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Oxidative dehydrogenation of ethane on Pt–Sn impregnated monoliths

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The oxidative dehydrogenation of ethane was studied over Pt–Sn impregnated monoliths at 1 bar, 600–900 °C and with different contents of oxygen, hydrogen and steam in the feed gas. As expected a decrease in oxygen in the feed led to a decrease in the conversion of ethane due to lower temperatures in the reactor. Adding steam to the feed showed no effect on the ethane conversion or the ethene selectivity. When the hydrogen/ethane ratio in the feed was varied from 0 to 0.5 at 700 and 850 °C, it resulted in a significant increase in the selectivity to ethene while the ethane conversion remained relatively unchanged. At 700 °C the selectivity increased from about 50% to 93% (carbon basis) with only a small decrease in the conversion of ethane. The results clearly show that both Pt and Sn have a catalytic effect. Pt caused the ethane conversion to rise and addition of Sn resulted in much better ethene selectivity. However, even though Sn alone showed some catalytic effect at lower temperatures, it cannot explain the great difference between the Pt and Pt–Sn catalysts. A reasonable assumption is therefore that there exist interactions between Pt and Sn that gives the Pt–Sn catalysts excellent properties for oxidative dehydrogenation of ethane, in particular upon addition of hydrogen.

KEY WORDS: ethene; ethane; dehydrogenation; Pt–Sn catalysts; monoliths.

1. Introduction

Ethene is an important feedstock for many chemical processes [1]. Ethene is mainly produced by steam cracking and the process is normally carried out in large units. However, steam cracking suffers from several limitations. One promising alternative to steam cracking of ethane is oxidative dehydrogenation of ethane which offers several advantages such as short contact time, adiabatic operation and smaller reactor volumes. It could also possibly be carried out in smaller units.

Although not yet commercialized, there have been several studies on oxidative dehydrogenation of ethane over different types of catalysts operated at low temperatures (300–400 °C), moderate temperatures (400–600 °C) and high temperatures (600–900 °C). At high temperatures the focus has been on Pt-based catalysts and chromium oxides. Selectivities of 70% with ethane conversions of 80% were obtained with Cr_2O_3/ZrO_2-monoliths, but they exhibited a shorter lifetime than catalysts based on Pt [2]. Pt-based catalysts have proved to be useful giving high yields of ethene [3–19].

It has been shown that addition of hydrogen to the ethane/oxygen feed during oxidative dehydrogenation increases the selectivity to ethene significantly [3,6,9,16]. Bodke *et al.* have reported an increase in the ethene selectivity over a Pt/α-Al_2O_3 catalyst from 65% to 72% when hydrogen was added to the feed. Nevertheless, the ethane conversion dropped from 70% to 52%. However, by adding Sn to the Pt catalyst an improved catalytic system is obtained. Using a Pt–Sn/α-Al_2O_3 catalyst the ethene selectivity increased from 70% to more than 85% with hydrogen addition keeping the conversion at ~70% [9]. The addition of hydrogen to the feed causes oxygen to react with hydrogen to produce water rather than to react with hydrocarbons, which will ultimately lead to products like carbon oxides [7,9,14].

Yokoyama *et al.* have investigated the addition of several metals to Pt catalysts. The results showed that promotion with either Sn or Cu to Pt monoliths enhanced both the conversion of ethane and the selectivity to ethene significantly compared to only Pt, giving higher yields of ethane [5]. Later studies support the idea that promoting Sn to Pt catalysts increases the selectivity to ethene [6,9,14,16]. Silberova *et al.* reported high yields of ethene (~63%) using Pt–Sn monoliths in a continuous flow reactor at 850 °C when hydrogen was added to the feed [16].

The purpose of the present work has been to obtain a better understanding of the effect of the catalyst on oxidative dehydrogenation of ethane. Experiments have been carried out in the temperature range of 600–900 °C over Pt, Sn and Pt–Sn catalyst as well as over wash-coated monolith without any catalyst. Furthermore, experiments were performed adding small to moderate amounts of hydrogen in the feed in order to study the effect on the selectivies, in particular to carbon oxides. The amount of oxygen was also altered and steam has been added to the feed. The goal has been to establish suitable feed compositions for oxidative dehydrogenation of ethane with respect to both ethane conversion and ethene selectivity.

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2. Experimental

The monolithic substrate consisted of extruded Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$; Corning) with a cell density of 62.2 cells/cm^3 washcoated with a dispersion of Disperal P2 (Condea). The monoliths were prepared as cylindrical pieces (15 mm in diameter and 10 mm in height). After washcoating, the monoliths were dried vertically for 4 h at 120 °C and the washcoating step was repeated until the weight increase was about 15% of the original monolith weight. The washcoated monoliths were calcined in a flow of air at 550 °C for 4.5 h. Four different types of catalysts were used; Pt, Sn and Pt–Sn on an alumina washcoat as well as the washcoated monoliths without any metal. Impregnation with 1 wt% Pt was done by an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Alfa Products) with subsequent drying for 4 h at 100 °C. The monoliths were then calcined in a flow of air at 550 °C for 4.5 h. Impregnation with 7 wt% Sn was done by an aqueous solution of $SnCl_2 \cdot 2H_2O$ (Merck), dried for 4 h at 100 °C and calcined in a flow of air at 100 °C for 0.5 h and at 700 °C for 1.5 h. The Pt–Sn catalyst was impregnated with Pt prior to impregnation with Sn.

The oxidative dehydrogenation of ethane was performed at 1 bar and high temperatures (600–900 °C). In the experiments where the furnace temperature was varied, the total flow rate was 2000 mL/min with 308 mL/min ethane, 30.8 mL/min hydrogen, 366.6 mL/min air and the rest of the feed consisting of argon. The same feed composition was also used during the stability tests. This composition gives a hydrogen/ethane ratio of 1/10 and an ethane/oxygen ratio of 4/1. A total flow rate of 2000 mL/min with 308 mL/min ethane and 30.8 mL/min hydrogen was kept constant in the experiments where the amount of oxygen in the feed was altered. In these experiments the oxygen flow was increased from 146.7 to 733.3 mL/min, but the total flow rate was kept constant at 2000 mL/min by reducing the amount of argon in the feed. In the experiments where the hydrogen/ethane ratio was varied, 308 mL/min ethane and 366.6 mL/min air were kept constant. The hydrogen flow was increased from 0 to 154 mL/min at a constant total flow rate of 2000 mL/min by reducing the amount of argon in the feed.

The oxidative dehydrogenation of ethane was studied in a continuous flow apparatus consisting of a quartz reactor with an inner diameter of 15 mm. The catalyst was placed between two inert monoliths acting as radiation shields. Temperature profiles were measured by a movable thermocouple placed inside a small quartz tube inside the monoliths. The temperature referred to as the reactor temperature in this paper was measured at the exit of the catalyst bed while the furnace temperature is the temperature measured between the quartz reactor and the inside of the furnace. The catalyst was reduced *in situ* in a flow of hydrogen at 600 °C for 0.5 h prior to the experiments. Two water-cooled condensers were installed at the outlet of the reactor to remove any water from the product gas. Dry samples of the product gas were then analyzed by two gas chromatographers (HP 5880 and HP 5890). A detailed description of the experimental set-up is described elsewhere [20].

3. Results and discussion

The main reaction products were ethene, water, hydrogen and carbon oxides. In addition to the carbon oxides, by-products like CH_4, C_3H_8, C_3H_6, C_3H_4, C_4- and C_5-components were also detected. After the experiments reported here were finished, some product analyses were made with another gas chromatograph (Agilent 6890N) using another column. These results showed that also ethyne could be produced in considerable amounts depending on the conditions. High temperatures favoured the formation of ethyne. In fact, the maximum selectivity to ethyne was about 3%.

3.1. Effect of catalyst

Figure 1(A, B) compare the results obtained over the monoliths impregnated with Pt–Sn/alumina and the washcoated monolith without any metal. The conversion of ethane is somewhat lower for the experiment performed without Pt–Sn in the whole temperature interval. While the conversion of oxygen is almost complete over the entire temperature range for the Pt–Sn catalyst, this is not the case using washcoated monolith where oxygen is detected in large amounts in the product gas at furnace temperatures below 750 °C. However, the main difference is observed in the two experiments at furnace temperatures below 800 °C for the selectivity to ethene. The selectivities to the carbon oxides, presented in figure 1(B), show that for the washcoated monolith, the selectivity to CO is much higher at furnace temperatures below 800–850 °C compared to the CO selectivity obtained by the Pt–Sn impregnated monolith. The Pt–Sn catalyst suppresses the formation of CO at lower temperatures. At 800 °C the selectivity to CO_2 is also very low. However, at higher temperatures the gas phase reactions start to play an increasingly important role.

Experiments have also been carried out over washcoated monoliths impregnated with only Pt. A comparison between the Pt and Pt–Sn catalyst is given in figure 2(A, B). In figure 2(A) the ethane conversion and ethene selectivity are measured as a function of furnace temperature. Figure 2(A) clearly shows the large effect Sn has on the selectivity to ethene when added to a Pt catalyst. Adding Sn greatly enhances the ethene selectivity by reducing the formation of CO as shown in figure 2(B) where the selectivities to CO and CO_2 and reaction temperatures are given as a function of furnace

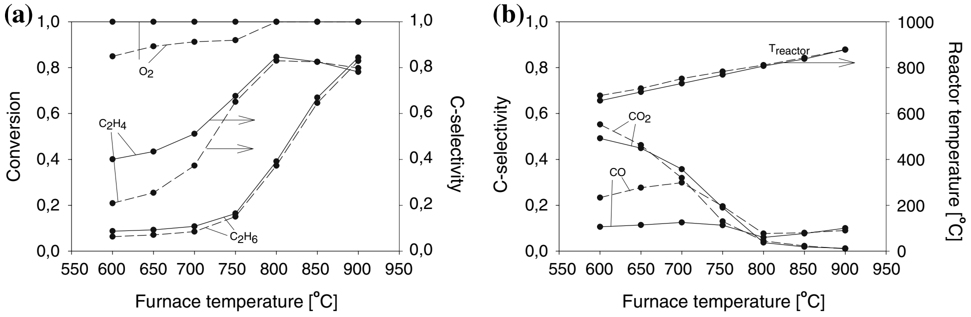

Figure 1. Comparison of a Pt–Sn catalyst (solid lines) and a washcoated monolith (dashed lines). Feed [NmL/min]: C_2H_6 (308), air (367), H_2 (31) and Ar (1295). Total flow rate: 2000 NmL/min.

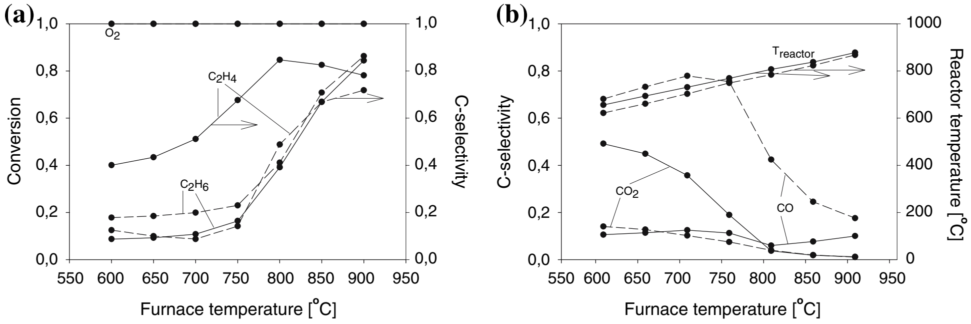

Figure 2. Comparison of a Pt–Sn catalyst (solid lines) and a Pt catalyst (dashed lines). Feed [NmL/min]: C_2H_6 (308), air (367), H_2 (31) and Ar (1295). Total flow rate: 2000 NmL/min.

temperature. The selectivity to CO_2 on the other hand is higher over the Pt–Sn catalyst at a furnace temperature of 800 °C than over Pt. When comparing the formation of other by-products such as propene, propyne, C_4- and C_5-components, they appear to be produced in larger amounts over the Pt–Sn catalyst. At furnace temperatures below 800 °C the selectivity to methane was higher over the Pt catalyst, but at higher temperatures no clear difference was observed.

The observed increase in ethene selectivity when adding Sn to the Pt catalyst is consistent with results obtained elsewhere [5,6,9,14,16]. However, the lower ethane conversion is in contradiction with the results achieved by Yokoyama *et al.* where addition of Sn gave increased ethane conversion in addition to higher ethene selectivity [5].

A washcoated monolith impregnated with only Sn was also tested at temperatures in the range of 600–900 °C and compared with washcoated monoliths without any metal as shown in figure 3. Figure 3(A) indicates that Sn alone has a positive effect on the ethene selectivity at lower furnace temperatures. Figure 3(A) also shows that the conversion of O_2 is not complete at furnace temperatures below 800 °C for the Sn impregnated system. Thus, it might appear that Sn has a catalytic effect at lower temperatures, but as the temperature rises the contribution from the gas phase reactions starts to dominate. Above 750 °C the conversion of ethane is even decreased by the addition of Sn. This is not, however, explained as a temperature effect since both maximum and reaction temperatures are higher in the experiment where Sn is used in this area. Reaction temperature and selectivities to the carbon oxides are given in figure 3(B). The observed increase in ethene selectivity when Sn is added to the monolith seems to be caused by less production of CO. The selectivity to methane, propene and propane is slightly higher over the washcoated monolith without Sn and there was not observed any evident difference between selectivities to propyne, C_4- and C_5-products for the two sets of experiments.

Even though it seems that Sn has some catalytic properties, it can still not account for the large difference between Pt and Pt–Sn catalysts. Bodke *et al.* suggested that the effect of Sn is caused by intermetallic components like Pt_3Sn, PtSn, $PtSn_3$ and a combination of these. This claim is based on a characterisation of a Pt–Sn-catalyst. There was not observed any free Pt [5,9].

3.2. *Effect of ethane/oxygen ratio*

It is evident from figure 4(A) that a decrease in the ethane/oxygen ratio results in an increase in the conversion of ethane for the Pt–Sn catalyst. Similar results were obtained by Yokoyama *et al.* [5] who altered the ethane/oxygen ratio between 1.5 and 2.1. The results also show that the conversion of oxygen is

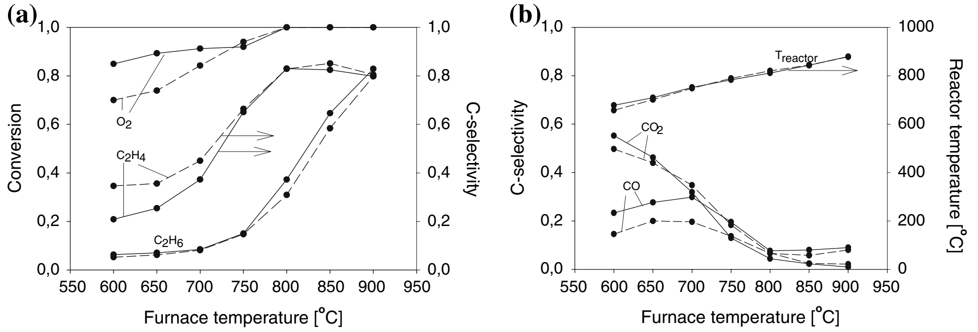

Figure 3. Comparison of a washcoated monolith (solid lines) and a Sn catalyst (dashed lines). Feed [NmL/min]: C_2H_6 (308), air (367), H_2 (31) and Ar (1295). Total flow rate: 2000 NmL/min.

complete in the entire interval. The selectivity to ethene decreases with decreasing ethane/oxygen ratio until an ethane/oxygen ratio of 4. Increasing the amount of oxygen in the feed even further, seems to increase the selectivity to ethene.

As expected, the temperature increases when the oxygen content in the feed increases. The behaviour of the ethene selectivity seems to follow closely the formation of CO_2. The selectivity to the other by-products increases when adding more oxygen to the feed and is probably due to the enhancement of reactor temperature.

The effect of the catalyst with varying ethane/oxygen ratios has also been studied at 700 °C. The Pt–Sn impregnated monolith has been compared to the washcoated monolith containing no metal. The results are presented in figure 5 and they show a significant effect of the catalyst at these reaction conditions. The ethane conversion, and in particular the selectivity to ethene, were much higher when the washcoat is impregnated with Pt–Sn. Figure 5(B) shows the selectivities to CO and CO_2. The formation of carbon oxides are reduced when using the Pt–Sn catalyst and the difference is especially evident for CO. The selectivities to methane, propane and C_4-components are higher over a washcoated monolith until an ethane/oxygen ratio of 4 where the trend shifted. The selectivity to propene was always higher over the Pt–Sn catalyst than the washcoated monolith. Propyne and C_5-components were not detected for ethane/oxygen ratios higher than 2.

The temperature profiles for the experiments over the Pt–Sn catalyst and the washcoated monolith are shown in figure 5(C, D), respectively. Large temperature gradients through the reactor are observed for the Pt–Sn catalyst and the maximum temperature is located in the first half of the catalyst bed (1.0–1.5 cm). For the washcoated monolith more even profiles are observed and the maximum temperature is at the exit of the reactive monolith (about 2 cm). The maximum temperature is also much higher using the Pt–Sn catalyst explaining the high ethane conversion. The results presented in figure 5(C, D) together with the conversion and selectivity data shows that oxygen reacts with hydrogen instantly when coming into contact with the catalyst. The large temperature increase caused by the combustion increases the endothermic dehydrogenation of ethane resulting in a temperature drop. This is in good agreement with results obtained elsewhere. Henning and Schmidt [14] studied the oxidative dehydrogenation of ethane over Pt–Sn monoliths using a multiport reactor where they were able to measure temperatures and product concentrations along the entire length of the reactor. They suggested that the combustion occurs on the surface leading to high

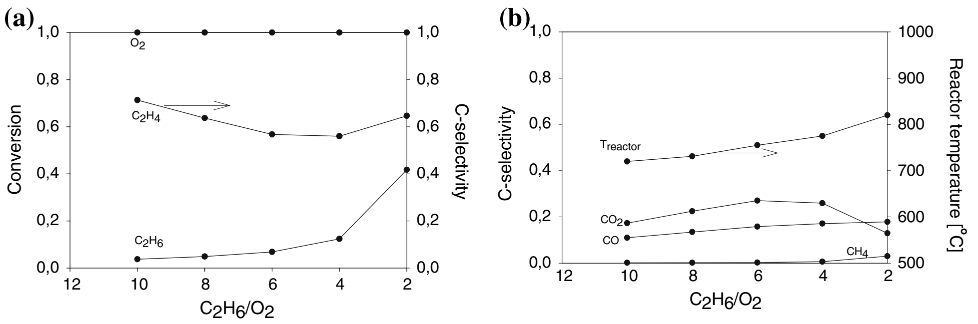

Figure 4. Effect of oxygen content in the feed over a Pt–Sn catalyst. Feed [NmL/min]: C_2H_6 (308), air (147–733), H_2 (31) and Ar (1514–928). Total flow rate: 2000 NmL/min. Furnace temperature: 700 °C.

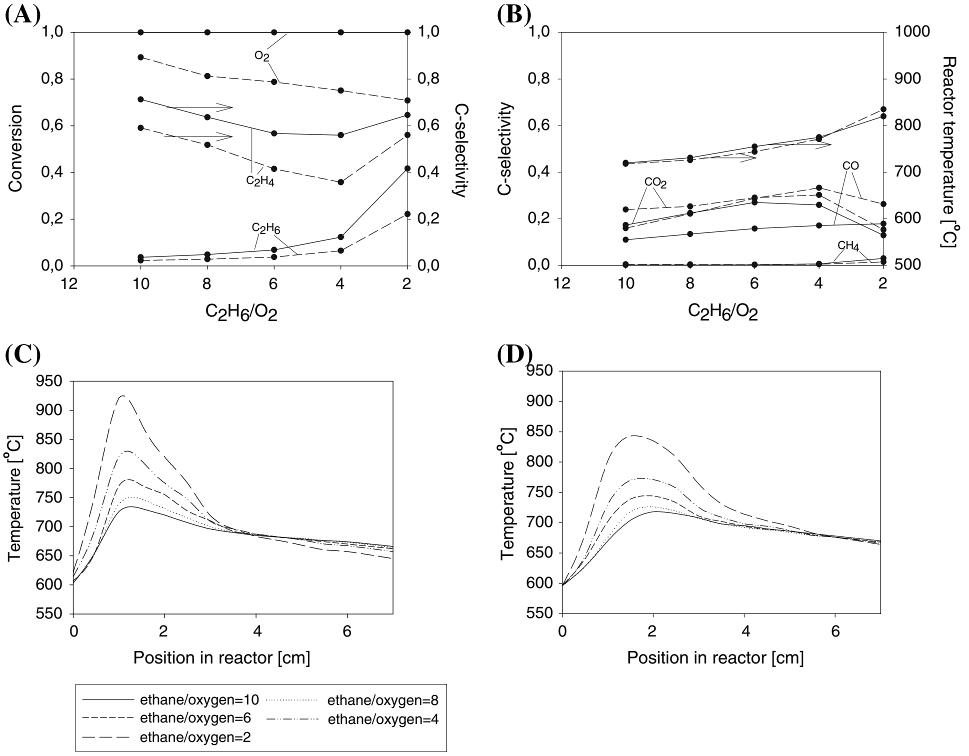

Figure 5. (**A**) and (**B**) show a comparison of variation of oxygen with a Pt–Sn catalyst and washcoated monolith where solid lines present experiment with catalyst and dashed without. (**C**) and (**D**) show temperature profiles through the reactor with and without catalyst, respectively. 0 cm represents the top of the upper inert monolith, 1.0 cm the entrance of the active monolith and 2.0 cm the exit. Feed [NmL/min]: C_2H_6 (308), air (147–733), H_2 (31) and Ar (1514–928). Total flow rate: 2000 NmL/min. Furnace temperature: 700 °C.

temperatures which initiates the homogeneous dehydrogenation to ethene. Lødeng *et al.* [11] and Beretta *et al.* [8] used a Pt catalyst to study the same reaction. No evidence of the heterogeneous production of ethene was found. This theory was later supported by Silberova *et al.* [7] who performed a comparative study for ODE under conventional flow and under Temporal Analysis of Products (TAP) reactor conditions. They concluded that ethene was formed in the gas phase and not via surface reactions.

3.3. *Effect of steam*

The effect of adding steam to the feed is shown in figure 6 where the conversion of ethane and the selectivity to ethene are given as a function of the ethane/oxygen ratio when 0%, 5% or 22.5% of the total feed consisted of steam. Figure 6(A) shows that neither the selectivity to ethene nor the ethane conversion seems to be affected by the addition of steam. In figure 6(B) the selectivities to ethene and the carbon oxides are shown

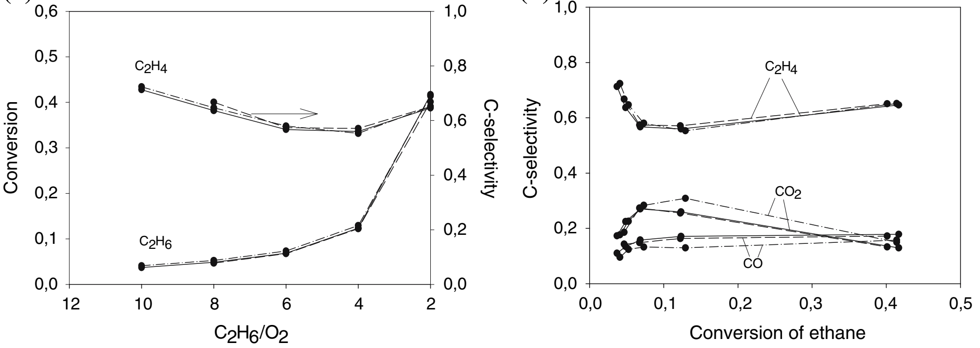

Figure 6. Effect of addition of steam. Solid lines represent 0% steam, dashed lines 5% steam and dash-dot lines where 22.5% of the total feed consists of steam. Feed [NmL/min] (0% steam): C_2H_6 (308), air (147–733), H_2 (31) and Ar (1514–928). Total flow rate: 2000 NmL/min. Furnace temperature: 700 °C.

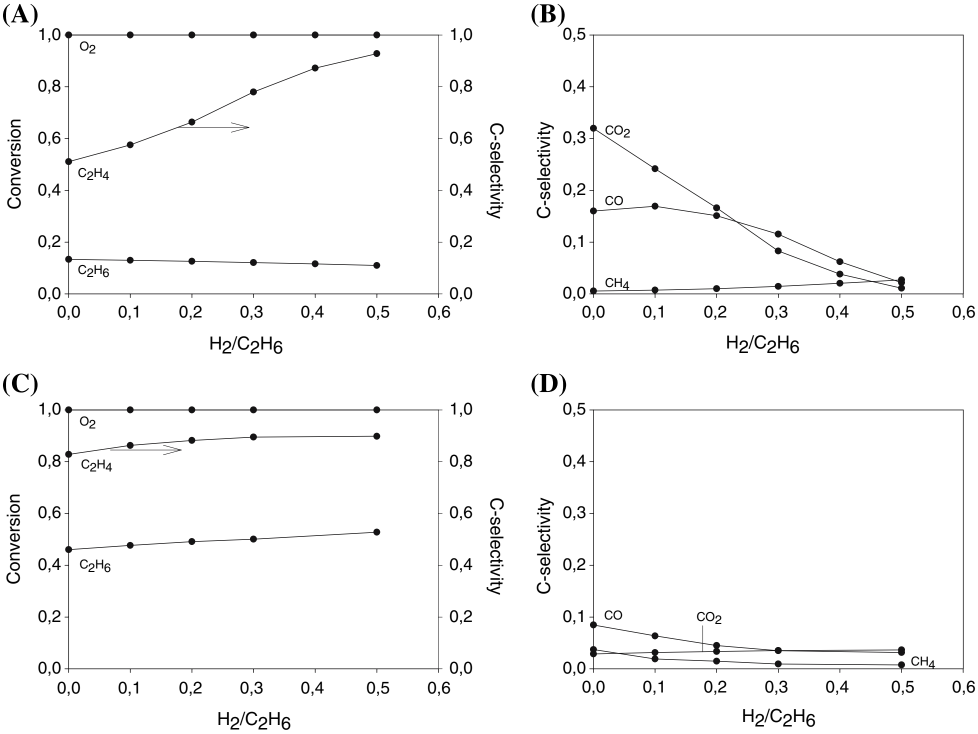

Figure 7. Effect of hydrogen addition (**A**) and (**B**) at a furnace temperature of 700 °C and (**C**) and (**D**) at a furnace temperature of 850 °C. Feed [NmL/min]: C_2H_6 (308), air (367), H_2 (0–154) and Ar (1325–1171). Total flow rate: 2000 NmL/min.

as a function of the ethane conversion. The results indicate that when steam is added to the feed, the selectivity to CO_2 increases and the selectivity to CO decreases probably as a result of the water–gas shift reaction. However, this does not seem to influence the selectivity towards ethene. The rest of the by-products were not affected by the addition of steam.

3.4. *Effect of adding hydrogen*

The conversions and the selectivity to ethene as a function of hydrogen/ethane ratio in the feed are given in figure 7(A, C) for experiments carried out at 700 and 850 °C, respectively. The results show that the ethene selectivity is strongly increased while the conversion of ethane remains relatively stable. The selectivities to carbon oxides at a furnace temperature of 700 °C are shown in figure 7(B) and it is evident that the increase in the ethene selectivity is caused by the reduced formation of carbon oxides upon addition of hydrogen. The selectivities to CO and CO_2 at 700 °C were greatly reduced as the hydrogen content in the feed was increased; from 16.0% to 32.0% without hydrogen to 2.2% and 1.1% at a hydrogen/ethane ratio of 0.5, respectively. The selectivities to methane and C_{3+} -components increased in the same interval.

At a furnace temperature of 850 °C the effect of hydrogen addition is not as obvious as at 700 °C, but the selectivity to ethene increased from 82.8% to 89.8% when the hydrogen/ethane ratio was increased from 0 to 0.5 (see figure 7(C)). Figure 7(D) shows that the selectivities to the carbon oxides and methane decreases when adding more hydrogen to the feed. For C_{3+}-components there is observed an increase in selectivity except for propane where the opposite effect is noticed.

3.5. *Stability test*

Figure 8(A) shows the conversions of ethane and oxygen and selectivity to ethene as a function of time. The catalyst seemed to be very stable for a period of almost 300 min. The selectivities to methane and carbon oxides are given in figure 8(B). As expected there was observed a slight increase in the selectivity to the carbon oxides. For methane and C_3-products almost no change in selectivity was observed. This was not however the case for C_4-components which showed an uneven curve the first 135 min. C_3H_4 and C_5-components were not detected in the product gas in this experiment.

4. Conclusion

The main products in oxidative dehydrogenation of ethane were ethene, water, hydrogen, methane, CO, CO_2 and ethyne. In addition smaller amounts of C_3–C_5 components were also detected.

Both Pt and Sn showed catalytic effect. While Pt increased the conversions of oxygen and ethane, addition of Sn to the Pt catalyst resulted in a significantly better selectivity to ethene. Even though Sn alone showed some catalytic effect in the lower temperature

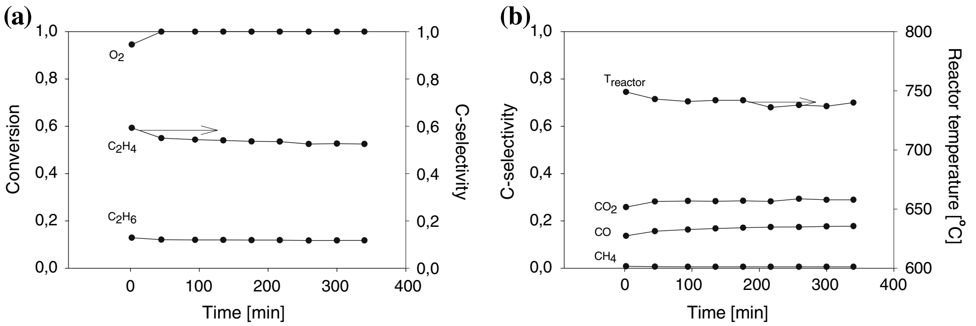

Figure 8. Time dependence of the Pt–Sn catalyst. Feed [NmL/min]: C_2H_6 (308), air (367), H_2 (31) and Ar (1295). Total flow rate: 2000 NmL/min. Furnace temperature: 700 °C.

range, it cannot account for the large difference in ethane conversion and selectivities observed over the Pt catalyst and the Pt–Sn catalyst.

Varying the amounts of oxygen and in particular the content of hydrogen in the feed showed large effects in the product distribution. A decrease in ethane/oxygen ratio led to a significant increase in ethane conversion due to larger extent of the exothermic oxidation of hydrogen to water, which gave a temperature rise in the reactor. Addition of only small amounts of hydrogen resulted in a considerable increase in ethene selectivity while the ethane conversion remained unchanged. Adding steam to the reaction mixture did not seem to affect either ethane conversion or ethene selectivity.

The results strengthen the theory that gas phase reactions play an important role in oxidative dehydrogenation of ethane. This reaction is on the other hand driven by heterogeneous combustion reactions. Ethene yields of ~66% were obtained at a furnace temperature of 900 °C over Pt–Sn catalysts.

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