Propene epoxidation over gold/titania and silver catalysts

A. Zwijnenburg
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Propene epoxidation
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Aalbert ZWIJNENBURG

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Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. J.A. Moulijn

Toegevoegd promotor:
Dr. ir. M. Makkee

Samenstelling promotiecommissie:

Rector Magnificus voorzitter
Prof. dr. J.A. Moulijn Technische Universiteit Delft, promotor
Dr. ir. M. Makkee Technische Universiteit Delft, toegevoegd promotor
Prof. dr. ir. H. van Bekkum Technische Universiteit Delft
Prof. dr. G.J. Hutchings Cardiff University
Prof. dr. ir. L. Lefferts Universiteit Twente
Dr. C.M. Lok Synetix
Dr. D.T. Thompson World Gold Council

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Each chapter in this thesis is written based on separate publications and can be read independently. Consequently, some overlap among the chapters is unavoidable.
Introduction

In this introduction the use and current production processes of propene oxide are briefly reviewed to illustrate the need for a new propene epoxidation process. Furthermore, current research activities for new propene oxide processes are discussed with respect to industrial application. Finally, the outline of this thesis will be presented.
Introduction

Propene oxide (PO) is one of the most important intermediates in chemical industry. The global PO production capacity is 6 Mton/y (1999, [1]). The major application (60%) of PO is in the production of polyether polyols [2], which are for example useful for making rigid as well as flexible urethane foams. PO can also be hydrolyzed with water to form 1,2-propane diol, which due to its low toxicity is used in foods, pharmaceuticals and cosmetics.

Current processes

Currently, there are two commercial propene oxide (PO) processes, namely: a chlorohydrin and a hydroperoxidation route [2]. The first process employs hypochlorous acid as oxidant, the latter uses an organic hydroperoxide. A detailed description of both commercial propene oxide processes has been given by Nijhuis [3].

The chlorohydrin is the oldest process, in which propene is reacted with hypochlorous acid to form propene chlorohydrin. Before the 1940s also ethene oxide (EO) was produced via this route [4], but this process has been abandoned since the introduction of a heterogeneous silver catalyst. The propene chlorohydrin is subsequently dehydrochlorinated with a base to form PO. If caustic soda is used, the sodium chloride can be recycled to a chlorine caustic plant. The main disadvantage of this process is the costly wastewater treatment due to the formation of environmentally unfriendly chlorinated by-products. Therefore, the process is outdated, and no new major chlorohydrin PO plants have been built over the last 20 years [5].

Scheme 1. Relevant reactions in the chlorohydrin process.

In the hydroperoxide process an organic compound is oxidized to its hydroperoxide, which is subsequently used to form the epoxide from propene. Besides PO a coproduct is formed out of the organic compound. Main examples are coproduction of t-butyl alcohol (TBA, from isobutane) or 1-phenylethanol (from ethylbenzene). TBA is commonly used as feedstock for methyl t-butyl ether (MTBE), while 1-phenylethanol is dehydrated to form styrene (SM or styrene monomer) [2].

Scheme 2. Relevant reactions in the hydroperoxide process with butyl alcohol as coproduct.

The advantage of this process over the chlorohydrin route is the good selectivity and low waste production. However, a fixed amount of coproduct is formed (typically 2.3 kg of TBA or styrene for 1 kg of PO) [5]. Markets for PO and its coproducts are not linked. For example, PO markets continue to grow, but the coproduct MTBE, after its introduction in the early 1990s as fuel additive, becomes less popular nowadays due to its low biodegradability and high solubility in ground water.

The chlorohydrin process is mainly carried out by Dow Chemical in North America, but other companies practice this process in Germany, Italy, Brazil, Japan, Eastern Europe, and Asia [1]. TBA coproduct plants are operated by Lyondell in the United States, France, and the
Netherlands and by Huntsman in the United States. Styrene monomer (SM) coproduct plants are located in United States and Japan (Lyondell), the Netherlands and Singapore (Shell), Spain (Repsol), and South Korea (Yukong) [1]. In Figure 1 the production capacities of the different processes are given. It should be noted that worldwide 36 chlorohydrin, 4 TBA, and 9 SM plants exist, indicating that the chlorohydrin plants are older and smaller in scale.

Main disadvantage of the current (coproduct) PO processes is the use of an organic hydroperoxide as oxidant. After the epoxidation of propene to propene oxide, an organic compound has to be transformed into a useable product or even to be disposed of. In the following section several options for improved processes are briefly discussed.

Choice of reagents

The six-million-ton/year market for propene oxide requires an abundant feedstock. Propene is produced on a 48 Mton/year scale (1998, [6]) and is, therefore, a good hydrocarbon source. Long-term research might focus on propane as feedstock, because of its lower price.

With respect to the oxidation species more options are currently under investigation. A schematic overview is given in Figure 2.

Alkenes like ethene and styrene, which have no allylic hydrogen groups can be directly epoxidized with molecular oxygen over silver catalysts. The alkene is epoxidized by a mild electrophilic oxygen (O^{5+}) [7]. The epoxidation of ethene is one of the most important industrial oxidations (with respect to volume) and typically carried out at 500 K and 1-3 MPa [4]. Also the epoxidation of butadiene to epoxybutene has recently been commercialized [8]. For hydrocarbons containing allylic hydrogens, like propene, till date no industrial direct oxidation process exists. One of the solutions may be a reduction in temperature to favor selective oxidation (by minimizing consecutive reaction of the wanted product to other oxygenates or CO_{2} and H_{2}O). Unfortunately, at temperatures typically below 400 K molecular
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oxygen needs to be activated before it can be used in oxidation reactions. One exception might be the CO oxidation, which takes place at 200 K over gold catalysts. This reaction and its mechanism will be discussed in a subsequent chapter.

Activation of molecular oxygen can be carried out by application of a suitable catalyst, if necessary in combination with:

1. an electrochemical epoxidation process (given in Figure 2 as e'): in particular, the indirect electrochemical generation of PO via propene halogenohydrid has been extensively studied. Again, main disadvantage is the production of chloro- or brominated byproducts [1].

2. adding photons to the reactor (photochemistry, given in Figure 2 as hγ): it has been shown that TiO₂ [9] and SiO₂ [10] can be used as photocatalysts. Photocatalysis is still characterized by low productivities and is, therefore, at present not a good option for PO production on a large scale.

3. using a reductant: oxygen is reduced to form organic (organic peroxides, ROOH) and inorganic (N₂O and H₂O₂) oxidants.

Different organic peroxides to generate propene oxide have been reviewed previously [11]. Main disadvantage of these routes is the need to regenerate the organic compound after use, or the production of a coproduct in considerable amounts.

N₂O can be used as precursor for active oxygen species. For benzene oxidation to phenol Panov and coworkers [12] have shown that N₂O can be a selective oxidant. Main advantage is that only N₂ is formed as byproduct. Recently, for propene epoxidation Duma and Hönike [13] showed yields up to 2 % with maximum 70 % selectivity using Fe/SiO₂ catalysts. N₂O is formed as by-product in adipic acid manufacture. The largest adipic acid plants produce about 300 kton/y of adipic acid, which would enable a PO production of about 30 kton/y. However, current PO plants typically have 200-300 kton/y production [1]. N₂O can be produced by oxidation of NH₃, which makes it, however, a rather expensive oxidant, more suitable for synthesis of high value products [14]. This is due to the fact that for one molecule of N₂O, two molecules of NH₃ (and, therefore, 3 molecules of H₂) are needed.

\[
N₂ + 3H₂ \rightarrow 2NH₃ + O₂ \rightarrow N₂O + 3H₂O
\]

**Scheme 3. Production of N₂O**

The use of hydrogen peroxide as oxidant was made possible by the discovery of Titanium-Silicalite-1 (TS-1) as catalyst by Enichem [15]. Only water is formed as byproduct. H₂O₂ is mainly produced by the anthrahydroquinone autoxidation process, with a typical production capacity of up to 60 kton/y [16]. When reacted with propene, ideally this would give 100 kton/y PO production. Again, the scales of PO and oxidant production do not match. A solution may be the in situ production of H₂O₂ that is immediately converted with propene to form PO and water. The reaction can be either carried out in two steps (first H₂O₂ formation, then epoxidation) or in one step [17] using Pd/Pt to form H₂O₂ from H₂ and O₂, and the TS-1 support as epoxidation catalyst. Industrial application of TS-1 in PO synthesis is impeded by its deactivation behavior. Deactivation is either due to leaching of the active Ti into solution [18] or pore blocking by oligomers formed out of PO [19]. Furthermore, solvent recycles are essential for the development of a continuous process [19].

As discussed in the sections above, application of a suitable catalyst (if necessary in combination with a suitable (cheap) reductant) to create an active and selective epoxidation species is needed for a new PO production process. However, mechanistic information that is obtained from steps 2 and 3 can also be important to optimize the new epoxidation catalyst. An overview of epoxidation mechanisms will be given in chapter 1.
Current research

To illustrate the current research activities in Figure 3 a patent distribution over 1995-2000 is given [20]. With respect to the commercial technologies, clearly it can be seen that the coproduct route has prevailed over the chlorohydrin route. On the developing technologies both H₂O₂ and the direct oxidation gain a lot of attention.

![Patent distribution over 1995-2000 (20).](image)

The latter will be the subject of this thesis. A competitive H₂O₂ route is being developed by Degussa-Hüls and Krupp Uhde [21]. Recently, it was announced by Sumitomo Chemical [22] that a 200 kton PO plant will be operational in 2002. This plant will use cumene hydroperoxide (cumene HP) as oxidant, which is subsequently recycled. Therefore, no coproduct will be produced.

Outline of this thesis

As PO remains an important intermediate in chemical industry, and its current production processes suffer from several disadvantages, a new process is highly desired. It was shown that due to market size of PO, propene and molecular oxygen are the best options as feedstock for a new PO process. A catalyst (that may require combination with a suitable reductant) is needed to create an active and selective epoxidation species.

In chapter 1 an overview of literature on direct gas-phase epoxidation of propene is given. Both silver and gold catalysts are currently under investigation and their differences and similarities will be discussed.

In chapter 2 and 3 the propene epoxidation over silver catalysts will be discussed. A lot is known on ethene epoxidation over silver, but propene is less studied. Over silver a maximum selectivity of 60% has been reported, and the causes of this low selectivity are investigated. These chapters will mainly focus on the application of an advanced TAP system to elucidate some aspects of the epoxidation mechanism, like the dissociation of oxygen on silver (chapter 2) and reaction of propene and oxygen (chapter 3).

Chapter 4 and 5 will focus on characterization of gold catalysts which exhibit a higher (> 99%) selectivity to PO, but require the presence of hydrogen in the feed mixture. Both the influence of the gold (chapter 4) and the Ti-containing support (chapter 5) will be discussed.
In chapter 6 and 7 new epoxidation catalysts are discussed. Both the metal (chapter 6) and the support (chapter 7) have been modified to improve the performance of the existing gold catalysts. It will be shown that a significant improvement in hydrogen efficiency can be achieved.

In chapter 8 an evaluation of both gold and silver catalysts will be given and the remaining research challenges for future industrial application are discussed.

References


A literature review on the mechanism of propene epoxidation over gold/titania and silver catalysts

In this chapter literature on the mechanism of propene epoxidation over gold/titania and silver catalysts is reviewed. Differences and similarities of gold and silver, with respect to the active (ep)oxidation species, particle size effects, influence of promoters and the support are discussed. Design rules for new and more selective epoxidation catalysts are given.
Introduction

Propene oxide is used in the production of numerous speciality chemicals and materials such as polyether polyols, propene glycol, alkanolamines, and glycol ethers [1]. The global PO production capacity is 6 Mton/y (1999, [2]). Currently, the production of propene oxide is roughly split between two indirect processes, the chlorohydrin and the peroxidation processes (mainly a propene oxide/styrene monomer (PO-SM) process and a propene oxide/tert-butyl alcohol (PO-TBA) process, respectively). Both of the indirect processes have significant drawbacks environmentally as well as economically depending on the coproduct value, and much effort has been spent trying to develop a catalyst for the direct partial oxidation of propene.

An option for the direct oxidation process can be a silver-based catalyst system. Silver catalysts may be able to directly oxidize propene into propene oxide without any coproduct analogous to the current industrial ethene oxide process. Silver catalysts are not only widely used for the commercial production of ethene oxide [3], but also for the oxidation of methanol to formaldehyde [4], and epoxybutene [5]. Selectivities in excess of 90 % are realized for the partial oxidation of ethene to ethene oxide over supported silver catalysts. Unfortunately, the highly selective supported silver catalysts for ethene epoxidation are reported to show unacceptably low selectivities for propene partial oxidation with selectivities of less than 6 % [6]. However, silver catalysts have recently drawn attention by reports of Arco (now Lyondell) researchers, who found higher selectivities by employing a Ag/CaCO₃ catalyst [7]. PO selectivities up to 60 % have been reported [8,9].

Haruta and coworkers discovered that also highly dispersed gold on a titanium-containing support can be used in the direct epoxidation of propene [10]. These catalysts show remarkably high selectivities to PO (> 99 %) using a mixture of hydrogen and oxygen. The reaction is usually carried out at temperatures between room temperature and 450 K and at atmospheric pressure. However, the propene conversion remains low (< 2 %) [11]. The hydrogen efficiency on the catalyst is low (indicating that the larger part of H₂ reacts with O₂ to form water) and obtaining a higher efficiency is probably one of the key factors for the realization of this process [12].

In this chapter, firstly, some of the requirements for a selective epoxidation of propene are defined. Secondly, the existing literature on propene epoxidation mechanisms over both gold/titania and silver will be reviewed. Differences as well as similarities between epoxidation mechanisms over gold and silver will be explored. For ethene epoxidation over silver excellent reviews exist [3,13], and extensive reviews have also been published by Bond and Thompson for general aspects of gold catalysis [14] and CO oxidation over gold [15]. Furthermore, Haruta and coworkers have summarized most of their findings [16]. No reviews of the mechanism of propene epoxidation over gold and silver are available yet. As a result, relevant findings for ethene epoxidation over silver and CO oxidation over gold will be briefly discussed and used for establishing insights in the mechanism of propene epoxidation over silver and gold.
Propene epoxidation over silver and gold/titania catalysts

Epoxidation of propene

To convert propene to propene oxide, an oxygen atom has to be added to the double bond, thus forming an epoxide ring. The double bond has a high electron density. Under oxidizing conditions, however, the partially positively charged hydrogen atoms on the allylic position also show reactivity [17]. The reactivity of the allylic hydrogens is due to their lower C-H binding energies in comparison with the other C-H bonds within the propene molecule [17]. In other words, the allyl intermediate formed after allylic C-H bond breaking is stable. The selectivity of the epoxidation reaction will, therefore, be dependent on the type of oxygen species. Generally, the scheme as given in Figure 1 can be drawn [18-20].

A mild electrophilic oxygen species will preferentially attack the π-bond, forming propene oxide. However, if the oxygen atom does not bind symmetrically, but binds with one of the two carbon atoms, propenal or acetone are formed [19], which occurs more favorably at higher temperatures. A strong electrophilic oxygen will in principle attack all C-C (and C-H) bonds, leading to oxygenated hydrocarbons with less than three carbon atoms, including CO and CO₂. Attack of the allylic hydrogens leads to allylic oxidation products, like allyl alcohol and acrolein.

To complicate matters, the product propene oxide can also be isomerized to acetone and propanal [21,22] and oxidized via other oxygenated intermediates to CO₂ and H₂O. Usually these routes are favored at higher temperatures over acidic and/or basic catalysts [19]. This conversion of the wanted product PO to other compounds will be further denoted as “secondary reaction”.

![Figure 1. Reaction of oxygen species with a propene molecule [18-20].](image)

In this chapter on silver and gold/titania, for each catalyst system first the structure of the active catalyst is discussed. Main reason is to elucidate whether or not surface science studies can be used to model the real catalyst. Secondly, models on the formation of oxidizing species and the interaction of propene with the catalyst are given. Thirdly, the epoxidation reaction between the oxidizing species and adsorbed propene is discussed. Finally, the influence of promoters and secondary reaction will be reviewed. Main objective will be to show that the concepts of epoxidation chemistry over gold and silver are similar. However, there is a difference with respect to metal particle size and support effects, and this will be treated. For example, for epoxidation over silver the support should be inactive, while for gold catalysts the titania-based support is necessary for activity.

Propene epoxidation over silver catalysts

The industrial process of ethene epoxidation is carried out with catalysts consisting of large silver particles (~ 500 nm) supported on crystalline α-alumina at 500 K and 1-3 MPa [23]. The low surface area of the catalyst and small conversion per pass (< 10 %) allow the produced heat to be efficiently removed. Most research efforts have concentrated on an increase in selectivity to ethene oxide. In the 1940s selectivities were around 60 %, and mainly by addition of promoters nowadays 90 % and more is achieved [24]. Chlorine is
continuously added to the catalyst system by cofeeding a Cl-containing hydrocarbon, and alkali are added to decrease acidity of the catalyst [3]. There have been many experimental and theoretical efforts to elucidate the reaction mechanism using supported, non-supported silver catalysts as well as silver single crystals.

Silver surface

The Ag(110) single crystal surface is the most active low index silver surface for oxygen adsorption and, therefore, studies related to the partial oxidation have predominantly been on the Ag(110) surface [25]. Oxygen interacts much more strongly with Ag(110) than with Ag(111) [26,27]. However, recent studies use Ag(111) as a model catalyst [28], as the Ag(111) single crystal catalyzes the formation of ethene oxide with kinetics that resemble those of supported catalysts [29]. This may be due to the general fact that densely packed low-indexed terminating crystal structures are thermodynamically preferred. Therefore, under reaction conditions, the main part of the silver surface may have a low index of Ag(111). Studies on Ag(111) (e.g. [30]) apply a high-pressure dosing of oxygen previous to the surface analysis to overcome the much lower oxygen sticking probability of about $10^{-7}$ to $10^{-6}$ [31,32] compared with the value of about $10^{-4}$ to $10^{-3}$ for Ag(110) [26,32].

Silver is known to undergo pronounced morphological changes following high-temperature treatment in various gas atmospheres [32]. Not only the temperature but also the atmosphere surrounding silver can significantly affect the morphology and properties of silver surface. Polycrystalline silver is investigated for more realistic measurements, while Ag(110) and Ag(111) are often chosen to investigate the surface properties and reactivity of silver.

Formation of oxidizing species over silver

Although the states of active oxygen species on silver are still subject of discussion, more and more realistic models of oxygen adsorption and oxygen states on the surface have been proposed by recent surface science studies. Generally, chemisorbed oxygen is considered as active species towards partial and total oxidation.

There are two concepts about the active oxygen species towards epoxidation on silver surface. One of them connects the epoxidation route with molecularly chemisorbed oxygen [33,34], while the other connects it with atomic oxygen [3,13,35]. Some researchers claim that both oxygen species are active in ethene epoxidation [36].

Recent discussions tend to converge on atomic oxygen as active species. Originally, the hypothesis of molecular oxygen as the active species was dominant. Especially, the lower selectivities towards epoxidation than 85.7 % (6/7 as the stoichiometric upper limit for molecular active oxygen species) supported this hypothesis. However, the appearance of patent examples [37] and academic studies [38] claiming selectivities over the limit has forced most followers of the molecular oxygen hypothesis to change their opinion. In addition, the observation of ethene oxide among the products of Temperature-Programmed Reaction (TPReact) of ethene with atomically chemisorbed oxygen supported the atomic oxygen hypothesis [29]. The recent detailed surface science studies by in situ X-ray Photoelectron Spectroscopy (XPS) with TPReact and in situ Ultraviolet Photoelectron Spectroscopy (UPS) come to the same conclusion [39-41].

The molecular oxygen hypothesis has recently drawn attention again by the paper of Boronin et al. [33]. Based on the observation of UPS spectra, they claim that the oxygen species being active towards ethene oxidation are molecular. However, this interpretation was questioned due to the depth probed by UPS [41]. UPS is not a fingerprint method for oxygen adsorbed at surfaces; therefore, the observed oxygen species in UPS spectra are probably not chemisorbed molecular oxygen but subsurface oxygen.
Recently, Nagy et al. have thoroughly investigated the states of relevant oxygen species on silver surface at the reaction conditions of methanol and ethene partial oxidation. Several facts of the different oxygen states are elucidated ([32,42] and references therein). Nagy defines three types of atomic oxygen species on and in silver: atomic surface oxygen and two types of subsurface oxygen species (Figure 2). Dissociatively adsorbed oxygen on silver is called \( \text{O}_\alpha \). This \( \text{O}_\alpha \) is located on the surface. One of the two subsurface oxygen species is known as \( \text{O}_\beta \). This species \( \text{O}_\beta \) is formed when oxygen dissociatively adsorbed and the resulting atomic surface oxygen (\( \text{O}_\alpha \)) diffuses into the bulk (\( T > 573 \, \text{K} \) under oxygen). The second subsurface species, \( \text{O}_\gamma \), is formed at higher temperatures (\( T > 873 \, \text{K} \)). It has been suggested that \( \text{O}_\gamma \) is formed via the segregation of \( \text{O}_\beta \) to the surface. Under reaction conditions of ethene and propene epoxidation, \( \text{O}_\alpha \) and \( \text{O}_\beta \) are important. These oxgens most probably correspond to atomic oxygen and subsurface (near-surface) oxygen, respectively. Although Nagy et al. studied silver surfaces under oxygen intensively, it should be noted that oxygen states and silver morphology might be influenced by the existence of the reaction medium to a great extent (i.e. under the mixture of oxygen and ethene/propene [40]). The effects of a reaction medium will be discussed later in this section.

Desorption behavior of oxygen species from silver surfaces differs depending on the type of silver investigated, i.e., Ag(110), Ag(111), foil, film, or supported silver. When more defects and/or adsorption area are present, it is expected that the interaction between oxygen and silver is larger, leading to a higher desorption temperature. Molecular oxygen desorbs at least 220 K ([43] and references therein). In general oxygen desorbs from silver surfaces at about 560 K – 575 K when silver is treated below 470 K under oxygen. At higher oxygen treatment temperatures, a new peak at higher temperature appears [39]. Also when silver is treated with a reaction medium (ethene and oxygen), oxygen tends to diffuse into silver bulk and desorbs at a broad range of temperature [40]. In the following sections those TPD spectra will be shown with XPS spectra.

Active oxygen species on the silver surface can be studied by a number of techniques. Recently, experimental results are reported by various \textit{in situ} techniques. Those \textit{in situ} spectroscopic techniques are often combined with temperature programmed desorption/reaction and provide more detailed information about what is happening on silver surface at reaction temperatures. These combined techniques give more detailed information of oxygen properties on a silver surface. Especially TPD/TPReact and XPS spectra of oxygen species on silver surface are often encountered. The general knowledge of those spectra will be briefly summarized here.

There are mainly two O 1s binding energy (BE) values observed in XPS spectra for oxygen species on a silver surface. In Figure 3, the schematic XPS spectra are shown. Nucleophilic oxygen (\( \text{O}^{\delta^-} \)) appears at around 528.0 - 528.5 eV. The other oxygen species, which is called covalent or electrophilic oxygen (\( \text{O}^{\delta^+} \)) appears at around 530.0 - 530.5 eV. As shown in Figure 3, the two different oxygen species can exist on a silver surface at the same time. In contrast, molecular oxygen is generally reported to have a binding energy of above 532.0 eV ([43] and references therein).
Figure 3. Schematic O 1s XPS spectra of silver surface with (a) electrophilic oxygen, (b) nucleophilic oxygen, and (c) both of electrophilic and nucleophilic oxygen.

Figure 4. (a) O 1s spectra and (b) TPD spectra of O$_2$ for silver (polycrystalline silver foil) treated by O$_2$ for 30 min at $P = 100$ Pa and various temperatures [39].
As mentioned earlier, TPD/TPR(react) and in situ XPS give insights of the oxygen state on the silver surface. Bukhtiyarov et al. investigated the effect of oxygen treatment temperatures on the desorption behavior [39]. The treatment temperature significantly affects the oxygen states in silver (Figure 4). The higher the treatment temperature is, the larger and higher the second peak is. The results indicate that at higher temperature (above 470 K) oxygen can diffuse into bulk silver followed by slow desorption. They also found that a higher pressure enhances oxygen diffusion. On the other hand, the XPS spectra did not differ at different treatment temperatures, which is probably due to the limited depth probed by XPS.

Bukhtiyarov also examined the binding energy of oxygen at room temperature and an elevated temperature (420 K) on Ag(111) [43]. The binding energy of O 1s shifted from 530.0 eV to 528.2 eV with no change in intensity when the silver crystal was treated at a higher temperature (Figure 5).

**Figure 5.** (a) O 1s spectra and (b) TPD spectra of O₂, recorded after the oxygen adsorption on the clean Ag(111) surface for 10 min at P = 100 Pa and T = 300 K (1), followed by heating up to 420 K (2). TPD spectrum of CO₂ is also shown to prove the absence of carbonates on the surface due to the background CO₂ [43].

By also recording the Ag 3d₃/₂ spectra, Bukhtiyarov and coworkers found that the appearance of BE(O 1s) = 528.2 eV changes the BE(Ag 3d₃/₂) of surface silver into the BE of Ag⁺ ions, while atomic oxygen with BE(O 1s) = 530.0 eV did not change the Ag 3d₃/₂ spectrum. This result shows that moderate heating (above ~ 400 K) of silver under oxygen can form ‘nucleophilic’ or ‘ionic’ oxygen. As opposed to XPS spectra, TPD peaks of oxygen for both temperatures of adsorption coincide (560 K).

The results imply that oxygen states keep changing while TPD measurements are conducted due to the much higher temperature in the TPD experiment than the pretreatment (at 300 or 420 K). This indicates the difficulty to assign the oxygen species from TPD measurements only. Furthermore, this also complicates the assignment of O₆, O₈, and O₇ as defined by Nagy et al. [32,42], and the nucleophilic and electrophilic oxygen as defined by Bukhtiyarov [43].

Bukhtiyarov et al. also looked into the concentration profile of oxygen species with binding energy of 528.2 eV and 530.0 eV by Angular Dependent X-ray Photoelectron
Spectroscopy (ADXPS). The oxygen species with BE(O 1s) = 530.0 eV was assigned to electrophilic oxygen on the surface, while oxygen species with BE(O 1s) = 528.2 eV was assigned to nucleophilic oxygen incorporated into the second silver layer (Figure 7).

![Graph showing concentration profiles of oxygen in silver by ADXPS.](image)

**Figure 6.** Concentration profiles of oxygen in silver by ADXPS [43]. The XPS intensity is plotted versus the ratio of penetration depth and inelastic mean free path.

The treatment of silver surfaces by oxygen at high temperatures and pressures results in oxygen dissolution into the silver bulk, however the treatment does not activate the surface towards epoxidation [39,43]. Grant and Lambert studied ethene epoxidation on Ag(111), and demonstrated that modification of clean silver by $\text{C}_2\text{H}_4 + \text{O}_2$ mixtures produces the surface sites active for ethene epoxidation [29]. Recently, the effects of reaction medium ($\text{C}_2\text{H}_4 + \text{O}_2$ and $\text{CO} + \text{O}_2$) on oxygen states on silver surface were investigated by Bukhtiyarov et al. [43]. In Figure 6, XPS (O 1s) and TPRReact spectra for silver treated with oxygen and reaction medium ($\text{C}_2\text{H}_4 + \text{O}_2$) are shown.

![Graph showing XPS(O 1s) and TPRReact spectra.](image)

**Figure 7.** Schematic XPS(O 1s) and TPRReact spectra after the treatment of oxygen and reaction medium [39,40]. Treatment condition: (a)(b) $P(\text{O}_2, \text{C}_2\text{H}_4+\text{O}_2) = 10$ Pa at 300 K for 10 min, (c) $P(\text{O}_2) = 10^{-2}$ Pa at 420 K for 10 min.

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This figure shows that only oxygen treatment (a) does not form active species towards ethene epoxidation. After the reaction medium treatment (b), ethene adsorption changes the electronic state of oxygen from nucleophilic oxygen to electrophilic oxygen. However, this oxygen species, through TPRreact, could not epoxidize ethene. Interestingly, only when silver is treated again under oxygen, the silver can form the active oxygen towards epoxidation. When the oxygen species are active towards epoxidation, two values of binding energy are found.

Furthermore, the effects of CO + O2 treatment on oxygen states on silver surface were examined [40]. While a C2H4 + O2 mixture provided not only the appearance of active oxygen states but also the dissolution of oxygen and carbon atoms in the silver bulk, the use of the CO + O2 mixture also produced two different adsorbed oxygen states without modification of silver bulk by dissolved atoms of carbon or oxygen.

The existence of two types of oxygen species seems a key factor to understand the epoxidation mechanism. The function of these two different oxygens in ethene epoxidation are summarized as follows:

1. Nucleophilic oxygen (BE(O 1s) = 528.4 eV) located in the second silver layer creates adjacent Ag+ cations, which can adsorb ethene
2. Electrophilic oxygen (BE(O 1s) = 530.5 eV) located on the top most surface epoxidizes ethene

Therefore, the presence of the both oxygen species is crucial for ethene epoxidation and most probably the same logic can be applied to propene epoxidation.

**Epoxidation reaction over silver**

Most literature assumes an Eley-Rideal mechanism between a gaseous ethene or propene and an adsorbed oxygen species [18,44]. Also some theoretical work has been published on the Eley-Rideal pathway [45,46]. However, based on the XPS and TPD studies discussed in the previous section, the silver surface is modified by the presence of an alkene. Therefore, a Langmuir-Hinshelwood mechanism involving both adsorption of propene and oxygen is more likely. Already in 1985 the inadequacy of the Eley-Rideal mechanism was shown by a kinetic study on Ag(111) [29].

Recently, an oxametallacycle intermediate (Figure 8) was proposed by Barteau and coworkers [47]. It has been demonstrated that 1-epoxy-3-butene (EpB) undergoes ring opening on Ag(110) to form a stable oxametallacycle. During TPD near 500 K EpB desorbs again [47,48]. However, no experimental evidence exists so far of formation of ethene or propene oxide from these intermediates. For example, adsorption of iodoethanol also gives a oxametallacycle, but during TPD no ethene oxide is formed [49].

Clearly, more theoretical work is needed to elucidate the Langmuir-Hinshelwood mechanism in combination with studies on model catalysts. An interesting approach may be the study of homogeneous complexes where the choice of ligands determines whether or not oxidant and alkene can coordinate simultaneously. Recently, an example with molybdenum has been given [50].

![Figure 8. Oxametallacycle species as proposed by Barteau et al. [47].](image-url)
Secondary reaction

The secondary reaction (conversion of PO to other products) may explain part of the low selectivity of silver catalysts. Interestingly, silver itself is not very active in conversion of PO, as shown by Bare [51] and given in Figure 9.

The desorption temperature is 170 K for the clean silver surface and increases up to 230 K with an increase in atomic oxygen coverage. In this temperature range there is no reaction of propene oxide with adsorbed oxygen. However, conversion of PO at higher temperatures under reaction conditions may still be possible. Bulushev and coworkers [52] found that ethene oxide is converted to glycol-like species on the alumina support, which are converted to CO₂ and H₂O at the silver-alumina interface. Therefore, alkali (K⁺, Ca²⁺) are added to industrial ethene oxide catalysts to reduce acidity of the Al₂O₃ support [3]. Recent patents on silver catalysts focus on the use of non-acidic supports, like carbonate [53] and silicate [54].

Silver particle size effect

In this section silver particle size effects will be discussed. For silver these effects are not very well known, but for gold these will be shown to play an important role in literature on mechanisms.

For silver a particle size effect is observed in the 30 – 50 nm range [35,55]. The influence of silver particle size on ethene epoxidation rate is given in Figure 10. The increase in ethene epoxidation rate with silver particle size is accompanied by a decrease in the Ag 3d₅/₂ binding energy value. The change in binding energy cannot be explained by a change in the metallic character of silver. As will be shown in the gold section, these changes occur for much smaller particles in the order of a few nanometers or less. Also based on XPS measurements of Ag particles supported on graphite [56,57] these changes in binding energy are assigned to the relative population of nucleo- and electrophilic oxygen during epoxidation. Electrophilic oxygen is present on small (< 30 nm) silver particles, but from 30 nm onward also

Figure 9. TPD spectra of propene oxide (heating rate 2 K/s) as a function of increasing atomic oxygen coverage on Ag(110). No other desorbing species were observed [51].

Figure 10. Variation of ethene epoxidation rate (filled symbol) and Ag 3d₅/₂ binding energy (open symbol) with mean silver particle size for unpromoted catalysts [55].
nucleophilic oxygen is observed. As discussed in the previous sections, both types of oxygen are needed for ethene epoxidation (nucleophilic oxygen creates ethene adsorption sites, while electrophilic oxygen is selective in the epoxidation reaction. To date, no reports exist whether or not these size effects also play a role for propene epoxidation over silver.

The difference in behavior between small (< 30 nm) particles and large (> 50 nm) particles has been assigned to geometrical effects [35]. The smaller particles are spherical, while the larger particles are well cut and have more regular surfaces exposed. Therefore, nucleophilic oxygen is more likely to be formed on a regular surface, and electrophilic oxygen formation is favored on an amorphous ("defect-rich") structure.

**Influence of promoters on silver**

One of the first type of promoters used for silver catalyst were the alkali metals (K, Rb, Cs), later followed by combinations with alkali earth metals (mostly Ba) [24]. There is an effect of these promoters on both the Ag and the support. For example, K can enhance oxygen adsorption on Ag [58], but also play a role in the decrease of the support acidity [3]. Another important promoter is chlorine. A ppm level of chlorine is added in the form of, for example, ethyl chloride to the feed stream of an industrial reactor. Cl is thought to create a more electrophilic oxygen, because it withdraws electrons [3,29]. There are many studies on the precise role of chlorine [27,59-63], but the topic is still controversial. Recently, also the addition of nitrogen oxide species to the reactor feed has been proposed. The role of nitrate species on the silver surface is still under investigation [59,64,65].

**Conclusion on silver**

Several aspects of the silver-catalyzed epoxidation are summarized in Figure 11.

![Epoxidation mechanism on silver](image)

**Figure 11. Epoxidation mechanism on silver [35].**

As shown in the previous, epoxidizing electrophilic oxygen is preferentially located on "defect" sites, while nucleophilic oxygen is located on the regular silver surfaces and associated with alkene adsorption. Nucleophilic oxygen is also responsible for total combustion. However, it should be noted that as oxygen states change during (for example, TPD) analysis, elucidation of the silver-catalyzed epoxidation mechanism depends on more in situ characterization studies. For ethene epoxidation isomerization and combustion over the support were found to be of minor importance [52].

Most of the mechanistic information on ethene epoxidation will also be applicable for the epoxidation of propene. It has been shown that propene and the product propene oxide interact with silver comparable to ethene and ethene oxide. The difference between ethene and propene is the presence of the allylic hydrogens of the latter. These are bound to show more interaction with nucleophilic oxygen than in the ethene epoxidation. Based on the
discussion above, a catalyst with small Ag particles may be more selective to PO because less nucleophilic oxygen will be present. Furthermore, the Al₂O₃ support used for ethene may not be suitable at all for propene, due to its activity in decomposing the wanted product.

**Propene epoxidation over gold/titania-based catalysts**

Propene epoxidation over gold was discovered by the group of Haruta at the Osaka National Research Institute in Japan [10]. In the late 1980s Haruta's group prepared small Au particles on TiO₂ and other oxides like Fe₂O₃ and Co₃O₄, primarily for low temperature CO oxidation [66]. However, the TiO₂ supported samples proved also to be active in propene epoxidation in the presence of both H₂ and O₂, at temperatures between 323 and 423 K. This inspired research groups from both academia and industry to study gold catalysts. The reason that gold has been neglected as catalyst is due to the fact that it only becomes appreciably active when applied as small (few nm or less) particles. Contrary to, for example, Pd and Pt, simple impregnation methods usually do not give well-dispersed gold catalysts [14].

**Gold surface**

In the above section it has been shown that surface science studies can provide valuable insight into the propene epoxidation mechanism over silver. This is due to the fact that large (> 50 nm) silver particles consisting mostly of low index Ag planes are active in both oxygen dissociation and propene adsorption. However, the reactivity of gold single surfaces is very small and difficult to distinguish from impurity contributions [14]. General agreement exists on the fact that Au(110) and (111) surfaces do not (dissociatively) adsorb molecular oxygen [11]. By application of gold films or particles, gold becomes more active. However, as dispersed gold in the form of particles or thin films is more difficult to characterize (many possible catalytic sites are present), general conclusions from literature are difficult to draw. Furthermore, many studies do not disclose gold particle size and tend to focus on one characterization technique only.

**Formation of oxidizing species over gold**

Discussions still exist on oxygen dissociation over small (< 10 nm) gold particles. Recent studies on CO oxidation over gold nanoparticles and polycrystalline gold tend to assign the oxygen species as being molecular [15,67,68] although other researchers believe dissociative oxygen adsorption is slow but possible [69]. With respect to propene epoxidation, no reports exist of gold being capable of epoxidizing propene in the presence of molecular oxygen only, whereas CO oxidation proceeds over gold powder [70] at 273 K. For epoxidation reactions, therefore, oxygen has to be activated.

Hydrogen does chemisorb on gold films [71]. This is also evidenced by the reactions involving hydrogen, like H-D exchange, hydrogenation of alkenes, alkadienes, alkynes, and ketones, and hydrogenolysis, which have been reviewed by Bond and Thompson [14]. Naito and Tanimoto found an increase in H₂-D₂ exchange reaction over < 0.05 wt.% Au catalysts by addition of oxygen, and were the first to propose a peroxo-like oxygen species that favors hydrogen dissociation [72].

Haruta's group originally proposed a peroxo-species located on the perimeter interface of gold and support to be responsible for the observed epoxidation activity [73]. Nijhuis et al. [12] proposed that a hydrogen peroxide-like species is formed on the gold. Based on a D₂ kinetic isotope effect Stangland et al. [74] came to a similar proposal. Main difference is that Haruta favors propene adsorption on Au, while Nijhuis and Stangland propose propene to be adsorbed on the Ti-containing support. In later reports [75] also Haruta and coworkers adapted the view of propene to adsorb on the support.
Propene does interact with a Au(111) and (100) surface as recently reported by Goodman and coworkers [76], albeit very weak. The activation energy of desorption was found to be 39 kJ/mol (compared to 41 kJ/mol for clean Ag(110) [77] and 70 kJ/mol for the frequently used TiO₂ support [78]). Furthermore, total combustion of propene with preadsorbed atomic oxygen was observed, and some partial oxidation products with masses 56 (acrolein) and 58 (propene oxide, acetone, and/or propanal). Although a similar pressure gap may exist comparable to Ag (low epoxidation selectivity observed under UHV conditions compared to reactions at atmospheric or higher pressures [3]) the high epoxidation selectivity probably can not be assigned to Au only. However, propene TPD experiments by Haruta and coworkers on both TiO₂ and Au/TiO₂ indicated some propene adsorption on gold, but these findings may be invalid due to the small intensity differences between the desorption peaks [73].

If hydrogen is dissociatively adsorbed onto small gold particles, and reacts with molecular oxygen, it may be possible to synthesize H₂O₂ directly from hydrogen and oxygen over gold catalysts. Most H₂O₂ direct synthesis literature is on homogeneous or heterogeneous application of Pt and Pd compounds [79,80]. Generally, Pd/C in the presence of strong mineral acids and halide ions is reported to be the most active and selective [81]. In a theoretical study by Paredes Oliveira and coworkers [82] it has been predicted that catalysts based on gold and silver would be better due to the higher stability of molecular oxygen. Dissociation of oxygen is said to lead to excessive water formation. Indeed, in some patents also gold is claimed to be beneficial for H₂O₂ formation [83,84], but Pt and Pd seem to work better. Under the conditions described in the patents (oxygen partial pressures, liquid phase, low pH) both Pd and Pt may be present in (partially) oxidized form, which can explain their better performance compared to gold. Unfortunately, the formation of H₂O₂ is favored under acidic conditions and in the presence halogen promoters. A good H₂O₂ synthesis catalyst will, therefore, not necessarily lead to a good propene epoxidation catalyst.

**Epoxidation reaction over gold/titania catalysts**

When a hydrogen peroxide-like species is formed over small gold particles, the oxidation species may spill over to the Ti-containing support and perform the epoxidation chemistry over a Ti site [12,74,75]. Ti is well known to epoxidize propene with both organic and hydrogen peroxide to PO in liquid-phase applications. A heterogeneous Ti catalyst was first developed by Shell [85] in the 1970s and is still in use today for the reaction of ethylbenzene hydroperoxide with propene to form PO in the SMPO (Styrene Monomer - Propene Oxidation) process [86]. The Shell catalyst consists of TiO₂ dispersed on SiO₂ to yield isolated tetrahedrally coordinated Ti units. Unfortunately, water adsorbs strongly on the Ti site due to its strong Lewis acidity, rendering it impossible to use this catalyst with H₂O₂. In the 1980s Enichem researchers prepared Titanium-Silicalite-1, that consists of isolated Ti units in a hydrophobic matrix of silicalite-1 (MFI) [87,88]. TS-1 is active in liquid-phase epoxidations using aqueous solutions of hydrogen peroxide.

A vast amount of literature exists on both the active site in TS-1 and its interaction with H₂O₂ and propene. TS-1 is made by isomorphous substitution of part of the Si atoms by Ti. The Ti in TS-1 is generally reported to be stable with respect to aqueous reaction mixture [89], although recent reports indicate some by-products may induce leaching in epoxidation of allyl alcohol [90,91] and propene [92]. In Figure 12 four proposed models for the Ti center in TS-1 are given. Originally, structure (4) has been proposed [93,94], also based on reports by Sheldon on the Shell TiO₂/SiO₂ catalyst [86]. However, it has been shown that in the as-prepared material Ti is tetrahedrally coordinated [95], so structure (4) has been discarded.
Figure 12. Proposed models for Ti species in TS-1 (taken from [95]). From left to right: (1) tetrapodal, (2) tripodal, (3) dipodal with Ti-OH, and (4) dipodal with Ti=O.

Also structure 3 was discarded as a truly heterogeneous catalyst should be at least tripodally coordinated [96]. The possible presence of structures (1) and (2) is currently under investigation by a combination of several characterization techniques, like FTIR, UV-Vis, Raman, and X-ray spectroscopy [95], $^{29}$Si MAS NMR [97] and neutron diffraction studies [98-100]. Furthermore, disagreement exists on the interaction of H$_2$O$_2$ and propene with this active center. Interestingly, it has been observed that addition of solvents enhances reaction rate, and methanol is considered to be the best solvent [101]. In Figure 13 an overview of different solvents is given.

![Graph](image)

**Figure 13.** Solvent effect on first order reaction rate constant for propene epoxidation over TS-1 (413 K, 1 % H$_2$O$_2$, 3 bar propene) [101].

These observations have led to the proposed active centers as given in Figure 14 [94,102,103]. The influence of solvents on the species in Figure 14a is interpreted in terms of hindrance by physisorbed solvent molecules in zeolite channels, in other words, a competitive adsorption effect. By using a tracer chromatographic method to determine preferential adsorption, Langhendries *et al.* [104] found that methanol increases the concentration of 1-hexene and higher alkenes in TS-1. In the species of Figure 14b the solvent is also coordinated to the catalytically active center and may have electronic or steric hindrance effects. However, no spectroscopic evidence exists of the coordination of a solvent molecule to the active site. Therefore, the structure as proposed in Figure 14b may not be valid.
Propene epoxidation over silver and gold/titania catalysts

![Chemical structures](image)

**Figure 14.** Catalytic sites proposed for the epoxidation of propene [102].
(a) Ti(η⁶-O₂) species [94]. (b) hydperoxo species with a coordinated solvent molecule (ROH, R = alkyl or H) [103].

As has been discussed above both the H₂O₂ direct synthesis as well as liquid-phase epoxidation literature indicate that formation of OOH-like species on gold and subsequent epoxidation over the Ti-containing support is likely. More evidence is given by the reports on Pd/Pt catalysts supported on TS-1 [105-107]. It has been shown by Hölderich and coworkers [107] that H₂O₂ is formed over Pd/Pt and reacts with propene over TS-1. Autoreduction of the catalyst and addition of Pt lead to the formation of a partially oxidized Pd⁵⁺ species, which is thought to be essential for the formation of oxidizing species [107,108]. Addition of AuCl₃ decreased PO yield and gave more unwanted propane. A comparable Pd/Pt supported on TS-1 was tested by Baiker and coworkers under the high pressures of 50 – 120 bar [109]. The catalyst initially had 99% selectivity and 3.5% yield to PO, but PO yield dropped to near zero after 35 h on stream. This was shown to be due to the oxidation of the solvent methanol to methylformate. The formation of methylformate induces acid-catalyzed conversion of propene oxide to oligomers and unselective oxidation of propene to acrolein and acetone. Formation of OOH-like species from H₂ and O₂ on Pt and spillover to a Ti site is also indicated by a recent report of Bal and coworkers [110]. An overview of reactions catalyzed by TS-1 and in situ generated H₂O₂ is given by Clerici and Ingallina [81].

**Secondary reaction**

Although the first reports of propene epoxidation over gold were based on TiO₂ supports [10], many other TiO₂ containing supports, like TiO₂/SiO₂ [12], TS-1 [12,111], and Ti-MCM [112] are active and selective. Only the TiO₂ support suffers from severe deactivation during several hours on stream, and this has been assigned to a secondary reaction of propene oxide [12,74].

As discussed in the sections above, TS-1 is an active and selective catalyst for propene epoxidation with H₂O₂. For example, Thiele and Roland found typical yields of 97% with respect to H₂O₂ and 97% with respect to PO, using methanol as solvent [101]. One of the reasons for the high selectivity to PO is the absence of strong acidic centers in the TS-1 (no Al³⁺ present) [113]. Nevertheless, the by-products formed are mainly related to an acid-catalyzed ring opening of PO and a subsequent reaction with either methanol or water. These acid-catalyzed ring opening reactions can be suppressed by impregnation of TS-1 with basic salts, but this also decreases the activity. This is due to the fact that the Ti epoxidation center is a Lewis acid, which forms a Brønsted acid with a coordinated water molecule. Reaction with a basic salt may, therefore, deactivate the epoxidation center. However, upon addition of neutral salts, like Na₂SO₄, activity could be maintained. This indicates that the acidic sites that cause by-product formation are different from the epoxidation center [101]. Thiele and
Chapter 1

Roland [101] assign these acidic sites to silanol groups on defect sites, a spectroscopic study by Gao and Wachs [114] indicates acidity may also be related to (part of the) Ti that is present in oligomeric TiO₂ units. Preparation of TS-1 with monodispersed TiO₂ units is, therefore, necessary for selectivity. Furthermore, the acid-catalyzed conversion of PO is said to lead to oligomer formation, which blocks the pores of TS-1 and gives deactivation [101,115].

Influence of promoters

In the previous paragraph the addition of salts to TS-1 has been discussed. With respect to the gas-phase epoxidation, also the effect of some promoters has been reported. Using the aforementioned model of formation of oxidizing species over gold and subsequent epoxidation over the Ti-containing support, promoters from H₂O₂ direct synthesis and TS-1 literature are interesting. Halides are reported as promoters for H₂O₂ formation from H₂ and O₂ [80], and indeed CsCl has been reported to decrease the water formation (increase in hydrogen efficiency) for gas-phase epoxidation. Unfortunately, also Cs is needed to decrease the Cl-induced acidity, and the presence of Cl leads to sintering of the gold particles under reaction conditions (gas phase, 373 K) [116].

There are also indications that trace amounts of Na and K can be beneficial for activity and selectivity [117]. The same effect has been observed for Na-promoted Fe₂O₃/SiO₂ catalysts with N₂O as oxidant [19,118], and as stated in the paragraph above for H₂O₂-based epoxidation over TS-1 [101,119,120]. In general, a decrease in acidity of the catalyst is said to account for the influence of alkali promoters.

Gold particle size effect

In the silver section it was shown that size effects appear between 20 and 50 nm due to the increase in regular (low index) surfaces as the particle size increases. For gold a much smaller critical particle size is reported, and catalytic differences are either assigned to the charge of the gold particle as a whole, or changes in the exposed surfaces.

Haruta’s work on propene epoxidation [11] indicates the existence of a critical size for gold in the reaction of propene with oxygen and hydrogen over Au/TiO₂, in this case, at around 2 nm. When gold particles are larger than 2 nm, propene oxide is selectively formed, when they are smaller than 2 nm only propane is formed [11]. According to Haruta below 2 nm gold particles are oxidized (carry a positive charge) and show comparable behavior compared to Pt, which is capable of propene hydrogenation [73]. Oxygen-enhanced hydrogenation of propene has been observed by Naito and Tanimoto for Au/SiO₂ [72], but water production and effects of subsequent hydroxy-group formation on propene adsorption/propane desorption may play a considerable role [25]. Particle size effects were also studied by Goodman, who by Scanning Tunneling Spectroscopy (STS) found for Au/TiO₂ a metal to non-metal transition at about 4 nm. For CO oxidation, clusters of 3.2 nm were shown to exhibit the highest activity [121,122]. A catalyst mainly consisting of oxidized gold was claimed by Dow Chemical to be active in propene epoxidation [123], unfortunately no gold particle size was reported.

The particle size effect has also been studied in our laboratories for a 0.2 wt.% Au/TiO₂/SiO₂ catalyst prepared via deposition-precipitation of Au(OH)₃. TEM studies (not shown) indicated for the three samples a uniform gold particle size and a gradual increase in mean gold particle size from 0.5 nm for the sample calcined at 673 K to 3 nm for the catalyst calcined at 773 K. As can be seen in Figure 15, both PO and propane are formed throughout the observed particle size range. The largest (3 nm) gold particles even produce propane and no PO. Therefore, it is tentatively concluded that not only the gold particle size, but also the structure of the surface may play an important role.
Propene epoxidation over silver and gold/titania catalysts

Figure 15. PO and propane yield as a function of calcination temperature (gold particle size) for 0.2 wt.% Au/TiO₂/SiO₂.

For example, another particle size effect may be assigned to the relatively large fraction of steps on small particles. A theoretical study by Mavrikakis et al. indicates that two or more layers of gold atoms are essentially metallic, and an increased adsorption strength is due to high step densities on the small particles and/or strain effects due to the mismatch at the Au-support interface [124]. This metallic character of small gold particles was confirmed by Mössbauer [125].

As stated in the paragraphs above an important aspect of the particle size effect is the state of the gold atoms at the surface of the gold particle and at the gold-support interface. Several characterization techniques have been carried out to elucidate the nature of the active site(s), like FTIR [126], and XPS [74], but so far no conclusive answer has been found. Main challenge is the low concentration of gold in active catalysts. However, in general an increase in gold loading will decrease the catalytic epoxidation activity, as higher gold loadings will usually result in larger gold particles. Furthermore, preparation of uniform gold particles is difficult, in general a particle size distribution is obtained. Preparation of model systems, with an increased gold loading, and defined gold particle size is needed for elucidation of this complex problem. Recent progress in colloid synthesis (see [127] for a review) has opened new field in mechanistic research. For example, 2 and 17 wt.% Au on TiO₂ samples for CO oxidation with almost identical gold particle size (5 nm) have been prepared and tested [128].

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Conclusion on gold

As stated in the sections above, contrary to silver, gold is most probably not able to activate oxygen for the epoxidation reaction at temperatures between 323 and 423 K. However, if the particles are sufficiently small (high surface area) and hydrogen is present, an active epoxidation species is formed. Based on the literature of H$_2$O$_2$ direct synthesis and liquid-phase epoxidation chemistry over Ti-based catalysts, a mechanism as given in Figure 16 is tentatively proposed.

Based on this scheme it can also be envisaged that the presence of propene on the gold particles would give rise to the formation of propane. Based on experiments with different gold particle sizes, it is concluded that propane formation is not due to the charging of gold particles smaller than 2 nm as proposed by Haruta [11], but due to the increased number of steps.

![Diagram of the reaction mechanism](image)

**Figure 16. Schematic reaction mechanism proposed for gold-catalyzed propene epoxidation.**

Uniqueness of gold?

With respect to epoxidation the literature shows that both Au and Ag can generate epoxidizing species, albeit under different conditions. Recently, also reports on gas-phase epoxidation over copper were published [129], however, the reaction was shown to be stoichiometric rather than catalytic [130]. Based on the proposed scheme in Figure 16 also metals like Pt and Pd are expected to be active in gas-phase epoxidation under H$_2$ and O$_2$ atmosphere. This was shown in liquid phase epoxidation under H$_2$ and O$_2$ atmosphere for Pt [131] and (Pt-promoted) Pd [107]. Furthermore, also Ag supported on TiO$_2$ seems to be active in gas-phase epoxidation in the presence of H$_2$ and O$_2$ [132]. Therefore, gold may not be the only metal for gas-phase propene epoxidation.
Conclusion on gold and silver for PO production

In this chapter the similarities and differences of PO formation over gold and silver are discussed. Based on literature reports it is shown that the formation of electrophilic oxygen is catalyzed by silver at temperatures above 473 K, and by gold between 323 and 423 K in the presence of hydrogen. For gold catalysts a second site (a Ti epoxidation center on the support) is necessary to coordinate propene, as the presence of propene and hydrogen on the same sites would probably lead to formation of propane.

Most silver literature is based on ethene, and it is not clear whether all mechanistic information can be applied to propene. A good ethene epoxidation catalyst has a low PO selectivity, so the influence of Ag particle size and support may very well be different. For gold many questions exist on the oxidation state of the gold as a function of particle size and contact with the support. Based on the proposed mechanism, application of similar promoters compared to liquid-phase applications may be beneficial. Furthermore, addition of methanol to the feed, may give comparable effects as observed in liquid phase (either by competitive adsorption or participation in the catalytic cycle), but has not been tested before.

Clearly, both gold and silver show promising leads towards a new PO process. For silver, the low selectivity to PO has to be overcome. Possible solutions may be different supports or silver particle sizes. For gold, the main problem is the inefficient use of hydrogen and the low activity. Promoters may enhance the H_{2} efficiency and several modifications of the support are available to increase the activity.

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References


Propene epoxidation over silver and gold/titania catalysts


On the interaction of oxygen with silver:

An advanced TAP reactor study

The interaction of oxygen with CaCO₃- and α-Al₂O₃- supported Ag catalysts was studied in an advanced Temporal Analysis of Products (TAP) reactor. Oxygen response peak broadening was observed at temperatures above 373 K and assigned to an activated adsorption mechanism, rather than an increased metallic silver surface area at higher temperatures. The high signal-to-noise ratio of the advanced TAP reactor rendered it possible to study oxygen uptake on the reduced silver catalyst samples by determination of the peak areas of the oxygen pulse responses. Adsorption of oxygen was modeled using a Langmuir-Hinshelwood approach taking into account both molecular oxygen adsorption and dissociation. The activation energy of oxygen dissociation was found to be 17 kJ/mol on a promoted Ag/α-Al₂O₃ catalyst and 52 kJ/mol for a Ag/CaCO₃ sample.
Introduction

Silver catalysts are widely used for the commercial production of ethene oxide [1], oxidation of methanol to formaldehyde [2], and epoxybutene [3]. Ethene oxide is an industrially important chemical compound: the total production capacity in the world is estimated to an amount of over 1000 kton/year [4]. The influence of the different types of oxygen (molecular and atomic, surface, subsurface and bulk) on – for example – the selectivity towards ethene oxide is still under debate [5]. Furthermore, silver has a high permeability for both oxygen and hydrogen [6] and is, therefore, subject for many membrane studies.

With respect to the interaction of oxygen with silver both adsorption of oxygen on silver and diffusion of oxygen into the silver bulk are of importance. Diffusion and solubility of oxygen have already been studied in the 1960s by Eichenauer and Müller [7]. The values for diffusion coefficients and activation energies were confirmed by membrane studies [8] and electrochemical experiments [9]. Adsorption of oxygen on silver catalysts was also studied recently by volumetric and gravimetric measurements [10,11] and in a TAP reactor by Gleaves and coworkers [12].

This study is a part of our research on silver catalysts for use in propene epoxidation. Silver usually exhibits low selectivities towards propene oxide, but CaCO₃ supported Ag was reported to be highly selective. Researchers of Arco (now Lyondell) [13,14] claimed propene conversions up to 20 % with up to 60 % epoxide selectivity. The selectivity of the epoxidation reaction may be influenced by the amount and type of oxygen adsorbed on the catalytic surface. Therefore, oxygen interaction over both conventional Ag/α-Al₂O₃ ethene oxide catalysts and Ag/CaCO₃ samples has been studied.

\[
\begin{align*}
\text{O}_2 \ (\text{g}) & \quad \uparrow \quad \downarrow \quad 1 \\
\text{O}_2^* & \quad \downarrow \\
\text{2O}^* & \quad \uparrow \quad \downarrow \\
\text{2O}^{*,\text{dif}} & 
\end{align*}
\]

**Figure 1. Reaction scheme for oxygen-silver interaction:** (1) molecular oxygen adsorption, (2) dissociation, and (3) atomic oxygen diffusion.

**Reactor model**

In this paper Temporal Analysis of Products (TAP), a transient response technique, has been used. A reduced catalyst is subjected to oxygen pulses. As the catalyst is oxidized, the oxygen pulse will increase in intensity during the experiment. An oxygen mass balance can be given by:

\[
V \cdot \frac{dP_{O_2}}{dt} = m_{Ag} \cdot R \cdot T \cdot \left( F_{O_2} - \frac{dU}{dt} \right) - D \cdot P_{O_2} \tag{1}
\]

In this equation, the pressure change inside the vacuum chamber is dependent on the flow into the vacuum chamber \((F_{O_2})\), the change in oxygen uptake and the exit flow of oxygen. The transfer coefficient \(D\) was estimated is be 2.9 m³/s based on the standby pumping capacity of the turbomolecular pumps of the MultiTrack setup [15]. The volume of the vacuum chamber \(V\) is 0.015 m³.

**Kinetic model**

In Figure 1 a reaction scheme for the adsorption of oxygen on silver is given. The following equations can be defined for steps 1 and 2. The oxygen uptake \(U\) is related to the surface coverage of atomic and molecular oxygen:
\[ U = N_i \cdot \left( \frac{\theta_{o_2}}{2} + \theta_{o_2} \right) \]  

(2)

In this equation it is assumed that molecular and atomic oxygen compete for the same silver sites. Based on a mean Ag particle size of about 0.4 \( \mu \text{m} \) for the promoted Ag/\( \alpha \)-\( \text{Al}_2\text{O}_3 \) catalyst [16] and under the assumption of atomic oxygen adsorption on semi-spherical shapes consisting mostly of the closely packed Ag(111) surface [17], the maximum amount of oxygen that can be adsorbed \( (N_i) \) is 14 \( \mu \text{mol} \) \( \text{O}_2 \)/g\( \text{Ag} \). For the unpromoted Ag/\( \text{CaCO}_3 \) catalyst a value of 5.7 \( 10^2 \) \( \mu \text{mol} \) \( \text{O}_2 \)/g\( \text{Ag} \) is estimated (based on Ag particle size measurements by TEM analysis (not shown)). The surface coverages of atomic and molecular oxygen are related to the total amount of surface sites by the site balance:

\[ l = \theta_{o} + \theta_{o_2} + \theta^* \]  

(3)

Furthermore, assuming that dissociation is rate limiting, the molecular adsorption (step 1 of Figure 1) is considered to be in quasi equilibrium with the gas-phase oxygen.

\[ \theta_{o_2} = K_1 \cdot P_{o_2} \cdot \theta^* \]  

(4)

where the molecular oxygen adsorption constant is given by:

\[ K_1 = \frac{k_1}{k_{-1}} \]  

(5)

Finally, the change in the atomic oxygen concentration can be given as:

\[ \frac{d\theta_o}{dt} = k_2 \cdot \theta_{o_2} \cdot \theta^* - k_{-2} \cdot \theta_o^2 \]  

(6)

By combination of equations (2-4), equation (6) can be given as a function of the atomic coverage only:

\[ \frac{d\theta_o}{dt} = k_2 \cdot \frac{K_1 \cdot P_{o_2}}{\left(1 + K_1 \cdot P_{o_2}\right)} \cdot \left(1 - \theta_o\right)^2 - k_{-2} \cdot \theta_o^2 \]  

(7)

As the uptake \( U \) is a function of atomic oxygen coverage, from equations (2-4):

\[ U = N_i \cdot \left( \left( \frac{1}{2} - \frac{K_1 \cdot P_{o_2}}{\left(1 + K_1 \cdot P_{o_2}\right)} \right) \cdot \theta_o + \frac{K_1 \cdot P_{o_2}}{\left(1 + K_1 \cdot P_{o_2}\right)} \right) \]  

(8)

**Experimental**

In this study Multitrack, an advanced Temporal Analysis of Products (TAP) reactor system, was used. A fixed-bed reactor is located in an ultra-high vacuum system. Small amounts of reactants (\( 10^{15} \text{-} 10^{20} \) molecules) can be pulsed into the reactor. At the reactor exit the pulse responses are simultaneously analyzed by four quadrupole mass spectrometers. All four mass spectrometers are able to analyze one of the components in the exit gas stream with a maximum sample frequency of 1 MHz. A detailed description of the Multitrack setup has been previously reported [16]. As the signal-to-noise ratio in this system is excellent, no
averaging is needed to obtain good peak signals. This is an important aspect, as transient phenomena may remain unobserved when the peaks are averaged.

Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851\textsuperscript{e} thermobalance from Mettler Toledo equipped with a TSO 801RO sample robot using ca. 35 mg sample.

For the experiments promoted and unpromoted Ag catalysts were used. A 15 wt.% Ag/\(\alpha\)-Al\(_2\)O\(_3\) catalyst was prepared by an impregnation method. The desired amount of silver(I) oxide (Ag\(_2\)O, 99.0 %, Aldrich) was dissolved in an aqueous ethylenediamine (99.5 %, Fluka) solution. The solution was added to the dried \(\alpha\)-Al\(_2\)O\(_3\) support material (Engelhard), followed by drying at 353 K for 5 h and calcination at 623 K for 4 h. For comparison, a Ca\(^{2+}\), K\(^+\), and Cl\(^-\) - promoted 18 wt.% Ag/\(\alpha\)-Al\(_2\)O\(_3\) catalyst was used. The promoter loadings were 0.2, 0.04, and 0.01 wt.% for Ca\(^{2+}\), K\(^+\), and Cl\(^-\), respectively.

A 53 wt.% Ag/CaCO\(_3\) catalyst was prepared by the procedure described in the patent by Arco (currently, Lyondell) [18]. Oxalic acid (98 %, Aldrich) was dissolved in an aqueous ethylenediamine solution. Slowly, silver(I) oxide was added to the solution and dissolved, followed by the addition of solid CaCO\(_3\) (99 %, Sigma) into the solution. The resulting suspension was mixed and dried at 373 K for 4 h, followed by calcination at 573 K for 4 h. The lump of solid was ball milled and shaped into powder [18,19]. Catalysts were sieved to obtain a particle size between 300 and 425 \(\mu\)m for Multitrack testing.

Oxygen uptake was determined by performing multiple-pulse experiments in the Multitrack setup. At each studied temperature, silver catalysts were reduced by propene (99.8 %) pulses (1 Hz, typically \(1.10^{16}\) molecules until a steady state is reached). Even though propene may irreversibly adsorb on the catalyst surface and reduce the surface sites available for oxygen adsorption, propene is used instead of hydrogen. This procedure is based on reports that hydrogen can reduce only the surface oxygen [20]. Furthermore, during the oxygen uptake experiments at all studied temperatures a negligible amount of total oxidation products (CO\(_2\) and H\(_2\)O, < 1 %), compared to the amount of oxygen taken up by the catalyst, was observed, showing that the amount of irreversibly adsorbed propene is negligible. In this work, a gas pulsing frequency of 0.6 Hz and a mass spectrometer sampling frequency of 250 Hz are used. When a 20 % O\(_2\)/Ar mixture is pulsed over the reduced Ag catalyst, initially there is a significant difference in the responses of Ar and O\(_2\) pulses. The differences in the peak areas correspond to the uptake of oxygen molecules on or into the silver, since there is no interaction of Ar with the catalyst. Therefore, the amount and rate of oxygen uptake can be calculated.

The parameter estimation was performed using MICROMATH SCIENTIST version 2.0. The optimal parameter set was determined by minimizing the sum of squared residuals (least squares-fit). Equations (1), (7), and (8) were solved in SCIENTIST under the assumption of zero oxygen coverage and oxygen partial pressures at the beginning of the adsorption experiment, and fitted to the experimental data. Furthermore, it was assumed that the molecular adsorption constant \(K_1\) and dissociation constant \(K_2\) had a similar temperature dependence.
Results

Oxygen response peak shapes

In Figure 2, steady-state oxygen pulse responses over the promoted Ag/α-Al₂O₃ catalyst are shown. As can be seen in the left part of Figure 2, starting from 573 K, the sharp initial part of the oxygen peak at 0.1 s becomes significantly lower when the temperature is increased, and finally it disappears at 673 K. In a same scale, however, base line shifts of the response are observed when the initial peak height becomes lower (right hand side of Figure 2). This indicates that at higher temperatures oxygen has more intense interaction with the Ag catalyst. In contrast with O₂, the steady-state pulse responses of propene in Figure 3 show less interaction at higher temperatures.

![Graph showing oxygen response peak shapes](image)

**Figure 2.** Steady-state oxygen pulse responses over promoted Ag/α-Al₂O₃ (300-425 μm, 463 mg catalyst, feed composition Ar:O₂=4:1, 1.10⁻¹⁶ O₂ molecules/pulse) (left), and the response signals without shifts in y-axis (right).

In order to study the oxidation state of the Ag catalysts under Multitrack conditions, TGA and TPD experiments were carried out. In Figure 4 a TGA (Thermogravimetric Analysis) of silver(I) oxide shows that Ag₂O decomposes to silver and oxygen above 630 K. A decomposition temperature of 470-570 K is usually reported in literature [21,22]. This indicates that a steady-state oxygen coverage on the Ag surface (in other words Ag₂O formation) at temperatures below 600 K can perhaps not be ruled out. However, Temperature Programmed Desorption (TPD) spectra of both fresh and used catalysts are recorded in the Multitrack setup (not shown) and do not indicate oxygen desorption for any catalyst in the temperature regions studied. Therefore, it can be concluded that under Multitrack conditions the catalysts mainly consist of metallic silver.

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Figure 3. Steady-state propene pulse responses over promoted Ag/α-Al₂O₃ catalyst (300-425 μm, 465 mg catalyst, 1.10¹⁶ propene molecules/pulse).

Figure 4. TGA of Ag₂O and mass spectra for O₂ and CO₂ (in He, 10 K/min).
Oxygen uptake curves were constructed by recording oxygen (20 % O₂ in Ar) pulses over reduced (30 min, 10¹⁶ molecules propene/s) silver using argon as internal reference. Uptake results were fitted by the model that is discussed in the introduction.

Comparison of oxygen uptake with oxygen pulse size shows that at the beginning of the uptake experiment, typically up to 50 % of the oxygen pulse is consumed. The reactor model will, therefore, have to include an oxygen mass balance. During a pulse, the oxygen pressure in the reactor is assumed to be constant in time and over the length of the reactor (CSTR model). These assumptions may be justified since the adsorption process time constant is typically 10 s (for the promoted Ag/α-Al₂O₃, for the CaCO₃ sample it is in the order of minutes), which is large in comparison with the oxygen pulse frequency of 1 s⁻¹. Pressure variations during an oxygen pulse will therefore not have a large impact on the adsorption process.

![Oxygen uptake curve](image)

**Figure 5.** Oxygen uptake curve of the promoted Ag/α-Al₂O₃ catalyst at 473 and 573 K with different pulse sizes (0.735 mg catalyst in 12 mm inner diameter, bed height 6.5 mm). Lines represent the Langmuir-Hinshelwood model fit. Pulse sizes (μmolO₂/gAg/s) are given in the insert.

Determination of adsorption and dissociation parameters

In Figure 5 the oxygen uptake curves for the promoted Ag/α-Al₂O₃ catalyst at 473 and 573 K and with different oxygen pulse sizes are given. As can be seen in this figure, oxygen uptake increases with both temperature and pulse size. The data are fitted using an Arrhenius-like dependency of the parameters K₁, k₂ and K₂ on temperature, the lines in the figure represent the model. The fitting parameters are given in Table 1.
Table 1. Fitting parameters of oxygen uptake model.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>promoted Ag/α-Al₂O₃</th>
<th>Ag/CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$ (Pa⁻¹)</td>
<td>$9.7 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\Delta H$ (kJ/mol)</td>
<td>15</td>
<td>48</td>
</tr>
<tr>
<td>$k_2^0$ (s⁻¹)</td>
<td>$5.2 \times 10^{3}$</td>
<td>$2.8 \times 10^{6}$</td>
</tr>
<tr>
<td>$E_{a,diss}$ (kJ/mol)</td>
<td>17</td>
<td>52</td>
</tr>
<tr>
<td>$K_2^0$ (-)</td>
<td>$1.7 \times 10^{3}$</td>
<td>$8.0 \times 10^{5}$</td>
</tr>
</tbody>
</table>

For the experiment of Figure 5 a dissociation activation energy of 17 kJ/mol can be determined. The promoted Ag/α-Al₂O₃ catalyst was also tested in the temperature range from 573 to 673 K, but the peak broadening and increased interaction make it cumbersome to determine reliable peak areas. Oxygen peak broadening occurs for the unpromoted Ag/α-Al₂O₃ for all temperatures studied from 423 to 673 K. This clearly indicates that adsorption is greatly increased for the unpromoted sample compared to the promoted Ag/α-Al₂O₃, although this cannot be quantified. For the CaCO₃-supported catalyst the oxygen uptake curves are given in Figure 6. Similar to the Ag/α-Al₂O₃ catalyst, the equilibrium uptake above 473 K does not change much upon a temperature increase, but both the dissociation activation energy and adsorption enthalpy are higher (52 and 48 kJ/mol, respectively).

![Figure 6. Oxygen uptake curve of the Ag/CaCO₃ catalyst at 423-573 K (0.337 mg catalyst in 7 mm inner diameter, bed height 11 mm). Lines represent the Langmuir-Hinshelwood model fit. Pulse sizes were approximately 0.20 µmolO₂/gAg/s for all temperatures.](image-url)
Discussion
In Figure 2 oxygen response peak broadening at higher temperatures is observed. This oxygen peak broadening was also observed in a TAP study of Rh/γ-Al₂O₃ at 823-923 K [23]. These researchers have assigned the oxygen peak broadening to an enhanced readsorption due to the lower oxygen coverage at higher temperatures. Based on the TGA of Ag₂O in Figure 4, it can be envisaged that below 600 K steady-state oxygen coverage is high, but at higher temperatures oxygen desorbs due to its thermodynamic instability on silver. The increased number of oxygen adsorption sites then gives readsorption and oxygen peak broadening. However, several TPD spectra of the catalyst samples before and after oxygen adsorption experiments in Multitrack show that no oxygen desorbed, indicating that mainly metallic silver is present. Therefore, the increased interaction with oxygen observed in this study is assigned to an activated adsorption mechanism: the higher the temperature, the higher the rate of adsorption.

Oxygen uptake on Ag was recently described by Badani and Vannice [11] who used the dual-site adsorption expression proposed by Ritchie [24]:

\[
\frac{U_c}{U_c - U} = \alpha \cdot t + 1
\]  

In this equation \(U_c\) is the oxygen uptake measured at infinite time. This equation could not describe the initial rapid adsorption observed by Badani [11] and also did not give satisfactory fits of the oxygen adsorption in this study. In a gravimetric study by Kondarides and Verykios [10] the integrated Elovich equation was used. This equation gives a straight line when uptake is plotted against the logarithm of time. Again, the fits were not satisfactory for our set of data. Therefore, the adsorption was modeled by a Langmuir-Hinshelwood approach.

The kinetic model in this study has been derived on the assumption that oxygen dissociation (step 2 in Figure 1) is rate limiting. This assumption is based on the comparison of Figures 1 and 2 of oxygen and propene adsorption. For oxygen the peaks are broadened at higher temperatures, while for propene the opposite holds. The shape of a peak gives direct information. The front end of the peak is lower the larger the extent of adsorption whereas the tail is longer, the slower the rate of desorption. For O₂ it is clear that the front end intensity decreases with increasing temperature. This is attributed to the increasing dissociative adsorption at higher temperature. The tail for the case of O₂ is longer the higher the temperature. This can be explained by a with increasing temperature increasing extent of readsorption at vacant sites. At low temperature readsorption does not take place because of the activated dissociative adsorption.

The adsorption of propene on a completely reduced Ag sample is favored at low temperatures and decreases at higher temperatures. Iwasawa and coworkers [25] have recently studied oxygen adsorption on Au/TiO₂ catalysts and found peak broadening at temperatures above 373 K for pulses of 1.10¹⁶ molecules, and no broadening for peaks between 298 and 473 K when 1.10¹⁵ molecules were pulsed. Peak broadening at higher temperatures and oxygen gas-phase concentration (larger pulses) was assigned to dissociative oxygen adsorption. For temperatures below 373 K the researchers concluded that molecular oxygen adsorption rather than dissociation was rate limiting by comparing the oxygen peak shapes with theoretical curves based on a molecular adsorption process. In our case the results do not support such a model.

Another possibility for the occurrence of oxygen peak broadening is slow diffusion of oxygen into the silver bulk or to subsurface sites. Oxygen diffusion does probably not play a role under the experimental conditions, as the oxygen coverages are typically up to 5 % of a monolayer (ML) for the catalysts studied. Higher pressures and oxygen coverages may be
needed to observe oxygen diffusion to the silver bulk [7-9] or subsurface sites [26]. This was also shown in the TAP study by Gleave et al. [12] in which O₂ adsorption at 90 kPa and 473 K led to typical uptakes of 13 μmolO₂/gAg for unsupported silver powder compared to a maximum of 0.5 μmolO₂/gAg for the promoted Ag/α-Al₂O₃ catalyst with a comparable silver particle size.

The uptake curves have been fitted under the assumption that the molecular oxygen adsorption enthalpy (∆Hₒ₂) and the dissociation enthalpy (∆Hₒ) are equal. This is based on the observation that the equilibrium uptake does not increase much upon an increase in temperature for both the promoted Ag/α-Al₂O₃ and the Ag/CaCO₃ catalyst. In other words, at higher temperatures less molecular oxygen adsorbs, but this is compensated by an increase in dissociative oxygen adsorption.

For temperatures above 573 K (not shown) the uptake for the promoted Ag/α-Al₂O₃ seems to decrease. This might be attributed to a change in rate-limiting step (molecular oxygen adsorption), but that would not explain the peak broadening of Figure 2. If molecular oxygen adsorption would be the rate-limiting step, similar peaks and temperature dependencies as given in Figure 2 for propene would be expected. The observed decrease in oxygen uptake can most probably be related to the disappearance of the oxygen responses, which renders it difficult to reliably determine peak areas.

The uptake curves of oxygen over promoted Ag/α-Al₂O₃ give an activation energy of 17 kJ/mol for the dissociation constant k₂. This is in excellent agreement with the work by Dean and Bowker [27], who found an activation energy of 16 kJ/mol for an Al₂O₃-supported Ag catalyst by oxygen temperature programmed desorption (TPD) techniques. However, based on the work by Campbell [28], Dean and Bowker assign this activation energy to molecular oxygen adsorption by the electron pickup of O₂ to form O₂⁻. The proposal in this study that the 17 kJ/mol is indeed due to a rate-limiting dissociation step is supported by theoretical work on unpromoted silver clusters. An activation energy for dissociation of 17 kJ/mol was calculated by Salazar and coworkers [29]. Furthermore, Raukema et al. [30] reported a similar dissociation activation energy (16 kJ/mol) using molecular beam studies on a Ag(111) surface.

The oxygen uptake (4-5 μmolO₂/gAg) for the Ag/CaCO₃ catalyst is much higher than the one for the promoted Ag/α-Al₂O₃. This difference is mainly due to the difference in silver surface area of the two catalysts. However, the dissociation activation energy is 52 kJ/mol, which is in good agreement with estimates based on O₂-TPD over Ag(111) [31]. In general, the parameters indicate a decreased molecular adsorption and dissociation on Ag/CaCO₃ compared to promoted Ag/α-Al₂O₃. Part of this effect may be explained by the presence of promoters, which generally tend to decrease dissociation activation energy (for example K on Ag [32]) and adsorption enthalpy (for example Cl on Ag [1]).

In conclusion, the advanced TAP equipment used in this study made it possible to study oxygen uptake on silver catalysts. It has been shown that the rate-limiting step of adsorption is the dissociation of molecular oxygen. The applied Langmuir-Hinshelwood model can be used to determine the activation energy of the oxygen dissociation. For the unpromoted Ag/α-Al₂O₃ catalyst no quantification could be made as most of the oxygen was consumed at the initial stages of the uptake experiment. In principle, this can be easily solved by decreasing the catalyst amount or changing the oxygen pulse size. The promoted Ag/α-Al₂O₃ and the unpromoted Ag/CaCO₃ are clearly different in oxygen adsorption properties, but it is cumbersome to assign this to the effect of promoters, support, or the silver surface structure (particle size, surface roughness). More experiments are needed to investigate these important parameters.

For ethene epoxidation it is generally stated that the surface reaction of ethene and oxygen is reaction rate limiting [1]. However, for higher olefins, like butadiene, norborne,
and styrene, molecular oxygen dissociation was reported to be rate limiting [33]. In general, enhanced adsorption of the higher olefins is to be expected, but also the increased product inhibition was shown to play a role [33]. Therefore, in propene epoxidation the dissociation of oxygen may be rate-limiting under certain conditions and thus determine selectivity of the reaction.

Conclusion

A detailed analysis of oxygen uptake on Ag catalysts indicated that under the vacuum conditions of an advanced TAP setup the observed oxygen response peak broadening is not due to an increased metallic surface area at higher temperatures, but due to the oxygen adsorption being an activated process. Furthermore, oxygen dissociation is the rate-limiting step. The dissociation of oxygen explains the observed oxygen response peak broadening. Adsorption parameters of both a promoted Ag/α-Al₂O₃ and an unpromoted Ag/CaCO₃ could be determined. The oxygen dissociation activation energy for promoted Ag/α-Al₂O₃ was 17 kJ/mol and in good agreement with both theoretical and experimental studies on Ag(111) surfaces, that were previously reported in literature, indicating that dissociation takes place on the regular surface of the 0.4 µm silver particles. For the unpromoted Ag/CaCO₃ similar oxygen coverages were found, however the observed activation energy of 51 kJ/mol suggests a change in oxygen adsorption properties.

Acknowledgement

Dr. P.J. Kooymman of the National Centre for High Resolution Electron Microscopy is acknowledged for performing the electron microscopy investigations.

List of used symbols

- D transfer coefficient m³/s
- F gas supply rate mol/gAg·s
- K₁ molecular oxygen adsorption constant Pa⁻¹
- k₂ oxygen dissociation constant s⁻¹
- k₃ atomic oxygen association constant s⁻¹
- mAg silver amount gAg
- Nₛ number of adsorption sites on silver surface mol/gAg
- P pressure Pa
- R gas constant J/mol·K
- T absolute temperature K
- U oxygen uptake molO₂/gAg
- V vacuum chamber volume m³
- θ surface coverage (-)

_subscripts_

- O regarding atomic oxygen
- O₂ regarding molecular oxygen

_superscripts_

- dif diffused into the silver bulk
- 0 pre-exponential factor
- * adsorbed on the silver surface
References


Propene epoxidation over silver catalysts was studied in an advanced Temporal Analysis of Products (TAP) reactor. The activation of silver by the reaction mixture (propene and oxygen) as well as the interaction of the product (propene oxide, PO) with a conventional ethene epoxidation catalyst (Ag/α-Al₂O₃) were examined by TAP-unique experiments. In the absence of oxygen, PO was chemically converted to a surface species on the Ag/α-Al₂O₃ catalyst. In the presence of oxygen, the surface species were easily oxidized. The catalyst exposed to the reaction mixture showed higher epoxidation selectivity than the catalyst treated by oxygen only. A similar reaction mechanism and active oxygen species compared to ethene epoxidation are suggested.
Introduction

Propene oxide (PO) is a reactive chemical intermediate and used as a raw material for numerous specialty chemicals and materials such as polyurethane, polyether polyols, 1,2-propane diol, and glycol ether. Currently, the worldwide PO production is around 6 million metric tons per year and the PO production processes can be roughly divided in two indirect oxidation processes, the chlorohydrin process and the peroxidation processes [1]. The chlorohydrin process has environmental concerns and equipment corrosion problems caused by chlorine, and the peroxidation process has economical drawbacks due to the complexity of the process and the large capital investment. Much effort has been directed to the development of new direct propene epoxidation processes without any or with environmentally friendly by-products such as water. Most of the work on the new processes can be split evenly between processes based on hydrogen peroxide and so-called direct oxidation processes. Molecular oxygen can be the oxidant in the direct oxidation processes either in the absence or presence of H₂ [2].

A high activity and selectivity to PO can be attained with the hydrogen peroxide process, however the high cost of the oxidant cannot be neglected. Several H₂-O₂ direct oxidation processes are also reported, and the gas phase oxidation process using Au/TiO₂ catalysts received considerable attention [3]. However, the low conversion, the low efficiency of hydrogen, and the catalyst deactivation impede the development of the process.

A promising route for PO synthesis can be a direct oxidation process based on silver catalysts and O₂ as oxidant. Silver-based catalysts are used industrially for the partial oxidation of ethene to ethene oxide and methanol to formaldehyde. Selectivity in excess of 90 % is realized for ethene epoxidation. However, these highly selective ethene epoxidation catalysts are reported to show unacceptably low selectivity (< 6%) for propene epoxidation [4]. Generally, the low selectivity of propene epoxidation is attributed to the high acidity of propene and the formation of an allylic intermediate that is easily oxidized to CO₂ and H₂O [5,6].

It is important to understand the functions of oxygen species on silver in order to elucidate the reaction mechanism and further improve catalysts. The commercial importance and the unique partial oxidation activity of silver catalysts in ethene epoxidation led to numerous publications over the last 40 years. Although there are ongoing discussions about details, most researchers agree to the points that two types of oxygen species are involved in the ethene epoxidation; ‘electrophilic (covalent)’ and ‘nucleophilic (ionic)’ oxygen [7-10]. Based mainly on XPS and TPD studies, it is generally accepted that ‘electrophilic’ and ‘nucleophilic’ oxygen are responsible for epoxidation and total oxidation reaction respectively. Nucleophilic oxygen is readily formed on the regular surface of silver and has an atomic nature, and electrophilic oxygen is most probably formed on the defects of a silver surface. Whether this oxygen is atomic, molecular or of another type is currently under debate [8,11-13]. Although almost no comparison between ethene and propene epoxidation mechanisms has been made until now due to the low selectivity of propene epoxidation, it is important to examine the similarities and differences between the propene epoxidation mechanism and well-studied ethene epoxidation mechanism to be able to improve propene epoxidation over silver catalysts.

In this chapter Temporal Analysis of Products (TAP), a transient response technique, was used to study the causes of the low PO selectivity of ethene epoxidation catalysts (Ag/α-Al₂O₃) and to study the propene epoxidation mechanism. The effects of secondary reactions (further reaction of PO) on the selectivity over α-Al₂O₃-supported catalysts and the dynamic changes of the silver surface induced by reaction mixture were investigated and are discussed.
Experimental

A commercial-type ethene epoxidation catalyst (Ca\(^{2+}\), K\(^{+}\), and Cl\(^{-}\)-promoted 18 wt.% Ag/α-Al\(_2\)O\(_3\)) was used in this study. The promoter loadings were 0.2, 0.04, and 0.01 wt.% for Ca\(^{2+}\), K\(^{+}\), and Cl\(^{-}\), respectively. The use of scanning electron microscopy revealed a homogeneous silver particle size of \(\sim 0.4 \mu\text{m}\).

Steady-state experiments were performed in a microflow setup. In this setup oxygen (10 vol%), propene (20 vol%) and nitrogen (70 vol%) were continuously fed over a 10 ml fixed-bed reactor placed in a fluidized-bed oven. Experiments were carried out at WHSV 0.805 \(\text{g}_{\text{propene}}/\text{g}_{\text{catalyst}}\)h, atmospheric pressure, and 523 K. The analysis of the reaction products was performed using an automated sampling gas chromatograph with a Poraplot Q (0.52 mm diameter, 25 m length capillary column) and He as carrier gas. A flame ionization detector (FID) was used for the analysis. The configuration was able to separate all oxygenated organic components relevant in this study. The oxygen consumption and \(\text{H}_2\text{O}\) production were measured on the same gas chromatograph using a Molsieve 5Å (2 mm diameter, 3 m length column) with a thermal conductivity detector (TCD).

In this study an advanced TAP reactor system, Multitrack (Multiple Time Resolved Analysis of Catalytic Kinetics), was used. The setup has been described elsewhere [14]. Briefly, a fixed-bed reactor (7 mm inner diameter, 11 mm bed height) with a sieved catalyst (particle size of 300-400 \(\mu\text{m}\), 465 mg) is located in a high vacuum system (2.10\(^{-4}\) Pa). Small amounts of reactants (10\(^{14} - 10^{18}\) molecules) can be pulsed into the reactor. At the reactor exit (6.10\(^{-7}\) Pa) the pulse responses are analyzed by four quadrupole mass spectrometers. All four mass spectrometers are able to analyze one of the components in the exit gas stream with a maximum sample frequency of 1 MHz. As the signal-to-noise ratio in this system is excellent, no averaging is needed to obtain good peak signals. This is an important aspect, as transient phenomena may remain unobserved when the peaks have to be averaged. Propene (> 99.8%), 20 % O\(_2\)/Ar, and 1.5 % PO in He (HP or UHP grades, Hoek Loos) were used as reactants. The gases and the corresponding mass to charge ratios used in this study are assigned as follows: water (18), oxygen (32), argon (40), carbon dioxide (44), and propene oxide (58). The m/e 58 signal can also be assigned to acetone and propanal. However, among those compounds the formation of PO is most abundant at short contact time in the microflow setup. Therefore, it is concluded that under Multitrack conditions most of the m/e 58 signal can be assigned to PO. Furthermore, careful analysis of the fragmentation patterns of the m/e 58 signal could rule out the presence of acetone.
Chapter 3

Results

Atmospheric steady-state catalyst testing

In the steady-state testing of the Ag/α-Al2O3 catalyst in the microflow reactor 1.2 % conversion of C3H6 and 7.0 % epoxidation selectivity was found. During the experiment partial oxidation products (PO), total oxidation products (CO2 and H2O), and secondary/side reaction products (oxyglenates; ethanol, acrolein, propanal, acetone) were observed. The amount of oxygenates was low compared to the amount of partial/total oxidation products (about 1.5 % of all products).

Propene epoxidation in the Multitrack

The results of isothermal catalyst testing with simultaneous propene and oxygen pulsing over the promoted Ag/α-Al2O3 catalyst in the Multitrack reactor are shown in Figure 1. Propene epoxidation and total oxidation were observed above 423 K. Both partial and total oxidation products showed a maximum at 573 K, coinciding with the temperature where most of the pulsed oxygen was consumed. For different lower propene/oxygen ratio (propene:oxygen = 1:2, 1:6), more total oxidation products and slightly more partial oxidation product were observed, but the same tendency (maximum activity at 573 K) was found. Although PO was detectable throughout the experiments and it was possible to compare the activity for different temperatures, the epoxidation selectivity and activity were very low (< 0.5 %) under TAP conditions. In addition, the propene pulse response was affected by another large pulse (i.e. Ar/O2 mixture pulse) due to simultaneous pulsing; therefore it was not possible to quantify propene.

Secondary reaction

The responses of PO pulses at different temperatures are shown in Figure 2. The PO response showed a significant delay and broadening at 423 K. When the temperature was increased to 548 K, the peak became sharp. When the temperature was increased further to 673 K, the peak was not delayed but the intensity decreased remarkably. The PO peak areas at different temperatures are also compared and it shows a linear decrease of PO area with temperature (Figure 2). Also, during this experiment very small amounts of total oxidation products were observed. It indicates that in the absence of oxygen PO may react more easily with the Ag/α-Al2O3 catalyst at higher temperature, resulting in the formation of surface species on the catalyst.

PO oxidation in the presence of oxygen was also investigated in Multitrack in the same way as the isothermal catalyst testing. Similar to the propene/oxygen pulse experiment (Figure 1), the catalyst showed oxidation activity above 423 K, and the activity increased monotonously with temperature. Clearly, PO was highly reactive over the promoted Ag/α-Al2O3 catalyst in the presence of oxygen, forming CO2 and H2O.

A transient experiment in Multitrack was carried out to examine surface species formation. In this experiment (Figure 3), the catalyst surface was first treated with PO for 10 min (zone I) and left in HV for about 10 min until stable signals were obtained (zone II). Thereafter oxygen was pulsed and the formation of gas phase species was examined.

Figure 3 shows the transient responses of oxygen, H2O, CO2 and PO at 673 K. Clearly, CO2 and H2O were formed (zone III), and oxygen did not show up for a certain period (80 s) as it was fully converted to oxidize the surface species. A transient experiment at 523 K (not shown) showed less prominent but similar behavior and proved the existence of surface species formation already at the lower temperatures.
**Figure 1.** Reactant and products concentration profiles during isothermal propene and oxygen pulses over promoted Ag/$\alpha$-Al$_2$O$_3$ (feed composition, propene:oxygen = 1:1, $1.0 \times 10^{15}$ O$_2$ molecules/pulse, 1 s$^{-1}$ pulsing frequency).

**Figure 2.** (a) PO pulse responses over promoted Ag/$\alpha$-Al$_2$O$_3$ catalyst and (b) the peak area change ($3.0 \times 10^{15}$ PO molecules/pulse, 1 s$^{-1}$ pulsing frequency).
Figure 3. Transient response experiment over promoted Ag/α-Al₂O₃ catalyst at 673 K; zone (I): PO pulsing; zone (II): no pulsing; zone (III): oxygen pulsing (5.0×10¹³ PO molecules/pulse, 1.0×10¹⁶ O₂ molecules/pulse, 1 s⁻¹ pulsing frequency).

Similar experiments with a different gas composition (zone I: PO and O₂ for 10 min, zone II: no pulsing under HV for 10 min, zone III: O₂ pulsing for 10 min) were carried out at 523 and 673 K (not shown). Large amounts of CO₂ and H₂O were observed in zone I, while no CO₂ and H₂O were observed in zone III at 523 and 673 K.

Examination of silver surface activation

The activation of silver surface by the reaction mixture was first examined by multiple propene pulse experiments over an oxidized silver catalyst (Figure 4). A different reactor with a smaller bed height (12 mm inner diameter, 6.5 mm bed height) and catalyst content (300-400 μm, 765 mg) were used to decrease the interaction of reactants and products with the catalyst. In the multiple pulse experiment a small amount of propene was pulsed continuously with a constant pulsing frequency (1 s⁻¹). The formation of CO₂ and H₂O showed similar responses, the first peak having a maximum intensity, indicating a fast total oxidation over the oxidized silver surface. Contrarily, PO formation showed its maximum peak at the second pulse. It should be noted that this phenomenon was reproducible under the conditions examined.

In another experiment, the interval between the oxygen and the propene pulse was varied to examine the effect of the reaction mixture. Oxygen was always pulsed at 0.1 s and propene at 0.1, 0.6, 1.1, 3.1, 5.1, 7.1, and 9.1 s. Interestingly, when propene and oxygen were pulsed simultaneously (time-lag = 0), the PO formation showed a maximum, and the CO₂ formation a minimum (Figure 5). The epoxidation selectivity was highest when both propene and oxygen were pulsed simultaneously. When there was a time-lag, the amount of PO and CO₂ produced was hardly affected by the length of the time interval. This fact shows that adsorbed oxygen species created by the oxygen pulse at 0.1 s does not desorb easily and stays on the silver surface until propene reacts with the oxygen-covered surface in the time range of
10 s. At the same time, it shows that the oxygen species inducing selectivity is already converted in the non-selective oxygen form within 0.5 s.

Figure 4. Propene pulses over oxidized promoted Ag/α-Al₂O₃ catalyst at 573 K (1.0×10¹⁶ propene molecules/pulse, 1 s⁻¹ pulsing frequency, 1ˢ⁻¹ pulse at 2.1 s).

Figure 5. Effects of interval between oxygen and propene pulses on partial and total oxidation activity over promoted Ag/α-Al₂O₃ catalyst (feed composition, propene:oxygen=1:1, 1.0×10¹⁶ O₂ molecules/pulse).
Discussion

Propene epoxidation and secondary reaction in the Multitrack reactor

Epoxidation and total oxidation of propene occurred above 423 K, and a typical volcano-type behavior was observed for the Ag/α-Al₂O₃ catalyst. When propene peak shapes were analyzed in Multitrack, peak sharpening was observed at higher temperature (Figure 6). This peak sharpening indicates less non-reactive adsorption of propene with the catalyst. Therefore, one of the possibilities to explain the volcano-type activity of epoxidation and total oxidation is that the oxidation reactions are rate-limiting up to the temperature with the maximum yield, and above the temperature propene adsorption on the catalyst surface is rate-limiting. However, carefully comparing the profiles in Figure 1, oxygen consumption remained high and almost constant above the temperature with a maximum oxidation activity, contrary to the significant decreases in partial/total oxidation activities. If the propene adsorption is the rate-limiting step and oxidation products yield truly decreases above 573 K, the amount of consumed oxygen should also decrease.

![Figure 6. Propene pulse responses over promoted Ag/α-Al₂O₃ catalyst (1.0×10¹⁶ propene molecules/pulse, 1 s⁻¹ pulsing frequency).](image)

PO interaction with the Ag/α-Al₂O₃ catalyst was examined and a strong interaction of PO with the catalyst was observed at 423 K relative to higher temperatures (Figure 2). This might indicate a larger chance of secondary reaction when there is oxygen available on the surface at lower temperature. However, the results of PO oxidation in the presence of oxygen showed no oxidation activity below 423 K, and PO would not be further oxidized at this temperature. In the absence of oxygen, a significant decrease in the PO area was observed with a temperature increase (Figure 3), while almost no CO₂ and H₂O were formed. Further examination of other mass to charge ratios showed no other reaction products, indicating that PO remained on the catalyst surface. Thus, the formation of surface species on the catalyst is clearly confirmed. The surface species formation over Ag/α-Al₂O₃ catalysts for ethene epoxidation was reported by Bulushev and co-workers using a transient response technique with in situ infrared spectroscopy [15]. They found that ethene oxide can react with the hydroxyl group of α-Al₂O₃ surface and glycol-like species are formed on the surface. They did not observe deep oxidation products (CO₂, H₂O) formed by α-Al₂O₃ support. Silver was
essential to form the deep oxidation products; surface species are oxidized by activated oxygen on silver. Therefore, PO is reacting with the support and stored on the support surface most probably in the form of glycol-like species or polymer species. Also, PO does not seem to react further on silver itself [16].

The observation of the high oxygen consumption at high temperatures, despite less oxidation products are formed, is probably due to the secondary reaction. The decrease in epoxidation and total oxidation activity above 573 K may be caused by different reasons. The active sites (i.e. active oxygen species) for epoxidation and total oxidation are probably different, and above 573 K only or relatively more of the epoxidizing oxygen may exist on silver. Hence, the oxygen consumption remains high because of more PO formation at higher temperatures. A thermally more stable feature of electrophilic oxygen \( T_{\text{desorption}} \approx 770 \, \text{K} \) than nucleophilic oxygen \( T_{\text{desorption}} \approx 580 \, \text{K} \) supports this view [17]. The reported desorption temperature of nucleophilic oxygen coincides well with the temperature where the maximum activity was observed. Therefore, the decrease in ‘apparent’ epoxidation activity at higher temperature in Figure 1 is most probably related to the occurrence of the secondary reaction. Since there was almost no oxygen available at the high temperatures under the reaction conditions, formed PO is converted to surface species. This is consistent with the high reactivity of PO with the catalyst at these high temperatures.

**Activation of silver surface**

In the multiple propene pulse experiment over the oxidized silver catalysts, the largest formation of PO was observed at the second propene pulse, contrary to the largest formation of \( \text{CO}_2 \) at the first propene pulse. There are several possibilities to explain this phenomenon. Possible causes of the high PO formation at the second pulse could be:

1) \( \text{CO}_2 \) adsorption on silver deactivating total oxidation active sites.
2) Strong adsorption of propene oxide after the first pulse, released in the second pulse.
3) Low oxygen coverage.
4) Restructuring of silver by the first propene pulse.

Considering the possibility 1), adsorbed \( \text{CO}_2 \) may form surface carbonate species with surface oxygen, covering the total oxidation active sites. However, at 573 K the formation of stable carbonate species on silver is unlikely [10,18] and also the sharp peak of \( \text{CO}_2 \) (Figure 4) suggests that there is little interaction of \( \text{CO}_2 \) and the catalyst. The second possibility 2) is that PO formed during the first propene pulse is stored on the catalyst surface, and subsequently removed by the second propene pulse. However, a small amount of formed \( \text{CO}_2 \) by the second propene pulse indicates the existence of oxygen on silver after the first pulse. As has been previously discussed, PO or resulting surface species will be easily combusted above 423 K in the presence of oxygen. Therefore, coexistence of PO and ‘active’ oxygen is very unlikely. Regarding the hypothesis 3), oxygen coverage on silver at the second pulse will be much lower due to reaction in the first pulse. The low oxygen-covered silver surface might form an epoxidation favorable surface. However, generally higher oxygen coverage is reported to show higher epoxidation activity [10]. Finally, possibility 4) appears most likely to explain enhanced PO selectivity, since reconstruction by hydrocarbon species (i.e. propene) are probably possible, similar to the so-called reaction mixture effects in ethene epoxidation [9].

The single pulse time-lag experiment gives more insight in this phenomenon. When there was no time-lag between propene and oxygen pulses (i.e. simultaneous pulse), the selectivity towards epoxidation was the highest. This clearly shows the effect of reaction mixture and that total oxidation is more favorable than epoxidation over the catalyst surface oxidized by only oxygen. The reaction mixture effects on the oxygen species, i.e. an activation of silver surface in epoxidation, found in ethene epoxidation seem applicable to the
propene epoxidation. Most probably, the presence of propene with oxygen promotes the formation of epoxidizing electrophilic oxygen. In the multiple pulse experiment, the first propene pulse over oxidized silver surface modified the oxygen-covered silver surface towards a more epoxidation favorable surface.

The function of hydrocarbon species (ethene, propene) in a reaction mixture on the state of surface oxygen is not yet fully understood, however, the formation of electrophilic oxygen by the reaction mixture is firmly proved by several surface science studies [17,19]. It is also shown that electrophilic oxygen is favorably formed on the defect sites [12,20-22]. Hence the reaction mixture may reconstruct the surface and form defect sites on silver surface.

**Reaction routes**

The Multitrack studies suggest three reaction routes in the oxidation of propene over Ag/\(\alpha\)-Al\(_2\)O\(_3\) catalysts (Figure 7).

![Reaction routes diagram](image)

*Figure 7. Main reaction routes over Ag/\(\alpha\)-Al\(_2\)O\(_3\) catalysts.*

Based on the results of the isothermal testing and the activation of the silver surface in Multitrack, oxygen species on silver seem to determine the route towards PO (a) or towards CO\(_2\), H\(_2\)O (b). Also, a convincing evidence for reaction route (c) has been presented. In order to enhance the epoxidation selectivity, routes (b) and (c) have to be prevented. Commercially, large silver particles (> 50 nm) are preferred in ethene epoxidation in order to enhance the rate of the rate-limiting step (i.e. double-bond adsorption) on its regular surface, by forming ionic silver sites adjacent to nucleophilic oxygen on silver surfaces [7]. However, catalysts with large silver particles will not attain a high epoxide yield due to (i) high acidity of propene and (ii) high reactivity of PO. In the presence of nucleophilic oxygen on the silver surface, most probably the routes (b) and (c) will occur easily. The preferred conditions for ethene epoxidation, the existence of both electrophilic for epoxidation and nucleophilic oxygen for adsorption of double-bond by the adjacent ionic silver, may not be suitable for propene epoxidation. The high acidity makes propene and PO very sensitive to total oxidation and secondary reaction by nucleophilic oxygen, respectively. Therefore, catalysts consisting of small silver particles with many defects on surface (e.g. [20]) are probably preferred because of their ability to form ‘electrophilic oxygen rich’ silver surface. Furthermore, in order to prevent PO from reacting further, the use of inert supports will be crucial for highly selective catalysts in propene epoxidation.
Conclusion

An advanced TAP reactor, Multitrack, was found to be a useful tool to study the dynamic changes of molecular interactions of reactants and products with catalyst samples. Furthermore, comparable results with studies using surface science techniques could be obtained. The high sensitivity of Multitrack rendered it possible to detect PO in the vacuum condition and to study the reaction mechanisms.

Secondary reactions over a promoted Ag/α-Al₂O₃ catalyst were observed in Multitrack. In the absence of oxygen, PO was stored on the catalyst surface in the form of surface species, which was easily oxidized to CO₂ in the presence of oxygen. The secondary reaction mechanism of PO is most probably the same as the one of ethene oxide.

The coexistence of propene and oxygen favors epoxidation. This indicates similarities of active oxygen species in propene and ethene epoxidation. The selectivity enhancement is probably due to surface reconstruction of silver induced by a hydrocarbon, yielding defect sites to stabilize electrophilic oxygen.

Therefore, knowledge on ethene epoxidation, especially details in reaction mechanisms, will be useful to understand the mechanism and improve catalysts in propene epoxidation. The results of this study suggest that the prevention of total oxidation caused by high acidity of propene and secondary reactions caused by high reactivity of propene oxide is crucial to improve propene epoxidation over silver catalysts. The use of inert support and silver catalysts with more surface defects or reaction conditions forming surface defects will be advantageous.

References


XPS and Mössbauer characterization of Au/TiO₂ propene epoxidation catalysts

Gold catalysts supported on TiO₂ and TiO₂/SiO₂ were used in gas-phase propene epoxidation with a hydrogen-oxygen mixture. The catalysts were characterized by ¹⁹⁷Au Mössbauer Absorption Spectroscopy (MAS), X-ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM).

Gold particle sizes of 1 wt.% Au catalysts calcined at 673 K ranged from 3 to 6 nm. Two Au contributions were found in Mössbauer spectra, and assigned to bulk metallic Au atoms in the core of a gold particle, and metallic gold on the outer surface of this particle. Surface gold atoms exhibit a smaller recoil-free fraction than Au atoms in the core of a particle. This has been assigned to the surface atoms being less coordinated. By MAS no evidence for charge transfer from support to Au particle could be found. Active epoxidation catalysts containing 10 wt.% Au could be prepared with a similar gold particle size compared to the 1 wt.% samples. Auger lines of the 10 wt.% Au catalysts could be determined. From the combinations of photoelectron and Auger lines, the Auger parameters were calculated. These parameters were found to be more indicative of the chemical state of the gold than the photoelectron line alone. The Auger parameters confirmed that the surface layer of 3 - 5 nm gold particles is metallic. Shifts in Au 4f/2 binding energy with respect to metallic gold show that the C 1s reference should be used with caution. Furthermore, final state effects due to the reduced coordination of metallic surface gold atoms will also give shifts in binding energy.

Both XPS and MAS indicate that deactivation of Au/TiO₂ during propene epoxidation is not due to a change in the active gold species and has to be related to the TiO₂ support. In the preparation of Au/TiO₂ via deposition-precipitation Au(OH)₃ species are converted to metallic gold during calcination. Gold particles do not gradually grow during calcination, possibly due to the simultaneous conversion of Au(OH)₃ moieties with dehydroxylation of the TiO₂ support. Epoxidation activity was found to increase with the amount of metallic gold. Catalysts consisting of only oxidized gold were found to be inactive. No evidence for oxidized gold active in the propene epoxidation reaction using H₂ and O₂ could be found.
Chapter 4

Introduction

Gold has traditionally been regarded as chemically too inert to be of any catalytic interest. However, it was found recently that contrary to bulk gold, very small gold particles show exceptional catalytic activity [1]. Although gold nanoparticles have been prepared and studied since ancient times, especially for their use as pigments, their role in catalysis has been limited. This is mainly due to the fact that highly dispersed gold catalysts are difficult to prepare, contrary to the other precious metals for which impregnation routes easily yield supported metal nanoparticles [1].

The availability of new preparation routes and characterization techniques, like Transmission Electron Microscopy (TEM), has led to new catalytic systems that show remarkable activity. For example, Haruta and coworkers showed that highly dispersed gold on a titania support is very active for CO oxidation at low temperature. These researchers also reported that the same catalyst system can selectively produce propene oxide from propene, oxygen, and hydrogen [2]. These catalysts can be prepared by deposition-precipitation of Au(OH)₃ that typically yields 4-6 nm gold particles. Active Au/TiO₂-based propene epoxidation catalysts have typically a gold loading of up to a few wt.% and give up to 2 % propene oxide yield at > 99 % selectivity [3]. As the development of a direct gas-phase propene epoxidation process, comparable to that of ethene, is highly desired, a lot of effort is undertaken to understand this catalytic system and to come to new and/or improved catalysts.

The catalytic activity and selectivity of gold for epoxidation can be tuned by the selection of metal oxide supports, and control of the size of the gold particles.

Detailed studies highlighting the support influence on propene epoxidation with hydrogen and oxygen have been presented by Nijhuis et al. [3] and Mul et al. [4]. Gold catalysts based on titanium-containing supports as TiO₂, TiO₂/SiO₂, and Titanium-Silicalite-1 (TS-1) were prepared by deposition-precipitation. Nijhuis et al. propose a mechanism involving epoxidation of propene with a hydroperoxide-like species over a tetrahedral Ti site. Selection of the metal oxide support is important. Deactivation occurs over a TiO₂ support, while application of a dispersed titanium support (for example, TiO₂/SiO₂) prevents catalyst deactivation [3].

It is claimed that in propene epoxidation gold is responsible for the formation of hydroperoxide-like species from H₂ and O₂ [3]. In CO oxidation the role of the gold is different: it has been shown that the (reducible) support supplies oxygen to the gold-support interface to react with CO that is adsorbed on gold [5].

Haruta’s work on propene epoxidation [2] indicates the existence of a critical size for gold in the reaction of propene with oxygen and hydrogen over Au/TiO₂ at a gold particle diameter around 2 nm. It is proposed that for gold particles larger than 2 nm, propene oxide is selectively formed, while for particles smaller than 2 nm only propane is formed [2]. A similar particle size effect was also studied by Goodman and coworkers. From Scanning Tunneling Spectroscopy (STS) experiments on Au/TiO₂ they found for decreasing particle size a metal to non-metal transition at about 4 nm. Clusters of 3.2 nm were shown to exhibit the highest activity for CO oxidation [6,7]. Au/TiO₂-based catalysts consisting of gold in a (partially) oxidized state were recently claimed by Dow Chemical to be active in propene epoxidation [8]. The presence of oxidized gold was evidenced by XPS, TEM, and UV-Vis studies [8,9].

As stated in the paragraphs above, an important aspect of the mechanism is the state of the gold atoms at the surface of the gold particle and at the gold-support interface. Several characterization techniques have been applied to elucidate the nature of the active site(s), like FTIR [10] and XPS [11], but so far no conclusive answers have been found. Main challenge is the low concentration of gold in active catalysts. However, in general an increase in gold
loading will decrease the catalytic epoxidation activity, as higher gold loadings will usually result in larger gold particles.

In the present study the nature of the active gold species in Au/TiO₂-based catalysts has been investigated by X-ray Photoelectron Spectroscopy (XPS) and ¹⁹⁷Au Mössbauer Absorption Spectroscopy (MAS). Till date, most ¹⁹⁷Au Mössbauer catalyst characterization studies have been carried out on Au/Fe-based systems [12,13] and occasionally on the Au/TiO₂-based catalysts [14]. In combination with Transmission Electron Microscopy (TEM), which gives information on the gold particle size, ¹⁹⁷Au Mössbauer has been applied to elucidate the active gold species. As it is element selective and sensitive to the local surroundings of the atoms, ¹⁹⁷Au Mössbauer Effect Spectroscopy is an excellent probe for such purposes [15]. In addition, XPS has been used because of its surface sensitivity.

**Experimental**

Three 1 wt.% gold catalysts have been prepared by static deposition-precipitation of Au(OH)₃ at a pH between 9.5 and 10 [3]. AuCl₃ (Aldrich) dissolved in water was used as gold source. As a support TiO₂ (P25 Degussa), TiO₂/SiO₂ (prepared via reaction of titanium(IV)ethoxide (Fluka, 97 %) in 2-propanol with surface hydroxyls of SiO₂ and calcination at 873 K [4]) and SiO₂ (Aldrich Davisol 646) were used.

Both a 1 and 10 wt.% Au/TiO₂ have been prepared via a gold colloid route according to Grunwaldt et al. [16] using tetrakis(hydroxymethyl)phosphonium chloride (THPC) as reductant and stabilizer. Furthermore, gold colloids were prepared based on a method by Porta et al. [17] using LiBH₄ as reductant and polyvinylpyrrolidone (PVP) as stabilizer. For the colloid method, the required amount of TiO₂ was added to the colloid suspension, centrifuged and washed at least three times with its own volume with distilled water to yield a Au/TiO₂ catalyst. Again, both 1 and 10 wt.% Au catalysts were prepared. The samples were dried at 368 K for 8 h prior to calcination.

All catalysts have been calcined under static conditions at 673 K unless stated otherwise.

**Characterization**

Transmission Electron Microscopy (TEM) was employed to determine the gold particle size. A Philips CM30T electron microscope with a LaB₆ filament as the source of electrons was operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

¹⁹⁷Au Mössbauer Absorption Spectroscopy (MAS) was used to determine the valence state and the local coordination of the gold atoms. For the ¹⁹⁷Au MAS measurements, the applied ¹⁹⁷Au γ-ray sources were obtained by irradiating enriched platinum powder (97.4 % ¹⁹⁶Pt) with thermal neutrons for 24 hours in the nuclear reactor of the Interfacultair Reactor Instituut, Delft, The Netherlands. This resulted in a 200 MBq Mössbauer source due to the ¹⁹⁶Pt(n,γ)¹⁹⁷Pt reaction. The subsequent beta-decay process to the Mössbauer isotope ¹⁹⁷Au has a half-life of 18.3 hours, which determines the half-life of the ¹⁹⁷Au Mössbauer source. Mössbauer spectra have been recorded in transmission geometry. Both source and absorber were cooled to a temperature of 4.2 K unless stated otherwise. For detection of the transmitted photons a high purity Ge detector has been used. In the Mössbauer absorption spectrum contributions from different Au sites in the catalysts can be distinguished by their isomer shift (IS, center of gravity on the velocity axis, expressed in mm/s) and quadrupole splitting (QS, distance between the two minima of a doublet). The isomer shift (IS) is a measure for the s-electron density at the nucleus of a gold atom and yields information on its valence state. The quadrupole splitting (QS) gives information on the electric field gradient around the nucleus.
which can be influenced e.g. by differences in the coordination symmetry of the neighboring atoms. Combinations of IS and QS give information on the oxidation state. The source velocity has been calibrated by a Michelson interferometer. All IS values are given according to this (absolute) scale. For the data analysis, the peak position of the bulk gold contribution was fixed at -1.22 mm/s (the reference value obtained for metallic bulk gold), unless stated otherwise. Further details on the analysis procedures are given in the corresponding table captions.

X-ray Photoelectron Spectroscopy (XPS) was employed to determine the chemical state of the surface gold atoms of the catalysts. To this end not only the value of the binding energy of the Au 4f\textsubscript{7/2} electrons was considered, but also the so-called Auger parameter [18] by analyzing the Au M\textsubscript{3}N\textsubscript{67}N\textsubscript{67} electrons. In particular, the value of the Auger parameter reflects the chemical environment of the Au atom and without being effected by sample charging or Fermi-level shifts. For the XPS analysis, samples were prepared from the Au/TiO\textsubscript{2} catalysts by pressing the material into a soft indium foil (Alfa Products UK, 99.9975% In) on a flat specimen holder. XPS spectra of Au 4f, O 1s, C 1s, and Ti 2p photoelectron lines and the Au M\textsubscript{3}N\textsubscript{67}N\textsubscript{67} Auger line were recorded with a PHI 5400 ESCA instrument with a step size of 0.1 eV. The instrument was set at a constant analyzer pass energy of 35.75 eV and unmonochromatized incident Mg X-ray radiation (Mg K\textsubscript{α1,2} = 1253.6 eV) was used. The Au M\textsubscript{3}N\textsubscript{67}N\textsubscript{67} Auger electrons with a kinetic energy of about 2015 eV can only be generated with the 'Bremsstrahlung' produced by the X-ray source operating at 15 kV and 400 W using the Mg anode. Therefore, the Auger line is recorded at an apparent negative binding energy [19]. The energy scale of the Spherical Capacitor Analyzer (SCA) spectrometer was calibrated according to a procedure described in the literature [20]. The electrons emitted from the sample were detected at an angle of 45° with respect to the sample surface. An elliptic area of 1.1 x 1.6 mm was analyzed. As a reference for metallic Au, spectra were recorded from a film of pure Au, obtained after sputter cleaning with 4 keV Ar\textsuperscript{+} ion beam rastering an area of 5 x 5 mm for 10 minutes.

In order to exclude any effects on the values of binding energies due to charging of the sample during the XPS analysis, all data are corrected by a linear shift such that the peak maximum of the main line in the C 1s spectra corresponds with 284.8 eV. The photoelectron binding energies (BE) and the Auger electron kinetic energies were determined from the spectra by taking the value corresponding with the peak maximum after a 7-points Savitzky-Golay smoothing of the signal.

The Auger parameter \( \alpha \) of Au in the 10 wt.% Au on TiO\textsubscript{2} samples has been determined by using the formula [18,21]:

\[
\alpha = \text{BE(Au 4f\textsubscript{7/2}}) + \text{KE(Au M\textsubscript{3}N\textsubscript{67}N\textsubscript{67}})
\]

In this equation BE(Au 4f\textsubscript{7/2}) is the binding energy of the Au 4f\textsubscript{7/2} electrons, and KE(Au M\textsubscript{3}N\textsubscript{67}N\textsubscript{67}) the kinetic energy of the Au M\textsubscript{3}N\textsubscript{67}N\textsubscript{67} Auger electrons.

For determination of the propene epoxidation activity, steady-state experiments were performed in a microflow setup. In this setup nitrogen (70 vol%), oxygen (10 vol%), hydrogen (10 vol%), and propene (10 vol%) were continuously fed over a 10 ml fixed-bed reactor placed in a fluidized-bed oven. The Weight Hourly Space Velocity (WHSV) was 0.71 \( \text{g_{propene}}/\text{g_{cat}}/\text{h} \). The analysis of the reaction products was performed using an automated sampling gas chromatograph, analyzing a gas sample every 12 minutes. A Poraplot Q 0.53 mm diameter, 25 m length capillary column was used with He as carrier gas. A flame ionization detector (FID) was used for the analysis. The hydrogen and oxygen consumption could be measured on the same gas chromatograph using a Molsieve 5Å, 2 mm diameter, 3 m length column, and a TCD detector.
Results

In previous work propene epoxidation catalysts have been prepared by deposition-precipitation of Au(OH)$_3$ at a pH between 9.5 and 10 on TiO$_2$-based supports [3]. In a standard preparation procedure these samples are washed to remove Cl$^-$ ions and subsequently subjected to calcination at 673 K. Formation of metallic gold during calcination is evidenced by the change in color of the white sample after deposition-precipitation and washing to a red/purple sample after calcination (due to the surface plasmon resonance or Mie scattering [22] of the metallic gold particles).

The preparation procedure of 1 wt.% Au/TiO$_2$ catalysts has been investigated in more detail. To investigate the influence of Cl$^-$ on the gold, both washed and unwashed samples are tested in the gas-phase epoxidation reaction. Furthermore, a stepwise calcination of the washed samples is performed, whereby after each calcination step the epoxidation activity has been determined. Propene oxide (PO) yields over these stepwise calcined Au/TiO$_2$ samples are recorded after 2 hours reaction time at 323 K. PO is the only product observed and in Figure 1 the PO yield is given as a function of the calcination temperature. The non-calcined samples (both washed and unwashed) are not active in the epoxidation reaction, but activity of the washed samples increases with calcination temperature.

![Graph showing PO yield and metallic surface Au fraction as a function of calcination temperature](image)

**Figure 1.** PO yield (% of propene feed) and fraction of metallic surface gold species in the Mössbauer spectrum as a function of calcination temperature of Au/TiO$_2$ catalyst. Reaction data were taken after 2 hours on stream at 323 K. Under these conditions less than 5 % of the initial activity of the Au/TiO$_2$ is lost due to deactivation.

After each calcination step a Mössbauer spectrum of these 1 wt.% Au/TiO$_2$ samples is recorded. The spectra as given in Figure 2a are fitted with in total four gold species with fixed IS (isomer shift) and QS (quadrupole splitting). The analysis results are given in Table 1.
Figure 2. (a) MAS spectra of 1 wt.% Au/TiO$_2$ catalyst as a function of calcination temperature. Spectra were recorded at 4.2 K and have been fitted with four sets of $(I_S, Q_S)$ values. The spectra are given in the same intensity scale but vertically shifted.
Figure 2. (b) TEM micrographs of the Au/TiO₂ samples calcined at the temperatures as given in the insert.
Table 1. Relative intensity (%) of the four (IS,QS) contributions in the Mössbauer spectra of 1 wt.% Au/TiO\textsubscript{2} at different calcination temperatures.

<table>
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The spectra of the non-calcined samples can be described with two contributions at large IS and QS. These two contributions decrease in intensity during calcination and above 573 K and higher calcination temperature the spectrum consists of two other contributions with lower IS. The peak at IS and QS of -1.22 and 0 mm/s, respectively, is fixed at the position of the Au foil reference. At calcination temperatures above 473 K the spectrum is largely determined by this so-called bulk gold contribution. The increase in relative intensity of this bulk gold contribution with increasing calcination temperature is accompanied by an increase in intensity of the contribution at IS and QS of -1.26 and 2.69 mm/s, respectively. This latter contribution is also given in Figure 1 as a function of calcination temperature.

In Figure 2b the corresponding TEM micrographs are given. No gold particles are observed on the non-calcined washed sample, also not under prolonged exposure to the electron beam (not shown), although the TiO\textsubscript{2} crystals become more amorphous. Metallic gold particles (dark spots in the micrographs) appear after calcination at 373 K. Surprisingly, the particles do not increase in size, but only in number during the calcination procedure. The formation of metallic gold particles seems to proceed inhomogeneously throughout the TiO\textsubscript{2} sample, which is confirmed by visual inspection of the sample calcined at 373 K. Both white and light purple support particles can be observed separately. During calcination at 423 K and higher temperatures the sample becomes more purple and at the same time homogeneous by color (all particles have the same color).

The Mössbauer spectrum of the 1 wt.% Au/TiO\textsubscript{2} catalyst (calcined at 673 K) is given in Figure 2 (bottom spectrum). In Figure 3 and Table 2 Mössbauer Absorption Spectroscopy (MAS) data of this fully calcined catalyst are compared with MAS data of 1 wt.% Au on a TiO\textsubscript{2}/SiO\textsubscript{2} and on a SiO\textsubscript{2} support.
Table 2. Mean gold particle sizes as determined by TEM and (IS, QS) of the two contributions in the Mössbauer spectra of 1 wt.% Au catalysts on different supports. One contribution was fixed at (-1.22, 0) mm/s. The relative intensity of the contributions is also given. All samples were calcined at 673 K. The Au/TiO₂ catalyst was both tested before and after epoxidation reaction (spent).

<table>
<thead>
<tr>
<th>sample</th>
<th>size (nm)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>intensity (%)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂ 673 K</td>
<td>5.2</td>
<td>-1.22</td>
<td>0</td>
<td>90</td>
<td>-1.26</td>
<td>2.69</td>
<td>10</td>
</tr>
<tr>
<td>Au/TiO₂ 673 K spent</td>
<td>5.2</td>
<td>-1.22</td>
<td>0</td>
<td>90</td>
<td>-0.64</td>
<td>1.77</td>
<td>10</td>
</tr>
<tr>
<td>Au/TiO₂/SiO₂ 673 K</td>
<td>3.2</td>
<td>-1.22</td>
<td>0</td>
<td>78</td>
<td>-1.09</td>
<td>2.52</td>
<td>22</td>
</tr>
<tr>
<td>Au/SiO₂ 673 K</td>
<td>6</td>
<td>-1.22</td>
<td>0</td>
<td>66</td>
<td>-0.98</td>
<td>2.58</td>
<td>34</td>
</tr>
</tbody>
</table>

A preliminary report on these three spectra has been published previously [23]. The spectra typically consist of a predominant bulk gold contribution (IS = -1.22 mm/s, QS = 0 mm/s), indicating the presence of metallic gold that is not perturbed by the support. Besides the bulk gold contribution, one other Au species is found with varying IS and QS. The spectral contribution of this second Au species is depending on the support. TEM analysis of these catalysts (not shown) was carried out to determine the average gold particle sizes. Gold particle sizes stated in Table 2 are depending on the support and the observed sizes are in good agreement with previously reported results [3]. The TiO₂ and TiO₂/SiO₂-based catalysts show a small particle size distribution (2σ = 2 nm), but for the Au/SiO₂ a broad particle size distribution is found in the form of large agglomerates (up to 30 nm in size), consisting of primary Au particles about 6 nm in diameter. As already pointed out by Nijhuis and coworkers [3] the 1 wt.% Au on TiO₂/SiO₂ catalyst shows 1.0 % propene oxide (PO) yield with > 99 % selectivity at 373 K. The TiO₂ based catalyst is already active at 323 K, where propene conversion to PO is 0.8 % at > 99 % selectivity (Figure 1). The Au/SiO₂ catalyst is not active in epoxidation, which has been assigned to the absence of a Ti epoxidation center [3,4].

As reported in the literature [3,4] the Au/TiO₂ catalyst shows deactivation after several hours on stream above 348 K. This was shown to be due to the ring opening of PO (propene oxide) and irreversible adsorption of the formed glycol-like species to the Ti epoxidation center [4]. The Au/TiO₂ catalyst was subjected to the epoxidation reaction at 348 K and showed only 25 % of its initial PO yield after 10 hours on stream, maintaining > 99 % selectivity and a constant water production over the investigated time interval. Subsequently, its Mössbauer spectrum was recorded and it is given in Figure 3. TEM analysis (not shown) did not indicate sintering of the gold particles, and the spectral contributions (Table 2) are in good agreement with the fresh Au/TiO₂ sample.
Figure 3. MAS spectra of fresh Au/TiO$_2$ catalyst compared to Au/TiO$_2$ after reaction (spent), Au/TiO$_2$/SiO$_2$, and Au/SiO$_2$. All catalysts had a 1 wt.% Au loading and were calcined at 673 K. The spectra were recorded at 4.2 K and have been fitted with two gold contributions, one with IS being fixed at -1.22 mm/s, one with varying (IS, QS). The spectra are given in the same intensity scale but vertically shifted.
XPS measurements have been carried out on some of the Au/TiO₂ samples. The two Au/TiO₂ samples calcined at 673 and 423 K, and the spent Au/TiO₂ have been analyzed and the Au 4f lines are given in Figure 4.

![Figure 4. XPS spectra of 1 wt.% Au/TiO₂ samples, from bottom to top: Au/TiO₂ calcined at 673 K, same catalyst after propene epoxidation reaction, and Au/TiO₂ calcined at 423 K.](image)

The Au 4f₇/₂ BE (binding energy) is given in Table 3.

**Table 3.** Au 4f₇/₂ binding energy and Au M₅N₆₇N₆₇ kinetic energy with reference to C 1s at 284.8 eV for different Au catalysts and the Au reference material. The Auger parameter α has been determined from the Au 4f₇/₂ binding energy and Au M₅N₆₇N₆₇ line positions (see text for details).

<table>
<thead>
<tr>
<th>sample</th>
<th>BE(Au 4f₇/₂) (eV)</th>
<th>KE(Au M₅N₆₇N₆₇) (eV)</th>
<th>α (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt.% Au/TiO₂ 673 K</td>
<td>83.29</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 wt.% Au/TiO₂ 673 K spent</td>
<td>83.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 wt.% Au/TiO₂ 423 K</td>
<td>84.21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10 wt.% Au/TiO₂ (THPC)</td>
<td>83.47</td>
<td>2015.61</td>
<td>2099.08</td>
</tr>
<tr>
<td>10 wt.% Au/TiO₂ (PVP)</td>
<td>83.49</td>
<td>2015.39</td>
<td>2098.88</td>
</tr>
<tr>
<td>Au reference</td>
<td>84.05</td>
<td>2015.10</td>
<td>2099.15</td>
</tr>
</tbody>
</table>
The C 1s line position is used as a reference, which results in negative Au 4f_{7/2} BE shifts of up to 0.7 eV relative to the 84.00 eV value for metallic gold [24]. Clearly, it can be seen that the Au 4f BE of Au/TiO₂ calcined at 673 K does not change much after propene epoxidation reaction. For the spent Au/TiO₂ catalyst two C 1s peaks (not shown) are observed, the second peak has 1.45 eV higher BE than the first peak of the usual hydrocarbon impurity and can be assigned to C-O bond containing carbon species [25]. In Figure 4 and Table 3, it can be seen that the Au/TiO₂ sample calcined at 423 K has a higher BE of about 0.9 eV compared to the sample calcined at 673 K. The Auger signals for 1 wt.% Au samples are too weak to be observed. Therefore, higher gold loaded samples were additionally prepared using a different preparation method.

In Figure 5 TEM micrographs of the four catalysts prepared via the colloid routes are given.

![TEM micrographs](image)

**Figure 5.** TEM micrographs of 1 (a and c) and 10 (b and d) wt.% Au/TiO₂ catalysts prepared via a colloid synthesis route: (a) and (b) using colloid route via tetrakis(hydroxymethyl)phosphonium chloride (THPC), and (c) and (d) using colloid route via polyvinylpyrrolidone (PVP).

Both the 1 and 10 wt.% Au/TiO₂ catalysts prepared using tetrakis(hydroxymethyl)phosphonium chloride (THPC) as stabilizer and reductant yield gold particles in a narrow size range around 5 nm (4 - 6 nm), independent of gold loading.
However, these samples are not active in the epoxidation reaction, as shown in Figure 6. Using polyvinylpyrrolidone (PVP) as stabilizer and LiBH₄ as reductant, Au particles with a similar mean particle size appear on the support of both 1 and 10 wt. % samples. The distribution of particle sizes (3 - 10 nm) turned out to be somewhat larger than that observed for the THPC sample. For the 10 wt. % PVP sample also a few 15 nm agglomerates consisting of 5 nm primary particles were observed. However, the overall particle size is reasonably uniform and the mean particle size is comparable to the THPC-based catalysts. The resulting PVP catalysts are both active and selective in propene epoxidation.

![Figure 6. PO and propane yield (% of propene feed) as a function of gold loading and preparation route. DP = deposition-precipitation, THPC = colloid route via tetrakis(hydroxymethyl)phosphonium chloride, and PVP = colloid route via polyvinylpyrrolidone. Reaction data were taken after 30 minutes on stream at 348 K. Under these conditions less than 5 % of the initial activity of the Au/TiO₂ is lost due to deactivation.](image)

Using XPS, no profound differences in C 1s intensities of these 10 wt. % Au samples (not shown) were observed, indicating that calcination at 673 K removes all hydrocarbon impurities remaining from the stabilizers used in the colloid synthesis. The epoxidation inactivity of the Au/TiO₂ (THPC) catalyst might be attributed to remaining phosphorus. A P 2p₃/2 peak in the XPS spectrum has been observed at BE 133.8 eV for the 10 wt. % Au/TiO₂ (THPC) sample, which corresponds to either phosphate or Au-P complexes [24]. No profound differences for the Au and O intensities are observed, so that P may be present on the TiO₂ support as well as on the Au particles.

For the 10 wt. % Au/TiO₂ catalysts, the Auger parameters were determined from the Au 4f XPS and the Au M₅N₇M₆7 Auger peaks as given in Figure 7. The relevant parameters are given in Table 3. For comparison, also the spectra of the gold film reference are reported. The unsmoothed Au 4f XPS and the M₅N₇M₆7 Auger signals are given in Figure 7. All signals were smoothed before the peak maximum was determined. This gave less than 0.05 eV change in BE for the Au reference peak as determined with and without smoothing. The Au 4f spectra of the two 10 wt. % catalysts clearly show a shift to lower BE compared to the Au reference.

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Figure 7. XPS spectra of Au 4f (left) and Auger $M_{55}N_{67}N_{67}$ (right) for 10 wt.% Au on TiO$_2$ catalysts prepared via THPC or PVP route compared to Au reference (Au film). BE = binding energy, KE = kinetic energy

The Auger parameter $\alpha$ of Au in the 10 wt.% Au on TiO$_2$ samples has been determined by use of Equation (1). These $\alpha$-values are given in Table 3 relative to the value determined for the Au reference. The table shows for both samples a negative shift in Auger parameter compared to the Au film reference.
Discussion

Propene epoxidation activity over Au/TiO$_2$ catalysts increases as a function of calcination temperature. In Figure 1 it can be seen that at the maximum calcination temperature of 673 K the highest PO (propene oxide) yield is found. During calcination the white samples turn into their characteristic purple color, which is indicative of the presence of small particles of metallic gold [22]. As can be seen in Figure 2, Mössbauer Absorption Spectroscopy (MAS) is an excellent tool to study the nature of the gold species. A profound change is found for gold species during the calcination treatment. The spectra in Figure 2 can be described by in total four contributions with different IS (isomer shift) and QS (quadrupole splitting). Combinations of IS and QS are indicative of oxidation state of gold. Therefore, in Figure 8, the obtained (IS, QS) combinations are summarized. Literature values of several gold compounds containing Cl and O, and gold colloids are also shown for comparison. In order to illustrate the reliability of the MAS method, IS and QS values of HAuCl$_4$ were taken from the literature [13] as well as experimentally determined in this study and showed a maximum difference in IS and QS of only 0.2 mm/s. The lines in Figure 8 correspond to the region in which usually Au compounds with two-coordinated planar (Au$^1$) or four-coordinated square-planar (Au$^{III}$) appear [26].

**Figure 8.** IS and QS plot of propene epoxidation catalyst data (closed symbols) compared to literature values (open symbols, Au/Mylar from [32], Au$_2$O$_3$ from [27], and other Au compounds from [13]). Lines indicate the regions in which Au$^1$/Au$^{III}$ compounds are usually reported [26]. IS and QS combinations denoted as Au(OH)$_2$/TiO$_2$ are the two contributions found for the non-calcined TiO$_2$ samples of Figure 2. Catalysts calcined at 373 K and higher consist of two contributions: bulk gold and a contribution depending on support (TiO$_2$, TiO$_2$/SiO$_2$, SiO$_2$ as given in Figures 2 and 3). Furthermore, the (IS, QS) of a spent Au/TiO$_2$ (taken from Figure 3) catalyst is given.
The spectra of both the washed and unwashed Au(OH)$_3$/TiO$_2$ samples consist of two contributions at (IS, QS) of (2.38,3.32) and (2.84,4.27). The IS-QS parameters for the two species are well in the range of what is usually measured for Au$^{III}$ compounds, but both IS and QS are higher than reported in the literature for Au$^{III}$-oxyhydroxide [13] and Au$_2$O$_3$ [27]. These literature values show that both IS and QS increase going from Au$_2$O$_3$ to Au(OH)$_3$. Therefore, probably the two species observed for non-calcined wet samples are indeed both due to Au(OH)$_3$ supported on TiO$_2$. The (IS, QS) sets of the two species are in good agreement with the two species found for Au(OH)$_3$ on Mg(OH)$_2$ as reported by Kobayashi et al. [14]. A shift of IS and QS to higher values was also observed for HAuCl$_4$ and AuCl$_4$/C as reported by Wagner et al. [13]. For AuCl$_4^-$ on activated carbon both IS and QS increase relative to the starting material HAuCl$_4$. Part of this shift can be explained by the amorphous character of the supported Au species and a less symmetric coordination. Furthermore, based on the comparison of both washed and unwashed non-calcined samples, it can be concluded that the presence of Cl$^-$ has no detectable influence on the gold atoms. In other words, it is likely that only Au(OH)$_3$ and not a gold chloro-hydroxy species is deposited on the TiO$_2$ support at room temperature and pH 9.5-10. At this high pH the existence of chlorohydroxy species is unlikely, which is also supported by spectroscopic studies in the literature [28].

When calcined up to a calcination temperature of 423 K, the two just-mentioned Au$^{III}$ species gradually decrease in intensity. For both spectra after calcination of 373 and 423 K a misfit can be observed in Figure 2 (in the 3 - 6 mm/s range on the velocity axis), which indicates that the IS-QS parameters of the two Au$^{III}$ species slightly change during calcination. In fact, doublets with slightly different (IS, QS) would give better analyses. If the IS and QS positions are not fixed, the IS of the third contribution (Table 1) is decreased from 2.4 mm/s without calcination to 2.2 mm/s after calcination at 373 and 423 K, respectively. At 573 K, the spectrum is comparable to the Au/TiO$_2$ catalyst calcined at 673 K. These spectra of samples calcined at high temperature can also be described by two contributions, but with lower (IS, QS) values compared to the two Au(OH)$_3$ species. From 373 K onward these two other contributions appear in the spectra. One contribution is predominant and has IS = -1.22 mm/s and no quadrupole splitting. This peak is fixed at the values obtained for the gold foil reference and is assigned to metallic (bulk) gold. The presence of metallic gold particles is also supported by the observation that this sample is light purple after calcination at 373 K. In agreement with MAS studies on Au clusters of similar size available in the literature [29-32] this contribution is assigned to gold in the core of a metal particle and further denoted as bulk gold.

Comparison of the data with different supports as given in Figure 3 shows that the spectra in all cases exhibit a predominant bulk gold contribution at (IS, QS) = (-1.22,0). Apparently, the gold in the core of the particle is not influenced by the support. In principle, the IS value of the gold atoms in the cores of the particles are dependent on the chemical nature of the gold atoms on the surface of the particle. However, if there are delocalized electrons present in the metal core, the influence of the surface gold atoms on the core atoms will be greatly reduced. This electronic screening effect is very effective over short distances. Mulder and coworkers [30] found for Au$_{55}$ clusters (size 1.5 nm) that the screening effect for the 13 core atoms is not perfect and the IS changes from -0.28 to -0.16 mm/s with respect to the bulk gold value and depending on the ligands used. Due to the symmetry of the atoms in the core (cubic-close-packed atoms), the quadrupole splitting is zero. As expected, since the Au/TiO$_2$-based samples used in this study have a mean gold particle size of more than 3 nm (about 10$^3$ atoms), the electronic screening of core atoms is perfect and an IS value for core atoms indistinguishable from bulk gold is observed.

For Au/TiO$_2$, the other contribution at (IS, QS) of (-1.26,2.69) observed at higher calcination temperatures appears to be also present for gold supported on TiO$_2$/SiO$_2$ and SiO$_2$,
with an IS and QS of -1.1 ± 0.1 and 2.6 ± 0.1 mm/s, respectively. As can be seen in Figure 8, the observed IS-QS combinations close to values obtained from spectra of 1.5 - 6 nm Au metal particles in a Mylar matrix as reported by Stevano et al. [32]. Stevano and coworkers assign these contributions to surface atoms of gold particles. Furthermore, other reports in the literature [30,31] indicate that spectra of gold particles can usually be described by a metallic core of identically coordinated atoms and a contribution from the surface shell of one atom layer thick. In line with these interpretations, the second contribution found in this study at (IS,QS) = (-1.1 ± 0.1, 2.6 ± 0.1) is assigned to the surface atoms. In Figure 1 it is shown that the increase in PO yield nicely correlates with the increase of the fraction of these surface atoms during calcination.

The relative intensity of this surface species is given as a function of the particle size in Figure 9. In this figure also the fraction of surface Au atoms is calculated assuming hemispherical gold particles [1] and a recoil-free fraction (f-factor) of 0.04 compared to the bulk gold value of 0.189. In the study by Paulus et al. [31] a ratio of 1.35 between f-factor for bulk and surface gold species (0.189/0.14) for 6-17 nm gold colloids was reported. The lower f-factor of Au atoms on the surface of the particle (0.04 vs 0.14 as observed by Paulus et al. [31]) can be attributed to their lower coordination and the absence of ligands. The f-factor of the surface atoms would be higher if the Au atoms that form the contact between gold and support would also be treated as "surface" atoms. However, these atoms on the boundary of gold particle and support are expected to exhibit (slightly) different MAS parameters (IS around -1.22, QS in the 1 - 3 mm/s range for metallic species) and this is not observed experimentally. These atoms either are present in low concentration (leading to low spectral intensity) or not much different from the bulk gold species in the core of the metal particles.

![Figure 9](image_url)

**Figure 9.** Fraction of Au surface species on different supports plotted versus mean particle size determined by TEM. The line represents the fraction of surface atoms calculated by assuming hemispherical gold particles and a surface atoms f-factor of 0.04 compared to the bulk value of 0.189.
The data for the Au/SiO₂ sample are not shown in Figure 9, as for this sample a broad particle size distribution is observed by TEM. Large agglomerates up to 30 nm in size consisting of about 6 nm primary Au particles are found. The definition of a mean particle size is, therefore, not possible and the data in Table 2 indicates that the mean particle size is smaller than 6 nm, as a large fraction of the surface species is found.

The main question regarding the surface species is whether they can be attributed to oxidized gold species or not. As described in the experimental section, the IS yields information on the valence state of the gold, while the QS gives information on the coordination of the neighboring atoms. In Figure 8, it can be seen that IS values for the surface contributions (-1.1 ± 0.1 mm/s) are concentrated around the value of bulk Au (-1.22 mm/s). Furthermore, Figure 8 shows that the IS-QS combinations of the surface species do not fit within the regions that are known for the ionic Au⁺ or Au³⁺ species. The observed behavior of the surface sites can thus be explained in terms of a metallic surface layer with an IS value close to bulk gold and QS values depending on the symmetry of the local coordination of the surface atoms. This interpretation of the spectra agrees with the investigations on molecular Au and Pt clusters and colloids that showed that surface sites can best be described as disturbed but metallic atom shells [30,31]. As stated previously for 1.5 - 6 nm Au metal particles in a Mylar matrix [32] the observed IS-QS combinations are similar.

In conclusion, MAS spectra of 1 wt.% Au on different supports indicate that Au particles of about 5 nm in size can be described by a bulk gold and surface species contribution. No contribution of the atoms on the boundary between Au particle and support is observed. Either, these boundary atoms are present in a too small amount to be detected, or they are not much different compared to the bulk gold or surface species. The last option would rule out the presence of Au³⁺ atoms as “chemical glue” between Au metal particle and support, as proposed by Bond and Thompson [33] for CO oxidation catalysts.

The deposition-precipitation of Au(OH)₃ at pH 9.5-10 yields active epoxidation catalysts. This route yields a uniform gold particle size distribution for supports that have a point of zero charge at a pH range of about 4-6 [34], like TiO₂ and TiO₂/SiO₂. The broad particle size distribution obtained for SiO₂ (point of zero charge at pH = 2) is an indication of a weak interaction of the precipitating Au(OH)₃ species with the highly negatively charged support. The inactivity of the Au/SiO₂ catalyst in the epoxidation reaction should, however, not be related to the broad gold particle size distribution, but to the absence of a Ti epoxidation center [3,4].

It has been shown by TEM that the deactivation observed for Au/TiO₂ [3] is not due to sintering of gold particles. Furthermore, the intensity ratio of bulk versus surface species (90:10) as found by MAS (Table 2) for the spent catalyst is identical to that observed for the fresh sample. Sintering is also not to be expected at the reaction temperature of 348 K, as the catalyst was already calcined at 673 K. The small deviations in IS and QS of fresh and spent Au/TiO₂ samples might be attributed to small changes in valence state/coordination of surface atoms. However, as only 10% of the spectrum consists of the surface species contribution, determination of the IS-QS parameters is difficult. The water production of a deactivated Au/TiO₂ remains constant. Also based on the knowledge on deactivation of TiO₂ by formation of glycol-like species on the Ti epoxidation center [4], it is concluded that the gold remains active during deactivation of the Au/TiO₂ catalyst. This is in agreement with the previously proposed mechanism with an OOH-like species over gold, which may be the intermediate in water formation [3].

During calcination no indication of a preferential conversion of one of the two oxidized gold species observed in the non-calcined sample into metallic gold is found. Most probably the two species are related to the same Au(OH)₃ moieties, where one species can be assigned to the “bulk” and another (probably the higher IS,QS one) to surface Au(OH)₃. Furthermore,
the MAS data indicate that the reduction of Au(OH)$_3$ to Au does not have a gold oxide intermediate.

Both MAS and TEM indicate that metallic gold particles do not grow gradually in size during calcination. Furthermore, TEM analysis indicates that Au(OH)$_3$ is highly dispersed as its particle size is below the detection limit of the equipment (0.5 nm). As a uniform gold particle size distribution is obtained during calcination, a homogeneous deposition of Au(OH)$_3$ species is not to be expected, as this would lead to a broad particle size distribution. Also based on the deposition-precipitation chemistry [35] the presence of discrete islands of Au(OH)$_3$ (of typically less than 1 nm thickness) is more likely. Blick and coworkers observed moiré fringes of up to 20 nm for 0.04 wt.% Au/MgO catalysts that were assigned to two-dimensional surface patches of oxidized gold. They observed an (IS, QS) of (1.38, 0) mm/s for these species that confirmed their assumption. These patches were mobile under the influence of the electron beam and tended to disappear within a few seconds [36]. This may explain the difficulty of observing the Au(OH)$_3$ species of this study in TEM.

These thin Au(OH)$_3$ islands are not active in propene epoxidation, Figure 1 clearly shows that the PO yield is correlated with the presence of metallic gold. From calcination at 573 K the amount of metallic surface gold species is constant, while the PO yield still increases from 0.61 to 0.75 %. One effect may be the disappearance of OH groups on TiO$_2$ during calcination. These groups are known to adsorb PO [4]. The hydrogen and oxygen treatment at the reaction temperature of 323 K will, however, lead to water formation and subsequent rehydroxylation of the TiO$_2$ surface.

Haruta and coworkers [37] found for Au/Fe$_2$O$_3$ catalysts that the formation of metallic gold was accompanied by the conversion of ferric hydroxide to crystalline Fe$_2$O$_3$. Furthermore, Park and Lee [38] observed that oxidized gold of a catalyst calcined at 373 K could be stabilized during CO oxidation at 310-330 K for both Au/Fe$_2$O$_3$ and Au/Al$_2$O$_3$ catalysts operating under wet conditions. Under dry conditions the amount of metallic gold increased during the CO oxidation reaction. Based on these reports and the characterization data presented here, the inhomogeneous formation of metallic gold on the TiO$_2$ support during the calcination process can be related to the different phases present in P25 TiO$_2$ (which is a mixture of 80 % anatase and 20 % rutile [39]) and crystal surfaces. These different TiO$_2$ surfaces will show a different dehydroxylation temperature and, therefore, a different temperature of metallic gold particle formation.

As MAS is element-selective, it is an excellent probe to study coordination and oxidation state of gold species. However, the active epoxidation catalysts studied here have particles larger than 3 nm, and the gold surface atoms contribute typically 10 % to the spectrum. The active gold site, which can be located at or near the Au-support interface might, therefore, not be visible in the Mössbauer spectrum. Furthermore, charging of the Au particle due to interaction with the support will not have a large influence in the Mössbauer spectrum. For gold particles larger than 55 atoms a shift in IS of less than 0.1 mm/s has been calculated upon charging by the addition of one electron [40]. Therefore, XPS analysis was carried out, as it is more surface sensitive.

The interpretation of Au 4f binding energies (BE) as determined by XPS is still subject of debate with respect to metal-support interaction (charging of the metal particle) and particle size effects [7]. As metallic gold has a BE of 84.00 eV [24], higher BEs (positive shifts) are usually assigned to (partially) oxidized gold. However, Table 3 clearly shows lower BE values for different 1 wt.% Au/TiO$_2$ samples.

In the literature negative shifts in Au 4f/BE have been observed before and explained by electron transfer to the gold. For 7.5 - 12.5 nm Au particles supported on Fe$_2$O$_3$, Gucci and coworkers [41] found a decrease in BE from 84.3 to 83.9 eV upon oxidation of the catalyst. These researchers concluded that Au$^{5+}$ was converted to Au$^{6+}$ by charge transfer involving O$_2^-$.
species [41]. Electron-rich gold species were proposed by Claus et al. to play a role in the hydrogenation of acrolein over 1 nm gold particles on TiO₂. Claus and coworkers did not report XPS spectra, but their conclusions were based on Electron Spin Resonance (EPR) studies [42].

Besides oxidation state, in XPS of nanosized gold particles both initial and final state effects can cause shifts in BE. The initial state effect involves a decrease in BE with a decrease in gold particle size, due to the increased number of surface atoms. Surface atoms have less neighbors than bulk atoms, which decreases the surface valence-band width. Therefore, the Au 5d electrons are more localized and this decreases the Au 4f BE [43,44]. Final state effects involve an increase in BE with a decrease in gold particle size. Smaller particles have more discrete conduction bands and more surface atoms with reduced coordination. Upon creation of a core hole by the incoming X-ray, the screening of this hole will be less for smaller particles. Therefore, the photoelectron will experience a higher BE. Both initial and final state effects are influenced by charging of the gold particle. Charging is dependent on the ability of the support to neutralize the particle within the lifetime of the core hole [43].

Firstly, the validity of the C 1s reference was checked. Using C 1s as reference may lead to small shifts in Au 4f½ BE due to presence of C-O as well as C-C bonds on TiO₂ supported catalysts [4]. This is illustrated by the spent Au/TiO₂ catalyst, for which a second C 1s peak at 286.25 eV is observed. This is due to the presence of a C-O bond containing carbon species. If the C 1s reference peak of the TiO₂ catalysts should be higher than 284.8 eV, this would imply that the determined BE is too small, causing negative BE shifts with respect to the gold reference. The use of Ti 2P½ as reference may also result in small shifts as Ti⁴⁺ can be reduced in situ to Ti³⁺. Therefore, it is concluded that the use of C1s as reference is only valid for comparison of similar (oxide-) supported catalysts. The shift in BE relative to the gold film reference is not a good measure for chemical state of the gold particle.

Comparable to the IS-QS plots for gold compounds studied with Mössbauer, combinations of photoelectron and Auger lines are more indicative of the chemical state [18] than the photoelectron line alone. Use of an unmonochromatized X-ray source renders it possible to generate Auger electrons. Generally, these lines are overlooked, as it is a relatively weak phenomenon and, for example, the Au M₅N₅N₆₇ are observed in the negative BE region (1253.6 - 2015 = -761.4 eV) [19].

As the oxidation state of the gold may change as a function of distance from the surface, the penetration depth of both photoelectron and Auger electrons is important. The kinetic energy of the Au 4f½ electrons (1253.6 - 84.0 = 1169.6 eV) implies an Inelastic Mean Free Path (IMFP) of 1.4 nm, while for the Au M₅N₅N₆₇ Auger electrons (2015 eV) an IMFP of 2.2 nm is reported [45]. Therefore, mostly the surface atoms of the 5 nm gold particles will appear in the XPS spectra. As the Auger electrons have a similar IMFP, combinations of Au 4f½ and Auger electrons will yield information on the same surface species.

Only samples containing more than 1 wt.% Au can be used to determine the Auger lines. Ideally, both 1 and 10 wt.% Au catalysts with identical particle sizes and catalytic properties should be prepared. When gold metal particles are prepared before the introduction of the support, gold particle size can be varied independently of gold loading. These colloid routes can also be applied to different supports with higher/lower points of zero charge. A disadvantage of gold colloid synthesis is the use of organic stabilizers (to prevent the clustering of the gold colloids in solution), which may affect the catalytic activity. Both the 1 and 10 wt.% Au/TiO₂ catalyst prepared via tetrakis(hydroxymethyl)phosphonium chloride (THPC) show no epoxidation activity. The gold particle size is comparable to the active Au/TiO₂-based catalysts prepared via deposition-precipitation. Therefore, the inactivity may
be due to the P remaining after calcination at 673 K. This has been indicated in the literature [16] and also P is observed in the XPS spectrum. According to Grunwaldt et al. [16], this method should provide active CO oxidation catalysts, but that has not been verified in this study. Whether the remaining P is related to Au or to the Ti epoxidation center, cannot be deducted from the XPS data. Apparently, the polyvinylpyrrolidone (PVP) used for the other colloid can be removed sufficiently during calcination at 673 K. In this case, no evidence has been found in XPS for remaining nitrogen (oxide) species.

It is noteworthy that the epoxidation activity increases between the 1 and 10 wt.% Au PVP samples, but never exceeds the activity of the 1 wt.% Au/TiO₂ prepared via deposition-precipitation. This indicates that an increase in gold loading will not overcome the low PO yields (< 2 %) generally observed over these catalyst systems [3] and this can be explained by the fact that PO desorption from a Ti site is rate limiting [4]. Furthermore, no difference in Au 4f BE is observed before and after reaction for the Au/TiO₂ catalyst calcined at 673 K. This indicates that the slight changes observed in (3S,3Q) of the metallic surface species are not significant and supports the conclusion that deactivation is due to the TiO₂ support [4].

For the 10 wt.% Au samples the XPS and Auger spectra (Figure 7) allow determination of the Auger parameter α. As given in Table 3, α shows a shift for the active 10 wt.% (PVP) Au/TiO₂ catalyst of -0.27 eV with respect to the Au reference (α = 2099.15 eV), while for the THPC sample only -0.07 eV is found. The difference between the two catalysts is mainly due to the difference in Auger line position. The value of 84.05 eV obtained for the Au reference is in good agreement with literature (84.00 eV) [24].

The 1 wt.% Au/TiO₂ and the 10 wt.% (PVP) Au/TiO₂ are both calcined at 673 K and active in propene epoxidation. TEM indicated a similar particle size distribution. Therefore, it is concluded that the active gold species of these two catalysts are similar. From the 4f7/2 BE of the 1 wt.% Au/TiO₂ a shift of -0.76 eV with respect to the measured gold reference is observed, while the Auger parameter of the active 10 wt.% (PVP) Au/TiO₂ catalyst gives a shift of only -0.27 eV.

Analysis of the Auger parameter will not suffer from charging of the gold particle as the photoelectron and the Auger electron are related to the same gold species. Furthermore, it has been shown that a change in the Auger parameter compared to the gold reference is indicative of final state effects [21, 46]. This would imply that the Au 4f7/2 BE of the studied gold particles would be higher than the 84.00 eV reported for metallic gold. The real value of BE can even be higher if charging of the gold particle occurs, while the occurrence of initial state effects would decrease the BE [21]. As the real BE value is not known, both the influence of initial state effects and charging cannot be elucidated.

The value of -0.27 eV for the shift in Auger parameter should be compared with a range from -1.30 eV up to -0.12 eV that has been reported for gold particles of increasing size on yttria-stabilized ZrO₂ [21]. In this study it has been shown that for small gold particles initial state effects are important, while for larger gold particles final state effects will give non-metallic BE. These larger gold particles have a shift in Auger parameter of -0.36 eV up to -0.12 eV. Unfortunately, no results on gold particle sizes were reported. Dalacu and coworkers [43] showed that initial state effects start to appear at sizes below 2 nm.

In conclusion, the shift in Auger parameter is within the range of what is reported for metallic gold particles. Therefore, the negative shift is not related to the gold particles being negatively charged, but to the increased fraction of surface atoms. These surface atoms are less coordinated and exhibit reduced screening of the photoelectron core hole. For elucidation of chemical state of the gold (for example the Au/TiO₂ catalyst calcined at 423 and 673 K) either the Auger parameter, or a metallic gold sample with a comparable dispersion should be used.
Based on the XPS and Auger data, the 10 wt.% (THPC) Au/TiO₂ sample is expected to have either larger gold particles (not supported by TEM and MAS, not shown here) or an increased coordination of the surface atoms and, therefore, an enhanced screening. The latter option is supported by the presence of P in this sample, which may be coordinated to Au. Phosphorus may have contaminated the surface of the Au particles and reduced its activity for propene epoxidation.

Figure 4 and Table 3 show that also the 1 wt.% Au/TiO₂ calcined at 423 K has a Au 4f BE of 84.21 eV, which would imply mostly metallic gold. However, a better reference in this respect is the 1 wt.% Au/TiO₂ calcined at 673 K. Compared to the latter sample, the catalyst calcined at 423 K has a 0.92 eV higher BE. Based on the discussion in the previous paragraphs, this would either imply a difference in gold particle size, or a more oxidized gold species. TEM indicates that the mean gold particle size is comparable and, therefore, the higher BE is assigned to oxidized gold. Park and Lee reported 2.4 and 3.8 eV relative to Au metal for Au₂O₃ and Au(OH)₃, respectively [38], but also 1.9 eV for Au(OH)₃ is stated in literature [47]. The surface sensitivity of XPS is nicely illustrated by Figure 4 and Table 1 for the Au/TiO₂ catalyst calcined at 423 K. Although in MAS 36% of the spectrum consists of metallic gold particles and their metallic surface atoms, XPS mainly detects the oxidized gold species. This indicates the oxidized gold species is highly dispersed, probably in the form of the Au(OH)₃ moieties that were previously proposed.

A schematic picture of the phases present during preparation of Au/TiO₂ catalysts is given in Figure 10. After the deposition-precipitation of Au(OH)₃ on TiO₂, during calcination gold is reduced and water is removed by dehydroxylation. The temperature dependence of the Au metal particle formation is probably due to the different crystal phases and surfaces that are present in TiO₂ P25. After calcination treatments at temperatures above 573 K, and for gold particles larger than 3 nm, all gold is present in a metallic form. Both XPS and MAS show the presence of metallic gold surface atoms after high temperature calcination.

**Figure 10. Schematic impression of conversion of Au(OH)₃ species supported on TiO₂ into Au/TiO₂ during calcination.**
It is shown that both XPS and MAS are excellent tools in the characterization of catalysts with nano-sized gold particles. Therefore, both MAS and Auger parameter analysis can play an important role in the elucidation of gold particle size effects in propene epoxidation, but also for CO oxidation. Application of higher gold loadings enhances MAS sensitivity and enables the determination of the Auger parameter. Future challenges are, therefore, the preparation of higher gold loaded samples with a uniform gold particle size around 2 nm. Correlation of catalytic activity with different gold particle sizes will then be possible. Colloid preparation routes may be a valuable tool in this respect, although these will not always yield catalytically active samples.

Conclusion

1 Wt.% Au/TiO₂-based propene epoxidation catalysts calcined at 673 K have been characterized by TEM, XPS, and ¹⁹⁷Au Mössbauer Absorption Spectroscopy. Gold particle sizes ranged from 3 to 6 nm. All techniques indicate that metallic gold was the active phase during propene epoxidation over these catalysts. The two Au species found in Mössbauer spectra were assigned to Au atoms in the core of a metal particle, and metallic gold on the outer surface of a metal particle. Based on TEM analysis, it was shown that the surface atoms have a smaller recoil-free fraction due to their lower coordination. For Au/TiO₂ it was observed that during calcination Au(OH)₃ species formed after deposition-precipitation are converted into metallic gold. Gold particles were shown not to grow gradually during calcination, and it is tentatively concluded that the conversion of Au(OH)₃ moieties occurs simultaneously with dehydroxylation of the TiO₂ support.

Both 1 and 10 wt.% gold catalysts with similar particle size have been prepared via a colloid route. The use of polyvinylpyrrolidone (PVP) in the colloid synthesis catalysts. XPS analysis showed that Au ⁴f₇/₂ binding energy based on the C 1s reference should be interpreted with caution. Determination of the Auger parameter of 10 wt.% Au catalysts confirmed that the surface layer of 3-5 nm gold particles is metallic. The negative shift in Auger parameter with respect to metallic bulk gold has to be related to final state effects. These effects are due to the less coordinated but metallic gold surface atoms, which exhibit reduced screening.

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References


Stability and selectivity of Au/TiO₂ and Au/TiO₂/SiO₂ catalysts in propene epoxidation

An *in situ* FT-IR study

*In situ* FT-IR spectroscopy was used to study the surface species involved in the selective epoxidation of propene with an O₂/H₂ mixture over a 1 wt.% Au/TiO₂ catalyst and a 1 wt.% Au/TiO₂/SiO₂ catalyst. Propene adsorbs weakly on both catalysts via γ-hydrogen bonding with surface hydroxyl groups of the TiO₂, or TiO₂/SiO₂ support. Propene adsorption is completely reversible at temperatures between 300 and 400 K. Irreversible adsorption of propene oxide (PO) was observed on both catalysts, yielding bidentate propoxy moieties. Similar propoxy species are formed after prolonged exposure of the catalysts to a propene/oxygen/hydrogen mixture. Deactivation of TiO₂ catalysts is explained by the formation of these propoxy groups on active and selective Ti sites. Neighboring acidic Ti sites are involved in coupling of PO onto these sites. Occupation of selective sites with propoxy groups is limited on TiO₂/SiO₂ catalysts. On this support, propoxy groups are located on acidic agglomerated TiOₓ sites, and linked to an Si-OH functionality. These groups are not involved in the selective epoxidation of propene, which occurs over isolated tetrahedral sites.

Besides propoxy groups, surface compounds with absorptions in the C=O stretching range (such as acetone and propanal) were observed on both catalysts. Formate and acetate species (implying C-C bond cleavage) were identified exclusively on the Au/TiO₂ catalyst. The relevance of these species will be discussed with respect to the selectivity of the catalysts investigated.
Chapter 5

Introduction

Highly dispersed Au/TiO₂ catalysts have recently received considerable attention, as these catalysts were found very active in low temperature CO oxidation [1]. Furthermore, an extraordinary selectivity in the oxidation of propene to the corresponding epoxide was claimed (> 99%), using a combination of H₂ and O₂ as oxidation mixture [2]. Additional studies of the epoxidation reaction indicated several drawbacks of the Au/TiO₂ catalyst. Firstly, the low conversion (1-2 %) obtained under typical reaction conditions (atmospheric pressure, 323 - 423 K) cannot be improved by increasing the reaction temperature, because this leads to extensive by-product formation. Secondly, the low efficiency of hydrogen (relatively large amounts of water are formed) is hard to prevent. Finally, significant deactivation of Au/TiO₂ catalysts within several hours on stream has been observed.

Many aspects of Au/TiO₂-based catalysts are still not very well understood. A hydrogen peroxy species has been proposed as oxidant in the epoxidation reaction [3], but this is still speculative [4,5]. The mechanism of deactivation has neither been investigated in much detail. Nijhuis [3] proposes oligomerized propene oxide to be responsible for deactivation of Au/TiO₂, based on TG/DSC profiles. Interestingly, deactivation of Au catalysts can be prevented by application of dispersed TiO₂ supports, like TiO₂/SiO₂ and Titanium-Silicalite-1 (TS-1) [3,6]. These catalysts usually show epoxidation activity at temperatures between 398 and 423 K, which is 50 degrees above the temperatures where Au/TiO₂ catalysts yield PO selectively.

InfraRed studies on Au/TiO₂-based catalysts were mainly focused on the active gold species in low temperature CO oxidation, discussing the interaction of CO with Au particles [7,8]. The water gas shift reaction was also previously studied using in situ IR by Bocuzzi [9]. The interaction of propene, propene oxide and a reaction mixture of H₂, O₂, and propene with Au/TiO₂-based catalysts has not been investigated previously using IR spectroscopy, although PO has been used as probe molecule to characterize catalyst acidity by infrared analysis [10]. Recently, an IR study on propene oxidation of Ti-modified sulfated ZrO₂ catalyst was carried out, but these catalysts exhibit a low selectivity to PO [11]. In this chapter IR spectra of reactants (propene, hydrogen, and oxygen) and propene oxide, interacting with deactivating Au/TiO₂, and non-deactivating Au/TiO₂/SiO₂ catalysts, are presented. Several aspects of the deactivation mechanism, as well as the selectivity of the Au/TiO₂ and Au/TiO₂/SiO₂ catalysts will be discussed.

Experimental

A 1.6 wt.% TiO₂ (0.1 monolayer) TiO₂/SiO₂ support was prepared by reaction of titanium(IV)ethoxide (Fluka, 97 %) in 2-propanol with surface hydroxyls of SiO₂ (Aldrich Davisil 646) based on a method by Rajadhyaksha and coworkers [12]. TiO₂ (P25, Degussa) was used as received. Catalysts containing 1 wt.% Au were prepared by deposition precipitation of Au(OH)₃, by slowly adding a AuCl₃ solution to a suspension of the support at pH 10 [3]. All catalysts were thoroughly washed before calcination at 673 K to prevent chlorine contamination. TEM analysis showed the formation of Au metal particles in the 3-6 nm range for both supports. Diffuse Reflectance UV-Vis Spectroscopy confirmed that the TiO₂/SiO₂ support did not contain anatase (only a band of isolated tetrahedral Ti at 230 nm was observed), indicating a high dispersion of Ti species.
The FT-IR measurements were performed using an in situ IR cell with CaF$_2$ windows [13]. A schematic picture of the in situ cell is given in Figure 1. Gas could be fed to the cell using a 4-way valve (Valco), which was configured to select two separate gas feeds. Using a flow of 30 ml/min, the cell was completely refreshed in about 30 seconds after switching the valve.

The samples were prepared in the form of self-supporting wafers (~ 20 mg/cm$^2$) at pressures of 3-4 ton/cm$^2$. Pretreatment of the wafers consisted of drying at 398 K in He. Spectra were recorded using a Nicolet Magna IR 860 spectrometer equipped with an MCT detector. Unless stated otherwise, spectra were recorded against a background of the sample at the reaction temperature under He at 4 cm$^{-1}$ resolution, using co-addition of 64 scans.

Gases applied (propene, 1.5 % PO in He, H$_2$, O$_2$, and He) were of HP or UHP grade and dried before use. The IR measurements were performed using a 10 % propene in He mixture, 1.5 % PO in He mixture, and a mixture of 10/10/10/70 vol% of propene, O$_2$, H$_2$, and N$_2$, respectively. Reference compounds (propanol and 1,2-propane diol, Fluka > 99.5 %) were fed to the in situ cell by saturation of N$_2$ with the required solvent in a 10 ml glass saturator at room temperature, followed by addition of dry N$_2$ leading to a 10 times dilution of the concentration of the reference compound. In situ reactivity studies were performed at temperatures ranging from 348 to 423 K.

**Results**

**Catalysts**

Spectra of the Au/TiO$_2$ and Au/TiO$_2$/SiO$_2$ catalysts using the empty cell as reference are shown in Figure 2. The hydrocarbon signals around (3000 cm$^{-1}$) in the catalysts are of only low intensity (Figure 2b), suggesting that little contamination was present after the preparation procedures and calcination at 673 K. This is in agreement with several observations in the literature [14]. The IR spectra of TiO$_2$ (not shown) and Au/TiO$_2$ are quite similar and comparable to the spectra recently published by Martra [15]. The spectra presented in the following paragraphs were recorded using the spectra shown in Figure 2 as a background. Hence, the interactions of various molecules were studied on catalysts calcined at 673 K in the preparation procedure, and dried in He at 398 K in the IR cell.
Figure 2. IR spectra of Au/TiO$_2$/SiO$_2$ (398 K, in He) and Au/TiO$_2$ (348 K, in He) catalyst.

Figure 3. Changes in the OH stretch region upon interaction of propene (top spectrum) and propene oxide (PO) (bottom spectrum) at 323 K with Au/TiO$_2$. Proposed absorption complexes are given in the inset.
Adsorption of propene

Changes in the hydroxyl stretching region of the Au/TiO₂ catalyst upon propene adsorption at 300 K are shown in Figure 3 (top spectrum). The intensity of the hydroxyl vibrations is clearly affected by the presence of gas-phase propene. Since the spectrum of Au/TiO₂ was used as background, decreasing intensities show as negative bands. Ti-OH stretching bands are located at 3737, 3726, 3686, 3674, 3657, 3646 and 3608 cm⁻¹. Spectroscopic identification of the OH-groups of various TiO₂ morphologies has been extensively discussed in [14-21]. The (negative) spectrum corresponds to spectra presented by Tanaka and White [14], although various bands are shifted to slightly higher wavenumbers. The 3737 cm⁻¹ band is probably due to a silica impurity [18,19]. The presence of about 0.25 wt.% SiO₂ in the P25 TiO₂ sample was confirmed by XRF analysis. The 3686 cm⁻¹ band contains contributions at lower (at 3674 cm⁻¹), as well as higher frequencies. The 3726 and the shouldered 3686 cm⁻¹ bands have previously been assigned to the isolated OH groups of rutile and anatase, respectively [16,21]. The P25 TiO₂ support consists of about 80 wt-% anatase and 20 wt-% rutile [22]. The bands at 3657, 3646, and 3608 cm⁻¹ have been assigned to hydrogen bonded OH groups, as well as water molecules adsorbed on different crystal phases [17,21,23]. Intensity differences between literature spectra, and the presented (negative) spectrum are likely related to the relative contribution of the hydroxyl groups to the interaction with propene. Besides the negative bands, a broad positive band is developed upon propene adsorption, centered around 3550 cm⁻¹, which can be assigned to H-bonded OH groups. Adsorption of ethene and propene on TiO₂ has been studied by Davydov et al. [24]. These authors showed that ethene adsorption did not result in decreasing Ti-OH intensities. This suggests that hydrogen interactions occur via the methyl group of propene, as illustrated in Figure 3. It should be noted that the 1635 cm⁻¹ band of adsorbed propene was hard to identify in the presented spectra, since the O-H bending deformation of physisorbed water is in close proximity to this band, located around 1620 cm⁻¹.

Upon propene adsorption, the spectrum of the Au/TiO₂/SiO₂ catalyst (not shown) is dominated by a negative band at around 3737 cm⁻¹, which is assigned to silanol groups of the silica support. In the Ti-OH region, only a weak negative band at 3716 cm⁻¹ is present, assigned to an isolated Ti-OH group [21,25]. Isolated Ti species were also identified by DR-UV-Vis analysis of these catalyst samples [3,6].

The interaction of propene with both catalysts is completely reversible: after removal of gas-phase propene the spectra in the OH-region were rapidly restored (the negative and positive bands disappeared), and adsorbed species did not remain on the surface. Furthermore, at temperatures above 473 K interactions of propene with the Ti-OH and Si-OH groups were no longer observed.

Adsorption of propene oxide - Au/TiO₂

The changes in the OH spectral region of Au/TiO₂ upon propene oxide (PO) adsorption are also presented in Figure 3. Compared to the adsorption of propene several differences can be identified:

(i). The acidic (lower wavenumber [26]) OH groups have a relatively stronger interaction with PO than with propene. The OH vibrations located at 3657 and 3646 cm⁻¹ are more affected. Introduction of PO also leads to a decrease of the OH stretching vibration located at 3410 cm⁻¹, which was not observed upon propene adsorption. This band has been assigned both to H-bonded hydroxyls of the rutile phase [21] and isolated OH, bridged between two adjacent Ti moieties [16]. The latter assignment seems more likely, as H-bonded hydroxyls would give rise to broader bands.

(ii). The maximum of the broad positive band is located at 3320 cm⁻¹ (not shown) upon PO adsorption, which is at a significantly lower wavenumber than observed after propene
adsorption (3550 cm\(^{-1}\)). This larger shift in OH-group frequencies indicates that the hydrogen bonds formed upon interaction with PO are stronger compared to propene adsorption [23].

(iii) Removal of gas-phase PO does not restore the original spectrum; the broad feature at 3320 cm\(^{-1}\) disappears, suggesting reversible adsorption, but the negative OH absorption bands hardly change. This suggests that also a chemical transformation of the OH-groups occurs by irreversible PO adsorption.

\[ \text{Figure 4. (a) Adsorption and desorption of propene oxide (PO) from the Au/TiO}_2 \text{ catalyst at 323 K by flushing in He. Top to bottom: in 1.5\% PO in He, in He after 3, 10 and 25 min, respectively. Region: 2600-3200 cm}^{-1}. \text{(b) Adsorption and desorption of PO from the Au/TiO}_2 \text{ catalyst at 323 K by flushing in He. Top to bottom: in 1.5\% PO in He, in He after 3, 10 and 25 min, respectively. Region: 1050-1800 cm}^{-1}. \]
The C-H stretching and bending regions of the adsorbed species are shown in Figures 4a and 4b, respectively. In the presence of PO, absorptions at 3049, 3001, 2970, 2931, and 2870 cm\(^{-1}\) can be identified in the C-H stretching region. The 2870 cm\(^{-1}\) has two shoulders on the low- and high-frequency side (at around 2855 and 2880 cm\(^{-1}\), respectively). Changing the gas-phase composition to He results in desorption and decomposition of adsorbed PO, as indicated by the decreasing 3049 cm\(^{-1}\) band (which is related to the CH\(_2\) stretch of the methylene group), and the decreasing intensity of the 3005 cm\(^{-1}\) band, which is assigned to the methine C-H stretching vibration of the PO molecule. The decreasing band at 1270 cm\(^{-1}\) (Figure 4b) is indicative for the symmetrical ring breathing mode of adsorbed PO [27]. Additional decreasing bands of adsorbed PO are located in the C-H bending region (1550 to 1300 cm\(^{-1}\)) at 1486, 1445, and 1410 cm\(^{-1}\) (CH\(_2\) and CH\(_3\) bending and deformation modes).

Weak C=O stretching vibrations can be observed in the spectra at 1660, 1690 (sh), and 1730 cm\(^{-1}\) (Figure 4b) suggesting that some adsorbed PO is converted to an oxidized, C=O containing surface species. This might be an adsorbed ketone (acetone [28]), or aldehyde (propanal). The 1660 cm\(^{-1}\) band is decreasing as a function of reaction time in He, while the 1730 cm\(^{-1}\) vibration and a shoulder at 1690 cm\(^{-1}\) are not affected.

The remaining C-H stretching vibrations of the adsorbed species formed by transformation of adsorbed PO can be assigned to CH\(_3\) and CH\(_2\) (as)symmetric stretch vibrations. The band at 1451 cm\(^{-1}\) can be assigned to \(\delta_{as}(\text{CH}_3)\), and the 1373 and 1339 cm\(^{-1}\) bands to \(\delta(\text{CH}_3)\) and \(\delta(\text{CH})\), respectively [29]. Strong bands are also located at 1142 (which is mainly the C-O-Ti stretch vibration) and 1097 cm\(^{-1}\) (C-C stretch) [30]. The spectral characteristics of the adsorption, desorption, and decomposition of PO are independent on the presence of gold or the amount of adsorbed water on the catalyst. This was verified by studying the interaction of PO with a TiO\(_2\) P25 support-only, and by recording reference spectra of a catalyst that was not dried at 398 K in He before use. These samples show identical bands in the IR spectra.

The spectral characteristics indicate that besides a minor amount of species containing a C=O functionality, a large fraction of the adsorbed epoxide is converted to another irreversibly adsorbed species. Adsorbed (intact) PO is probably H-bonded to acidic OH groups as given in the insert of Figure 3. Therefore, it is likely that the irreversibly adsorbed species are formed via acid-catalyzed opening of the epoxide ring, yielding a monodentate (1-, or 2-propoxy), or bidentate propoxy species. To further validate the assignment, the adsorption of 1-propanol, 2-propanol, and 1,2-propane diol on Au/TiO\(_2\) was studied at 348 K. These spectra are compared with the spectrum of the catalyst after PO adsorption at 348 K in Figure 5.
Figure 5. Comparison of spectra after adsorption of 1,2-propane diol, 1-propanol, 2-propanol, and PO on the Au/TiO$_2$ catalyst at 348 K.

Figure 6. Time dependent spectra taken upon introduction of PO to the IR cell, containing Au/TiO$_2$/SiO$_2$ catalyst at 323 K (after 30, 60, 90 and 120 s, respectively).
Unfortunately, the type of species formed by interaction of the alcohols with the catalyst appears quite different from the species formed upon PO adsorption. Spectra of the adsorbed alcohols, and especially of 1,2-propane diol, contain a large C=O band at 1695 cm\(^{-1}\). This indicates conversion of the alcohols over the Au/TiO\(_2\) catalyst to acetone. The assignment to the ketone is evidenced by the fact that no CH stretch of an aldehyde (HCO) at about 2740 cm\(^{-1}\) is observed [10], while the aldehyde C=O stretching vibration is also expected at lower wavenumbers [27]. The diol does not form propoxy linkages, which is in agreement with the extensive acetone formation. On the other hand, the spectra of 1- and 2-propanol contain bands in the 1500 to 1150 cm\(^{-1}\) region that are indicative of the corresponding adsorbed propoxy product. The observed frequencies of adsorbed 2-propanol on Au/TiO\(_2\) are in good agreement with literature data of adsorbed 2-propanol on TiO\(_2\) [29,31] and the Ti-(O-CH\(_2\)(CH\(_3\)))\(_2\) complex [32]. The spectra of the adsorbed n- and 2-propanol show profound differences in the \(\nu(C-O)\) and \(\nu(C-C)\) region (1050-1200 cm\(^{-1}\)), mainly related to different C-C stretching frequencies. In this region the PO spectrum resembles that of 1-propanol, but the spectra of the reference compounds are significantly different in the C-H stretching region. Concluding, the spectrum of adsorbed PO does not unambiguously correspond to that of one of the adsorbed alcohols. It appears most likely that a bidentate propoxy species is formed. This will be discussed in the following paragraph.

**Adsorption of propene oxide - Au/TiO\(_2\)/SiO\(_2\)**

In Figure 6 the changes in the spectrum of the Au/TiO\(_2\)/SiO\(_2\) catalyst upon introduction of PO in the \textit{in situ} cell is shown. Both the Si-OH (3745 cm\(^{-1}\)) and a Ti-OH group located at 3730 cm\(^{-1}\) participate in the reactive adsorption of PO. The Ti-OH seems to decrease before the silanol absorption is affected (after 30 s), but after 60 s the spectrum is dominated by the Si-OH vibration. The intensity of the C-H stretching vibrations increases, due to the increasing PO concentration in the \textit{in situ} cell. The desorption and decomposition of adsorbed PO is shown in Figures 7A (broad adsorption at 3325 cm\(^{-1}\) and the CH stretch frequencies) and Figure 7b (CH bending vibrations). Upon desorption of PO, the intensity of the Si-OH and Ti-OH frequencies at 3745 and 3715 cm\(^{-1}\), respectively, are partially restored (become less negative), in agreement with the decreasing 3325 cm\(^{-1}\) band. Apparently a significant fraction of PO is reversibly adsorbed on the Au/TiO\(_2\)/SiO\(_2\) catalyst. The signals at 3067 and 3011 cm\(^{-1}\) are indicative for adsorbed PO. After desorption and transformation of adsorbed PO (decreasing bands at 3067, 3011, (Figure 7a), and 1495, 1462, 1450, 1410, and 1374 cm\(^{-1}\) (Figure 7b)), the remaining adsorbed species gives rise to C-H bands at 2979 (\(\nu_{as}CH_3\)) and 2939 cm\(^{-1}\) (\(\nu_{as}CH_2\)), with a shoulder of the symmetric methyl stretching at 2883 cm\(^{-1}\). The remaining bands at 1460 and 1382 cm\(^{-1}\) can be assigned to \(\delta_{as}(CH_3)\), and \(\delta(CH_3)\), respectively [29]. As was previously discussed for the Au/TiO\(_2\) catalyst, the spectral changes are related to the formation of propoxy species. Characteristic absorptions of the propoxy compounds in the 1200 to 1100 cm\(^{-1}\) region could not be analyzed for the Au/TiO\(_2\)/SiO\(_2\) catalyst, due to the opacity of the sample in this spectral region.
Figure 7. (a) The interaction of PO (1.5 % in He) with the Au/TiO₂/SiO₂ catalyst at different temperatures. Top to bottom: in PO at 323 K, 353 K, 378 K, 400 K, in He at 400 K. Spectral region 2500 to 4000 cm⁻¹. (b) The interaction of PO (1.5 % in He) with the Au/TiO₂/SiO₂ catalyst at different temperatures. Top to bottom (1410 band): in PO at 323 K, 353 K, 378 K, 400 K, in He at 400 K. Spectral region 1200 to 1550 cm⁻¹.
Figure 8. Comparison of spectra recorded at 348 K: PO on Au/TiO₂, PO on Au/TiO₂/SiO₂, and 1,2-propane diol on SiO₂.

The C-H stretching vibrations are in excellent agreement with those observed in the spectrum of 1,2-propane diol adsorbed on the SiO₂ support (Figure 8c). The diol mainly yields the bidentate propoxy species. Only a small fraction of the diol was converted into acetone. The different behavior of the diol on TiO₂ and TiO₂/SiO₂ suggests that dehydration and ketone formation is favored on TiO₂, while alkoxy formation is favored on TiO₂/SiO₂. On the other hand, formation of alkoxy species does not occur when silica is exposed to ethene oxide (EO) [33] or PO [10], which was confirmed by experiments with the Davisil SiO₂ support (not shown). For temperatures between 348 and 423 K, PO was found to adsorb reversibly via H-bonding with the Si-OH group located at 3745 cm⁻¹. This suggests that acidic Ti sites of the Au/TiO₂/SiO₂ catalyst are involved in the formation of the bidentate propoxy species. Activation of the PO molecule by Ti rather than Si is also in agreement with the spectra shown in Figure 6, where first the Ti-OH band at 3730 cm⁻¹, and then the Si-OH band at 3745 cm⁻¹ responds to PO adsorption. In conclusion, in the case of TiO₂/SiO₂ it is very likely that bidentate propoxy species are formed, although the presence of some monodentate propoxy species cannot be excluded.

In situ reaction

To further investigate which surface species causes deactivation of the Au/TiO₂ catalyst, this catalyst and Au/TiO₂/SiO₂ were exposed to the reaction mixture. The resulting spectra are presented in Figure 9, and compared with those obtained after decomposition of adsorbed PO.
Figure 9. Spectra of Au/TiO₂/SiO₂ and Au/TiO₂ catalysts. (a) Au/TiO₂/SiO₂ (H₂O₂/propene mixture, 30 mins, 373 K), (b) Au/TiO₂/SiO₂ (PO adsorption and decomposition, He, 5 mins, 400 K), (c) Au/TiO₂ (H₂O₂/propene 150 mins, 373 K), and (d) Au/TiO₂ (PO adsorption and decomposition, He, 323 K).

Obviously, the adsorbed species after reaction are quite similar in nature to the ones obtained after adsorption and decomposition of PO. The catalysts apparently convert the reaction mixture to PO, which is strongly adsorbed on the surface of both catalysts, yielding the bidentate propoxy species. It should be noted that interaction of the reaction mixture with the supports in the absence of Au, did not show any propoxy group formation. Furthermore, in the presence of propene and O₂ only, no adsorbed species were found at the reaction temperatures studied. This suggests that the H₂/O₂ mixture yields a stronger oxidizing species over Au than O₂ alone. The frequencies of the bidentate propoxy species show some intensity differences, explained by different reaction times and temperatures. The chemical interaction of PO with Au/TiO₂ was obtained at 323 K, while a temperature of 400 K was applied to establish interaction with the Au/TiO₂/SiO₂ catalyst. Furthermore, specific absorption frequencies are located at slightly higher wavenumbers for the Au/TiO₂/SiO₂ catalyst, compared to the Au/TiO₂ catalyst (e.g. the band at 1443 is shifted to 1456 cm⁻¹), in agreement with the spectra of adsorbed (and decomposed) PO. This suggests a somewhat different interaction of the propoxy species with the two catalysts. Furthermore, after exposure to the reaction mixture a band at 1682 cm⁻¹ can be observed in the spectrum of the Au/TiO₂ catalyst, while the C=O band is more pronounced and located at 1716 cm⁻¹ in the Au/TiO₂/SiO₂ spectra. These bands are assigned to adsorbed acetone and/or propanal. Based on spectra of propanal adsorbed on SiO₂ (not shown), it appears likely that the 1716 cm⁻¹ band has a predominant contribution of adsorbed (hydrogen-bonded) propanal, while the 1682 cm⁻¹ band of Au/TiO₂ is most likely related to adsorbed acetone, as previously discussed.

For Au/TiO₂, strong additional bands are located at 1570 and 1540 cm⁻¹, which are absent in the Au/TiO₂/SiO₂ spectra. These bands are in good agreement with the absorption
frequencies of formate and acetate species. Oxidation of the bidentate complex apparently leads to acetate and formate species (thus implying C-C bond breaking). Contrary to Au/TiO₂, exposure of the propoxylated Au/TiO₂/SiO₂ catalyst to (hydrogen and) oxygen did not change the spectra, which indicates that the bidentate propoxy species on Au/TiO₂/SiO₂ are stable under oxidizing conditions.

Discussion

Deactivation of Au/TiO₂ catalysts

When the high selectivity of Au/TiO₂ catalysts in the oxidation of propene to PO was first discovered, deactivation of the catalyst was not considered [2]. In more recent studies [3,5] deactivation of the Au/TiO₂ was observed within the first hours of operation. Surprisingly, when TiO₂ was supported on SiO₂ or other modified supports, deactivation occurred to much less extent [3]. Stangland et al. recently observed that deactivation was also less severe at relatively high temperatures (473 K), suggesting that a strongly adsorbed species causes deactivation [5]. In this study both the adsorption of propene and propene oxide was studied to elucidate which compound was the precursor of the deactivating species.

In the absence of an oxidizing species, the adsorption of propene is reversible on both catalysts between 300-473 K. Above 473 K no adsorption could be observed. As no irreversible species are found it is very probable that deactivation of the Au/TiO₂ catalysts is not due to irreversible non-oxidative interactions of propene with the catalyst.

The interaction of PO on the Au/TiO₂ catalyst showed both reversible and irreversible adsorption. Interaction of PO with the acidic OH groups (see the insert of Figure 3) results in the acid-catalyzed epoxide ring opening to form a proproxy species. Based on comparison of the spectrum of the PO decomposition product with spectra of adsorbed alcohols, the formation of a bidentate propoxy species is proposed. This interpretation is also supported by a study of Cant and coworkers [33], who studied ethene oxide (EO) adsorption in the presence of oxygen on Ag/TiO₂ catalysts at 493 K. These authors concluded that ethene oxide reacts instantaneously with surface hydroxyl groups to form glycol-like species. The experiments were very illustrative showing only two C-H stretching frequencies at 2930 and 2880 cm⁻¹, indicating that ethoxy groups were not formed (absence of the CH₃ vibrations at 2980 cm⁻¹). These spectral features also ruled out the formation of adsorbed polymeric species, since they would give rise to only one C-H stretching frequency [33]. PO oligomerization was suggested as the cause of deactivation by Nijhuis et al. [3]. Dimerization of PO to the corresponding 1,4-dioxanes was observed [3]. However, the spectra presented in this study, did not show the characteristic C-O-C vibration of the dioxane compound (at 1260 cm⁻¹), in agreement with the results of Cant [33]. The formation of the 2,5- and 2,3-dimethyl dioxane compounds may only occur at the higher partial pressures used by Nijhuis (34 kPa compared to 1.5 kPa of PO in this study). The presence of minor amounts of these compounds on the surface cannot be ruled out, but oligomeric or polymeric species appear not very likely to be responsible for catalyst deactivation.
The spectral observations and the different behavior of both catalysts with respect to deactivation, are proposed to be explained by the chemical transformations schematically illustrated in Figure 10.

![Figure 10. Formation of bidentate propoxy species over the TiO\textsubscript{2}/SiO\textsubscript{2} and TiO\textsubscript{2} support. Ti\textsubscript{e}: selective epoxidation site, Ti\textsubscript{a}: acidic PO coupling site.](image)

On Au/TiO\textsubscript{2}, interaction of PO with an acidic OH group results in the acid-catalyzed epoxide ring opening to form a monodentate propoxy species. It is proposed that the formed alcohol intermediate rapidly reacts with a neighboring selective Ti-OH epoxidation site, forming structure A. The facile acetone formation upon exposure of the TiO\textsubscript{2} support to propane diol might be related to the initial presence of 2 OH groups in this molecule, which apparently reduces propoxy formation. To explain the stability in the epoxidation reaction of the Au/TiO\textsubscript{2}/SiO\textsubscript{2} catalyst [3], it has to be assumed that active Ti-OH epoxidation sites are not affected by the adsorbed bidentate propoxy groups. It is therefore proposed that the intermediate alcohol reacts with a neighboring Si-OH group (structure B). This is in agreement with the slightly different absorption frequencies observed in the spectra of both catalysts (Figure 9). Apparently, due to the absence of neighboring acidic PO coupling sites (Ti-OH), the epoxidation sites of the Au/TiO\textsubscript{2}/SiO\textsubscript{2} catalyst remain active. It should be noted that the Si-OH group itself is not reactive towards ring opening of PO [38]. In the initial stage of PO adsorption (Figure 6) a Ti-OH group reacts before the Si-OH group frequencies are changed. Furthermore, it has been reported that formation of alkoxy species does not occur when silica is exposed to EO [33] or PO [10].
To further discuss the role of specific TiO₅-sites in the epoxidation reaction, Figure 11 schematically shows the surface composition of Au/TiO₂ and Au/TiO₂/SiO₂ catalysts. As was recently discussed by Gao and Wachs [34], two types of Ti-species are usually present on supported TiO₂ systems; segregated oligomeric domains, and isolated Ti-species (Figure 11). The degree of homogeneity is associated with the relative amount of Ti-O-Si linkages in TiO₂/SiO₂ mixed oxides. Isolated tetrahedral sites (Ti₅O₄) have been postulated as the active centers for the epoxidation of olefins by organic peroxides. This suggests that on Au/TiO₂/SiO₂ catalysts only agglomerates of TiO₅ on SiO₂ are involved in the propoxy formation, while isolated tetrahedral epoxidation sites are not, as schematically indicated in Figure 11. This is in excellent agreement with the acidity of the specific TiO sites. It has been stated that Bronsted acidity is associated with Ti-O-Si bridges where Ti atoms reside not in tetrahedral sites, but in pentahedral or octahedral sites [34] of agglomerated TiO₅ moieties. These sites induce reaction of PO to propoxy groups on the TiO₂/SiO₂ surface, while on SiO₂ this does not occur. Whether on unsupported TiO₂ specific sites (Ti-OH groups) are involved in the epoxidation reaction, or whether the reaction principally occurs on all Ti sites, could not be resolved from the spectra presented in this chapter. It is obvious from the presented spectra and reaction data, however, that on TiO₂ all Ti-OH groups, including the epoxidation centers, are involved in the formation of propoxy groups, explaining deactivation.

Contrary to reaction with Bronsted acidic OH groups, it can also be envisaged that the oxygen of propene oxide reacts directly with the Ti center, either forming linear Ti alkoy compounds or titanium glycolate-type species (Figure 12). An analogous activation of ethene oxide (EO) over Lewis acidic Al⁺⁺ sites was proposed to explain EO isomerization activity of Ag/Al₂O₃ catalysts [35]. Ti alkoy species were described by Rust and Spalter [36] in the 1950s, more recently Gainsford and coworkers synthesized titanium glycolate [37]. However, the activation of the propene oxide by the Bronsted acidic hydroxyl groups as proposed in this chapter can be supported by the following:

(i). Mechanisms according to Rust [36] or Gainsford [37] occur with any type of Ti. The epoxidation catalysis as shown for TS-1 in liquid phase and Au/TiO₂-based catalysts in gas phase would not be possible if all titanium centers would form alkoy or glycolate species.
The acidic Ti species as proposed in this chapter are clearly different from the active epoxidation centers and can, therefore, exhibit different chemistry. (ii). Complexes as proposed by Gainsford would not give the shift in $\nu_{CH}$ as shown for TiO$_2$ and TiO$_2$/SiO$_2$ in this chapter. A glycolate-type of species is only dependent on the Ti center. The proposed bidentate structure is dependent on two support sites, one being a Ti, the other Si.

(a) \[ \text{TiOR} + \text{H}_2\text{C} = \text{C} - \text{H} \xrightarrow{X} \text{OR} \]

(b) \[ \text{O} - \text{Ti} - \text{O} \]

\[ \text{R} = \text{alkyl} \]
\[ \text{X} = \text{halogen} \]

Figure 12. Other titanium alkoxide compounds: (a) formation of Ti alkoxy species (after [36]) and (b) structure of Ti glycolate (after [37]).

The location of Au in the catalysts and the role of the Au particles in the oxidation mechanism are not clear. The postulate of the formation of hydrogen-peroxide intermediates, followed by interaction with the propene molecule is yet the most accepted reaction pathway. This intermediate is formed by Au activation of H$_2$ and O$_2$ (H$_2$O$_2$), as illustrated in Figure 12. Proximity of the Au particles to the isolated TiO$_x$ epoxidation centers seems likely. This does not affect the formation of propoxy groups, which are formed by interaction of PO with the catalytic surface, i.e. after the catalytic epoxidation of propene occurred.

In conclusion, it is proposed that deactivation of Au/TiO$_2$ catalysts is due to the formation of propoxy species over (Brønsted) acid sites, blocking selective epoxidation sites. On the Au/TiO$_2$/SiO$_2$ catalysts, the epoxidation reaction probably occurs over isolated TiO$_x$ sites, which are not involved in propoxy formation. At longer reaction times than the time applied in this study, and in the presence of higher concentrations of PO, oligomerized species might also contribute to deactivation.

Activity and selectivity of Au/TiO$_2$-based catalysts

The unique behavior of Au-based propene epoxidation catalysts is the excellent selectivity (usually reported to be above 99%). The IR spectra show, however, that bidentate propoxy groups and other products containing C=O entities are present on the surface of both catalysts. As indicated in Figure 13, the bidentate propoxy species is oxidized to formate and acetate species upon exposure to oxygen on TiO$_2$, while the bidentate propoxy species on Au/TiO$_2$/SiO$_2$ could not be oxidized by prolonged exposure to oxygen or a hydrogen/oxygen mixture. Apparently, the Si-O-C bond increases the stability of the adsorbed molecule towards oxidation.
The discrepancy between the gas-phase and surface product distribution can be explained by the assumption that the surface species are only formed in the initial stages of the reaction, and act as non-reactive spectator species during the subsequent course of the reaction. However, it should also be considered that products of PO decomposition can be present in the gas phase in too low amounts to be detected.

Principally, formates and acetates observed on the Au/TiO₂ catalyst, are precursors for the formation of CO₂. Formation of ethanal and CO₂ from PO with H₂ and O₂ has been observed by Stangland et al. [5]. Also the bidentate propoxy compound might be converted to propanal and acetone. For the Au/TiO₂/SiO₂ catalyst the main C=O band is in good agreement with hydrogen-bonded propanal, which is formed under inert atmosphere. Formation of propanal from PO has been observed by Piers and Rochester [38]. These authors found that PO dissolved in CCl₄ reacts to propanal in minor amounts over aerosil SiO₂ at room temperature. This isomerization activity might be attributed to an increased acidity of the silanol groups induced by CCl₄. This is supported by a Si-OH band shift from 3740 to 3687 cm⁻¹ in the IR spectra as reported by Piers and Rochester [38]. For Au/TiO₂/SiO₂ it is tentatively proposed that reaction of the propoxy species to propanal involves recombination of Si-O and Ti-O to Si-O-Ti, as given in Figure 13, since in view of the IR spectra, water is not likely to play a role in this transformation.

By-products, like ethanal, CO₂, acetone, and propanal have been observed in the gas phase at higher temperatures [2,3], but (precursors) might be present at reaction temperatures which appear to induce high selectivity. Industrial application of Au catalysts will be complicated if the PO product has to be separated from a stream containing oxygenates such as propanal, acetone and ethanal. Dow Chemical has recently filed a patent on oxidized Au on dispersed Ti catalysts, in which selectivities of only 97 % were reported after 168 hours on stream, suggesting by-product formation [39].
Based on the presented results, the formation of adsorbed by-products is due to the presence of acidic Ti sites. To prevent the ring opening of PO, catalyst modifiers may be added to block these sites. Thiele and Roland [40] have shown for liquid-phase epoxidation that this approach can be successful. By addition of a neutral salt (such as Na₂SO₄) the sites with high acidity were neutralized, while the active Ti site remained active.

Conclusions

Irreversible adsorption of propene oxide (PO) was observed on both a 1 wt. % Au/TiO₂ and a 1 wt. % Au/TiO₂/SiO₂ catalyst, yielding bidentate propoxy moieties. Spectroscopic evidence for oligomerization or dimerization of PO was not found. Similar propoxy species were observed after prolonged exposure of the catalysts to a propene/oxygen/hydrogen mixture. Additionally, formate and acetate species were formed exclusively on the Au/TiO₂ catalyst after exposure to the reacting mixture at 400 K or decomposition of the adsorbed bidentate propoxy species in a hydrogen/oxygen mixture. Supporting Au and TiO₂ on SiO₂ apparently reduces the activity towards C-C bond breaking. Based on the spectroscopic results, deactivation of Au/TiO₂ catalysts is likely related to the irreversible adsorption of a propoxy species on the active Ti site. On the TiO₂/SiO₂ catalyst the acidic Ti sites that cause ring opening of PO are apparently not located near the active epoxidation center. Therefore, no deactivation of the dispersed Ti catalysts was observed. Analysis of the Au/TiO₂/SiO₂ catalyst showed the formation of acetone and propanal. However, these side-products remain adsorbed on the catalyst surface under reaction conditions, maintaining a gas-phase selectivity of > 99 %.

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References


Bimetallic catalysts in propene epoxidation

Gold catalysts are compared with Pd and Pt catalysts in the direct gas-phase epoxidation of propene. In literature reports on liquid-phase epoxidations it has been shown that Pd and Pt can catalyze the formation of propene oxide in the presence of hydrogen and oxygen. However, both Pd and Pt yield mainly propane in gas-phase conditions. This has been assigned to the presence of metallic Pd and Pt.

Both Pd and Pt have also been added in promoter levels to Au catalysts. The presence of small amounts of Pd added to Au catalysts prepared by deposition-precipitation also leads to unwanted hydrogenation to propane. This is explained by the presence of monometallic Pd particles.

Addition of 5% of Pt relative to Au yields bimetallic Au catalysts that are more active and selective. The water-propene oxide ratio decreases upon addition of Pt to a Au/TiO₂/SiO₂ catalyst, while the epoxidation activity is maintained. Hydrogenation of propene to unwanted propane does not occur at temperatures below 373 K. Based on comparison of different preparation routes it is concluded that Pt is present as a highly dispersed phase in the gold particles.
Introduction

The direct gas-phase synthesis of propene oxide, by the use of molecular oxygen, has long been desired. Highly dispersed Au/TiO₂ catalysts show an extraordinary selectivity in the oxidation of propene to the corresponding epoxide (> 99 %), using a combination of H₂ and O₂ as oxidation mixture [1]. Additional studies of the epoxidation reaction have indicated several drawbacks of the Au/TiO₂ catalyst. Firstly, the low conversion (1-2 %) obtained under typical reaction conditions (atmospheric pressure, 323 - 423 K) cannot be improved by increasing the reaction temperature, because this leads to extensive by-product formation. Secondly, the low efficiency of hydrogen (relatively large amounts of water are formed) is hard to prevent. Finally, significant deactivation of Au/TiO₂ catalysts within several hours on stream has been observed. Deactivation can be partly prevented by using dispersed TiO₂ supports, such as TiO₂/SiO₂ and Titanium-Silicalite-1 (TS-1) [2,3] and Ti-MCM [3-5].

For industrial applications the efficiency of hydrogen should be increased, as process economics will be favored by a decrease in hydrogen consumption. Additionally, the direct reaction of H₂ and O₂ to form water is highly exothermic. Improving hydrogen efficiency will, therefore, decrease the amount of heat released in the reactor.

In recent literature [2,6] a hydroperoxide-like intermediate has been proposed to be responsible for the selective epoxidation. This oxidizing species is said to be formed over gold and subsequently used for epoxidation over the Ti-containing support. Although gold is known to catalyze the formation of hydrogen peroxide from H₂ and O₂ – and this is also supported by theoretical work [7] - most patents describing H₂O₂ direct synthesis are based on bimetallic Pd and Pt catalysts (for example [8,9]). As the reaction is favored under low pH conditions, the metals are usually supported on carbon.

H₂O₂ formation from H₂ and O₂ and subsequent propene epoxidation has been shown by Hölderich and coworkers [10,11] for Pd/Pt supported on Titanium-Silicalite-1 in the liquid phase. An oxidized Pd species was reported to be active in H₂O₂ formation. Interestingly, Kuznetsova and coworkers reported that both metallic and oxidized Pt are needed for cyclohexene oxide from cyclohexene with H₂ and O₂ over Pt/SiO₂ catalysts [12,13]. Metallic Pt was said to be responsible for H₂O₂ formation, and it was proposed that Pt ions facilitate epoxide formation [12].

In this chapter catalytic concepts established from H₂O₂ direct synthesis have been applied to the gas-phase propene epoxidation to both improve hydrogen efficiency and gain insight into the epoxidizing species. Pd and Pt catalysts based on liquid-phase epoxidation reactions have been tested in the gas phase. Also the standard gold catalysts have been modified with promoter levels of Pd and Pt. The addition of a second metal to the gold catalyst complicates the preparation and characterization. Consequently, several preparation routes have been assessed for their ability to yield active gold-only catalysts. The most promising preparations have been used to modify the gold with Pd or Pt.

Experimental

Palladium and platinum catalysts

To test a typical H₂O₂ catalyst in gas-phase epoxidation, a 2 wt.% bimetallic Pd:Au supported on γ-Al₂O₃ was prepared according to Lückoff et al. [8]. To test the influence of support, reference samples were prepared using TiO₂ instead of Al₂O₃. Lückoff's method is based on reduction of Pd and Au salts in a suspension of the support by sodium formate at 353 K and pH 6.

The catalysts were compared with samples obtained from the Boreskov Institute of Catalysis, which consisted of Pt and a heteropolyacid (HPA) supported on SiO₂. H₂PtCl₆ was
Bimetallic catalysts in propene epoxidation

used as Pt precursor, which was reduced at 573 K to yield 1 wt.% Pt catalysts. More details of these catalysts will be given in the results section.

Gold catalysts
In the next series of experiments several gold catalyst preparation routes were assessed. Gold was deposited on a TiO$_2$/SiO$_2$ support [2] by deposition-precipitation (DP) [14], ion exchange (IE) [15], and via size-controlled gold colloids (SGC) [16].

For the deposition-precipitation preparation the support was dispersed in water (approximately 10 ml/g$_{support}$) to which ammonia was added to raise the pH to a value between 9 and 10. Over a period of 2 h the required amount of gold (in the form of AuCl$_3$ solution) was added dropwise to the support under vigorous stirring. The suspension was stirred for another half an hour after which the mixture was centrifuged and washed with at least ten times its own volume of distilled water. Furthermore, the DP method was used to assess the promoting effect of Pd and Pt. Several 1 wt.% bimetallic catalysts were prepared. The corresponding metal chlorides were dissolved in water and used similar to the AuCl$_3$ solution for DP preparation as described above. Both the simultaneous deposition of gold and Pt or Pd, as well as deposition of Pd and Pt onto gold catalysts was studied.

For the ion-exchange preparation a [Au(ethylenediamine)$_2$]Cl$_3$ complex was made by the method of Block and Bailar [17]. A suspension of TiO$_2$/SiO$_2$ was heated to 343 K in aqueous ammonia of about pH 11. The [Au(ethylenediamine)$_2$]Cl$_3$ solution was added dropwise into the slurry of TiO$_2$/SiO$_2$. After addition of the solution, the slurry was maintained at 343-335 K for one hour and then cooled to room temperature. The treated TiO$_2$/SiO$_2$ was centrifuged and washed with at least ten times its own volume of distilled water.

In order to prepare Au stabilized as colloid, the sol preparation of Baiker and co-workers was performed [16]. The TiO$_2$/SiO$_2$ support was suspended in water at pH 2, and the appropriate amount of a H$_2$SO$_4$-treated solution (pH = 2) with gold colloids was added with stirring. After 10 min the suspension was filtered and washed three times with distilled water.

The samples prepared by DP, IE, or SCG were dried at 353 K for 2 hours and calcined at 673 K for 4 hours.

Characterization
Transmission electron microscopy was performed using a Philips CM30T electron microscope with a LaB$_6$ filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

Performance testing
Steady-state experiments were performed in a micro-flow setup. In this apparatus nitrogen (70 vol%), oxygen (10 vol%), hydrogen (10 vol%), and propene (10 vol%) were continuously fed over a 10 ml fixed-bed reactor placed in a fluidized-bed oven. The Weight Hourly Space Velocity was 0.71 g$_{propene}$/g$_{cat}$h. The analysis of the reaction products was performed using an automated sampling gas chromatograph, analyzing a gas sample every 12 minutes. The column used for analysis was a Poraplot Q 0.53 mm diameter, 25 m length capillary column, with He as carrier gas. A flame ionization detector (FID) was used for the analysis. This configuration was able to separate all oxygenated organic components relevant in this study. The hydrogen and oxygen consumption was measured on the same gas chromatograph using a Molsieve 5Å, 2 mm diameter, 3 m length column and a TCD detector.
Results

**Palladium and platinum in gas-phase epoxidation**

The oxygenate product yield for a Pd catalyst prepared according to the formate reduction as proposed by Lückoff et al. [8] is compared to a Au catalyst in Figure 1. The gold catalyst was prepared using the same preparation procedure.

![Graph](image1)

![Graph](image2)

**Figure 1.** Oxygenate product yield (left axis) versus time as a function of temperature (right axis): 2 wt.% Pd/Al₂O₃ (top) and 2 wt.% Au/TiO₂ (bottom).

Main oxidation product for both the Pd/Al₂O₃ and Au/TiO₂ catalyst is acetone, although for the TiO₂-based catalysts also minor amounts of PO, propanal en ethanol are found. The Pd catalyst is active already at 323 K and shows higher acetone yields. Especially for the Pd catalyst temporarily higher yields for acetone upon a temperature increase are observed, indicating a slow product desorption [2].
The acetone yield is compared to the hydrogenation activity (propane formation) for several Pd-Au catalysts prepared via formate reduction in Figure 2.

![Graph showing acetone and propane yield at 373 K for catalysts prepared via formate reduction as a function of Pd and Au content and type of support. Total metal loading was 2 wt.%. Bimetallic samples contained 1 wt.% Pd and 1 wt.% Au.]

Figure 2. Acetone and propane yield at 373 K for catalysts prepared via formate reduction as a function of Pd and Au content and type of support. Total metal loading was 2 wt.%. Bimetallic samples contained 1 wt.% Pd and 1 wt.% Au.

It should be noted that for the all samples mainly acetone was observed as oxidation product, only the Pd-Au/Al₂O₃ catalyst produced ethanal in < 0.02 % yield between 348 and 448 K. The oxidation products of Au/TiO₂ are given in Figure 1, while Pd-Au/TiO₂ only gave acetone.

For comparison, in literature PO yields of 1 % over 1 wt.% Au/TiO₂ are reported at > 99 % selectivity [2]. TEM analysis of the samples prepared by formate reduction (not shown) indicated a very broad particle size distribution (2-50 nm), the larger particles consisting of clusters. Furthermore, the metal was not homogeneously distributed over the support.

The Pt-HPA (heteropolyacid) catalysts obtained from the Boreskov Institute of Catalysis were tested between 323 and 423 K. A description of these 1 wt.% Pt samples together with their catalytic activities can be found in Appendix 1. All samples yield propane, ethanal and acetone as major products, while traces of formaldehyde, propanal and acrolein are found. All hydrogen is converted over these catalysts, at higher temperatures more water is formed and the propane yield is decreased. If no hydrogen is added, no propane and less acetone are formed. Comparison of reduced and calcined samples shows that the calcined sample gives less propane and more acetone. Furthermore, the conversion of PO and 2-propanol over the 20 % Cs₂₅H₁₀₅PW₁₂O₄₀-1 % Pt/SiO₂ was tested (not given in the table). It was found that PO is readily converted to propanal and trace amounts of ethanal. 2-Propanol is converted to acetone, while directly after addition of 2-propanol, propanal is detected. Furthermore, upon removal of the catalyst from the reactor for all samples acetic acid was found to be present on the catalyst. The concentration of acetic acid in the gas-phase was below the detection limit of the GC equipment.

As shown in the above, the tested Pd and Pt catalysts known from liquid-phase epoxidation are not active in PO formation. Therefore, in the following the activity of gold is assessed.
Gold-based propene epoxidation catalysts

Different preparation routes have been evaluated for their ability to yield active gold catalysts. The results are given in Table 1.

**Table 1.** Product yields for Au/TiO$_2$/SiO$_2$ catalysts at 373 K. Other products are ethanal, acrolein, propanal and acetone.

<table>
<thead>
<tr>
<th>Preparation</th>
<th>PO (%)</th>
<th>propane (%)</th>
<th>H$_2$O/PO (-)</th>
<th>other (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP</td>
<td>1.2</td>
<td>&lt; 0.1</td>
<td>29</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>IE</td>
<td>0.05</td>
<td>9.0</td>
<td>110</td>
<td>0.06</td>
</tr>
<tr>
<td>SGC</td>
<td>&lt; 0.01</td>
<td>3.5</td>
<td>∞</td>
<td>0.16</td>
</tr>
</tbody>
</table>

It is shown that the highest yield of propene oxide (PO) was achieved with the catalyst prepared according to the deposition–precipitation method. On a TiO$_2$/SiO$_2$ support, the DP catalyst gives propene oxide with a yield of 1.2 % and no propane, while the IE (ion exchange) catalyst gives propane as a major product. Also the formation of water is favored over the IE sample as shown by the higher H$_2$O/PO ratio. TEM analysis (not shown) showed for both DP and IE samples gold particles with sizes between 4 and 10 nm, with a mean particle size of 6 nm. Furthermore, the gold particles were found to be homogeneously distributed over the support. The SGC method also gives a uniform gold particle size of around 5 nm, but only shows propane formation.

The effect of particle size has also been studied for a 0.2 wt.% Au/TiO$_2$/SiO$_2$ catalyst prepared via deposition–precipitation of Au(OH)$_3$. TEM studies (not shown) indicated for the three samples a uniform gold particle size and a gradual increase in mean gold particle size from 0.5 nm for the sample calcined at 673 K to 3 nm for the catalyst calcined at 773 K. As can be seen in Figure 3, both PO and propane are formed throughout the observed particle size range. The largest (3 nm) gold particles even produce propane and no PO.

![Figure 3. PO and propane yield as a function of calcination temperature (gold particle size) for 0.2 wt.% Au/TiO$_2$/SiO$_2$.](image-url)
The DP method was chosen for investigation of bimetallic catalysts. To the AuCl₃ solution the corresponding Pd or Pt salts were added (Pt:Au = 5:95). TEM micrographs are given in Figure 4.

![TEM micrographs](image)

**Figure 4.** TEM micrographs of (a) 1 wt% Pd-Au (5:95)/TiO₂/SiO₂ and (b) 1 wt% Pt-Au (5:95)/TiO₂/SiO₂ catalyst.

Both catalysts show homogeneously distributed metal particles up to 5 nm. No separate Pt or Pd metal particles were found. XRF analysis confirmed the presence of Pd and Pt in the bimetallic samples. In Table 2 the hydrogenation and epoxidation activities are compared for the bimetallic catalysts obtained.

<table>
<thead>
<tr>
<th>Metal</th>
<th>PO (%)</th>
<th>propane (%)</th>
<th>H₂O/PO (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au only</td>
<td>1.2</td>
<td>&lt; 0.1</td>
<td>29</td>
</tr>
<tr>
<td>Pd-Au</td>
<td>&lt; 0.01</td>
<td>10</td>
<td>∞</td>
</tr>
<tr>
<td>Pt-Au</td>
<td>1.0</td>
<td>0.1</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Table 2. Product yields for bimetallic catalysts compared to Au only at 373 K.

Clearly, it can be seen that both Pt and Pd induce hydrogenation of propene to the unwanted propane. The DP Pd-Au catalyst only shows propene hydrogenation and no oxidation activity. Also the addition of Pt leads to formation of propane at 373 K, but this catalyst exhibits less water formation compared to the Au-only catalyst. The ratio of H₂O to PO is 9.3 for the Pt-modified catalyst compared to 29 for the Au-only sample. The effect of Pt concentration was further investigated and the results are given in Figure 5.
It can be seen that at even higher Pt concentrations the H$_2$O/PO ratio is again increased. This might be due to the formation of separate Pt particles that enhance the water formation reaction. The hydrogenation of propene does not occur below 373 K even with the highest Pt concentration investigated, while the PO yield is still high (1.1 % at 348 K against 1.5 % for the 1:9 Pt-Au at 373 K).

![Graph](image)

**Figure 5. Effect of Au fraction in Pt-Au bimetallic catalysts on PO yield and H$_2$O/PO ratio at 373 K.**

As a reference, a Pt/TiO$_2$/SiO$_2$ catalyst was prepared with a 0.05 wt.% Pt loading. By TEM analysis (not shown) no metal particles were observed, although Energy Dispersive X-ray (EDX) analysis indicated the presence of Pt in the sample. This indicates the Pt particles are below 0.5 nm in size. This catalyst yielded 0.2 % PO and H$_2$O/PO was 1550. Furthermore, trace amounts of ethanal, propanal and acetone were formed at 373 K.

The DP method to prepare Pt-Au catalysts was repeated for another support (TiO$_2$) and base (Na$_2$CO$_3$ instead of NH$_3$OH). For comparable PO yields (0.2 %) at 348 K, the H$_2$O/PO ratio decreased from 73 to 33 upon addition of 5 % Pt relative to Au. No propane was formed at these temperatures.

In order to investigate whether the Pt is present as separate metal particles or homogeneously distributed in the gold, samples in which Pt was added after deposition of Au were prepared. The addition of 5, 10, or 15 % Pt induces hydrogenation to propane and formation of ethanal, propanal, and acetone. The gold catalyst before the addition of Pt does not show this byproduct formation, and has a lower H$_2$O/PO ratio. Diffuse Reflectance UV-Vis analysis of the Pt-Au samples was carried out, but the Pt loading was too low to observe any changes in the surface plasmon resonance of the metallic gold particles located at 500-550 nm. No changes in the relative amount of octahedral Ti on TiO$_2$/SiO$_2$ [18] were found to account for the by-product formation.
Discussion

Pd catalysts - effect of support and metal particle size

By taking promising examples from H₂O₂ direct synthesis literature it was tried to prepare a good propene epoxidation catalyst. In the original patent [8] the Pd-Au/Al₂O₃ catalyst yielded H₂O₂ with 40 % selectivity at 298 K and 8 MPa. The reaction was carried out in a slurry reactor in the presence of sulfuric acid and NaBr. However, in propene epoxidation, the Al₂O₃-based catalysts are not active, and the same holds for TiO₂-supported samples (Figures 1 and 2). Based on the proposed model for oxidation species formation over the metal and subsequent epoxidation over the support [2], it can be envisaged that Al₂O₃ does not epoxidize, but TiO₂ is reported to be active. Therefore, the observed lack of epoxidation activity is assigned to the metal particles. As for both TiO₂ and Al₂O₃ supports acetone and propene are observed, the formation of these products is related to reactions catalyzed by the metal particles, rather than the (TiO₂−) support. As can be seen in Figures 1 and 2, both Au and Pd are active in hydrogenation of propene to propane and propene oxidation to form acetone.

TEM analysis showed a broad metal particle size distribution for the catalysts of Figure 2. This may indicate that there is a weak interaction between metal and support during reduction by formate, causing primary metal particles to cluster in solution before adsorbing onto the support. It is surprising that the Au-only samples also exhibit hydrogenation. According to Haruta and coworkers [1], this is due to the presence of small (<2 nm) gold particles. TEM analysis does not rule out the presence of these particles, but indicates that also larger particles are present, which should give PO formation.

The formation of propane over Pd containing catalysts can be explained by the presence of metallic Pd that is known to catalyze hydrogenation reactions. The formation of propane over gold catalysts supported on both TiO₂ and Al₂O₃ cannot be explained by only a gold particle size effect. As a range of particle sizes is present, also PO should have been formed.

Both the hydrogenation and oxidation activity are assigned to Pd and Au prepared by formate reduction, as there is not much influence of the TiO₂ and Al₂O₃ support. Two possible explanations remain for the epoxidation inactivity of Au, Pd, and Pd-Au samples:
1. the structure of the Pd and Au metal particles formed by formate reduction does not permit formation of the OOH-like oxidation species
2. the metal-support interface does not permit spill-over of OOH-like species to the support.

The presence of both propene and hydrogen on a metal surface will lead to hydrogenation and supports the first explanation. As hydrogenation is not observed for active epoxidation catalysts based on Au/TiO₂ [2], the structure of the metal particles should be different. The formation of OOH-like species can be envisaged by considering the oxidation activity. Acetone is the main oxidation product, and two likely reaction routes are either the hydration of propene to propanol and subsequent oxidation to acetone, or reaction of propene with a peroxy species. The hydration route is not probable as it is acid-catalyzed and most probably related to the support. Furthermore, in literature [19] it has been shown that peroxy species on oxidized Pd can give rise to ketone formation. In conclusion, the OOH-like species may be formed on the Pd-Au catalysts, but the co-adsorption of propene on the metal particles gives rise to both hydrogenation and oxidation with acetone as main product. For Pd, hydrogenation may be related to metallic and oxidation to oxidized Pd phases. Due to the broad metal particle size distribution it is not clear whether these phases exist in the same metal particle or are related to different particles with a different size.
Pt catalysts

Another promising metal is Pt, which is known to catalyze epoxidation reactions in the presence of hydrogen and oxygen [12]. Kuznetsova and coworkers have proposed H₂O₂ species formation over Pt and subsequent epoxidation over Pt ions. To enhance selectivity and activity, a transfer agent was added. In this study, HeteroPolyAcid (HPA)-based compounds were used. Tungsten present in this compound has a comparable role as the Ti in Ti epoxidation catalysts. In Appendix 1 it can be seen that under gas-phase conditions all Pt/HPA catalysts yield acetone and propane as major products, instead of propene oxide. Not surprisingly, the formation of propane is due to the presence of hydrogen. Without hydrogen present, no propane is formed. At higher temperatures the formation of water is preferred over propane formation. Furthermore, without hydrogen also less acetone is formed. Experiments using propane as reagent show that this is not due to the formation of acetone from propane. The presence of ethanal and trace amounts of formaldehyde indicate also C-C bond breaking activity of these catalysts. Based on these results it can be concluded that under the test conditions only the Pt is active, and no indications of spill-over of oxidizing species to the HPA compound is observed. This is comparable to the Pd catalysts.

The hydrogenation activity of Pt can be explained by the presence of metallic Pt (which is supported by the grey/black color of these catalysts). Again, formation of acetone can be explained by either acid-catalyzed reactions or an OOH-like species comparable to the Pd catalyst. For these catalysts conversion of 2-propanol to acetone is observed. Without hydrogen present, less acetone is formed. This can be explained by the fact that without H₂ less water is present. In the discussion on Pd the formation of acetone via acid-catalyzed hydration of propene was discarded as the support was shown not to have much influence. The same holds for the Pt/HPA catalysts, as the HPA support will be clearly different in acidic properties. However, the formation of small amount of acetic acid also occurs under these conditions, which may explain the acid-catalyzed formation of acetone. Acidity is also indicated by the conversion of PO under reaction conditions to propanal and other oxidation products.

In conclusion, for Pt the same catalytic effects as for Pd are observed. The catalytic activity is mainly due to the metal particles and not due to the support. Pt apparently is active in both hydrogenation and unselective oxidation of propene. The acidity of the unselective oxidation products, like acetic acid, also induces hydration of propene that results in acetone (via an oxidative step). The results for both Pd and Pt indicate that under gas-phase conditions the formation of propene is preferred over the formation of OOH-like species in the presence of hydrogen. This can be explained by the adsorption of propene on Pd or Pt particles. Furthermore, both Pd and Pt show oxidation activity, but no selective epoxidation to PO. Formation of an OOH-like oxidation species over Pt and Pd may be possible, but any formed PO will be rapidly converted to other products. This is illustrated by the 0.05 wt.% Pt/TiO₂/SiO₂ catalyst that yielded 0.2 % PO, also ethanal, propanal, and acetone. Furthermore, this sample showed a high rate of water formation, but no propane was formed.

The main difference between liquid-phase and gas-phase epoxidation with Pd and Pt may very well be the oxidation state of the metals. Results by the groups of Hölderich [10] and Kuznetsova [12] clearly show that both oxidized and reduced Pd or Pt species are present in selective epoxidation catalysts. Under gas-phase conditions, the partial pressure of hydrogen is higher than under liquid-phase conditions. Furthermore, for H₂O₂ direct synthesis over Pt/Pd usually acids are added that may stabilize oxidized phases. It should be noted that acidic phases are not preferred as they may lead to hydrolysis and oligomerization of the formed PO. In conclusion, both Pd and Pt will be mainly in the reduced form under gas-phase conditions. This will lead to propane formation. Both Pd and Pt only are also active in unselective oxidation of propene.
Modification of gold catalysts

The influence of preparation route on PO production was further investigated by assessing activity of gold catalysts prepared by deposition-precipitation (DP), ion-exchange (IE), and size-controlled gold colloids (SGC). TEM analysis indicated a similar particle size distribution for the DP and IE catalyst. However, the IE sample does not give PO, again indicating that not only the gold particle size, but also the metal-support interface or the structure of the gold particle might be important for epoxide selectivity. The stabilizer (Tetrakis(Hydroxymethyl)PhosphoniumChloride, THPC) used for the SGC method apparently diminishes the epoxidation activity. In the original article [16] and in XPS studies [20] phosphorus was found to remain on the catalyst. Stangland et al. [6] investigated several preparation routes and also concluded deposition-precipitation was the best to obtain active gold catalysts. Recently, it was found that by using polyvinylpyrrolidone (PVP) as stabilizer, and LiBH₄ as reductant to produce colloids also active Au/TiO₂ catalysts can be prepared (at 348 K, 0.05 and 0.2 % PO for 1 and 10 wt.% Au, respectively [20]), but this method was not further investigated in this study.

As only the DP sample was found active for propene epoxidation, it was decided to use deposition-precipitation for the addition of promoting elements to the Au catalyst. Contrary to the IE preparation, which was originally proposed for obtaining well-mixed Pd-Au catalysts [15], the DP method does not necessarily give alloy formation [21]. Hydrogenation is observed, while for the IE and SGC catalyst samples no indication of the presence of < 2 nm gold particles is obtained. Again, the gold particle size effect as proposed by Haruta’s group [1] is not observed here.

Both Pd and Pt addition during DP preparation of gold catalyst lead to hydrogenation activity at 373 K. This result is supported by claims in the patent literature [3] that promotion by Pd is not to be applied for selective gas-phase propene epoxidation, as it will lead to hydrogenation. However, below 373 K no propene is observed for the Pt-containing samples. TiO₂-supported catalysts, which are known to be active at lower temperatures than TiO₂/SiO₂-based samples [2], show the same promoting effect of Pt at 348 K.

Based on the TEM characterization and reaction data Pt seems to be incorporated into the Au metal particles using the DP preparation. Formation of the oxidizing species is more efficient for these bimetallic samples compared to Au-only catalysts, as less water is formed. The effective Pt loading is too low to be observed in any changes of the surface plasmon resonance of gold metal particles at 500-550 nm. This is in good agreement with the work by Wu et al. on bimetallic Pt-Au particles [22].

Researchers of Tosoh reported a Pd/TS-1 catalyst that could give 99 % PO selectivity and no propane in a liquid-phase epoxidation using H₂ and O₂ at 300 K [23]. Hölderich and coworkers [10] found at addition of up to 10 % of Pt relative to Pd to this catalyst had a positive effect on selectivity and activity due to the stabilization of small Pd particles and an oxidized Pd phase. Both large (metallic) particles of Pd and larger amounts of Pt are reported to catalyze hydrogenation to propane. Analysis was hampered by the broad particle size distribution.

This study indicates that under gas-phase conditions Pd is too good a hydrogenation catalyst to enable selective PO production. Apparently, Au is able to dissociate hydrogen (shown by its hydrogenation activity and supported in literature [6] by a kinetic isotope effect), but for some gold metal particles no propene is able to adsorb onto gold. Based on Haruta’s reports [1] gold particle size seems important, but no evidence is found for a transition around 2 nm. From the results presented in Figure 3, it is tentatively concluded that not only the gold particle size, but also the structure of the surface may play an important role. Most probably the change is related to the amount of steps/structure of the gold surface. Hydrogen dissociation but no propene adsorption on gold would enable epoxidation over the
Ti site instead of hydrogenation to form propane. A schematic explanation of the observed side reaction is given in Figure 6.

From the presented catalytic data it can be concluded that small amounts of Pt have a beneficial effect on the hydrogen efficiency. It may be that some gold sites responsible for water formation are poisoned by Pt. However, a change in the coverage of oxygen and hydrogen on the gold is more likely. Recently, it was shown that small amounts of Pt on Au(111) surfaces could increase CO adsorption [24]. In general, water formation is dependent on the coverage of H₂ and O₂, more oxygen usually gives a higher efficiency for H₂O₂ direct synthesis [25] and a higher PO yield [1]. Therefore, it is assumed that Pt increases the oxygen coverage on the metal particles.

Clearly, more characterization studies are needed to determine the location of the Pt and the nature of its promoting effect. However, for both TiO₂ and TiO₂/SiO₂ the promoting effect is observed and addition of Pt to Au catalysts could be useful for possible future industrial application.

Conclusion

Based on the proposed mechanism of oxidizing species formation using hydrogen and oxygen, H₂O₂ direct synthesis catalysts have been tested in the gas-phase propene epoxidation. Contrary to what has been reported for liquid-phase applications, Pd may not be a suitable catalyst in the gas phase, as the metal will catalyze unwanted hydrogenation reactions. Both Pd and Pt were used as promoter for gold catalysts. The results show that deposition-precipitation is a good technique for obtaining active and selective epoxidation catalysts. However, upon addition of Pd or Pt this method is not expected to yield alloy metal particles. The results for Pd-Au catalysts made by DP indicate that although Pd seems well dispersed over the support, hydrogenation of propene to unwanted propane occurs. This is probably due to the presence of monometallic Pd particles.

Results for Pt show an increase in the hydrogen and oxygen efficiency, combined with a stable yield in propene oxide. Hydrogenation of propene to propane occurs at higher temperatures, but can be prevented by operation below 373 K. Both hydrogenation to propane and by-product formation at more than 15 % Pt relative to Au may be related to the formation of separate Pt phases.

Acknowledgements

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References


[18] Chapter 5 of this thesis.

[20] Chapter 4 of this thesis.
## Appendix

### Results of the Pt-HPA catalysts

**Table A.1.** Propane, acetone, and ethanal yield as a function of temperature for the Pt-HPA catalysts obtained from the Boreskov Institute of Catalysis. TBA = t-butyl alcohol, standard reaction conditions $N_2$:O$_2$:H$_2$=propene = 7:1:1:1, WHSV 0.71 g$_{\text{propene}}$/g$_{\text{cat}}$/h. No H$_2$ indicates that no hydrogen was used. The 20%(TBA)$_3$H$_2$PW$_{11}$O$_{39}$-1%Pt/SiO$_2$, calcined at 573 K was also tested with propene instead of propene as reactant.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>T (K)</th>
<th>propane (%)</th>
<th>acetone (%)</th>
<th>ethanal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%Cs$<em>2$H$</em>{0.5}$PW$<em>{12}$O$</em>{40}$-1%Pt/SiO$_2$</td>
<td>323</td>
<td>22</td>
<td>0.30</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>19</td>
<td>0.35</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>17</td>
<td>0.50</td>
<td>0.10</td>
</tr>
<tr>
<td>20%H$<em>3$PW$</em>{12}$O$_{40}$x11H$_2$O-1%Pt/SiO$_2$</td>
<td>323</td>
<td>24</td>
<td>0.087</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>20</td>
<td>0.35</td>
<td>0.075</td>
</tr>
<tr>
<td>20%(TBA)$<em>3$H$<em>2$PW$</em>{11}$O$</em>{39}$-1%Pt/SiO$_2$</td>
<td>323</td>
<td>20</td>
<td>0.38</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>18</td>
<td>0.49</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>16</td>
<td>0.65</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>16</td>
<td>0.58</td>
<td>0.045</td>
</tr>
<tr>
<td>20%(TBA)$<em>3$H$<em>2$PW$</em>{11}$O$</em>{39}$-1%Pt/SiO$_2$, calcined at 573 K</td>
<td>323</td>
<td>21</td>
<td>0.0</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>17</td>
<td>0.55</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>13</td>
<td>0.52</td>
<td>0.079</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>11</td>
<td>0.59</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>323 (2)</td>
<td>19</td>
<td>0.39</td>
<td>0.14</td>
</tr>
<tr>
<td>20%(TBA)$<em>3$H$<em>2$PW$</em>{11}$O$</em>{39}$-1%Pt/SiO$_2$, calcined at 573 K, propane as reactant</td>
<td>348</td>
<td>-</td>
<td>0.046</td>
<td>0</td>
</tr>
<tr>
<td>20%(TBA)$<em>3$PW$</em>{12}$O$_{40}$x11H$_2$O-1%Pt/SiO$_2$</td>
<td>348</td>
<td>23</td>
<td>0.46</td>
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<tr>
<td></td>
<td>373</td>
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<td>0.56</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>373 no H$_2$</td>
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<td>0.051</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>23</td>
<td>0.29</td>
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<tr>
<td>20%(TBA)$<em>3$PW$</em>{12}$O$_{40}$x11H$_2$O-1%Pt/SiO$_2$, calcined at 573 K</td>
<td>323</td>
<td>16</td>
<td>0.23</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>14</td>
<td>0.51</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>348 no H$_2$</td>
<td>0</td>
<td>0.051</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>12</td>
<td>0.64</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>8.2</td>
<td>0.67</td>
<td>0.050</td>
</tr>
<tr>
<td>20%Na$<em>7$PW$</em>{11}$O$_{39}$-1%Pt/SiO$_2$</td>
<td>323</td>
<td>11</td>
<td>0.20</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>12</td>
<td>0.38</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>9.5</td>
<td>0.64</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>7.5</td>
<td>0.70</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>6.4</td>
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</tr>
<tr>
<td></td>
<td>473 no H$_2$</td>
<td>0</td>
<td>0.052</td>
<td>0</td>
</tr>
<tr>
<td>20%H$_3$[PO$_4$(WO$_2$)$_2$]$_4$-1%Pt/SiO$_2$</td>
<td>323</td>
<td>14</td>
<td>0.27</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>11</td>
<td>0.64</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>9.4</td>
<td>0.045</td>
<td>0.086</td>
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<tr>
<td></td>
<td>373 no H$_2$</td>
<td>0</td>
<td>0.052</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>423 no H$_2$</td>
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What is causing the low yield in propene oxide over gold/titania-based catalysts?

In this chapter new catalysts and process options for propene epoxidation with hydrogen and oxygen are discussed. One of problems connected with the use of gold/titania-based catalyst systems is the low yield in propene oxide. It is shown that the low propene oxide yield is due to product inhibition. A modified Langmuir-Hinshelwood model is developed and will be used to discuss the underlying kinetic mechanism.
Introduction

The direct gas-phase synthesis of propene oxide, by the use of molecular oxygen, is still aimed at. Highly dispersed Au/TiO₂ catalysts show an extraordinary selectivity in the oxidation of propene to the corresponding epoxide (> 99 %), using a combination of H₂ and O₂ as oxidation mixture [1]. Additional studies of the epoxidation reaction indicated several drawbacks of the Au/TiO₂ catalyst. Firstly, the low conversion (1-2 %) obtained under typical reaction conditions (atmospheric pressure, 323 - 423 K) cannot be improved by increasing the reaction temperature, because this leads to extensive by-product formation. Secondly, the low efficiency of hydrogen (relatively large amounts of water are formed) is hard to prevent. Finally, significant deactivation of Au/TiO₂ catalysts within several hours on stream has been observed. Deactivation can be almost completely prevented by using dispersed TiO₂ supports, such as TiO₂/SiO₂ and Titanium-Silicalite-1 (TS-1) [2].

In recent literature [2,3] a hydroperoxide-like intermediate has been proposed to be responsible for the selective epoxidation. This oxidizing species is said to be formed over gold and subsequently used for epoxidation over the Ti-containing support. The support is responsible for the slow desorption of PO. One of the problems for future industrial application might be the low yield in propene oxide. Furthermore, the presence of minor amounts of by-products, not detected on lab-scale catalyst testing, might complicate the separation unit in an industrial process.

In this chapter the support effect will be investigated. It has been reported that the Au/TiO₂ and Au/TiO₂/SiO₂ show activity at different temperatures. As already pointed out by Nijhuis et al. the 1 wt.% Au on TiO₂/SiO₂ shows 1.0 % propene oxide (PO) yield at > 99 % selectivity at 373 K. The Au/TiO₂ catalyst is already active at 323 K, where propene conversion to PO is 0.8 % at > 99 % selectivity [2,4]. The PO yield of Au/TiO₂ decreases above 348 K, due to the secondary reaction of PO (to form acetone, propanal, ethanal, etc). PO is stable at higher temperatures on TiO₂/SiO₂, but below 373 K the activity is low. Therefore, the catalysts cannot be compared at the same reaction temperature. Other dispersed Ti supports, like TS-1, exhibit a similar behavior to TiO₂/SiO₂.

In this chapter a Langmuir-Hinshelwood model will be discussed to explain the catalytic behavior of these catalysts. Main objective is to find ways to enhance PO yield. From this model a catalytic cycle is proposed together with its consequences for the maximum yield in PO. Finally, several process and catalyst options are discussed in view of potential future industrial application.

Experimental

For the TiO₂/SiO₂ support preparation a method proposed by Rajadhyaksha et al. [5] was used. This method was also used in previous work [2,6]. Tetraethyl orthotitanate (TEOT, Fluka, 97 %) was dissolved in dry 2-propanol, after which the silica support (Aldrich Davisil 646, 290 m²/g) was added. The 2-propanol was evaporated in a rotating vacuum evaporator at 333 K. The catalyst support was dried in air for 2 hours and calcined at 873 K for 2 hours. This sample will be denoted as selective TiO₂/SiO₂ support. A non-selective TiO₂/SiO₂ support was prepared via the same procedure, except that wet 2-propanol was used. The presence of water was evidenced by the presence of a white precipitate in the TEOT/2-propanol solution. A TiO₂ support (Degussa P25, 90 m³/g) was used as received.

1 Wt.% gold catalysts were prepared by a deposition-precipitation of Au(OH)₃ at a pH between 9.5 and 10 on the supports [2,4]. The catalysts have been calcined at 673 K after the deposition-precipitation, but prior to use.
Steady-state experiments were performed in a microflow equipment. In this apparatus nitrogen (70 vol%), oxygen (10 vol%), hydrogen (10 vol%), and propene (10 vol%) were continuously fed over a 10 ml fixed-bed reactor placed in a fluidized-bed oven. The Weight Hourly Space Velocity (WHHSV) was 0.71 gpropene/gcat h unless stated otherwise. Solvents like methanol and acetone could be added to the reaction mixture via a separate N₂ feed equipped with a liquid saturator. Saturation was carried out at room temperature unless stated otherwise. The analysis of the reaction products was performed using an automated sampling gas chromatograph. The column used for analysis was a Poraplot Q 0.53 mm diameter, 25 m length capillary column, with He as carrier gas. A flame ionization detector (FID) was used for the analysis. This configuration was able to separate all oxygenated organic components relevant in this study. The hydrogen and oxygen consumption was measured on the same gas chromatograph using a Molsieve 5Å, 2 mm diameter, 3 m length column and a Thermal Conductivity Detector (TCD).

The Multitrack, a TAP-like system [7], was used to record Temperature Programmed Desorption (TPD) spectra after adsorption of PO. The Multitrack consists of a small reactor (7 mm inner diameter, bed height 10 mm) that is located in an ultra-high vacuum system [8]. Small amounts of reactants (10¹⁵-10²⁰ molecules) can be pulsed into the system. At the reactor exit the reaction products and reactants were analyzed by four quadrupole mass spectrometers. Known amounts of PO (1.5 % PO in He, Scott) were fed to the catalyst bed via the pulse valves after which TPD spectra were recorded (heating rate 10 K/min).

The FT-IR measurements were performed using an in situ IR cell with CaF₂ windows. This cell was designed and built at the University of Amsterdam [9]. Gas could be fed to the cell using a 4-way valve (Valco), which was configured to select two separate gas feeds. The samples were prepared in the form of self-supporting wafers (~ 20 mg/cm²) at pressures of 3-4 ton/cm². Pretreatment of the wafers consisted of drying at 398 K in He. Spectra were recorded using a Nicolet Magna IR 860 spectrometer equipped with a Mercury Cadmium Telluride (MCT) detector. Unless stated otherwise, spectra were recorded against a background of the sample at the reaction temperature under He at 4 cm⁻¹ resolution, using co-addition of 64 scans. Gases applied (propene, 1.5 % PO in He, H₂, O₂, and He) were dried before use. The IR measurements were performed using a 10 % propene in He mixture, 1.5 % PO in He mixture, and a mixture of 10/10/10/70 vol% of propene, O₂, H₂, and N₂, respectively.

Diffuse Reflectance UV-Vis spectra were recorded on a Cary UV-Vis spectrophotometer using BaSO₄ as reference.

Transmission electron microscopy has been performed using a Philips CM30T electron microscope with a LaB₆ filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.
Model development

A simple Langmuir-Hinshelwood model was derived to elucidate whether or not the yield over the gold/titania-based catalysts can be increased. A schematic representation of this model is given in Figure 1.

\[ C_3 = \]

\[ C_3 = * \rightarrow \text{PO} \]

\[ \text{PO} \]

**Figure 1.** Scheme of elementary steps used for the Langmuir-Hinshelwood model; \( C_3^* \) represents propene, PO is propene oxide.

For simplicity, in the following equations \( C_3^* \) and PO will be replaced by A and B, respectively. The following assumptions are used:

1. propene adsorbs (step 1) and irreversibly reacts (step 2) to propene oxide which desorbs (step 3)
2. \( \text{H}_2 \) and \( \text{O}_2 \) are not taken into account, the formation of oxidizing species is fast compared to the conversion of propene to propene oxide

Furthermore, it was assumed that the rate-limiting step is the desorption of propene oxide (step 3):

\[
 r_3 = k_3 \cdot N_T \cdot \theta_B - k_3' \cdot p_B \cdot N_T \cdot \theta_A.
\]  \( (10) \)

As step 2 is irreversible, the rate equation of this step is:

\[
 r_2 = k_2 \cdot N_T \cdot \theta_A
\]  \( (11) \)

The adsorption of propene (step 1) is in quasi-equilibrium, for the coverage of propene then the following equation holds:

\[
 \theta_A = K_1 \cdot p_A \cdot \theta_B.
\]  \( (12) \)

Based on step 2 and 3 having an equal rate and the site balance:

\[
 1 = \theta_A + \theta_B + \theta_C
\]  \( (13) \)

for the reaction rate the following expression is found \( [10] \):

\[
 r = \frac{k_2 \cdot N_T \cdot K_1 \cdot p_A}{1 + (1 + \frac{k_3}{k_3'}) \cdot K_1 \cdot p_A + \frac{p_B}{K_3}}
\]  \( (14) \)

In this equation \( K_1 \) and \( K_3 \) are the ratios of \( k_1 \) and \( k_1' \), and \( k_3 \) and \( k_3' \) respectively. Using the equation for a plug-flow reactor and integration of propene conversion \( X_A \) leads to:

\[
 \frac{W}{F_{A0}} = \frac{X_A}{k_2 \cdot N_T \left( 1 + \frac{k_2}{k_3} \cdot \frac{1}{K_1 \cdot K_3} \right)} \cdot \frac{\ln(1 - X_A)}{(p_{A0} + K_3') \cdot k_2 \cdot N_T \cdot K_1}
\]  \( (15) \)
Taking into account that propene conversion $X_A$ is below 2% equation (15) may be simplified to:

$$\frac{W}{F_{A0}} = \frac{X_A}{k_2 \cdot N_f \left( 1 + \frac{k_2}{k_3} - \frac{1}{K_1 \cdot K_3} + \frac{1}{(p_{A0} + K_3) \cdot K_1} \right)}$$ \hspace{1cm} (16)

The propene conversion $X_A$ as function of WHSV ($\frac{g_{propene}}{g_{cut} \cdot h}$) can then be expressed as:

$$X_A = \frac{k_2 \cdot N_f \cdot M_A \cdot 3600}{\left( 1 + \frac{k_2}{k_3} - \frac{1}{K_1 \cdot K_3} + \frac{1}{(p_{A0} + K_3) \cdot K_1} \right) \cdot WHSV}$$ \hspace{1cm} (17)

As can be seen, the conversion of propene (= PO yield, if the reaction is > 99% selective) is inversely proportional to the WHSV. In Figure 2, Equation (8) is fitted to previously reported data [2] on 1 wt.% Au supported on Titanium-Silicalite-1 (TS-1).

![Figure 2. PO yield versus WHSV. The line represents Equation (17) that is fitted to the experimental data (symbols) for Au/TS-1 reported by Nijhuis et al.[2].](image)

As can be seen in the figure, Equation (8) can represent the experimental data reasonably well. However, Figure 2 suggests that a lower WHSV leads to a higher yield in PO. Yet, except for one case (which will be discussed in a later section) PO yields above 2% at > 99% selectivity have not been reported in literature.
What is causing the limit in PO yield?

In this paragraph a discussion is given on the possible causes of the limited yield in PO. These causes are:

1. The epoxidation reaction is non-catalytic; i.e. one propene molecule reacts with only one Ti site.
2. The epoxidation reaction is catalytic, but also an irreversible and deactivating reaction occurs.
3. There are no irreversible reaction steps.
4. Competitive adsorption of water should be taken into account.

1. Stoichiometric reaction?

The first option is that propene epoxidation over gold/titania-based systems is non-catalytic. This option is ruled out, as more turnovers per Ti site occur. For example, the conversion reported in Figure 2 [2] for Au/TS-1 corresponds to turnover frequencies from 0.5 to 2.3 mol_{propene}/mol_{Ti} h in increasing WHSV range. As these catalysts are stable and no deactivation is observed, the reaction is catalytic and not stoichiometric.

2. Deactivation?

The second option is that an irreversible and deactivating reaction occurs. This may be due to the occurrence of secondary reactions at low WHSV. Both TiO_2/SiO_2 and TS-1 are active and selective supports, due to the presence of isolated TiO_2 units. However, the presence of TiO_2 islands containing Ti-O-Ti units may induce secondary reaction of propene oxide [6,11]. This is illustrated by using a TiO_2/SiO_2 supported gold catalyst with an amount of the Ti present in the form of TiO_2 islands. A Diffuse Reflectance UV-Vis spectrum of the non-selective support is given in Figure 3 and compared with a selective sample.

![Figure 3. Diffuse Reflectance UV-Vis spectrum of selective and non-selective TiO_2/SiO_2 supports. The presence of TiO_2 islands in the not selective sample is evidenced by a right shift of the absorption peak.](image-url)
What is causing the low PO yield?

The selective sample mainly consists of isolated TiO$_2$ units (atomically dispersed Ti) on SiO$_2$. These units contain tetrahedral Ti, as evidenced by the band at 190-200 nm [12]. The right shift in absorption for the non-selective sample is due to the presence TiO$_2$ islands (containing Ti-O-Ti bonds) besides the aforementioned isolated and tetrahedral Ti. Octahedrally coordinated Ti shows the absorption maximum at 240 nm [12,13].

For the TiO$_2$/SiO$_2$ support preparation a method proposed by Rajadhyaksha et al. [5] was used. Formation of TiO$_2$ islands for the non-selective catalyst can be assigned to the presence of water during preparation, which will lead to rapid hydrolysis of the tetraethyl orthotitanate (TEOT) precursor [13]. Carefully dried glasswork and mixing of the reagents in a glove box could be beneficial for the preparation of highly dispersed TiO$_2$ supported on SiO$_2$.

The PO and propanal production of the non-selective catalyst are given in Table 1.

Table 1. PO and propanal yield at 373 K for Au/TiO$_2$/SiO$_2$ with TiO$_2$ islands present on the support. PO and propanal where the only products observed.

<table>
<thead>
<tr>
<th>WHSV (g$<em>{propane}$/g$</em>{cat}$·h)</th>
<th>PO yield (%)</th>
<th>propanal yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.71</td>
<td>0.10</td>
<td>0.029</td>
</tr>
<tr>
<td>1.42</td>
<td>0.13</td>
<td>0.011</td>
</tr>
<tr>
<td>2.13</td>
<td>0.14</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Contrary to the results for a selective catalyst, PO yield and selectivity both decrease with contact time. This can be assigned to the secondary reaction of PO to propanal over this type of catalyst. Total propene conversion is constant in this small WHSV range.

These results indicate that the limit in PO yield can be dependent on the contact time in the reactor. Formation of by-products at high contact time may remain unobserved in laboratory reactors as the catalyst is under unsteady conditions. It has been shown that deactivation is associated to formation of bidentate propoxy species [11]. Therefore, the catalyst will be slowly covered by hydrocarbon species before by-products appear at the reactor exit. In conclusion, one of the explanations that the PO yield is limited to 2 % is that there are no 100 % selective catalysts. In previous work [6,11] it has been shown that even on the surface of > 99 % selective catalysts C=O containing species can be observed and that these are formed in the presence of oligomeric TiO$_2$ species (containing Ti-O-Ti bonds). The C=O compounds may only be spectator species, but they may also desorb in minor amounts.
To determine the amount of oligomeric TiO₂ (that leads to by-product formation), the Au/TiO₂/SiO₂ catalyst that gave >99 % selectivity to PO [6,11] has been tested in the Multitrack setup. After each adsorption experiment the catalyst was reactivated at 673 K to remove all remaining hydrocarbon species. As can be seen in Figure 4, the amount of adsorbed PO is decreased between 323 and 473 K. At the lower temperatures there is both reversible and irreversible adsorption, but at higher temperatures only irreversible adsorption on oligomeric TiO₂ sites occurs. Based on this plot, the titrated amount of oligomeric TiO₂ sites was calculated to be 3 % of the total Ti sites present.

![Graph showing the amount of adsorbed PO vs. temperature](image)

Figure 4. Amount of adsorbed PO vs. temperature for a Au/TiO₂/SiO₂ catalyst in the Multitrack setup.

There are indications, however, that the Ti ep oxidation center will not give rise to by-product formation [3,6,11]. For example, the work by Thiele and Roland [14] on TS-1 catalysts in liquid ep oxidation shows that modification with salts can decrease by-product formation, while ep oxidation activity is maintained. In other words, by-product (propanal) formation occurs over different sites and preparation of a truly 100 % selective catalyst is, therefore, possible. According to the Langmuir-Hinshelwood model such a catalyst would give higher PO yields at lower WHSV. Furthermore, increasing the catalyst load would lead to higher yields in PO, even in the case of deactivating catalysts. In conclusion, the limited PO yield cannot be assigned to a deactivating reaction.
3. Propene to PO reversible?
A limit in PO yield can appear in the model if there are no irreversible elementary steps. The conversion is then determined by the equilibrium conditions, 2% PO being the equilibrium concentration. However, it is very unlikely that reaction 2 is reversible. This would imply the conversion of PO to propene, which is thermodynamically unfavorable. Furthermore, several studies on PO decomposition over Ti-based catalysts have not reported propene to be under the decomposition products [3,15,16].

4. Competitive water adsorption?
The assumption of competitive adsorption implies that for step 3 (PO adsorption) to occur, empty sites should be present. Therefore, the Langmuir-Hinselwood model will never reach 100% PO-covered catalysts. A small fraction of empty sites will induce propene adsorption. Therefore, the irreversible reaction 2 will proceed over the whole catalyst bed length and a decrease in WHSV has to lead to higher conversions. A more elaborate model would take into account competitive adsorption of water on the active site or the storage of PO on OH groups not related to the active sites. To study both the desorption of PO and water, TPD studies were carried out in the Multitrack set-up. A blank TPD spectrum was recorded of the fresh catalysts, the water signal (m/e 18) is given in Figure 5.

![Figure 5. TPD spectra (m/e 18) of fresh Au/TiO2/SiO2 and Au/TiO2. Intensities are normalized based on the catalyst weight.](image)

For TiO2 water desorbs at 370 K, while TiO2/SiO2 has a desorption peak at 415 K. These low-temperature peaks are assigned to physisorbed water and removal of hydroxyl groups [17-19]. The high-temperature contribution in Figure 5 indicates that the TiO2 support has more OH groups than TiO2/SiO2.
After this TPD experiment, PO was adsorbed at different temperatures and subjected to TPD. In Figure 6 a TPD spectrum (mass to charge ratio (m/e) 58) after adsorption of PO at 323 K is given.

![Graph](image)

**Figure 6.** TPD spectra (m/e 58) for both Au/TiO₂/SiO₂ and Au/TiO₂ catalyst after adsorption of PO at 323 K. Intensities are normalized based on the catalyst weight.

In Figure 6 for both the Au/TiO₂ and Au/TiO₂/SiO₂ catalyst a desorption peak is observed at a temperature of about 373 K. Based on previous work [6,11] this peak is assigned to the desorption of hydrogen-bonded PO. At 530 K a second peak is observed for Au/TiO₂, that seems broadened and shifted to somewhat higher temperatures for the Au/TiO₂/SiO₂ catalyst. This peak was assigned to the release of propanal and acetone (note these compounds also give a signal for m/e 58). This assignment was based on analysis of fragmentation patterns and a PO TPD in He over Au/TiO₂ in the IR cell. PO was adsorbed at 323 K, and in TPD starting at 450 K a C=O band at 1720 cm⁻¹ appeared, which was removed after prolonged exposures to He at temperatures above 600 K.

As can be seen in Figure 6 both the Au/TiO₂ and Au/TiO₂/SiO₂ have a comparable PO desorption temperature (373 and 382 K, respectively). As the Au/TiO₂ catalyst shows activity between 323 and 348 K, a rate-limiting PO desorption can be understood. However, for the 1 wt.% Au on TiO₂/SiO₂ that is active at 373-423 K [2,4] Figure 6 suggests PO desorption is fast and no limitations are expected. The desorption of water as given in Figure 5 at 370 K (TiO₂) and 415 K (TiO₂/SiO₂) seems in better agreement with the reported activity temperatures [2].

From the TPD studies, the optimum reaction temperature seems not related to the PO desorption temperature only, but also to the desorption temperature of water. However, modification of the Langmuir-Hinshelwood model by taking into account the co-adsorption of water will not lead to a limit in PO yield. Water will decrease the θ-values but a comparable explanation will hold as for PO. The Langmuir-Hinshelwood model will predict a fraction of empty sites throughout the catalyst bed, which will enable propene adsorption and subsequent epoxidation.
Low PO yield due to non-Langmuir adsorption

To summarize all experimental data and the previously discussed options: the low yield in PO is due to non-Langmuir adsorption. The situation at low and high PO partial pressures will be dramatically different as illustrated in Figure 7. Apparently, at high PO pressures, PO is able to poison the surface for propene adsorption.

\[
\theta_A = K_1 \cdot p_A \cdot \left( \theta - \frac{p_B}{K_4} \right)
\]

\[\text{Equation (18)}\]

For a sufficiently high PO partial pressure (determined by adsorption equilibrium constant \(K_4\)), the fraction of empty sites available for propene adsorption will become zero and the epoxidation stops. Equation (9) and Figure 7 imply that **PO can adsorb on a PO-rich surface, while propene adsorption is prevented.** In other words, the empty sites of Figure 7 at the maximum PO yield are accessible for PO, but not for propene. It can easily be seen that by substitution of Equation (9) in Equation (2) and solving the equations, a limit in the PO yield will appear. In fact, the equation for WHSV versus PO yield (X) will be the same as for an equilibrium reaction.

Figure 7. Scheme of adsorbate coverages for catalyst at low (left) and the maximum PO yield (right). PO can adsorb on a PO-rich surface, while propene adsorption is prevented.

At low WHSV the epoxidation reaction can only stop if no propene is allowed to adsorb. Mathematically, the situation at the maximum PO yield of Figure 7 can be translated into \(\theta_A = 0\). This will only be possible if the \(\theta_A\) term in Equation (2) is replaced by:
A proposed reaction scheme is given in Figure 8.

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{C}_3 &= \text{epoxidation} \\
\text{H}_2\text{O} + \text{PO} + \text{PO} &= \text{condensed surface phase}
\end{align*}
\]

Figure 8. Proposed reaction scheme for propene epoxidation over gold/titania-based catalysts. At low PO yield, the catalytic cycle will proceed via pathway 3. At the maximum PO yield, the PO concentration is determined by equilibrium 4 and reaction via pathway 3 is inhibited.

At low PO yields, the reaction will proceed via pathway 3. However, at higher PO partial pressures (smaller WHSV), pathway 4 will become more important until the maximum PO yield is reached. Pathway 4 is not an irreversible reaction step, as this would imply catalyst deactivation. The formation of a condensed surface phase can be understood based on the polar nature of both PO and water. At low PO pressures, the adsorption of PO is small, but rapidly increases upon an increase in PO pressure. The less polar propene molecule cannot adsorb anymore.

The condensed surface phase in Figure 8 may seem like multilayer adsorption. The catalysts would then consist of a supported liquid phase. However, as reaction temperatures are well above the boiling point of PO (310 K) for TiO2 catalysts and both PO and H2O (373 K) for TiO2/SiO2-based samples this option has to be discarded. Therefore, the condensed surface phase is probably a relatively stable (sub)monolayer adsorption phase.

Why can PO adsorb on a PO-rich surface, while propene adsorption is prevented?

In this section, the adsorption of PO on a PO-rich surface will be further elucidated. Previous work [6,11] and the TPD studies indicate that the adsorption of PO is related to OH groups that are present on the oxide support. Robinson and Ross [20] have studied PO adsorption on SiO2 and they proposed two adsorbate structures as given in Figure 9. At low pressures PO mainly interacts with isolated OH groups (see Figure 9, left structure), as these hydroxyl groups have more acidic protons. However, at higher partial pressures, PO also interacts with less acidic hydroxyls as given in the right hand side of Figure 9.

Therefore, it is proposed that at high WHSV, where PO yield is typically below 1-2 %, mainly the isolated hydroxyl groups are associated with PO. These may be hydroxyls located on the inactive part of the support, like SiO2 or (octahedral) TiO2, but also on active Ti epoxidation centers. The equilibrium between adsorbed and gas-phase PO will then allow for propene adsorption and subsequent reaction.
What is causing the low PO yield?

![Chemical structures](image)

**Figure 9.** Adsorbed PO on hydroxyl-containing supports: at low PO pressures on isolated OH (left) and at high PO pressures on associated OH (right), after [20]. M denotes Ti or Si.

However, at higher PO partial pressures (low WHSV) PO will also interact with the less acidic associated OH groups. It is tentatively assumed that these sites are not accessible for propene adsorption. The adsorption equilibrium between gas-phase PO and the right hand structure of Figure 9 has been described in Equation (9) by the $p_0/K_4$ term. At decreasing WHSV, the fraction of adsorption sites will become zero for propene, while PO can still adsorb. Based on the described interaction with hydroxyl groups, the following detailed scheme is proposed.

![Chemical reactions](image)

**Figure 10.** Proposed mechanism for propene epoxidation over TiO$_2$/SiO$_2$ catalysts. At low PO yields the catalytic cycle will proceed via pathway 3. At the maximum PO yield, the PO concentration is determined by equilibrium 4 and reaction via pathway 3 is inhibited.
In conclusion, the low PO yields of TiO$_2$/SiO$_2$-based catalysts can be understood in terms of the yield determined by the equilibrium between gas-phase and adsorbed PO. PO molecules are most probably located on hydroxyl groups and inhibit the adsorption of propene. Important parameters for this equilibrium are:
1. the acidity of the interacting proton
2. hydrophobicity/hydrophilicity of the catalyst
3. temperature
4. PO partial pressure
In general, these parameters can be changed by catalyst and/or process development.

Catalyst development
As the limit in PO yield according to Figure 10 is dependent on hydrogen bonding of OH groups, both the acidity of the interacting proton and hydrophobicity/hydrophilicity are of importance. Therefore, the limit in yield may be solved by catalyst development. A good example in this respect is the difference in activity temperatures for the TiO$_2$- and TiO$_2$/SiO$_2$-supported gold catalysts. In the paragraph on competitive adsorption it was shown that these temperatures nicely correlate with the desorption peak of water.

All evidence points to (isolated) tetrahedral Ti sites being active and selective in epoxidation. In this work 0.1 monolayer of TiO$_2$ was dispersed on SiO$_2$ (290 m$^2$/g) and the spectroscopic (UV-Vis) and catalytic (> 99 % PO selectivity) studies indicated the presence of mainly isolated Ti sites. Another option can be the application of Titanium Silicalite-1, which is used for its hydrophobic properties in liquid-phase epoxidation with aqueous H$_2$O$_2$. For zeolite synthesis, the amount of Ti that can be isomorphously substituted in the Silicalite-1 framework is limited to up to 2 or 3 % [21,22].

It should be noted that the Au particles have to be located near the active Ti epoxidation center. Based on the proposed mechanism involving H$_2$O$_2$-like species formation over gold [6,11], spill-over of the oxidizing species to TiO$_2$ is required. For Au/TS-1 catalysts Nijhuis et al. [2,23] observed that Au particles were located on the outer surface of the TS-1 crystals. The oxidizing species may, therefore, not be able to diffuse to the Ti that is mainly located inside the crystal and may be decomposed to water. This was evidenced by SEM and TEM characterization studies that showed that only high surface area TS-1 (comprising of small zeolite crystals) was active in epoxidation [23]. Epoxidation reaction probably takes place on the outer surface of the crystals. This surface will exhibit similar properties as TiO$_2$/SiO$_2$, including the presence of isolated and associated OH groups.

In view of performing the reaction in a hydrophobic environment, gold should be located inside the zeolite crystals. Formation of SiO$_2$ or TiO$_2$ shells around gold or silver colloids has been recently reported [24,25]. Possible drawbacks of this route are the use of stabilizers to protect gold colloids from agglomeration and the dispersion of Ti in the surrounding TiO$_2$/SiO$_2$ matrix. Stabilizers can diminish epoxidation activity by their strong interaction with gold or the Ti epoxidation center [4]. However, performing the epoxidation reaction in a hydrophobic environment may not be successful. As shown by Langhendries et al. [26] TS-1 is hydrophobic, but the water located inside the zeolite is adsorbed on the Ti site. This is because Ti is a strong Lewis acid. In other words, changing the environment may not be enough for shifting the equilibrium. Also shown in Figure 10, the equilibrium of gas-phase and adsorbed PO involves the active epoxidation site. By removal of the hydroxyl groups, also the active epoxidation center will be affected. Modification of the active Ti epoxidation center may, therefore, not be possible. This is illustrated by a recent publication of Haruta and coworkers on Au/TiO$_2$/SiO$_2$ catalysts prepared from non-porous silica [27]. By the application of low surface area silica, the amount of hydroxyl groups is diminished, but this also complicates the preparation of highly dispersed TiO$_2$/SiO$_2$ supports. Titanyl
acetyladetionate was used as Ti precursor for which non-porous SiO₂ provided less anchoring sites. This was shown by the low PO selectivity over these catalysts (up to 60% for the support calcined at the highest temperature). By high temperature calcinations, more isolated TiO₂ units were formed and these sites had a beneficial effect on selectivity.

Sol-gel chemistry offers a great deal of possibilities to change hydrophilicity of the catalysts. A research group at Bayer reported PO yields up to 9.8% (95% selectivity, atmospheric pressure) over gold supported on TiO₂/SiO₂ hybrid materials prepared via sol-gel routes [28]. In these materials Si-OH groups are replaced by Si-H and Si-CH₃ units, that apparently have a beneficial effect on PO yield. As the Bayer researchers employ a lower propene concentration (6%) compared to the standard value used in this study (10%), the PO yield of these catalysts would be 5.9% under the conditions of this study. The maximum selectivity of only 95% still indicates that Ti-O-Ti units are present, although the nature of the by-products is not stated in the patent [28]. One of the challenges related to these organic/inorganic materials will be the stability during catalyst regeneration. Figure 6 indicates that temperatures above 500 K are needed to remove hydrocarbon impurities (secondary products of PO decomposition). However, it has been shown that the Si-C bond will break under oxidizing conditions at temperatures above 500 K [29].

In conclusion, the temperature difference for epoxidation activity between TiO₂ and TiO₂/SiO₂ supported catalysts implies that catalyst development may be beneficial for shifting the equilibrium. The TiO₂-supported catalyst will give higher PO yields at higher temperatures than 350 K, but, unfortunately, deactivating secondary reactions can occur over this catalyst. The TiO₂/SiO₂ (and TS-1) is selective at higher temperatures but this effect is diminished by the increased PO adsorption on these materials. Main challenge is that the limiting PO adsorption equilibrium is occurring on the active epoxidation center. Therefore, many modifications will lead to inactive catalysts.
Process development

To illustrate the options with respect to process development, in Figure 11 the effect of a temperature increase (from 348 to 373 K) on the PO yield over a selective Au/TiO$_2$/SiO$_2$ catalyst can be seen. Upon an increase in temperature at 2200 s a temporary increase in PO yield is observed. This is in agreement with previous reports [2] and due to a change in the PO adsorption equilibrium. At higher temperatures the equilibrium constant of PO adsorption is lower, so that an additional amount will be released upon a temperature rise.

![Graph showing methanol concentration and temperature vs. time](image)

**Figure 11.** Effect of temperature and methanol addition on PO yield for Au/TiO$_2$/SiO$_2$ catalyst.

A similar effect is observed upon saturation of the N$_2$ gas stream with methanol after 4000 s on stream (Figure 11). Based on the schemes presented in Figures 8 and 10, this can be explained by competitive adsorption of PO and methanol. Upon introduction of methanol, PO will be removed from the catalytic surface. An indication that it is a competitive adsorption effect rather than a coordination of methanol to the epoxidation intermediate (as proposed for liquid-phase epoxidations [30]) is given by the observation that both acetone and water (not shown) have a comparable effect. Furthermore, the steady-state PO yield is lower upon addition of methanol. If methanol would coordinate to the epoxidation center and facilitate epoxidation, the steady-state PO yield would be higher.

Addition of a co-feedant, like methanol, can be used to remove PO from the catalytic surface. In Figure 11 a PO yield of 3.2 % can be seen upon switching to the methanol stream. The GC analysis time of typically 6 - 12 minutes is too long to observe the real transients, so quantification of the amount of released PO is not possible.

Unlike acetone and water, methanol changes the selectivity of the reaction dramatically. The steady-state situation ends after 1 h of methanol addition at 373 K as besides PO propanal is formed (Figure 11 at 7600 s). Upon prolonged exposure to methanol (not shown), propanal even becomes the only oxidation product. The use of acetone and water did not lead to a change in selectivity.
The effect of methanol was further investigated in the FTIR setup. Spectra are shown in Figure 12 before and after methanol addition to the in situ FTIR cell. Upon exposure to the H₂/O₂/propene/N₂ mixture a negative band at 3740 cm⁻¹ accompanied by a broad adsorption at 3370 cm⁻¹ is developed. This can be assigned to the reaction of silanol groups (negative band) and formation of a hydrogen-bonded OH species (positive band) [31]. A shoulder at 3710 cm⁻¹, which is assigned to a Ti-OH species, can also be observed. C-H stretch vibrations of an adsorbed hydrocarbon species appear at 2979, 2939, and 2883 cm⁻¹. In the 1800-1350 cm⁻¹ region bands at 1460 and 1382 cm⁻¹ are formed. These hydrocarbon species are irreversibly adsorbed, as the bands do not decrease upon prolonged exposure to He. Based on observations by Cant and coworkers [32] that ethene oxide reacts with surface hydroxyl groups of Ag/TiO₂ catalyst at 493 K to form glycol-like species, this spectrum is assigned to a bidentate propoxy species [6,11] (shown in the insert of Figure 12).

![Figure 12. IR spectrum of Au/TiO₂/SiO₂ catalyst: (a) after 60 mins reaction with H₂O₂ and propene at 398 K, (b) after 60 mins cofeeding methanol. Inset: proposed bidentate propoxy species [6,11].](image)

This compound is probably formed via ring opening of propene oxide and subsequent reaction with surface OH groups. The broad band at 1716 cm⁻¹ is assigned to an adsorbed C=O containing species. Addition of methanol shows a further decrease in the silanol band at 3740 cm⁻¹ and C-H stretching bands typical of a methoxylated SiO₂ surface appear at 2965 and 2854 cm⁻¹ [33]. The intensities of the bands at 1460 and 1382 cm⁻¹ are increased. The formation of formate from methanol is unlikely, as no formate species (which give bands at 1570 and 1540 cm⁻¹ [6]) are observed. Apparently, methanol reacts with surface OH groups and enhances the formation of the bidentate propoxy species. The disproportionation of
methanol will probably create OH groups that can activate the ring opening of PO. This will lead to more bidentate propoxy species. These species probably desorb as propanal [11].

As methanol reacts with the catalyst, acetone and water are better options for removing PO from the surface, but still the yield is determined by equilibrium 4 of Figure 8. Addition of another compound to the reactor feed will eventually lead to a competitive adsorption, less PO adsorbed onto the catalyst and, therefore, less PO in the gas phase. In conclusion, to obtain higher PO concentrations in the reactor exit stream, periodic cycling of either the reactor temperature or feed mixture (pressure swing) is required. Periodic operation has been applied to overcome several chemical engineering challenges [34] and both temperature and pressure swing have been previously proposed to enhance PO concentrations [23].

Temperature swing would involve reaction at low temperature and PO removal at higher temperature. The temperature differences cannot be too high, to avoid the risk of by-product formation. Two aspects are important for temperature swing: the adsorption capacity of the epoxidation catalyst and the temperature dependence of PO desorption. An adsorption enthalpy of around 60 kJ/mol has been reported by Robinson and Ross [20] for PO on SiO2. For a reactor operating at 373 K, heating up to 473 K will remove 98 % of the adsorbed PO. Application of this option will involve the development of high surface area catalysts with a high PO storage capacity.

As for pressure swing, removal of PO from the catalyst at lower pressure will create even more diluted streams and, therefore, can be counterproductive. Pulses of acetone and water can also be seen as pressure swing operations. Industrially, water (or more probably low-pressure steam) would be the best option, because of the relatively easy water-PO separation. Again, the PO storage capacity of the catalyst is the main key to an economically viable process.

Conclusion

A modified Langmuir-Hinshelwood model has been developed to explain the limit of propene oxide (PO) yield at around 2 % over Au/TiO2-based catalysts. Previously reported results can be explained by a PO adsorption structure involving hydrogen-bonded OH groups.

An increase in catalyst load does not lead to a higher yield in propene oxide, either due to consecutive reaction over Ti-O-Ti containing units, or the existence of a PO adsorption-desorption equilibrium over active epoxidation centers. This limit in PO yield may be circumvented by a catalyst development or a temperature/pressure swing process. Catalyst development has to be focused on an increase in the hydrophobicity of the catalyst. More specifically for pressure swing, several cofeedants, like water, acetone and methanol can be used to remove PO from the catalyst by competitive adsorption. However, methanol reacts with the catalyst and increases the surface acidity, which leads to propanal formation. Propanal is probably being formed from bidentate propoxy species, which are already present on catalysts operating at > 99 % selectivity to PO. Minor amounts of other oxygenates than PO might complicate the product separation in future industrial applications. Steam would be a better option for possible future industrial processes.
List of used symbols

- $F_i$: flow rate of compound i
- $K_j$: equilibrium constant of reaction j
- $k_j$: reaction rate constant of reaction j
- $M_i$: molar mass of compound i
- $N_i$: total concentration of active sites
- $p_i$: partial pressure of compound i
- $r_j$: reaction rate of reaction j
- $X$: conversion
- $W$: catalyst mass
- WHSV: Weight Hourly Space Velocity
- $\theta$: surface coverage

subscripts

- A: propene
- B: propene oxide
- cat: catalyst
- *: empty sites
- 0: at the reactor inlet

References


and silvers. Similar discussions on propene epoxidation have been investigated. Both catalytic systems are compared and the best options towards a future propene oxide production process are discussed.

A summary and evaluation of the presented chapters is given. In this thesis, gold and titania-based systems are discussed.
Summary

Propene oxide (PO) is one of the most important intermediates in chemical industry. Currently, there are two commercial propene oxide (PO) processes, namely: a chlorohydrin and a hydroperoxidation route. The first process employs hypochlorous acid as oxidant, the latter uses an organic hydroperoxide. Both processes suffer from severe environmental and/or economic drawbacks, respectively. It has been shown in the introduction that due to the market size a new PO process should be based on propene and molecular oxygen as feedstock and the number of steps should be as small as possible to minimize by-product formation.

Both silver and gold/titania are interesting catalytic systems. Silver catalysts suffer from low selectivity to PO (up to 60%), while gold/titania catalysts are limited in PO yield (up to 2%). As shown in the literature overview (chapter 1), many mechanistic aspects of epoxidation over gold and silver are unclear yet. Most silver literature is based on ethene, and it is not clear whether all mechanistic information can be applied to propene. A good ethene epoxidation catalyst has a low PO selectivity, so the influence of Ag particle size and support are different. For gold many questions exist on the oxidation state of the gold as a function of particle size and contact with the support. Clearly, both gold and silver show promising leads towards a new PO process. The proposed reaction schemes are given in Figure 1.

![Figure 1. Proposed propene epoxidation mechanisms over gold/titania and silver catalysts.](image)

Characterization of gold/titania and silver catalysts

In chapters 2, 3, and 4 valuable characterization tools have been used and (further) developed to study silver and gold catalysts. Chapters 2 and 3 discuss silver in more detail, chapters 4 and 5 focus on the Au/TiO₂-based catalysts.

In chapter 2, the interaction of oxygen with CaCO₃- and α-Al₂O₃-supported Ag catalysts was studied in an advanced Temporal Analysis of Products (TAP) reactor. Adsorption of oxygen was modeled using a Langmuir-Hinselwood approach taking into account both molecular oxygen adsorption and dissociation. The activation energy of oxygen dissociation was found to be 17 kJ/mol on a promoted Ag/α-Al₂O₃ catalyst and 52 kJ/mol for a Ag/CaCO₃ sample. Determination of oxygen dissociation activation energy is important. For ethene epoxidation it is generally stated that the surface reaction of ethene and oxygen is reaction rate limiting. However, for higher olefins, like butadiene, norbornene, and styrene, molecular oxygen dissociation can become rate limiting. Therefore, in propene epoxidation the dissociation of oxygen may be rate-limiting under certain conditions and thus determine selectivity of the reaction.

Chapter 3 was focused on the reaction of oxygen and propene over a promoted Ag/α-Al₂O₃ catalyst, studied in an advanced Temporal Analysis of Products (TAP) reactor. In the absence of oxygen, PO was chemically converted to a surface species on the Ag/α-Al₂O₃ catalyst. In the presence of oxygen, this specific surface species were easily oxidized. The catalyst exposed to the reaction mixture showed higher epoxidation selectivity than the catalyst treated by oxygen only. The results suggest that the mechanism and the active oxygen
are similar compared to ethene epoxidation. However, both the high acidity of propene and the propensity of propene oxide to secondary reaction should be taken into account to improve propene epoxidation over silver catalysts. The use of inert support and silver catalysts with more surface defects or reaction conditions forming surface defects can be advantageous.

One of the main questions regarding gold catalysis is the oxidation state of the active gold species. In chapter 4, gold catalysts supported on TiO₂ and TiO₂/SiO₂ have been characterized by ⁴⁷Au Mössbauer Absorption Spectroscopy (MAS), X-ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM). Gold particle sizes of 1 wt.% Au catalysts calcined at 673 K ranged from 3 to 6 nm. Two Au contributions were found in Mössbauer spectra, and assigned to bulk metallic Au atoms in the core of a gold particle, and metallic gold on the outer surface of this particle. Surface gold atoms exhibit a smaller recoil-free fraction than Au atoms in the core of a particle. This has been assigned to the surface atoms being less coordinated. By MAS no evidence for charge transfer from support to Au particle could be found. Active epoxidation catalysts containing 10 wt.% Au could be prepared with a similar gold particle size compared to the 1 wt.% samples. Auger lines of the 10 wt.% Au catalysts could be determined. The Auger parameters confirmed that the surface layer of 3 - 5 nm gold particles is metallic. Shifts in Au 4f½ binding energy with respect to metallic gold show that the C 1s reference should be used with caution. Furthermore, final state effects due to the reduced coordination of metallic surface gold atoms will also give shifts in binding energy.

In the preparation of Au/TiO₂ via deposition-precipitation Au(OH)₃ species are converted to metallic gold during calcination. Gold particles do not gradually grow during calcination, possibly due to the simultaneous conversion of Au(OH)₃ moieties with dehydroxylation of the TiO₂ support. Epoxidation activity was found to increase with the amount of metallic gold. Catalysts consisting of only oxidized gold were found to be inactive. No evidence for oxidized gold active in the propene epoxidation reaction using H₂ and O₂ could be found.

Another main question is related to the effect of the TiO₂-based support on propene epoxidation over gold catalysts. TiO₂-supported catalysts deactivate, while dispersed TiO₂ on SiO₂ maintains its activity. Both XPS and MAS indicate that deactivation of Au/TiO₂ during propene epoxidation is not due to a change in the active gold species and has to be related to the TiO₂ support. In chapter 5, in situ FT-IR spectroscopy was used to study the surface species involved in the selective epoxidation of propene over a 1 wt.% Au/TiO₂ catalyst and a 1 wt.% Au/TiO₂/SiO₂ catalyst. At the low temperatures applied for Au/TiO₂-based catalysts (323 – 423 K) propene adsorbs weakly on both catalysts via γ-hydrogen bonding with surface hydroxyl groups of the TiO₂, or TiO₂/SiO₂ support. Propene adsorption is completely reversible at temperatures between 300 and 400 K. Both reversible and irreversible adsorption of propene oxide (PO) was observed on both catalysts, the irreversible adsorption yielded bidentate propoxy moieties. Similar proproxy species are formed after prolonged exposure of the catalysts to a propene/oxygen/hydrogen mixture. Deactivation of TiO₂ catalysts is explained by the formation of these propoxy groups on active and selective Ti sites. Neighboring acidic Ti sites are involved in coupling of PO onto these sites. Occupation of selective sites with propoxy groups is limited on TiO₂/SiO₂ catalysts. On this support, proproxy groups are located on acidic agglomerated TiO₂ sites, and linked to an Si-OH functionality. These groups are not involved in the selective epoxidation of propene, which occurs over isolated tetrahedral sites.

An important finding is that besides proproxy groups, surface compounds with absorptions in the C=O stretching range (such as acetone and propanal) were observed on both catalysts. Formate and acetate species (implying C-C bond cleavage) were identified.
exclusively on the Au/TiO₂ catalyst. The 1 wt.% Au/TiO₂/SiO₂ catalyst exhibits > 99 % PO selectivity under flow-conditions, but the FTIR study indicates that on the catalytic surface byproduct formation occurs.

**Catalyst development**

Compared to silver, gold catalysts show the highest selectivity to PO (> 99 % compared to < 60 %). However, these catalysts suffer from severe drawbacks that limit the possible industrial application. These are the low yield in PO (< 2 %) and the low efficiency in hydrogen (water production). The low H₂ efficiency has to be improved in view of raw material costs, but the direct reaction of H₂ and O₂ to H₂O will also produce heat. This heat has to be removed at low temperatures as reaction over gold/titania-based catalysts typically takes place below 473 K. In chapter 6 it is shown that the low efficiency in hydrogen can be solved by application of promoters, in chapter 7 the reasons for the low yield in PO are disclosed.

In chapter 6, gold catalysts are compared with Pd and Pt catalysts in the direct gas-phase epoxidation of propene. In literature reports on liquid-phase epoxidations it has been shown that Pd and Pt can catalyze the formation of propene oxide in the presence of hydrogen and oxygen. However, both Pd and Pt yield mainly propane in gas-phase conditions. This has been assigned to the presence of metallic Pd and Pt. Both Pd and Pt have also been added in promoter levels to Au catalysts. The presence of small amounts of Pd added to Au catalysts prepared by deposition-precipitation also leads to unwanted hydrogenation to propane. This is explained by the presence of monometallic Pd particles. Addition of 5 % of Pt relative to Au yields bimetallic Au catalysts that are more active and selective. The water-propene oxide ratio decreases upon addition of Pt to a Au/TiO₂/SiO₂ catalyst, while the epoxidation activity is maintained. Hydrogenation of propene to unwanted propane does not occur at temperatures below 373 K. Based on comparison of different preparation routes it is concluded that the Pt of these selective catalysts is present as a highly dispersed phase in the gold particles.

In chapter 7, options for the development of new catalysts and processes for propene epoxidation with hydrogen and oxygen are discussed. One of problems connected with the use of gold/titania-based catalyst systems is the low yield in propene oxide. It is shown that the low propene oxide yield is due to product inhibition. A modified Langmuir-Hinshelwood model is developed and used for discussion of both support and process options.

**Evaluation: Silver or gold?**

In future, research efforts can be allocated to improve the selectivity of silver-based catalysts or the activity of gold/titania-based catalyst systems. Based on the information presented in the preceding chapters the question arises on which route seems most promising in view of the development of a new propene epoxidation process.

Firstly, the requirements for the characterization tools are discussed as they may be important for catalyst research in general. Secondly, the potential of catalyst development, and thirdly, process options are treated.

**Characterization**

The advanced TAP reactor has been shown to be a valuable tool in silver catalyst research. Main finding is that within the order of seconds, epoxidation selectivity can change. This selectivity change has been related to the population of oxygen species. Therefore, the work presented in chapters 2 and 3 shows that relatively slow techniques like TPD (often applied in literature) will not be useful to characterize the different oxygen species and their effect on selectivity. However, even an advanced TAP reactor cannot elucidate all mechanistic aspects. Application of *in situ* spectroscopic tools, like Raman and XPS, are
needed to study both adsorbate coverages and resulting reaction products. For catalyst development, testing in fixed-bed reactors at higher pressures is still necessary because of the lower epoxidation selectivity under the lower pressures in TAP reactors combined with in situ spectroscopic techniques. Use of the TAP technique for gold-catalyzed epoxidation is limited due to the low activity and low reaction temperatures. In other words, the small amount of product that is formed will slowly desorb from the catalyst surface, leading to a negligible shift (if any) in baseline of the mass spectrometer signal.

With respect to the characterization of gold/titania-based catalysts, several observations are made in chapters 4 and 5. The active gold species in propene epoxidation, but also CO oxidation, are under much discussion. As shown in Chapter 4, combinations of a bulk (MAS) and surface (XPS) characterization technique are very powerful. Main challenge in this respect is that the active species may be present in a very small amount. Therefore, the amount of active material has to be as high as possible, while a well-defined and uniform metal particle size is maintained. Future research on the interesting particle size effects observed in (gold) catalysis is, therefore, dependent on the development in preparation techniques. For example, preparation of gold colloids in a desired size range has been studied extensively, however, not all these samples will exhibit catalytic activity due to the impurities introduced by the ligands. The next step will be the preparation of particles with a defined morphology (shape, surface structure) that allows elucidation of structure-activity relations. Furthermore, Chapter 4 illustrates the importance of FTIR analysis of the surface of a > 99% selective catalyst. Small amount of byproducts may remain unobserved at the reactor exit, but can be detected by FTIR.

**Catalyst development**

As shown in the above, characterization tools can be improved to facilitate catalysis research. Based on the reports in literature and the chapters presented in this thesis, also a direction (gold or silver) can be defined. In the following table the two investigated catalyst systems are compared.

**Table 1. Comparison of gold/titania and silver catalysts.**

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With respect to the oxidant needed for the epoxidation of propene, both gold and silver use molecular oxygen, but gold also needs hydrogen. The maximum H₂ efficiency that can be obtained for Au will be at H₂O/PO = 1, but this value has not been reached yet (Chapter 6). The direct conversion of H₂ and O₂ to H₂O is one of the problems related to gold chemistry. All experimental evidence obtained so far points to the gold metal particles being responsible for the excessive water formation. In literature and in Chapter 6 it has been shown that Pt promoters can have a beneficial effect, while maintaining the epoxidation activity. Whether this effect is due to poisoning of unselective gold sites, or a change in reactant coverages onto the Au metal particles remains to be solved in future. More research into the exact nature of the epoxidizing species (H₂O₂ or OOH?) will give an indication if the H₂O/PO of 1 is a real minimum or can be suppressed even further. The water formation is not only important for
raw material cost, but also for the heat produced in the epoxidation process. High \( \text{H}_2 \) efficiency will pose less problems associated with heat transfer.

Clearly, the activity of silver catalysts will not be much of a problem for industrial applications, as the maximum conversion is usually limited by the temperature rise that is allowed in the fixed-bed reactor. The activity for gold is lower, but catalysts operated at short contact times still exhibit reasonable productivity. Main problem for gold is that the PO yield is limited due to the strong inhibition of the epoxidation reaction by PO (Chapter 7). This limitation leads to diluted PO streams leaving the reactor. The reaction proceeds catalytically, but at the maximum PO pressure an equilibrium between gas-phase PO and catalyst will be reached. It is shown in Chapter 7 that this behavior is most probably due to the epoxidation chemistry over Ti centers. One solution may be an increased catalyst hydrophobicity. Last years significant progress has been made in sol-gel chemistry and post-treatment of TiO\(_2\)/SiO\(_2\) gels to remove unselective Ti sites and replacement of -OH by -CH\(_3\) and -H groups. A good example is given in a patent by Bayer researchers that claim a PO yield of 8% (although with only 95% selectivity) [1]. Another option may be the use of other epoxidation catalysts, like W and Mo, in the gas-phase epoxidation, but no examples other than Ti are known yet. One explanation may be that Ti\(^{4+}\) is stable in the reaction mixture containing propene and hydrogen, while W and Mo are reduced and not active in epoxidation. In conclusion, Ti may very well be the only epoxidation catalyst that is active in gas-phase applications.

Selectivity is one of the remarkable aspects of the gold catalysts. In view of the beneficial effect of the increase in active Ti sites as stated in the paragraph above, more research could be directed into isolated Ti units with a high loading on an inert support. The results presented in Chapter 5 show that even small amounts of clustered TiO\(_2\) will lead to by-product formation. In Chapter 7 it was shown that only 3% of the Ti present in the catalyst sample is enough to explain the by-product formation of Chapter 5. The low selectivity for Ag-based catalysts remains to be solved. Chapter 3 showed that Al\(_2\)O\(_3\) is not inert towards PO and possibly CaCO\(_3\) as proposed by Arco researchers [2] may suppress secondary reactions. Also many promoters (Cl\(^-\), NO\(_3^-\)) are claimed for these carbonate-based samples and their role should be further elucidated. Especially, in the presence of nitrogen oxide species (sub)stoichiometric reactions can occur and this should be carefully checked. Silver particle size and surface morphology may also be an important parameter for propene epoxidation as it influences the “active” oxygen species. The optimum silver particle size may be different from the large particles that are used for ethene epoxidation.

The maximum reaction temperatures for gold/titania-based catalysts are below 470 K. Above this temperature byproduct formation occurs, and the results of Chapter 5 indicate that this is mainly due to the secondary reaction of PO. In order to improve heat transfer, a high reaction temperature is favored. As silver is active and selective between 470 and 520 K, this catalyst is favored. Furthermore, the gold/titania catalyst leads to higher heat production due to the direct formation of H\(_2\)O from H\(_2\) and O\(_2\). For the gold/titania catalyst an optimum temperature will, therefore, be determined by the trade-offs between heat transfer, selectivity, and activity. For silver also the production of CO\(_2\) may give rise to unwanted heat production, but heat transfer is improved due to the higher reaction temperatures.

For both catalysts pressure seems to have a beneficial effect on activity. For gold catalysts the presence of hydrogen will complicate matters as the explosive region is easily reached. With respect to catalyst cost, no clear distinction can be made between the two routes. The ideal catalyst may very well employ metal particles in a distinct size range, which requires deposition-precipitation or the more costly colloid synthesis routes. Furthermore, the preparation of the support and the possible aftertreatment are also important for a cost comparison.
In conclusion, both gold/titania and silver have different pros and cons related to future industrial application. Gold catalyst research should be focused on improvement of the PO adsorption equilibrium on the Ti epoxidation units and increase of hydrogen efficiency, for example by addition of promoters to the gold particles. A lot of research has been performed already on silver epoxidation catalysts, but a thorough understanding of the oxygen species on the silver surface may lead to new insights. One of the main features of the gold/titania catalysts is their good selectivity but clearly more research is needed on the formation of epoxidizing species.

Process options

In the discussion above, possible future applications were based on the use of an adiabatic fixed-bed reactor. In view of the results presented in this thesis also other process layouts may come into mind. In Chapter 7 some options, like pressure- and temperature-swing have been discussed. Clearly, not enough has been investigated on the gold/titania-based catalysts to revert to engineering solutions only. Furthermore, the data presented in Chapter 7 suggest that some of the catalyst and process development targets are similar. For example, catalyst development would aim for a higher concentration of active sites in view of a higher steady-state PO yield, while in process development a higher concentration of active sites would be needed for a highly PO-loaded catalyst to be successfully applied in pressure-swing processes.

One of the short-term process options may still be the application of liquid-phase processes using H₂O₂ and TS-1. However, some of the problems related to the gold/titania catalysts (selectivity) will also hold for the TS-1 chemistry, and new problems as solvent recycle and catalyst reactivation at high temperatures appear [3].

Conclusion

It has been shown that both gold/titania and silver catalyst are currently the best candidates for a new propene epoxidation process. The gold/titania is interesting for its selectivity and while silver is preferred for its high activity. To date, no evidence exists that the activity or selectivity are limited by a theoretical maximum.

References
Samenvatting

Propeneoxide (PO) is een van de belangrijkste grondstoffen in de chemische industrie. In 1999 werd er in de wereld 6 miljoen ton PO geproduceerd. Er zijn twee processen waarbij PO wordt gemaakt uit propeen en een oxidant. In het chlorohydriโปรпроцесе wordt propeen omgezet met hypochloritzuur, het hydroperoxideproces maakt gebruik van een organisch peroxide als oxidant. Het chlorohydrinproces produceert naast PO ook milieu-onvriendelijke chloorhoudende verbindingen en daarom zijn de meeste nieuwe PO-fabrieken gebaseerd op het hydroperoxideproces. Het nadeel van het hydroperoxideproces is de equimolare hoeveelheid bijprodukt. In de huidige processen worden zowel isobutanol als styreen als bijprodukt geproduceerd.

Om deze nadelen te ondervangen, zou een proces waarbij propeen en zuurstof (of lucht) reageren tot propeneoxide ontwikkeld moeten worden. Zilverkatalysatoren kunnen PO produceren, maar de maximale selectiviteit bedraagt 60% (de overige hoeveelheid propeen wordt voornamelijk volledig tot CO₂ en H₂O verbrand). Goud/titania-katalysatoren kunnen zeer selectief (> 99%) PO produceren, maar zetten maximaal 2% van de hoeveelheid propeen om. Bovendien werkt de laatste katalysator alleen in de aanwezigheid van waterstof en produceert derhalve ook een grote hoeveelheid water.

In hoofdstuk 1 is een literatuuroverzicht gegeven. In de literatuur blijkt dat voor zilver de selectiviteit van de reactie wordt bepaald door de concentratie van electrofiele en nucleofiele zuurstof. Nucleofiele zuurstof speelt een rol in het adsorberen van propeen, maar leidt ook tot totale verbranding. Electrofiele zuurstof leidt tot selectieve epoxidatie. De grootte van de zilverdeeltjes en de structuur van het oppervlak zijn belangrijke parameters voor de selectiviteit. Voor goud/titania-katalysatoren lijkt de epoxidatie van propeen over een Ti-atoom in de drager plaats te vinden. Het goud katalysert de reactie van waterstof en zuurstof tot de oxidant. Deze oxidant, waarschijnlijk een waterstofperoxide-achtige verbinding, diffundeert naar de drager en zorgt voor epoxidatie.

Hoofdstukken 2, 3 en 4 gaan over de karakterisering van zowel zilver- als goud/titania-katalysatoren. In hoofdstuk 2 is de interactie van zuurstof met zilverkatalysatoren met CaCO₃- en α-Al₂O₃-dragers bestudeerd door middel van een Temporal Analysis of Products (TAP)-reactor. Adsorptie van zuurstof op gereduceerde monsters kon met een Langmuir-Hinselwoodmodel worden beschreven. Voor een gepromoteerde Ag/α-Al₂O₃ katalysator werd 17 kJ/mol als activeringsenergie voor de zuurstofdissociatie gevonden, voor een Ag/CaCO₃ monster bedroeg deze waarde 52 kJ/mol. Voor de epoxidatie van propeen kan de zuurstofdissociatie snelheidspalend worden en dus van belang zijn voor de epoxidatie-selectiviteit.

In hoofdstuk 3 is de reactie van zuurstof en propeen op een gepromoteerde Ag/α-Al₂O₃ katalysator nader bestudeerd in een TAP-reactor. In de afwezigheid van zuurstof reageert PO tot een oppervlakte-component. Deze stof wordt in de aanwezigheid van zuurstof snel geoxideerd. Het is gebleken dat de katalysator die voorbehouden is in het reactiemengsel (zuurstof en propeen) een hogere epoxidatie-selectiviteit heeft dan een katalysator die enkel in zuurstof is behandeld.

In hoofdstuk 4 wordt het onderzoek naar de oxidatietoestand van het goud in de actieve goud/titania-katalysatoren beschreven. Goudkatalysatoren met TiO₂ en TiO₂/SiO₂ als drager zijn gekarakteriseerd door middel van ¹⁹⁷Au Mößbauer Absorptie Spectroscopie (MAS), X-ray Photoelectron Spectroscopy (XPS) en Transmissie Electron Microscopie (TEM). De grootte van de gouddeeltjes lag tussen de 3 en 6 nm voor de monsters die bij 673 K gecalcineerd waren. Twee goudbijdragen zijn gevonden in de Mößbauer spectra en deze zijn toegekend aan metalen goudatomen in de kern van een gouddeeltje en verstoord metalen goudatomen op het buitenoppervlak van een gouddeeltje. Deze goudatomen aan
het oppervlak van een gouddeeltje hebben een lagere terugslagvrije fractie dan de
goudatomen in de kern van een gouddeeltje. MAS leverde geen aanwijzing voor een
ladingsoverdracht tussen gouddeeltje en drager. XPS analyse van 1 en 10 gewichts.% Au
katalysatoren met vergelijkbare gouddeeltjesgrootte is gebruikt om de Augerparameter te
bepalen. De waarde van deze parameter toonde ook het metalisch karakter van de
goudatomen aan het oppervlak van een gouddeeltje aan. Tevens werd aangetoond dat de
verschuivingen in Au 4f,22 bindingsenergie niet een goede maat zijn voor de oxidatietoestand
van goudatomen in kleine metaladeeltjes. Dit komt door een onzekerheid in het gebruik van
de C 1s referentie en “final state” effecten.

Tijdens de bereiding van goudkatalysatoren door middel van depositie-precipitatie en
calcinering wordt Au(OH)₃ naar metalisch goud in de calcineringsperiode omgezet. De
epoxidatie-activiteit hangt af van de hoeveelheid metalisch goud. Katalysatoren, die enkel
geoxydeerd goud bevatten, zijn niet actief. In dit onderzoek is dus geen bewijs gevonden dat
de activiteit van goud/titania-katalysatoren in de aanwezigheid van waterstof en zuurstof aan
goxydeerd goud is toe te schrijven.

Zowel XPS als MAS lieten zien dat de deactivering van Au/TiO₂ tijdens
proppeenepoxidatie niet te wijten is aan een verandering in de oxidatietoestand van het goud.
In hoofdstuk 5 is deze deactivering nader onderzocht door middel van infraroodspectroscopie.
De oppervlakte-componenten die ontstaan tijdens epoxidatiereactie over een deactiverende
Au/TiO₂- en een stabiele Au/TiO₂/SiO₂-katalysator konden zo worden geanalyseerd. Propeen
adsorbeerde reversibel op beide katalysatoren tussen 300 en 400 K, maar een gedeelte van het
PO adsorbeerde irreversibel en vormde een bidentaat propoxy-verbinding. Dezelfde
verbindingen werden gevormd tijdens reactie in de aanwezigheid van propaan, waterstof en
zuurstof. De deactivering van de Au/TiO₂ katalysator kan door de vorming van deze propoxy-
verbindingen op actieve en selectieve Ti atomen worden verklaard. Zure Ti atomen, die
vlakbij de actieve centra liggen, zijn hiervoor verantwoordelijk. Op TiO₂/SiO₂-katalysatoren
is de vorming van propoxy-verbindingen tot de geagglomereerde TiOₓ-plaatsen beperkt en
vindt niet plaats op de geïsoleerde Ti epoxidatiecentra.

In vergelijking met zilver geven goud/titania-katalysatoren de hoogste selectiviteit
(>99% vergeleken met <60%). De goud/titania-katalysatoren hebben echter als nadelen de
lage PO opbrengst (<2%) en de lage waterstoffefficiëntie (grote waterproductie). Dit lage
rendement in het gebruik van waterstof moet worden verbeterd in verband met
groondstoffen, maar ook om de warmteproductie tijdens de reactie binnen de perken te
houden. Deze reactiewarmte moet bovendien bij lage temperaturen worden afgevoerd, daar de
selectieve reactie naar PO beneden 473 K moet plaatsvinden.

In hoofdstuk 6 werden goudkatalysatoren vergeleken met Pd- en Pt-katalysatoren. De
aanwezigheid van Pd en Pt leidt in veel gevallen tot de vorming van propaan. Het toevoegen
van geringe hoeveelheden Pt (5% ten opzichte van de hoeveelheid goud) geeft echter geen
propaanvorming en bovendien een verlaging van de water-PO verhouding (hoger
waterstofrendement). In hoofdstuk 7 werden opties voor nieuwe katalysatoren en processen
beschreven. De lage PO-opbrengst over goudkatalysatoren is aan produktinhibitie te wijten.
Door de katalysator meer hydrofoob te maken, is de maximale PO-opbrengst te verhogen. Het
periodiek opereren van druk en/of temperatuur is tot nog toe geen goede optie voor het
vergroten van de PO-opbrengst.

In hoofdstuk 8 zijn zilver- en goud/titania-katalysatoren met elkaar vergeleken. Beide
systemen zijn geschikt voor nader onderzoek wat betreft de proppeenepoxidatie. Voor
zilverkatalysatoren zou de selectiviteit verhoogd moeten worden door middel van variatie van
zilverdeeltjesgrootte en de toevoeging van inerte dragers. Voor goud/titania-katalysatoren is
het modificeren van de drager het meest geschikt voor het verkrijgen van een grotere PO-
opbrengst.

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Publications and presentations

Publications


Publications in preparation


Oral presentations


A. Zwijnenburg, A. Urakawa, A. Vaccaro, B. van der Linden, G. Mul, M. Makkee, and J.A. Moulijn, “Propene epoxidation over silver: reaction mixture effect and O₂-Ag interaction”, Presented at 4th World Congress on Oxidation Catalysis, Berlin, Germany, 16-21 September 2001.


Poster presentations


