GAS-PHASE ALDOL CONDENSATION OVER TIN ON SILICA CATALYSTS

J. Venselaar

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CONTENTS

INTRODUCTION - SCOPE OF THESIS

In the period between the second World War and the mid-1970s, cheap oil and natural gas have become the dominant raw materials for the manufacture of a large variety of chemicals. Coal has all but disappeared as a chemical feedstock, whilst biomass contributed to the production of industrial chemicals to a limited extent, i.e. it was used mostly for chemicals with molecular structures similar to those of the feedstock, such as is the case for carbohydrates and fatty oil-derived products.

This industrial 'monoculture' is now changing rapidly. Among the causes are the rising prices and more limited availability of oil and gas, and the changing relations between oil producing, industrialized and developing countries. A growing need is felt by the latter two groups of nations to promote self-reliance as regards energy materials and feedstocks for the manufacture of chemicals. As a result, coal-based technology is being revived with growing haste in industrial countries; older technology is modernized and supplemented by new and improved processes to make the industrialized world less dependent economically and politically on the oil-producing cartel.

Many developing countries have been hit even harder by the rising prices of crude oil. Some of these having a large potential for biomass production have now turned to biomass-based processes to achieve a greater degree of self-reliance. A good example is Brazil, where large-scale ethanol production from biomass by fermentation is now an industrial reality.

Of course, carbohydrate-containing materials, such as molasses, have long been a substantial source of ethanol, although the main production of ethanol is from petroleum-derived ethylene. However, increasing quantities of crops such as sugar cane, cassave and wheat are now used to make ethanol. For instance, the production of ethanol in Brazil based on these crops planned for 1980 is 2,700,000 tons. Ethanol is planned to be used mainly as a source of energy, for instance as addition to gasoline, e.g. in the U.S.A. It can also serve as a base material for the chemical industry, e.g. to produce ethylene, an obvious intermediate from which a long line of other products can be derived.

For example, production of ethylene from ethanol is growing rapidly in Brazil. Old plants are modernized and extended and new plants under construction. A 120.000t/a ethylene plant is being built by Rhône-Poulenc and the production of vinyl chloride monomer from the ethylene (200.000 t/a) is being considered by Dow Chemical. (1,2).

Another potentially important intermediate is ethanal, probably the main alternative for ethylene. Part of the butanol production, the entire production of 2-ethylhexanol and many other compounds, aldehydes as well as alcohols, are obtained from it in processes in which aldol condensation is the central reaction (Figure 0.1). Butanol and 2-ethylhexanol are quite important for the manufacture of solvents and plasticizers. Their annual production is high: 50.000 tons butanol and 190.000 tons 2-ethylhexanol were produced in the USA in 1974 (3,4). However, most of the n-butanal required as an intermediate was obtained by hydroformylation of propene, the most economical process route since about 1960 (5).

The commercial processes via the aldol condensation route are all based on liquid-phase base-catalyzed condensation. Heterogeneous gas-phase processes have been proposed, especially for the condensation of ethanal, n-butanal and acetone, but economical and technical shortcomings have retarded their application. In principle, gas-phase processes have advantages over the liquid-phase process because reaction control in particular is easier, as is discussed in chapter 1.

Among the reasons why gas-phase aldol condensation has so far met with little success in industry is that the catalysts applied tend to have low selectivities and become rapidly deactivated. An exception to this rule seems to be a catalyst consisting of tin on silicagel, which is a promising catalyst according to Swift and co-workers (Gulf Research and Development Co.) (6, 7, 8, 9, 10). The aim of the work described in this thesis was to investigate the aldol condensation over this catalyst more fully, especially of ethanal. Aspects covered here are catalyst preparation and performance, the mechanistic background of the catalytic activity and the kinetics of the reaction.

Chapter 1. contains a literature survey on catalytic aldol condensation, with special attention to the work of Swift et al quoted above. Catalyst preparation and characterization are discussed in chapter 2. Several methods of preparing tin on silica catalysts were tried out to find the influence of the method of preparation on performance and to select the optimum catalyst. In this work, the self-condensation of ethanal was applied as the test reaction, ethanal being a highly reactive compound which is also interesting from the point of view of industrial application of the process.

Chapter 3 describes the activity, selectivity and deactivation of the catalysts and the factors that control them during the aldol condensation of ethanal.

A better understanding of the catalytic background of the reaction is believed to be necessary to improve the process. Therefore, kinetic measurements are presented in chapter 4 and the structure of the active site is dicussed in chapter 5.

Catalyst performance in the condensation of n-butanal, an industrially important reaction, is the subject of chapter 6. The final chapter also contains a proposal for a process based on the knowledge obtained in this study.

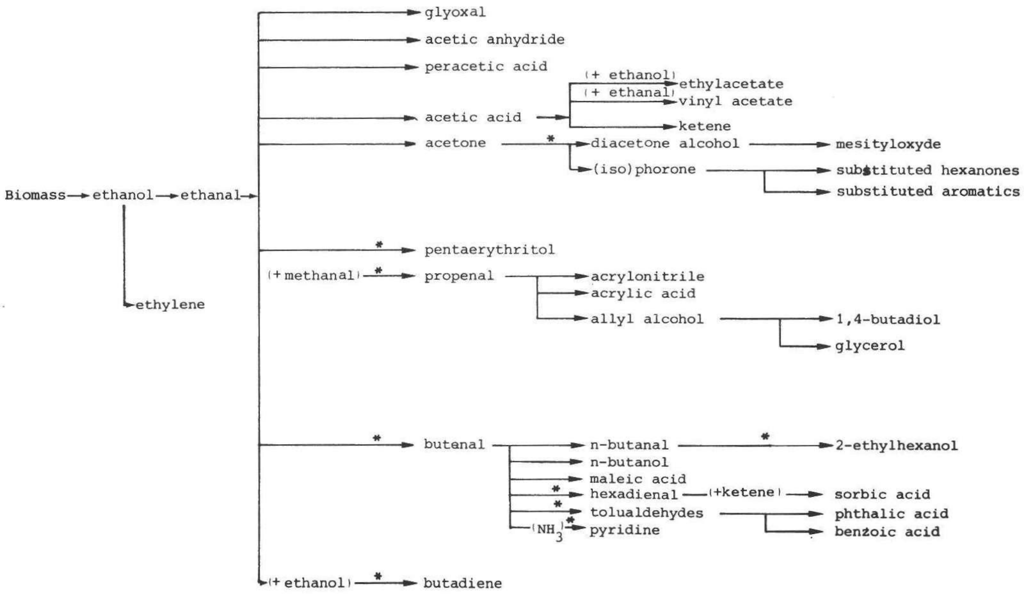


Figure 0.1 Ethanol as a raw material for industrial chemicals

** in this reaction the aldol condensation is an essential step.*

1. ALDOL CONDENSATION

1.1 Description of the reaction

Aldol condensation can be defined as an addition reaction between two reactants, each containing at least one carbonyl group, one of which contains at least one α-hydrogen as well. Reactions of aldehydes and ketones are common examples. The name comes from the self-condensation product of ethanal, which is called aldol because it contains a hydroxyl group as well as an aldehyde function:

$$2\ CH_3CHO \longrightarrow CH_3CHOHCH_2CHO \qquad \text{(3-hydroxybutanal)}$$

This configuration of a hydroxyl group in β-position to the carbonyl group is characteristic of the reaction product: β-hydroxy-aldehydes or β-hydroxy-ketones. The condensation may be followed by a dehydration step involving the β-hydroxyl group and an α-hydrogen and giving an α,β-unsaturated aldehyde or ketone. For instance, a 3-hydroxybutanal dehydrates easily to 2-butenal (crotonaldehyde):

$$CH_3CHOHCH_2CHO \longrightarrow CH_3CHCHCHO + H_2O$$

When two different reactants are used, both containing an α-hydrogen, four products can be formed, in proportions varying with the reactivity ratios of carbonyl groups and of α-hydrogens. When one reactant has no α-hydrogen, only two products are formed. Because aldehydes are generally more reactive than ketones, the self-condensation of the latter will only occur in minor amounts when mixed feeds are used.

Conversion to aldol products is not always quantitative because it may be limited by equilibrium. Ethanal condensation shows a favourable equilibrium at low temperatures, viz. nearly 100% conversion to aldol at 25 °C. Equilibrium conversion is, however, less favourable for the higher aldehydes and the ketones, e.g. for butanal 66% and for acetone 10% at 25 °C. Moreover, equilibrium conversion decreases with increasing temperature. The subsequent dehydration is also an equilibrium reaction; its conversion increases with increasing temperature.

The overall equilibrium conversion to the unsaturated product therefore becomes more favourable at higher temperatures. A review of the liquid-phase aldol condensation is given by Nielsen and Houlihan (11).

1.2 Catalysis

Liquid-phase aldol condensation is commonly performed at low temperature, e.g. 15 °C for ethanal and 50 °C for butanal, because of the unfavourable equilibrium and the risk of continuing aldol condensation of primary products at higher temperatures. An effective catalyst is applied since the reactants are not reactive at these temperatures. An aldol condensation without catalyst has been claimed only once, viz. a moderate conversion of ethanal to butenal by heating ethanal and water at 160 °C in an autoclave (12).
Four forms of catalysis can be distinguished, all following the same essential steps but having a different initial activation step:

- base catalysis
- acid catalysis
- amine catalysis
- metal coordination catalysis

For a reaction to occur two carbons must be coupled, the carbon of the carbonyl group of one reactant and the carbon atom in α-position relative to the carbonyl group of the other compound. The carbonyl group is strongly polarized, with a positive charge on the carbon. (Of course, the α-carbon is influenced too; it carries a small positive charge). Catalysis consists of two actions, viz. activation of the carbonyl carbon and of the hydrogen of the other reactant molecule. Activation of the latter, resulting in abstraction of an α-hydrogen is difficult. The carbonyl group, on the other hand, is quite reactive in itself, particularly when a proton is coupled to the carbonyl oxygen and a carbenium ion is formed which may lead to enolisation. Figure 1.1 summarizes the characteristic reaction steps of the four types of catalysis.

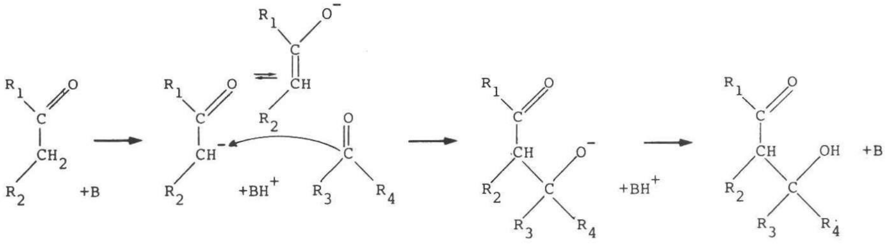
Base catalysis is most commonly used in preparative organic chemistry and technological practice. It gives the highest reaction rates, because a strong enough base effectively activates even less reactive α-hydrogens. Its mechanism has been proposed for the first time by Hann et al (11, 13, 14, 15). Generally NaOH, $Ca(OH)_2$ and basic ion exchangers are used as catalysts in industry.

Acid catalysis requires the simultaneous activation of both structures in the reactant molecules, because the enol intermediate is insufficiently reactive (14, 16, 17). Acid catalysis therefore is less effective, and inapplicable

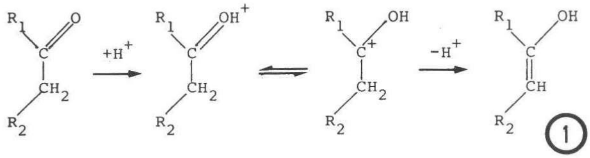
Figure 1.2.1 Catalytic mechanisms of the aldol condensation proposed for liquid-phase reactions.

B *is a Brønsted base,* M *is a free or not completely coordinated metal ion.*

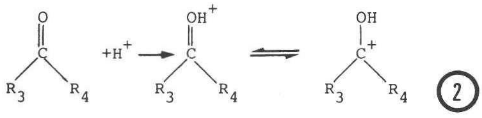
A. Base catalyzed



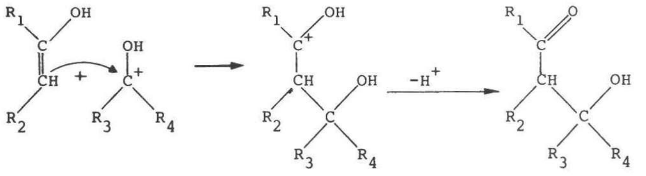
B. Acid catalyzed



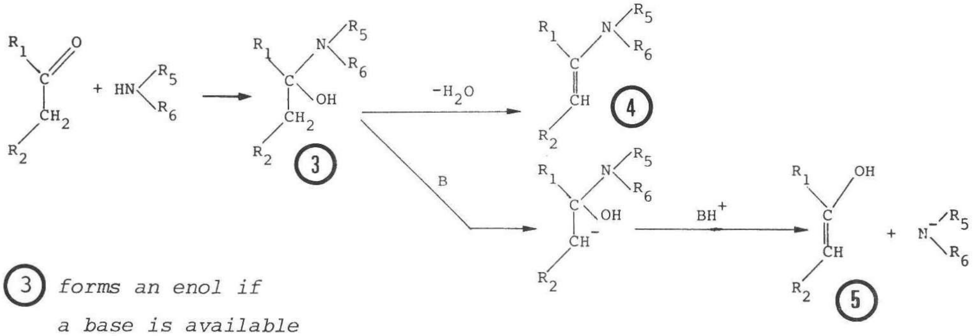
and



① *and* ② *react*

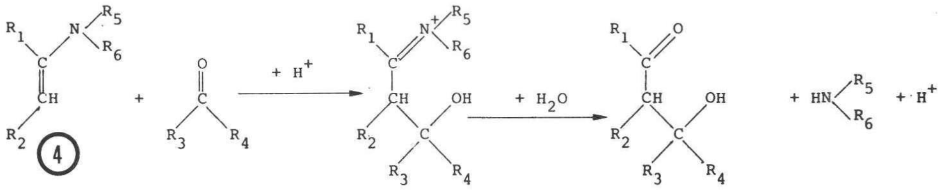


C. Amine catalyzed



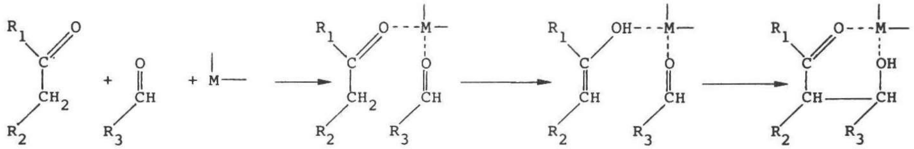
③ *forms an enol if a base is available*

C.1 if the pH is low enough, ④ *reacts with a protonated substrate*



C.2 another possibility is the reaction of ⑤ *with another substrate (as reaction of* ① *with* ② *)*

D. Metal-coordination catalyzed



for aldehydes, the more so because acid is a far better catalyst for a parallel reaction, viz. polymerization.

Amine catalysis proceeds via an intermediate formed by addition of the amine to the carbonyl carbon. Because such an addition requires that hydrogen is attached to the nitrogen atom, only primary and secondary amines are useful. The reaction path depends on the pH and the type of amine employed (18, 19, 20, 21).

Metal coordination catalysis is quite analogous to acid catalysis. Instead of the enol an enolate or a similar structure is formed, the metal ion acting as a Lewis acid. Free metal ions as well as alcoholates are mentioned as catalysts. Metal coordination catalysis by Copper(II) has been proposed by Iwata et al and was inferred from the action of the aldolases in biochemistry (22). Activation is by coordination of the reactants to the metal ion. Amines are added sometimes to enhance the activity and selectivity of the metal ion catalysis. These may activate the carbon atom in α-position (23, 24, 25). When using alcoholates of various metals, such as Al, Zn, Na, Mg and Sn (26, 27, 28, 29, 30, 31) activation can either be by coordination or by enol formation with the reactant . Since strong Lewis acidic metal alkoxides also catalyze the Cannizzaro reaction of aldehydes, the product mixture can be quite complex. An interesting aspect of metal coordination catalysis is the selectivity for crossed aldol condensation when working with a mixture of aldehydes and ketones. Reiff (32) describes such a selective co-condensation, viz. the addition of ketone to the α-carbon of an aldehyde effected by metallic Schiff bases. Iwata et al (22) found that crossed aldol condensation was favoured with copper (II) as catalyst, even when a large excess of ketone was used. This led them to the assumption that the aldehyde is coordinated to the metal ion somewhat more easily than the ketone.
Application of cobalt catalysts for the condensation of n-butanal is interesting because the same catalyst is applied in the preceding production of the aldehyde by hydroformulation (33, 34, 35, 36, 28, 39). Furthermore, these cobalt catalysts are claimed to be much more active for the condensation of the normal compound than for condensation of iso-butanal, which is also formed during hydroformylation.

Dehydration of the aldol/ketol compound is catalyzed by acids, the first step being the removal of the hydroxyl group, which is activated by a proton. The reaction is generally quite fast. For instance, the aldol condensation of butanal results directly in the unsaturated compound when carried out at temperatures higher than 70°C.

Gas-phase aldol condensations require rather high temperatures, viz. 200 °C and higher, and are catalyzed by heterogeneous catalysts. It is generally believed that acid/base catalysis proceeds according to similar mechanisms for heterogeneous reactions as for homogeneous reactions (40, 41). Because most heterogeneous catalysts consist of metal oxides, basic and acidic sites are available. Basic sites are associated with surface oxygen ions, (Lewis) acid sites with metal ions. Heterogeneous gas/solid catalysis may proceed according to a base or metal coordination-catalyzed mechanism, or a combination of these mechanisms. Not much has been done, however, to unravel the mechanism.

A mechanism with base catalysis has been proposed by Malinwski and co-workers (42, 43, 44), who employed basic solids obtained by impregnation of silica gel with alkali hydroxides as catalysts. Their findings were that

- the activity of the catalyst is proportional to the concentration of alkali atoms brought on the surface,
- the activity is proportional to the alkalinity of the metal ions used,
- the reaction rate is proportional to the acidity of the α-hydrogen atom and the reactivity of the carbonyl group.

Minachev et al observed the same for the condensation of butanal over rare earth oxides (45).
Some authors proposed an acid-catalyzed mechanism for the aldol condensation on silica gel (46, 47, 48), assuming the proton of the surface hydroxyl groups to be acid enough to activate the carbonyl group and start the enolisation. However, very pure silica gels and aerosils are much less active or not at all (48, 49, 50, 51). Thus the activity of silica gels must be due to impurities, the more so because the acidity of the surface hydroxyl group is quite low. A similar conclusion has been drawn by Van Roosmalen in a study of the isomerization of 1-butene on silicagel (52), who concluded the active sites to be aluminium ions present as an impurity, not the hydroxyl groups.

1.3 Liquid-phase versus gas-phase processes

At present, aldol compounds are usually produced by *liquid-phase processes*, generally employing homogeneous catalysts. Common catalysts are strongly basic substances, e.g. the hydroxides of alkali and earthalkali metals. The following characteristics have strongly influenced the form of liquid-phase processes.

a) The formation of the aldol is a strongly exothermic reaction. The heat of reaction for the ethanal condensation is-55 kJ.mol^{-1}, for the butanal condensation-67 kJ.mol^{-1} and for the acetone condensation-61 kJ.mol^{-1}. Thorough cooling is therefore necessary to keep the reaction temperature at the required low level. Many different systems are employed. One works at the boiling point of the substrate, and evaporation takes care of the excess heat (53, 54, 55). A more common method is external cooling of the liquid phase, with or without direct recirculation (56,57,58,59,60,61). Those circulation streams can be as much as 20-40 times the feed volume (62).
b) Subsequent condensation of primary products is dependent on the concentration of reactants, products and catalyst and on the temperature. The two factors mentioned last are the most important. Local overheating of the mixture and a locally high catalyst concentration must be prevented. Vigorous stirring of the reaction mixture, e.g. by circulation, and stepwise addition of the catalyst are used to this end (58,60). Dilution with large amounts of water, ethanol or ethers is also employed, particularly in older processes (63, 64, 65, 66).
c) The reaction is commonly stopped before equilibrium is reached because the concentration of the desired intermediate goes through a maximum, decreasing again at very long residence times. Even so the residence times required to obtain a reasonable conversion are quite long, i.e. up to 1.5 h for the condensation of ethanal and several hours for the condensation of acetone. To improve the process better catalysts have been sought, which give higher reaction rates and better selectivities even at higher temperatures, in particular for the butanal condensation. Amines (67) and metal ion catalysts, e.g. cobalt salts, have been proposed (37, 39, 33, 68). An amine catalyst has been claimed to give a high selectivity for the ethanal condensation even at 100 °C (69).
d) Acetone and ethanal are miscible with the catalyst solutions, aqueous or alcoholic, but many other aldehydes and ketones are not. Thus mixing of the catalyst solution and the reactants poses a problem. This is another reason for applying well-stirred reaction systems (62). Sometimes high concentrations of electrolytes are employed to stabilize the suspension. These may also act as catalyst (70, 71). High salt concentrations are reported, however, to decrease the selectivity (34, 36, 72). Phase transfer catalysts are reported to enhance the action of the catalysts in these suspensions, e.g. the salts of tertiary and quaternary amines (54, 73).
e) To avoid catalyst disposal problems heterogeneous catalysts such as basic ion exchangers have been proposed (54, 73, 74, 75, 76), but for aldehydes immiscible with water phase transfer agents or catalysts are still needed.

Other heterogeneous catalysts proposed are MgO, MoO_3 with ZnO on alumina (77, 78) for butanal condensation, and the hydroxides of barium, calcium and sodium for condensation of acetone (79, 80, 81, 82).
f) Since the α,β-unsaturated product is the most common product many processes contain two steps. The second step, dehydration of the aldol or ketol, is catalyzed by acids, is endothermic and takes place at temperatures normally higher than for the condensation step. Therefore, the reaction mixture has to be acidified between aldol condensation and dehydration.

Summarizing, the main characteristics of the liquid-phase processes are:
- thorough cooling, in particular in the case of ethanal condensation,
- vigorous mixing, especially in two-phase systems such as encountered in the case of butanal,
- long residence times and a relatively low degree of conversion,
- a non-recoverable catalyst,
- an unfavourable heat economy when a two-step process, condensation and subsequent dehydration, is needed.

Although no *gas-phase process* has yet been commercialized, some comparison with current liquid phase practice is possible on the basis of experimental data on the performance of heterogeneous catalysts for gas-phase aldol condensation at various process conditions.
The gas-phase reaction leads to the desired unsaturated product in a single step because of the high reaction temperature. This probably results in a more favourable energy economy for the reaction. Mixing of gases is of course easy, and the chance of hot spots or locally too high concentrations is small. In the gas-phase process catalyst recovery is not necessary and liquid waste streams containing catalysts and auxiliary chemicals do not occur. Moreover, the gas-phase reaction promises to be much easier to control than the liquid-phase reactions.
However, reactant concentrations are lower and the equilibria less favourable. Single pass conversions will therefore be lower.
The selectivity of the gas-phase process is of major importance for process economy and determines the feasibility of a gas-phase process to a large extent. The overall efficiency of the liquid-phase processes is between 90 and 95%.
As for gas-phase processes, the main factors controlling the selectivity are catalyst type and the conversion per pass.

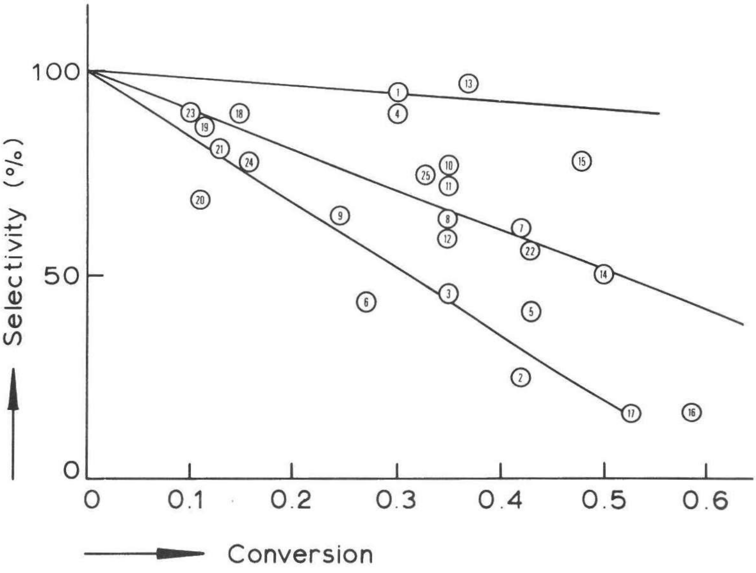


Figure 1.2. Performance of heterogeneous catalysts for the gas-phase aldol condensation of ethanal. Numbers refer to the catalysts with numbers (A) given in table 1.3.1.

Tables 1.3.1. - 1.3.5. and figure 1.2. give reaction data for several catalysts and feedstocks. From these data it can be concluded that the single pass yield for ethanal condensation should not exceed 35%. The catalyst showing the highest selectivity (97%) is Li_3PO_4 (83). Tin on silicagel may be a good alternative because of its high single pass yield (37%). The single pass yield for butanal condensation does generally not exceed 35%, the catalyst performing best in this reaction being tin on silicagel (7, 8); at 60% conversion the selectivity is 97%.

Acetone conversion to mesityloxide is quite low. Higher conversions can be reached when the unsaturated intermediate is hydrogenated in the same reactor. From the above data it can be concluded that for ethanal and butanal condensation gas-phase processes are promising although a large recycle of unconverted reactant(s) is necessary. Tin on silicagel may well be a suitable catalyst for such a process, and because few data are available on its action and methods of preparation, this catalyst was studied in some detail.

Table 1.3.1 Literature data on the gas-phase aldol condensation of ethanal (numbers (A) refer to figure 1.3.1)

year	lit	catalyst	(A)	temp °C	flow conditions	conversion %	yield %	selectivity a) %
1918	(84)	UO_2		360	(pure)			<40
1920	(85)	$Na_2Al(SO_4)_2$	(1)	200	0.1 LHSV	30	(28,5)	95
1931	(86)	CuO/Cr_2O_3 (1:1)	(2)	360	batch, H_2 $200 * 10^2$ kPa	42	(11)	36
1947	(87)	$MgO/ZnO/Al_2O_3$		300	N_2		15	
	(88)	o.8w% Ta_2O_3 on silicagel	(3)	320	0.57 LHSV eth./H_2O=1/2	35	(16.1)	46 25 (higher products)
1949	(89)	Cd-phosphate on glass wool	(4)	360	80 GHSV eth/N_2=1/1	30	(27)	90
	(90)	2.w% Ta_2O_3 on silicagel	(5)	350	0.4 LHSV 8w% H_2O	43	(18)	42
		id.	(6)	280	id.	27	(12)	44
		silicagel pure	(7)	350	id.	42	(26)	62
		id.	(8)	280	id.	35	(22)	63
1950	(91)	ZnO/Bi_2O_3 (94/6) on steel turnings		400	0.75 LHSV eth/H_2 = 1/1	24		
		MgO/Bi_2O_3 (94/6) id.		400	1.5 LHSV eth/H_2 = 1/3	6		
		MgO/V_2O_5 (94/6) id.		400	id.	4		
1954	(92)	$3CuO.H_2O$		200	recycle batch 1.5 g.gcat.$^{-1}$h^{-1} 2 h . 25 min	97	(54)	56
		AlO(OH)		230	id.; 4 h. 20 min	96	(79)	82
		$Fe(OH)_3$		170	id.; 7 h. 20 min	96	(75)	78
		β-H_2SnO_3		260	id.; 3 h. 35 min	90	(63)	70
		SnO		200	id.; 9 h	79	(49)	62
1957	(93)	MgO/TaO_5 (95/5)	(9)	300	1200 GHSV eth/H_2O/N_2= 1/3/3	24.5	(16)	65
1959	(94)	25w% Nb_2O_5 on asbestos		340			30	
1961	(49)	SiO_2	(10)	340		35	(27.3)	78
		ZrO_2/SiO_2 (55/45)	(11)	340		35	(26.6)	76
		id (85/15)	(12)	340		35	(21.7)	62
	(95)	0.1 mol NaOH on 100g silicagel		300		29		
1963	(96)	2w% Ta_2O_3 on silicagel		335	1 LHSV eth/H_2O =1/1		19	
1964	(83)	Li_3PO_4	(13)	250	5g.gkat^{-1}.h^{-1}	37	(33.3)	97
1965	(46)	sil/al (87/13)	(14)	185		∿50	(∿25)	∿50
	(8)	10w% Sn on silicagel	(15)	250	0.5 LHSV eth/H_2 = 1/1.5	48	(37.3)	78
1966	(97)	Mg/Cu/II)(Mn(II) oxide (65/25/10)	(16)	300	70 g cat.h.mol^{-1}	58.5	(10.2)	17.4
		id.	(17)		48 g cat.h.mol^{-1}	52.6	(8.7)	16.5
1967	(98)	$LiAlO_2$ on silicagel	(18)	295	1.5 LHSV eth/H_2O = 2/1	14.6	(13.1)	89.9
		id.	(19)	250	2.8 LHSV id.	11.2	(9.7)	86.8
		ZrO_2 on silicagel	(20)	305	1.5 LHSV id.	11.0	(7.7)	69.8
		id.	(21)	245	1.6 LHSV id. (35 kPa)	12.8	(10.4)	81.4
1968	(99)	sil/al (87.5/12.5)		220	0.873 LHSV		13	
1969	(100)	ZnO	(22)	230	0.5 LHSV eth/H_2 = 10/1	43	(24.1)	56
1970	(101)	Cd/Ca phosphate	(23)	360		10	(89)	89
		id.	(24)	400		15.8	(12.4)	78
1976	(102)	MgO/Al_2O_3 (with Li^+)	(25)	280	71g cat.h.mol^{-1}	32.8	(25.6)	78
	(103)	alumina with 10 mmol.Na^+.g^{-1}		400			30	

a) values are for single pass, if not stated otherwise yield is conversion to desired product.

Table 1.3.2 Literature data on the gas-phase aldol condensation of n-butanal.

year	lit	catalyst	temp °C	flow conditions	conversion %	(yield) %	selectivity %
1953	(104)	at 275°C dehydrated hydroxyde of					
		Cu(II)	275	0.2 LHSV	7	(3.9)	56
		Mg	id	id	33	(28.4)	96
		Al	id	id	49	(36.8)	75
		silicagel	id	id	25	(21.5)	86
		Sn(II)	id	id	44	(38.3)	87
		Sn(IV)	id	id	25	(20.8)	83
		Cr(III)	id	id	39	(30.0)	77
		Fe(III)	id	id	32	(24.5)	76.5
1956	(105)	silicagel with 0.08w% Pd	150	0.025 LHSV	25	(20)[a]	80[a]
1965 1969	(8) } (7)	10w% Sn on silicagel	250	0.5 LHSV but/H_2=1/2	62	(60.1)	97
1972	(106)	K,NaY zeolite	200	0.53 LHSV (after 1 hr op)	48.6	(36.5)	75
1976	(102)	MgO/Al_2O_3	280	125 gkat.hr.M^{-1} n/iso=1/1 $3.8* 10^2$ kPa	51	(35.7)	70
1978	(45)	La_2O_3	370	1.5 LHSV but/N_2=1/4	43	(14)	32.5
		Nd_2O_3	360	id	49	(20.4)	41.5 (40.5)[b]
1943	(107)	Cr_2O_3	330	autoclave; cat is 10w%; $20* 10^2$ kPa 1 hr; H_2	48.3		

a) as butanol

b) to dipropyl ketone

Table 1.3.3 Literature data on the gas-phase aldol condensation of acetone

year	lit	catalyst	temp °C	flow conditions	conversion %	(yield) %	selectivity %
1962	(108)	ZnO	550	5 GHSV		15[a]	
1964	(83)	Li_3PO_4	285	2.4 LHSV	23	(9.9)[a]	43[a]
1965	(109)	$ZnO/Cr_2O_3/CuO/$ Fe_2O_3/SiO_2	300	0.25 LHSV ac/N_2=4/1		14[a] 16[b]	
1965	(8)	10w% Sn on silicagel	300	1.0 LHSV ac/H_2=1/2	14	(9.8)[a]	64[a]
1965	(110)	5w% MoO_3 on alumina	275	1.0 LHSV ac/H_2=1/33	32	(2.3)[a,c]	7.2[a] 62[b]
1967	(111)	Mg-silicate (with 5w% Pd)	275	1.0 LHSV ac/H_2=1/1	51.5	(28.3)[a,c]	55[a] 80.5
1969	(100)	$MgO/SiO/Cr_2O_3/$ $CuO/Al_2O_3/CaO$	250	0.7 LHSV ac/H_2=12.5/1	41	(19)[a,c] (23)[b,c]	46[a]
	(112)	alkalicellulose	116		16.6	(15.2)[b]	95[b]
1970	(113)	Al_2O_3 (with Rh)	350	ac/H_2=1/1 $6* 10^2$kPa	36.2	(25)[a,c]	68.5[c]
1975	(114)	Zr Phosphate (with Pd)	120	4.0 LHSV ac/H_2=3/1 $20* 10^2$ kPa	28	(26.3)[a,c]	94[c]
1976	(115)	H_3PO_4(12w%) on silicagel	180	1.0 LHSV		11.2	
1977	(102)	MgO/Al_2O_3(50/3) with Li^+	300	1.0 LHSV $3.8* 10^2$ kPa(abs)	18.4	 (11.0)[a]	86.4 36.0
	(116)	Zr Phosphate (with 0.5w% Pd)	160	5.0 LHSV ac/H_2=2.5/1 $30* 10^2$ kPa	36.3	(33)[a,c]	90[a] 95.5[b]
1960	(117)	ZnO/ZrO_2 (82/18)	370	0.25 LHSV ac/H_2 = 1/1	34.3	(20)[a]	58[a] 78.5[b]

a) to mesityl oxide

b) to mesityl oxide, (iso)phorone, and other trimers

c) including direct hydrogenation of the compounds

Table 1.3.4 Literature data on the gas-phase aldol condensation of various compounds.

lit	substrate	catalyst	temp	flow conditions	Conversion	yield %
(83)	propanal	Li_3PO_4	275	2,5 LHSV	32	30
		$Cu(OH)_2$	280	0.8 LHSV	15	6
		Ca orthophos	235	0.8 LHSV	68	57
(118)	id	$Ca(OH)_2$	150	0.085 LHSV prop/N_2/H_2O= 2.8/1/7.5	80	60
(107)	id	Cr_2O_3	400	batch;autoclave; N_2;20* 10^2kPa;1h		18.7
(119)	2-butenal	BaO/CaO	300			40 (o-toluald.)
(120)	id	10% $Ca(CH)_2$ on alumina	300	0.07 LHSV	97.8	45.7 (toluald.)
	id	10w% $Sr(OH)_2$ on alumina	300	id	60.1	41.8 (toluald.)
(9)	id	10w% Cu/Sn(1/1) on silicagel	250	0.5 LHSV	61.7	35.4 (toluald.)
(121)	butanone	ZnO/ZrO_2 (94 6)	400	1.5 LHSV but/H_2=1/1	15.5	12.7 (C_8)
(83)	cyclopetonone	Li_3PO_4	240	2.2 LHSV	44.0	
(102)	cyclohexane	MgO/Al_2O_3 (50/1)with Li^+	280	0.5 LHSV 3.8* 10^2kPa	14.7	12.3
(83)	id	Li_3PO_4	270	1.57 LHSV	13.0	12.7
		Na-orthophosp.	275	0.47 LHSV	29.0	25.2
		$Cu(OH)_2$	275	0.34 LHSV	47.8	40.2
(6)	id	10w% Sn on SiO_2	250	0.5 LHSV	27.5	25.2
(8)	id	10w% Sn on SiO_2	250	1.0 LHSV cycl/H_2=1.2/1	27.5	25.6

Table 1.3.5 Literature data on the gas-phase aldol condensation of **mixed feeds.**

lit	feed	catalyst	temp °C	flow conditions	Conversions[a] %	yield[a] %
(122)	methanal/ethanal (1/3)	3w% La_2O_3 on silicagel	485	400 GHSV	38	33 (propenal)
(123)	id (3/1)	Li_2CO_3 on silicagel	350	0.2g.$gcat^{-1}h^{-1}$		52
(124)	ethanal/methanal (1/2)	5w% NaOH on silicagel	300	3 LHSV mixt /H_2O=1/3	80	
(95)	id (1/1)	7w% k_2TiO_2 on silicagel	225		56	
(122)	ethanal/propanal (1/3)	3w% La_2O_3 on silicagel	485	400 GHSV	45 (2 methyl-propenal)	41
(95)	id (1/1)	Na_2O/SiO_2 (1/3.18)	275		45	
(118)	id (1/1)	kOH on ceramic chips	300	0.085 LHSV mixt/N_2=3/1	93	73
	id (1/1)	10w% $Cu(H_2PO_4)_2$ on ceramic chips	300	id	74	62
(122)	methanal/n-butanal (1/3)	3w% La_2O_3	485	400 GHSV	34 (2 ethyl-propenal)	30
(95)	id (1/1)	Na_2O/SiO_2 (1/3.18)	275		49	
(95)	methanal/n-pentenal (1/1)	Na_2O/SiO_2 (1/3.18)	275		59 (2 propyl-propenal)	
(122)	methanal/acetone (1/3)	5w% La_2O_3 on silicagel	485	400 GHSV	40 (methyl-vinyl-ketone)	66
(83)	ethanal/benzaldehyde (1/1)	Li_3PO_4	333	2.2 LHSV	27 (cinnamic acid)	9
(125)	benzaldehyde/ethanal (1/3)	0.8w% Na on silicagel	430	0.6 LHSV		27.2
(126)	acetone/iso-butanal (1/1)	1% kOH on alumina	350	306g.$(lcat)^{-1}h^{-1}$ mixt/H_2 = 1/10	12.9 (methylhexenal)	3.9
	id	5w% Sn on silicagel	350	id	12.0	5.9

a) based on first mentioned reactant.

1.4 Previous work done on tin on silicagel catalysts.

The tin on silicagel catalysts described by Swift et al (6, 7, 8, 9, 10) give good results for the aldol condensation of ethanal and butanal. A 10w% Sn catalyst gave a single pass conversion of 48% for ethanal at a selectivity of 78%; for butanal the conversion was 62% at a selectivity of 97%. In both cases hydrogen was used as diluent. These conversions are high compared to those obtained on most other catalysts.
Earlier work has shown several other tin compounds to have some catalytic activity for the aldol condensation, but their performance was not as good. Examples are the tin(II, IV)hydroxides for butanal (104) and tin(IV) compounds for ethanal (92, 128) (see tables 1.3.1, 1.3.2)
In particular large amounts of acid and ketone are reported to be formed when applying these catalysts for the ethanal condensation. Furthermore tin compounds are mentioned along with many others as possible catalysts or additives without further specification , e.g. (129,127). Swift et al noticed aldol condensation as a side reaction when studying the dehydrogenation of cyclohexanone over nickel-tin-silica catalysts, and reported particulars about preparation and activation of the catalyst by reduction, using the butanal condensation as the test reaction (7). When describing their findings they claim many tin compounds with different solvents for the preparation of the catalysts, and invariably assume that a tin compound is present as fine particles well distributed through the support. The catalytic activity was found to depend on the duration of the reduction (figure 1.3). Swift and co-workers concluded from their experiments that metallic tin in the β-phase is the active agent, although initially they mentioned stannous-oxide as an other possibility. Their optimal catalyst was 10w% tin on silicagel. Other supports were tested but gave catalysts with much lower activity and selectivity.
Before reduction the catalyst showed some activity but a low selectivity. Pure silicagel had more or less the same activity as an unreduced catalyst but a much better selectivity. A study with adsorption of ammonia at 250 °C revealed that the unreduced catalyst had twice the number of acid sites as the pure silicagel support, and the reduced catalyst three times that number. Thus the activity is probably not directly related to the Lewis acidity of the catalyst. Catalyst deactivation could be delayed to a high degree by diluting the feed with an "inert" gas. Hydrogen proved to be the most favourable diluent. The optimal ratio of reactant to diluent was 0.2. According to the Swift patent (10), coke formation during butanal condensation is the main cause for deactivation, although oxidation by water and coalescence of metallic tin were suggested at first to be additional causes.(7).

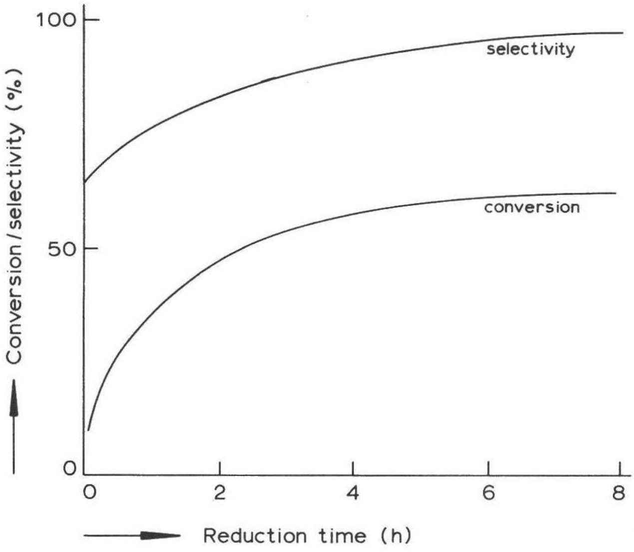


Figure 1.3 Effect of catalyst reduction time on conversion and selectivity. Reaction with butanal at 250 °C, 0.5 LHSV, H_2/butanal = 2 ;reduction with hydrogen at 375 °C (after (7)).

Regeneration of the catalyst was shown to be possible by a treatment with hydrogen at high temperature (350 - 500 °C). Reactivation is considered necessary when 10 - 20% coke has been deposited on the catalyst. This condition is reached after 2- 3 weeks. After reactivation 5 - 10w% coke remains in the catalyst but the activity and selectivity are about the same as for a freshly prepared catalyst.

The following is claimed in the Swift patents:

- a gas-phase process for aldol condensation,
- feeds include butanal, acetone, ethanal, possibly mixed with methanal,
- a heterogeneous catalyst "comprising metallic tin in the β-phase" on a support having a surface area of at least 50 $m^2.g^{-1}$,
- a support that is by preference silicagel,
- hydrogen as diluent for stable catalyst performance,
- a regeneration procedure consisting of a heat treatment under hydrogen.

Tin on silicagel catalysts have also been used by Droste et al (126) for a crossed aldol condensation of acetone with isobutanal. The reaction was found to be highly selective, viz. 50% and more, to the mixed aldol product. This selectivity is similar to the observed selectivity for crossed aldol condensation in liquid-phase metal coordination catalysis discussed earlier in this chapter. In a normal liquid-phase base-catalyzed reaction, mesityloxide is formed as the main product.

2. CATALYST PREPARATION AND COMPOSITION

2.1 Introduction

The conditions of preparation of a catalyst are of much importance for its ultimate performance as has been demonstrated by many authors (e.g. 130, 131, 132, 133). Two factors are often essential for a catalyst to be effective, viz. a fine dispersion of the active component and a proper interaction with the support. Therefore various supports and procedures were tested for the preparation of the tin on silica catalysts studied here.

Hydrogenic silicagel is the best support for the tin catalyst according to Swift et al (7, 8), other supports showing much lower activities. They do not make clear, however, why such is the case. A common property of hydrogenic silicagels is the large content of impurities, some of which are known to catalyze the aldol condensation to some extent. Pyrogenic silicas (silica powders) are less impure. These can be converted to an aerogel by wetting with water and drying the resulting gelatinous mass. After granulation the material is porous and can be used as adsorbent or catalyst carrier although its mechanical strength is not too good. Thermal and hydrothermal treatment improve the mechanical stability but also change surface structure and porosity (134, 135).

In view of the above, various types of silica supports have been applied in these studies. Moreover, the zeolite mordenite, which was not investigated before, has been tested. Mordenite is a mechanically strong support which is an interesting feature in a practical process. It is a crystalline aluminium-silicate having the overall composition $Na_8(AlO_2)_8(SiO_2)_{40} \cdot 24\ H_2O$. The sodium ions can be replaced by H^+. In acid solution the structure is partially dealuminated. Large amounts of hydroxyl groups are then formed (136, 137). Both the Na and the H-mordenite can adsorb other metal ions by ion exchange (138). The preparation of a tin mordenite has been described by Coughlan et al (139), who used dimethyltindichloride in aqueous solution at low pH.

The surface structure of silicagel and silica powders can be described as being regular on a short range but amorphous over a longer distance with many defects. The surface carries a large number of hydroxyl groups; four types can be distinguished: isolated single surface hydroxyl groups, isolated geminal groups and both types hydrogen bonded to other hydroxyl groups (see figure 2.1.1). A thorough discussion of the types of hydroxyl groups and their occurrence is given by van Roosmalen (140, 141). On silica powder only the two types of isolated hydroxyl groups are observed initially. After a thermal treatment followed by hydration other groups are also present. These are most likely geminal hydroxyl groups with hydrogen bonds formed by opening of siloxane bonds.

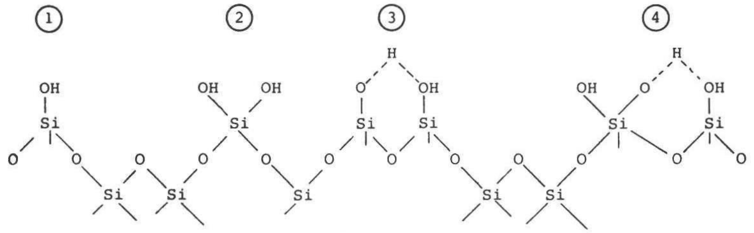


Figure 2.1.1 Types of hydroxyl groups on a silica surface:
(cf. van Roosmalen (140, 141)

1. *isolated single hydroxyl group*
2. *isolated geminal hydroxyl group*
3. *vicinal hydroxyl groups with hydrogen bonding*
4. *geminal group with hydrogen bonding*

Physical adsorption of water occurs only to a minor extent on the isolated hydroxyl groups of silicagel. There are indications that adsorption to these sites is stronger for silica powder. Moreover, there is evidence that the isolated hydroxyl groups are more reactive and give more easily chemisorption than the hydrogen bonded groups(142). For instance, such is found for reaction with $SnCl_4$ (161). However, this conclusion is opposed by others as follows from (143).

The amount of hydroxyl groups on silicagel is a subject of continuing discussion. Depending on the method of determination and the history of the gel, values ranging from 4.4 — 9.6 groups per nm^2 are found (144, 145, 146). Berendsen (142) argues on theoretical grounds and by comparison of published data that a value of 4.8 is likely after the surface has been annealed and has reached some degree of order. This value is found when physisorbed water is removed at 200 °C; about the same has been reported by several other authors (147, 148). Furthermore Berendsen supposes the amount of isolated hydroxyl groups to be 3.6 nm^{-2} and that of hydrogen-bonded groups 1.2 nm^{-2}. Less annealed silica gels show higher hydroxyl coverages. The short distance regularity of the silica surface seems to be described most appropriately by a β-tridymite structure (142, 149, 150, 151) (figure 2.1.2). Here the distance between two isolated hydroxyl groups is about 0.28 nm, but it is of course much smaller for groups with hydrogen bonds. For silica powder lower hydroxyl coverages have been reported, viz. from 2.3 to 4.8 nm^{-2} (147, 152, 144, 153, 149).

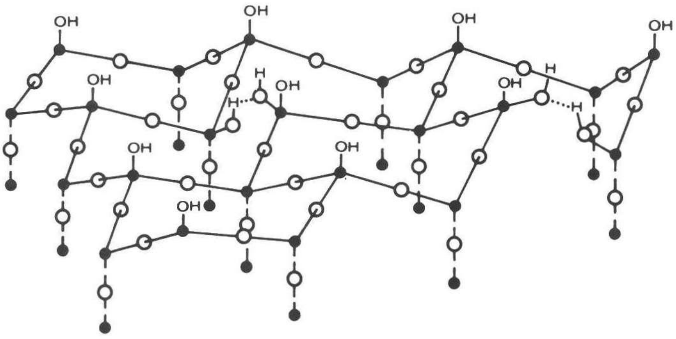


Figure 2.1.2 Model of the silicagel surface structure, which shows its short distance regularity;some defects caused by broken siloxane bonds are incorporated. (cf. 142). Copied by courtesy of the authors and Marcel Dekker Inc. N.Y.

The reactivity of the hydroxyl group is of importance when the silicagel is impregnated with active material to make a catalyst.

Exchange of protons by metal ions as well as adsorption or chemical reaction of the hydroxyl groups are feasible and have been described by many authors, e.g. for Cu, Pt, Co, Mn (155, 156, 157, 158, 159, 160). The pH plays an important role: if it is too low adsorption of most metal ions does not occur. At high pH the silica may dissolve slightly and the metal is precipitated as its silicate (161).

There is no agreement about the mechanism of adsorption. Chemisorption is possible, sometimes with one hydroxyl group, generally with two vicinal groups, but reaction with more groups has also been proposed. The latter is unlikely because of the tension of the resulting bonds. Coordination is possible with the hydroxyl groups acting as ligand; physisorption of a metal complex with a hydrogen bond to one of the ligands may also occur. Such bonds are less strong and probably unimportant for catalyst preparation.

Reaction with more reactive compounds is another effective method of preparation. The chlorides of several polyvalent metals are commonly used to modify the silicagel surface and to determine the surface of silicagels. Generally one or two hydroxyl groups are involved in this reaction because of the small size of the metal ions and the distance between the hydroxyl groups.

Rachkovskii et al (162) and Fink et al (163) have reported on the interaction of $SnCl_4$ with respectively silicagel and silica powder. On silicagel $SnCl_4$ reacts with two hydroxyl groups, but reaction is not quantitative. Only 40% of the groups react. On silica powder the reaction is complete. This underlines again the structural difference between silicagel and silica powder. It provides further evidence for the assumption that the isolated hydroxyl groups are the more reactive groups. Metal-organic compounds react in a similar way as the above metal chlorides. Dibutyldimethoxytin, used in our experiments, reacts with the hydroxyl groups by its methoxy groups, giving methanol and a tin compound attached to the surface with two bonds.

Uniform distribution of the active compound is dependent on the rate of precipitation on or adsorption to the surface, in relation to the rate of diffusion into the pores of the support. Extreme cases are (i) strong adsorption or fast precipitation with slow diffusion, and (ii) hardly any adsorption or precipitation with easy diffusion.

In the first case a large amount of the compound will remain at the periphery of the support particle. In the second case uniform distribution will be obtained at first, but during drying the compound will withdraw into the interior of the catalyst particle, with the liquid. It only precipitates when saturation of the liquid is reached.

Several tin compounds such as chlorides and organic tin compounds, are available for use in catalyst preparation methods. $SnCl_2$ is used in aqueous solution. The solution is acid (pH is about 2) because of Sn^{2+} hydrolysis and contains many different ions, mainly complexes of tin with chloride or hydroxide (171). Important complex species are $SnOH^+$ and $Sn_3(OH)_4^{2+}$ (164). Mixed complexes are not formed (167). The small amount of precipitate formed consists mainly $SnO.nH_2O$. Addition of acid causes the precipitate to dissolve. When hydrochloric acid is used, more chloride complexes are formed, of which $SnCl_3^-$ is most important (166, 167). When solutions are in contact with air, oxidation of Sn^{2+} to Sn^{4+} will occur. Large amounts of hydroxides are formed, i.e. $Sn^{4+}(OH)_n^{(4-n)}$ (with n = 1-4), as well as a precipitate of $Sn(OH)_4.nH_2O$ (168). As a result the pH decreases during oxidation.

$SnCl_4$ and dibutyldimethoxy **tin** are very reactive and are easily hydrolyzed. They must be handled under dry conditions. They dissolve easily in hexane. $SnCl_4$ has a low boiling point (114 °C) and thus a high vapour pressure at ambient temperature.
According to the above, the following methods appear to be attractive for use in studies for preparation of tin on silica catalysts:

- dry impregnation with aqueous $SnCl_2$ solutions, sometimes after acidification of the solution with HCl. The method implies the addition of just enough solution of the active compound to the support to fill the pores.
- wet impregnation, i.e. the support is brought into a solution of the active compound; aqueous solutions of $SnCl_2$ and solutions of $SnCl_4$ and dibutyldimethoxy tin in n-hexane, were used.
- adsorption of $SnCl_4$ from the vapour or liquid-phase
- granulation of the silica powder whilst in contact with an aqueous $SnCl_2$ solution.

After impregnation the catalysts must be dried, calcined and activated by reduction with hydrogen. Swift et al (7,8), who prepared their catalysts by dry impregnation of silicagel with an aqueous solution of $SnCl_2$, report that reduction is not easy (cf. figure 2.3.1). They also state that reduction proceeds through several stages with different activation energies towards β-tin crystallites with a mean diameter of 100mm, as was determined with X-ray diffraction.

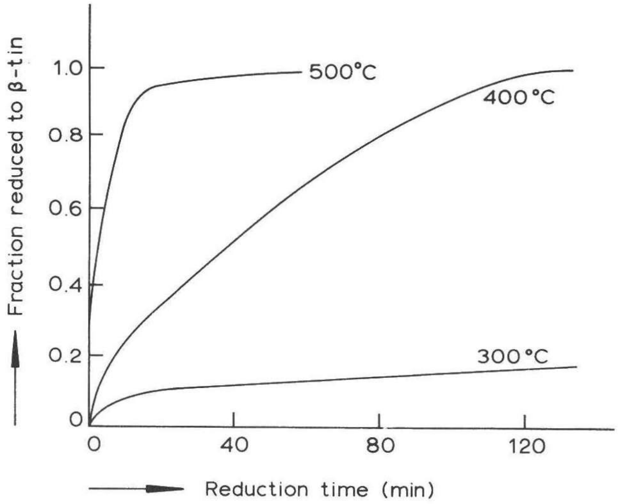


Figure 2.1.3 Reduction of a tin on silicagel catalyst with hydrogen at different temperatures, after Swift (7).

2.2 Experimental

2.2.1 Chemicals and supports

A number of carriers were obtained in small quantities from several producers. Their characteristics are given in table 2.2.1, together with the codes applied by us. For comparison the data of the support used by Swift and co-workers are included. Two types of hydrogenic silicagel have been tested. The material containing the least amount of Al^{3+} (D) has been used for most experiments. Three types of pyrogenic silicas have been applied, one of which (S) had been modified and sintered previously. Two types of mordenites were available. One had the normal form containing sodium, in the other one the sodium was ion exchanged with hydrogen.

The following tin compounds were used, all analytical grade chemicals:
$SnCl_2.2H_2O$ from, UCB, Belgium.
$SnCl_4$ from Aldrich, Belgium
$Sn(Bu)_2(Methoxy)_2$ from Alfa Research Chemicals, Ventron Cy, U.S.A.

Water and n-hexane were distilled and deoxygenated before use.

Table 2.2.1 Support characteristics

code	physical properties		analytical data
	Hydrogenic silicagels		
A	silicagel AT23 ex Gembo (AKZO), the Netherlands		
	D_{pores}	9.5 nm	Al 0.20 w%
	S_{BET}	385 m^2,g^{-1}	Ca 0.09 w%
	V_p	0.90 $cm^3.g^{-1}$	Na 0.03 w%
D	silicagel "weitporig" (special SP2-291.3451) ex Grace GmbH Germany		
	D_{pores}	16nm	Al 0.08 w%
	S_{BET}	380 $m^2.g^{-1}$	Ca 0.04 w%
	V_p	1.2 $cm^3.g^{-1}$	Na 0.08 w%
	(support used by Swift et al, Davison Grade 70)		
	D_{pores}	14 nm	Ca 0.07 w%
	S_{BET}	340 $m^2.g^{-1}$	Na 0.09 w%
	V_p	1.16 $cm^3.g^{-1}$	other 0.07 w%
	Pyrogenic silica (silica powder)		
F	Aerosil 130V ex Degussa GmbH, Germany		
	D_{part}	16nm	Al 0.10 w%
	S_{BET}	130 $m^2.g^{-1}$	Na 0.005 w%
G	Aerosil 300V ex Degussa GmbH, Germany		
	D_{part}	7 nm	
	S_{BET}	300 $m^2.g^{-1}$	as support F
S	Silica S, an experimental silica powder, modified hydrothermally by DSM, the Netherlands		
	D_{pores}	17 nm	Na 36 ppm
	S_{BET}	101 $m^2.g^{-1}$	
	V_p	1.05 $cm^3.g^{-1}$	
	Zeolites		
K	H-Mordenite Zeolon 900H ex Norton Chem.Proc.Prod. Ltd. Great Britain		
	S_{BET}	373 $m^2.g^{-1}$	
	$V_{micropores}$	0.17 $cm^3.g^{-1}$	(95% of total pore volume)
M	Na-Mordenite Zeolon 900Na ex Norton Chem.Proc.Prod. Ltd. Great Britain		
	S_{BET}	243 $m^2.g^{-1}$	
	$V_{micropores}$	0.113 $cm^3.g^{-1}$	

2.2.2 Preparation of catalysts

As stated earlier various methods were applied for preparation of the Sn-catalyst.

Dry impregnation with an aqueous solution of $SnCl_2$ was applied to silicagels A and D. This method was completely based on the method described by Swift et al (7). Before impregnation the silicagel was dried at 150 °C during 16h. Between 25 and 50g support was then wetted with just enough (i.e. 25 - 50 ml) solution to fill the pores. The amount of $SnCl_2$ dissolved was calculated to give the desired tin content. E.g. for a catalyst with 1w% Sn based on 50 g support 0.963 g $SnCl_2.2H_2O$ must be dissolved in 50 ml water.
The impregnated support was first dried in air at ambient temperature during 1h and then at 150 °C during 16h. After calcination at 450°C during 16h in a small flow of air and cooling in a flow of dry nitrogen to prevent adsorption of water, the product was stored in a desiccator. Activation of the catalyst was done immediately before use. Usual conditions for activation were a temperature of 450 °C, a hydrogen flow of 250 $ml.min^{-1}$, and a time of 30 minutes or longer.

Dry impregnation with an acidified aqueous solution of $SnCl_2$ was used with the silicagel D, the mordenites K and M, and the modified silica powder S. Support S adsorbed also about 1 ml water per gram, H-mordenite (K) about 0.15 $ml.g^{-1}$ and Na-mordenite (M) about 0.1 $ml.g^{-1}$.
The further procedure was identical with the method described above, except in that just enough concentrated hydrochloric acid was added to the $SnCl_2$ solution to dissolve the precipitate initially formed. Although no precipitate could be observed at the lowest concentration applied (for a catalyst with 0.5w% tin) a small amount (some drops) of acid was nevertheless added.

Wet impregnation with an aqueous $SnCl_2$ solution was carried out with silicagel D and mordenites K and M. No acid has been added to the $SnCl_2$ in these experiments, so any precipitate formed was not dissolved. The procedure was as follows: oxygen-free water was placed in a glass vessel with a jacket through which warm water could be led. Nitrogen was bubbled through. After addition of $SnCl_2.2H_2O$ the solution was heated to 70 °C. The support was then added. The amount and concentrations for these experiments are given in table 2.2.2. Vigorous stirring is necessary to keep the system well mixed. A cooler on top of the vessel prevents evaporation of water from the system which is maintained at 70 °C.

Table 2.2.2 Conditions for the wet-impregnation of silicagel and mordenite with an aqueous solution of $SnCl_2$

support code	amount of support (g)	amount of solution (ml)	concentration Sn^{2+} (mmol.l^{-1})	time of oxygen introduction min.	catalyst code
D	25	500	100	5	D6
D	12.5	500	100	5	D7
D	25	500	50	5	D8
D	12.5	500	50	90	D9
K	15	750	75	-	K4
M	15	750	75	-	M4

For three experiments with silicagel D as support air was passed through the solution from the start; in a fourth experiment the nitrogen was replaced by air 1.5h after the addition of the support D. During impregnation of mordenites no air was applied. The pH was measured continuously and two samples were taken from the solution at regular intervals, commonly 15 or 30 minutes, viz. one through a filter, so that only dissolved tin is present, and the other directly from the liquid after a short settling period, so that it contained precipitated tin but no tin adsorbed by the support. The experiment was stopped when the pH began to decrease appreciably, which is presumably due to Sn^{4+} formation and hydrolysis. The liquid was then decanted and the impregnated support rinsed three times with a hydrochloric acid-containing solution having about the same pH as the tin solution and then three times with water. The further treatment is identical with the one described for dry impregnation of silicagel.

Aerosil-based catalysts made with an aqueous solution of $SnCl_2$ were produced from silica powders F and G. To 10 g aerosil suspended in 110 ml of an aqueous solution of $SnCl_2$ some hydrochloric acid was added to dissolve the initially formed precipitate. The amount of $SnCl_2$ to be used was calculated from the desired tin content. The suspension was stirred vigorously at 95 °C for 20 minutes under nitrogen. The mixture was then heated to nearly dryness and the crust formed broken to fine catalyst particles. The further procedure was identical to the one described in the first catalyst preparation of this section.

Wet impregnation with a solution of dibutyldimethoxytin (DBDMT) was applied to silicagel D. The silicagel had been dried at 350 °C in a nitrogen flow for 3h. The DBDMT was dissolved in freshly distilled dry hexane. In most experiments 10 g support was suspended in 100 ml solution in a closed vessel under nitrogen. After 16h the silicagel was filtered off, washed twice with hexane and dried in a film evaporator at 80 °C. Thereafter three different methods were applied for further treatment: (i) direct reduction under hydrogen (100 ml. min^{-1}) during 1h at 300 °C and ½h at 450 °C, (ii) calcination at 450 °C in a flow of air for 16h followed by in situ activation at 450 °C with a hydrogen flow at 100 $ml.min^{-1}$ during 1.5h, (iii) heat treatment of the catalyst precursor in the reactor under nitrogen (100 $ml.min^{-1}$) at 300 °C followed by activation at 450 °C with hydrogen (100 $ml.min^{-1}$) during 1h.

Wet impregnation with a solution of $SnCl_4$ in hexane was applied to silicagel D. The impregnation was identical with that of DBDMT, described above; further treatment of the impregnated and dried support was done by two different methods: (i) direct calcination with air at 450 °C during 16h followed by the normal activation in the reactor (30 min; 450 °C; H_2 flow 250 $ml.min^{-1}$), (ii) the same method except for passage of air saturated with water over the impregnated support at 25 °C for 3h prior to calcination.

Reaction with $SnCl_4$ vapour was applied to make catalysts based on silicagel D. 10g silicagel was dried at 350°C under nitrogen during 3h and placed in a vessel under nitrogen. $SnCl_4$(1.2 g) was then introduced by heating this impregnant in a connected vessel whilst cooling the vessel containing the support in ice. The system was left at ambient temperature for 16h. The further treatment proceeded according to the two methods described previously.

Reaction with liquid $SnCl_4$ and silicagel D was accomplished by mixing 20 g silicagel (dried at 350 °C under nitrogen for 3h) with 60 ml $SnCl_4$. After 16h at ambient temperature the $SnCl_4$ was distilled off under a flow of nitrogen. The impregnated silicagel was treated with air saturated with water at 25 °C for 3h. Calcination and activation proceeded as described in the first method of this chapter.

2.2.3 Analytical methods

Several analytical methods have been used to define the catalyst at various stages of the preparation.

Tin content of the solid samples was determined by neutron activation analysis. This is a relatively easy and fast method for the simultaneous determination of the concentration of tin and other elements, e.g. Na.

The detection limits for tin and sodium are 300 and 1 ppm, respectively. Tin contents are given as weight percent of the calcined catalysts dried at 150 °C for 16h, unless stated otherwise.

Tin content of the solutions of some impregnation experiments have been determined by atomic absorption spectroscopy (A.A.S.). Sample preparation was by adding 10 ml concentrated hydrochloric acid to 1 ml solution and dilution of this mixture with water to exactly 50 ml. These solutions were stored in polyethene bottles to prevent loss of tin by adsorption to glass.

X-ray-diffraction has been applied to establish the occurrence of crystalline compounds. The Guinier-de Wolff method was followed. Four samples were analysed simultaneously using one film, which makes comparison easier. The size of the particles was estimated from the line width of the diffraction patterns. The method could be used quite easily because the support itself, silicagel, is totally amporphous.

X-ray fluorescence was applied to determine the distribution of tin in a catalyst particle. By this method the composition of a sample is measured from the intensity of the emission lines caused by electron bombardment. A line scan can be made over a catalyst particle when using a narrow band. Both tin and silicon can be measured by using a beam of 15 keV electrons.

Tin is detected by its L_α line, silicon by its K_α line. Sample preparation is done by casting the particles into a resin. A section through the particle is obtained by abrasion and polishing.

Structural analysis has been accomplished by nitrogen adsorption for pore size distribution and BET surface area, and by mercury penetration for pore size distribution. The BET surface is measured by the expansion method in which the pore distribution is obtained from nitrogen adsorption at -190 °C with semi-automatic apparatus, Carlo Erba 1800. Surface and pore sizes were calculated with the method of Broekhof (169, 170); the shape of the T-plot gives indications about the form of the pores, e.g. cylindrical or inkbottle-shaped.

Nitrogen adsorption can be used for pores with diameter 3 to 50 nm; mercury penetration for pores with diameter between 4 and 5000 nm. The latter measurements were done using a Micromeretics 905-1. For all methods samples were pretreated at 150 °C in vacuum.

Thermogravimetric analysis (TGA) has been performed to determine the thermal stability of the catalysts and catalyst precursors under different conditions. The apparatus used was a Stanton Redcroft TG-750; the experiments included reductio and oxidation runs with previously dried reactant gases. The apparatus was evacuate prior to a change of gaseous reactant. Reduction with TGA was done by two methods: temperature programmed up to 450 °C under hydrogen, or heating under nitrogen to the same temperature followed by introduction of hydrogen. The hydrogen supply was started as soon as the weight decrease by water desorption had become negligible. The reduction experiments were supplemented by data obtained during activation of the catalyst in the reaction apparatus(see the next chapter). The reactor was brought to 450 °C under nitrogen; activation proceeded isothermally. The reduction was followed by means of gaschromatographic analysis of water in the product gas, taking samples every 3 min.

Differential Scanning Calorimetry (DSC) has been used to determine the melting point and the amount of metallic tin in some catalysts. Samples were kept under nitrogen during the measurement. Results were poorly reproducible.

Moessbauer spectroscopy was used to determine the electronic state of tin compounds. The method uses a monochromatic beam of high energy gamma radiation. emitted by the tin isotope Sn^{119m}, of which the nuclei are in an excited state and emit a gamma quantum when returning to their ground energy state. The catalyst samples were powdered and enclosed in a sealed circular sample holder made of polyethene (diameter 20mm, thickness 0.5-1.0mm). For measurements on reduced catalysts the samples were transferred to the sample holder under nitrogen in a glove box. The Sn 119 m source has a short life, however, and must therefore be renewed regularly. Unfortunately, it became unavailable whilst this work was in process; as a consequence, a thorough investigation was impossible.

2.3. Results and discussion

The various methods applied and the supports used in preparing supported tin catalysts have been introduced in the preceding paragraphs. Since it will be shown later that the activity of the tin/silica catalysts is very much dependent on the various parameters of preparation, this paragraph gives some background on the phenomena occuring during preparation.

2.3.1 Tin content, distribution and crystallinity

The results of the catalyst preparation with regard to the tin content are given in table 2.3.1 and figures 2.3.1 and 2.3.2. In the latter figure the differences in specific surface area of the various supports have been accounted for by giving the tin per unit specific surface area.

Comparison with the intended tin content values shows that significant tin losses occur during preparation with aqueous $SnCl_2$ solutions. These losses are larger for silicagel when hydrochloric acid is added to the solution to dissolve

Table 2.3.1 Tin contents of catalysts, and the loss of tin occuring during preparation. (Tin contents in w%, measured by neutron activation analysis, tin loss in % of the original intended tin content*).

catalyst	tin content (w%)	tin loss (%)
a. dry impregnation, no acid added		
A3	7.2	28
A4	8.3	17
A5	4.2	16
A6	1.8	10
D1	7.4	27
D2	7.3	27
D3	3.6	10
D18	7.5	25
b. dry impregnation with acid added		
D10	7.5	50
D11	6.36	47
D12	3.74	58
D13	2.65	56
D14	2.00	50
D15	0.98	51
D16	0.51	49
D17	0.45	10
c. wet impregnation with aqueous $SnCl_2$		
D6	2.30	12
D7	1.70	19
D8	2.10	16
D9	1.79	28
d. wet impregnation with dibutyl-dimethoxytin in hexane		
D19	1.78	11
D20	3.72	7
D21	1.02	0
D22	5.64	6
e. wet impregnation with tintetrachloride in hexane		
D23(1)	0.80	60
D23(2)	0.65	68
D23(4)	0.80	60
D24(2)	0.77	81
f. with tintetrachloride vapour		
D25(1)	3.80	-
D25(2)	0.92	-
D25(4)	1.30	-
g. with liquid tintetrachloride		
D26(4)	4.00	-
h. mordenites dry impregnation with added acid		
K1	1.42	17
K2	3.19	36
K3	9.55	5
M1	1.54	9
M2	4.16	17
M3	6.75	33
i. mordenites, wet inpregnation with aqueous $SnCl_2$		
K4	5.39	4
M4	6.34	12
j. aerosils granulated with an aqueous $SnCl_2$ solution		
F1	0.53	0
F2	1.85	2
F3.1	3.15	13
F3.2	3.06	22
F4	6.70	13
G1	0.10	0
G2	0.23	8
G4	1.34	33
G5	2.30	42
G6	7.30	14
k. sintered aerosil, dry impregnation with added acid		
S1	1.83	9
S2	3.50	13
S3	4.00	33
S4	0.88	12

(1) after impregnation and drying only.
(2) after direct calcination
(4) after treatment with water vapour and calcination.

* The intended tin contents were determined as follows:

- for dry impregnation: from the tin concentration and the amount of solvent adsorbed,
- for wet impregnation with an aqueous $SnCl_2$ solution: from the amount of tin adsorbed from the solution,
- for wet inpregnation with the hexane solutions of DBDMT and $SnCl_4$: by assuming that tin has been adsorbed quantitatively.

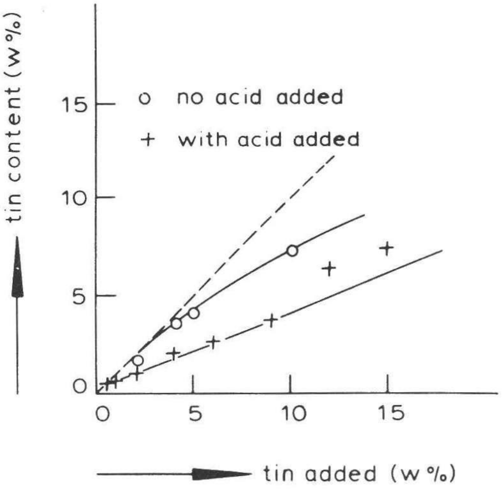


Figure 2.3.1 Comparison of actual and intended tin contents of dry impregnated silicagels.

any precipitate formed. Investigation showed that the losses occur only during the drying step, a transparent crystalline substance and a white powder being formed in cold parts of the reactor. The only tin compound which can be responsibl for this behaviour is $SnCl_4$ since it has a boiling point of 114 ^{o}C. No further tin evaporation takes place during calcination or reduction; besides water only HCl is detected in the off-gas. It is concluded that addition of hydrochloric acid to the solution promotes the formation of $SnCl_4$, because of the higher Cl/Sn ratio. This results in a higher tin loss with the silicagel (see e.g. fig. 2.3.1). Mordenites and the modified silica powder (S) give much lower tin losses under the same conditions, presumably because the $SnCl_4$ formed reacts more readily with these supports.

The maximum quantity of tin adsorbed by silicagel D during wet impregnation with a $SnCl_2$ solution was 2.6w%Sn. This is calculated from the decrease of the tin content of the solution. Figure 2.3.3a shows how the tin concentrations and pH change during some preparations. When oxygen is introduced a decrease of the pH is observed; in the absence of oxygen the pH increases. The change in dissolved tin is not directly related to pH changes when oxygen is present, but when oxygen is absent a decrease of the tin concentration is coupled to an increase in the pH. Therefore adsorption of tin on the silicagel is likely to occur by tin(II)hydroxides. The hydroxide is first physisorbed on the silica surface; then, a chemical addition takes place in which OH^- is produced.

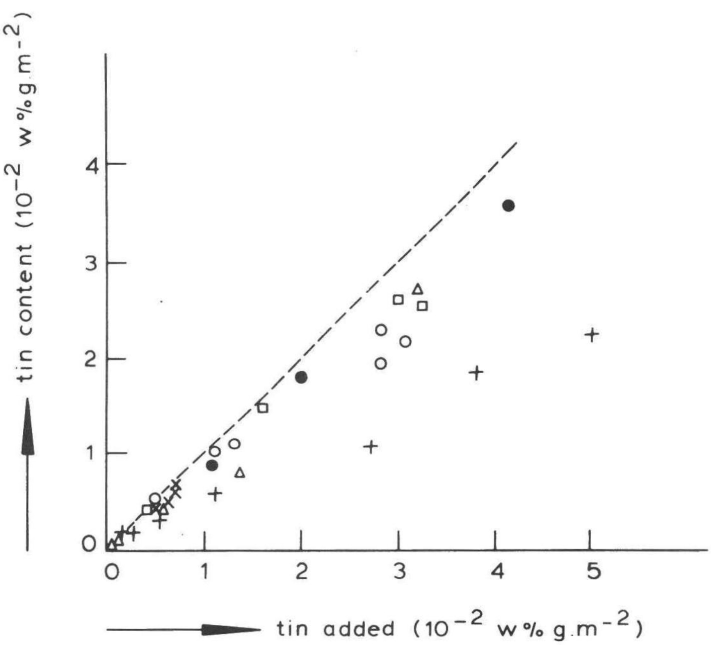
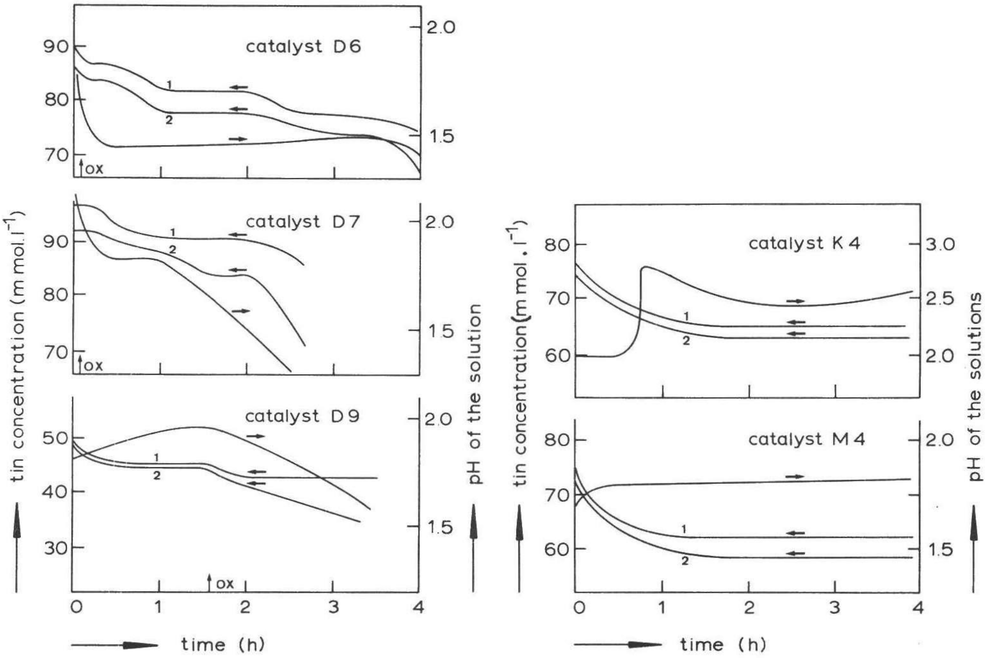


Figure 2.3.2 Comparison of actual and intended tin content for the impregnation of silica supports with aqueous solutions of $SnCl_2$*. (data are given as w%Sn per unit surface area).*

silicagel D:	○ *dry impregnation*
	+ *dry impregnation, acid added*
	× *wet impregnation*
silica powders:	□ *F catalysts*
	△ *G catalysts*
	● *S, dry impregnation, acid added*

The resulting increase in pH is counteracted when oxygen is present, because the Sn^{4+} formed hydrolyses.

The Na content of the support has decreased from the initial value of 800 to 40 ppm by the wet impregnation. As will be shown later the tin content in the particle bulk of the catalysts prepared by this method does not exceed 0.5w%. This value can be reached by ion exchange of one tin for one Na present in the silicagel, an exchange which also causes the release of OH^- ions. According to figure 2.3.3a it is a slower reaction than physisorption. At higher pH tin(II) forms more precipitate, part of which is deposited on the support.



(2.3.3.a)

(2.3.3.b)

Figure 2.3.3 Catalyst preparation by wet impregnation with an aqueous solution of $SnCl_2$.

a. with silicagel D

b. with mordenite K and M

The tin concentration is given as:

1 the amount of tin in the solution, dissolved and suspended

2 the amount of dissolved tin only

ox indicates introduction of air

However, the precipitate dissolves easily when rinsing the support. This is particularly so for catalysts D7 and D9, which were prepared in solutions of higher pH. Tin(IV) precipitates are much more difficult to dissolve, and therefore remain on the support.

The results obtained with the aerosils, F and G, show a relatively small loss of tin even though hydrochloric acid was added to the $SnCl_2$ solutions. This indicates that the tin compounds formed reacted more readily with the silica powder than with silicagel, as mentioned before. Here, too, $SnCl_4$ is most probably the key intermediate formed. Earlier tests showed that the silica powders did not adsorb any tin from an acidified solution of $SnCl_2$, even after one night's standing. Impregnation of silicagel with $SnCl_4$ from hexane solution showed that the reactivity at ambient temperatures is low: the dried sample (D23(O)) contained only 0.8 w%Sn. Direct calcination (D23(2)) caused tin losses, which could only be prevented by pretreatment with water vapour (D23(4)). Reaction with $SnCl_4$ vapour resulted in adsorption of more $SnCl_4$, but this component is not adsorbed strongly. Even pretreatment with water vapour did not prevent a large loss (compare D25(4) with D25(o)). The reaction with liquid $SnCl_4$ gave a much better retention of tin, which may be caused by the higher temperature used to vaporize the excess $SnCl_4$. The average tin coverage reached in this case is 0.5 at $Sn.nm^{-2}$. Assuming a coverage of 4.8 hydroxyl groups per nm^2, only 20% of the groups have reacted.

During impregnation of silicagel with DBDMT dissolved in hexane tin reacted almost quantitatively with silicagel. The various treatments after the impregnation step did not give any difference in the tin content.

Preparation of the mordenite-based catalysts also gave high tin contents and relatively small tin losses. The course of tin content and pH during wet impregnation are shown in figure 2.3.3b. The Na-mordenite shows the same phenomena as silicagel, considering no oxygen is available: Na^+ ions are exchanged for Sn^{2+}, which results in a pH increase. The H-mordenite behaves differently. Ion exchange of H^+ and Sn^{2+} is somewhat more difficult as follows from the longer time needed to reach equilibrium. This may also be due to the somewhat higher pH of the solution, which is ascribed to the difference in support.

The Na content of the Na-mordenite is about 5w%. If one Sn^{2+} would be exchanged for two Na^+, the maximal tin content would become 13w%.

The distribution of tin over the catalyst particles follows from X-ray fluorescence line scans of which some examples are given in figure 2.3.4. All samples were in calcined form. It follows that the tin distribution in the catalysts prepared by dry impregnation without acid addition (e.g. D2) is very uneven. This applies to single particles as well as to the particles of a batch. The catalysts prepared by dry impregnation with added acid, on the other hand, show an even distribution with small deviations, the concentration

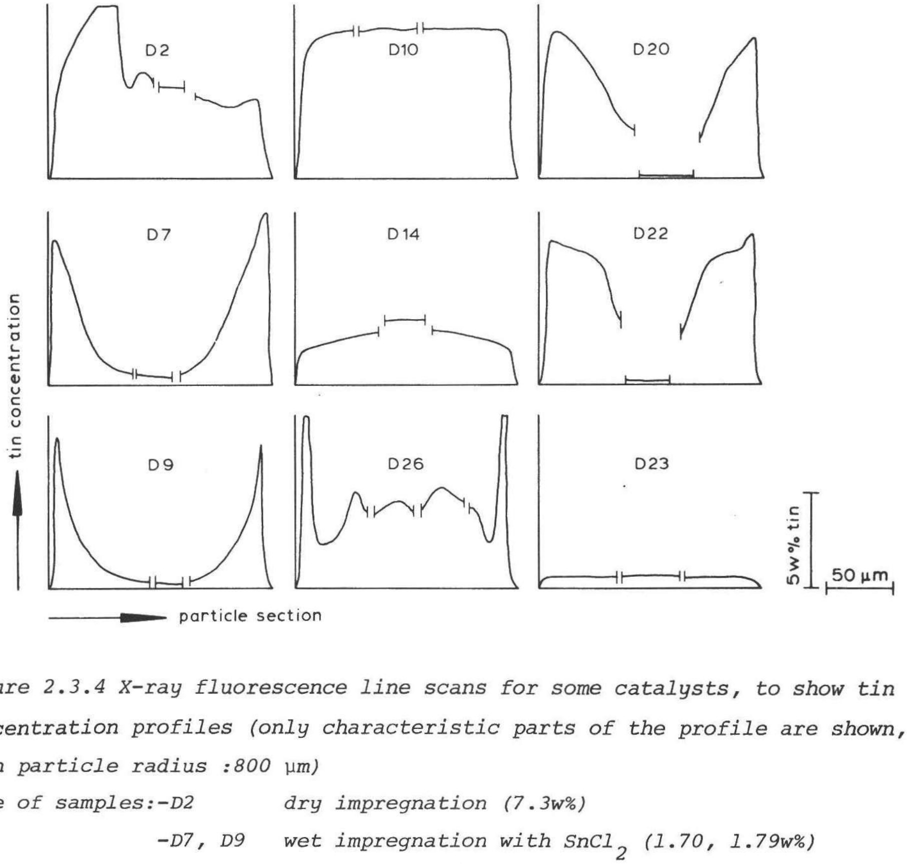


Figure 2.3.4 X-ray fluorescence line scans for some catalysts, to show tin concentration profiles (only characteristic parts of the profile are shown, mean particle radius :800 µm)

Type of samples:-D2 dry impregnation (7.3w%)

-D7, D9 wet impregnation with $SnCl_2$ (1.70, 1.79w%)

-D10, D14 dry impregnation, acid added (7.5, 2.0w%)

-D20, D22 wet impregnation with DBDMT (3.72, 5.64w%)

-D23 wet impregnation with $SnCl_4$ (0.80w%)

-D26 impregnation with liquid $SnCl_4$ (4.0w%)

in the center of a particle being somewhat higher in some particles. Impregnation with liquid $SnCl_4$ leads to an uneven tin distribution: near the outer surface of the particle there is a region with very high tin concentration (D26). By contrast, catalysts produced by impregnation with $SnCl_4$ solutions in hexane (D23, D24) show an even distribution but their tin content is quite low. This is caused by the slow reaction of $SnCl_4$ with the silica surface combined with the relative ease of diffusion of the $SnCl_4$ through the support pores when impregnating with this compound from the vapour phase or from a solution in hexane.

$SnCl_4$ is also formed during drying after dry impregnation with $SnCl_2$. The distribution obtained is generally good; apparently, the formation of $SnCl_4$ is vital for an effective distribution, because the direct interaction of $SnCl_2$ with the surface is rather weak (see below). Less $SnCl_4$ is formed when the impregnating solution is not acidified and, moreover, because a precipitate is present in such cases. The tin distribution then is much more uneven. The high concentration of tin near the outer surface of catalyst D26 is attributed to diffusion of $SnCl_4$ to the outer surface of the particle during drying, where it reacts to hydrolysis products with water with which the catalyst has been brought into contact during pretreatment.

Wet impregnation with a $SnCl_2$ solution results in low Sn concentrations within the particle and a high one at the outside. This may be caused by weak interaction between Sn^{2+} and the surface in aqueous solutions or by the fact that few sites are available for the addition of Sn^{2+}. The latter explanation is more likely because repeated washing did not remove the tin. The most probable explanation is the ion exchange of Sn^{2+} and Na^+, as was discussed earlier in this section. The large accumulation of tin at or near the outer surface is ascribed to the formation of insoluble hydrolysis products from Sn^{4+}. Wet impregnation with DBDMT gives catalysts with a tin distribution which is to be expected for the extreme case of high reactivity of the active compound combined with a relatively low diffusion rate. Nearly all the tin is adsorbed in an outer layer of 50 nm of the particles. The maximum concentration is equivalent to about 7w%, indicating a tin coverage of about 1.0 at $Sn.nm^{-2}$. Because DBDMT can react with two hydroxyl groups, 40% of these groups must have reacted since the hydroxyl group coverage is 4.8 nm^{-2}. This result is in close agreement with the findings of Rachkovskii et al (162).

The catalysts based on silica powder (F and G) do neither show a very even tin distribution over the individual particles, nor over the entire catalyst batch. This means that the tin distribution does not become fixed until most of the liquid in the suspension has evaporated. At an earlier stage the suspension is still homogenized by the vigorous stirring applied.

The $SnCl_4$ formed during drying is not well distributed over the crust of slightly sintered silica powder formed during the final phase of the evaporation.

X-ray diffraction of the catalysts showed that hardly any crystalline phase is present in the dried catalyst impregnated with aqueous $SnCl_2$. After calcination, lines of SnO_2 are clearly present and after reduction metallic β-tin was detected. The catalysts prepared by dry impregnation of silicagel with an acidified aqueous solution of $SnCl_2$ show an interesting phenomenon. The calcined catalyst with a low tin content (<2w%) contained SnO_2 particles with sizes of about 50 - 100 nm. The catalysts with higher tin contents contained smaller particles, i.e. about 5 - 10 nm. The reason for this may be the low tin concentration in the solutions used for the first group of catalysts.
It is probable that a certain minimum concentration of the tin compounds is necessary for precipitation to start. If the concentration is initially low, the liquid will first be concentrated in parts of the support particle. When precipitation eventually occurs conditions such as acidity are quite different from the conditions prevailing when one has started with a higher tin concentration. This may lead to different size of the tin-containing particles on the surface.
The β-tin crystallites formed during reduction are much larger, about 100 nm diameter, presumably because the tin melts and coalesces in the large pores.
T.G.A. analysis of the drying and calcination steps did not give useful information, the desorption of water blurring all other changes in weight. Calcination showed a fast drop in weight when raising the temperature from 25 to 250 °C. A continuing decrease occurred when keeping the temperature at 450 °C over a period lasting 10 to 15h after the start of the calcination. The catalysts lost 2 - 2,5% weight during calcination, i.e. the same weight loss as the untreated support.

Summarizing, the following conclusions are drawn:

- $SnCl_4$ is largely responsible for the adsorption of tin on the silica supports when using aqueous solutions of $SnCl_2$ for impregnation,
- Smooth tin distributions can be obtained under proper conditions of preparation,
- Reaction of $SnCl_4$ with the support is more effective at higher temperatures,
- The reactivity of silica powder is higher than that of silicagel
- If precipitates are present during impregnation these tend to concentrate near the outer surface of the particles; precipitates of tin(II) are easily dissolved but those of tin(IV) are hard to remove.

- Tin(II) ions are adsorbed on the surface by ion exchange with Na^+ ions present as impurity in the (hydrogenic) silicagels; the silica powders do not adsorb tin as tin(II).
- DBDMT is very reactive towards the silicagel surface, but only about 40% of the hydroxyl groups present can react. The distribution obtained is very unsatisfactory because of the high reactivity

2.3.2 Structure of the catalysts

The conditions during preparation may have much influence on the physical structure of Sn/SiO_2 catalysts. For instance, silicagel disintegrates to a powder when in contact with an aqueous $SnCl_2$ solution for 15h. Another factor that should be taken into account is the influence of the (hydro)thermal treatment occuring during other preparation steps. A decrease of the surface area at constant pore volume may occur during drying at 150 °C when the gel contains water and HCl (172, 173). Other structural changes are possible during calcination. Moreover, the possibility that tin affects the stability of the carrier during drying and/or calcination should not be overlooked. Metal ions are known to influence the structural stability of silicagels (146, 174, 173, 176, 175, 177, 178, 179, 180, 181). In particular Na^+ has an appreciable negative effect. Finally, the occurrence of structural changes during catalyst preparation, e.g. at conditions of high temperature and when in contact with water, may provide indications for instability during reaction at lower temperatures but over much longer periods of time. Accordingly, the changes of some structural parameters during catalyst preparation were studied.
Tables 2.3.2 and 2.3.3 show some physical characteristics and figure 2.3.5 contains pore distributions as measured by mercury porosimetry for some typical samples. In figure 2.3.6 the various supports are compared with respect to cumulative surface area versus pore size.
Comparison of DO and D10.6 shows that the pore size distribution remains almost the same, but also that pore volume and surface area decrease somewhat.
The same effects are observed for the G-catalyst. The F-catalyst, however, shows an increasing pore diameter and pore volume. When the diameters of the most frequently occuring pores found by nitrogen adsorption and by mercury porosimetry are compared, the former pore size value is found to be higher. The latter method measures the entrance diameter of the pore, whereas nitrogen adsorption gives the internal diameter. Although mercury penetration measurements are known to give values smaller by about 20-30%, the difference of a factor of about 2 is significant.

Table 2.3.3 Structural data obtained by nitrogen adsorption.
a. catalyst after drying step of preparation
b. after calcination step
c. after reduction

Catalyst	S_{BET} $m^2.g^{-1}$	V_{pore} $cm^3.g^{-1}$	R_{pore} at dV/d(logR)max	$R_{pore, mean}$ nm
D0	380	1.20	8.0	7.2
D0.b	372	1.16	7.0	6.7
D1.a	314			
D1.b	350			
D1.c	328	1.11	7.0	6.8
D2.a	332	1.06	7.0	6.4
D2.c	341	1.12	7.5	6.6
D3.a	334	1.07	7.5	7.0
D3.b	353	1.16	6.5	6.2
D6.b	387	1.12	7.0	7.6
D7.b	385	1.18	7.0	6.6
D10.b	323			
D11.b	344			
D12.b	350			
D13.b	362			
D14.b	374			
D15.b	379			
D16.b	382			
D17.b	382			
D20	349	1.01	6.5	6.4
D24(2).b*	382	0.96	7.0	6.5
D25(2).b*	369	1.23	6.5	7.0
D25(4).b*	344	0.85	7.0	7.4
D26(4).b*	374	1.13	6.2	6.0
F	128			
F0.b	130	1.39	30.0	20.0
F1.b	135			
F3.2.b	128			
F4.b	127	1.63	38.0	24.7
G	315			
G0.b	326			
G1.b	327			
G2.b	402			
G4.b	342	1.52	22.5	13.2
G6.b	280	1.38	18.5	10.8
S	101	1.05	17.0	
S2.b	89	0.78	18.0/27.0	22.1

* (2) after direct calcination
(4) with preceding treatment with water vapour.

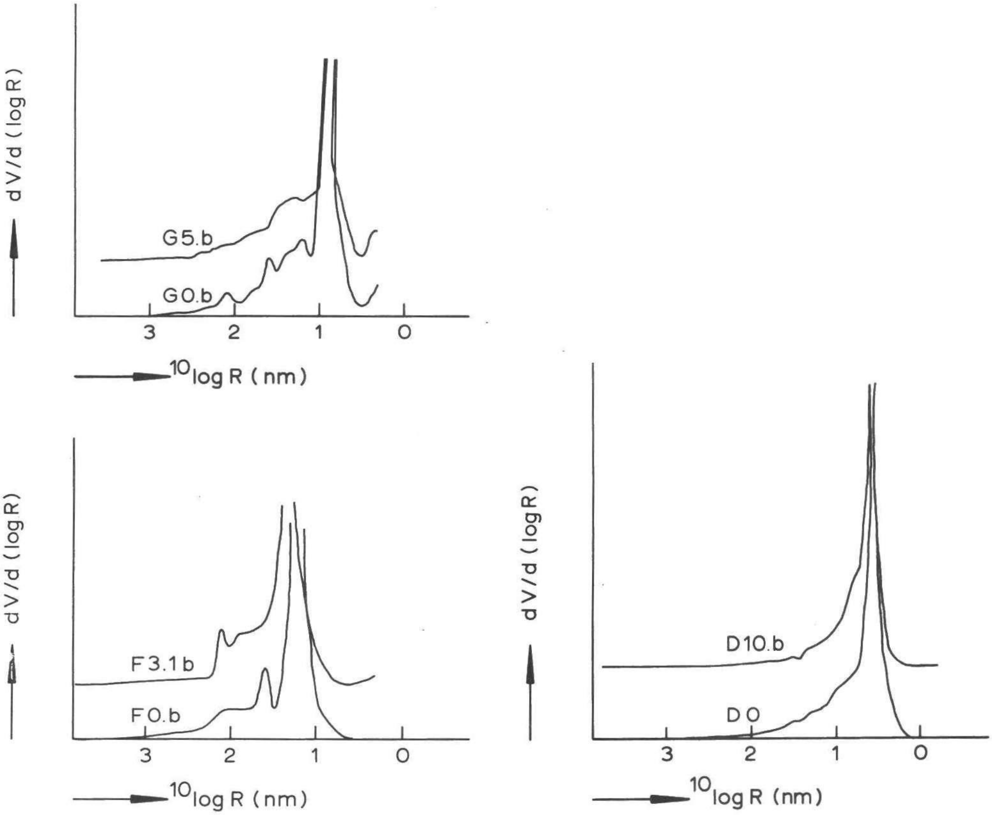


Figure 2.3.5 Comparison of pore distribution of supports and catalysts (method: mercury porosimetry)

Table 2.3.2 Structural data on calcined catalyst and support (method; mercury porosimetry).

Catalyst	S ($m^2.g^{-1}$)	Vp* ($cm^3.g^{-1}$)	R_{pore} at $dV/d(logR)_{max}$ (nm)	R_{pore} mean value (nm)
D0**	435	1.04	3.5	8.1
D10.b	371	0.89	3.5	8.2
F0.b	113	1.37	16.9	24.5
F3.1.b	101	1.49	22.9	31.4
G0.b	302	1.51	7.4	14.2
G5.b	271	1.28	7.4	14.1

* measured from 100 kPa(abs) on

** untreated support

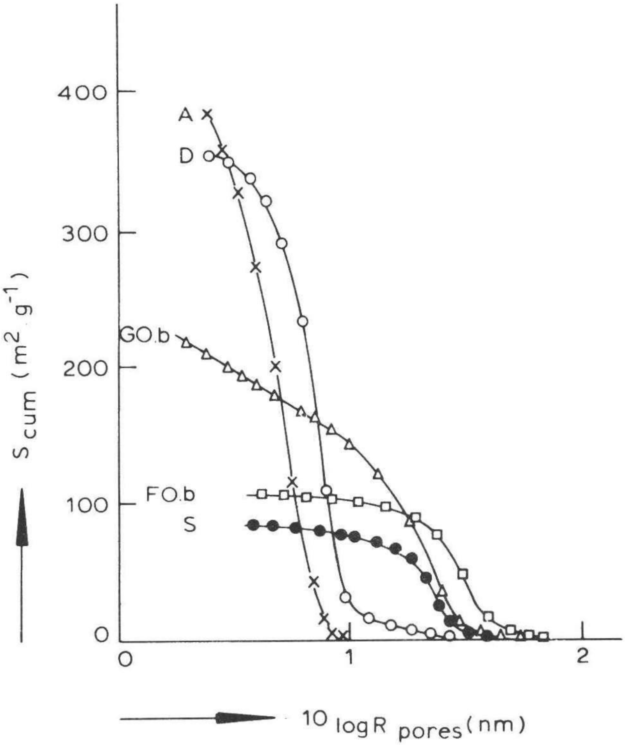


Figure 2.3.6 Cumulative surface versus pore diameter for the supports used.

The difference in surface area found by the two methods may indicate that an "ink bottle" shape is a characteristic of the pores. This is plausible, considering that the structure is built up from spherical primary particles.
The similarity in surface area of DO and DO.b shows that, in spite of the high Na content, the support hardly degrades during the various preparation steps.

Tin appears to influence the structural characteristics. After impregnation and drying, surface area and pore volume have decreased (D1.a, D2.a, and D3.a), but calcination restores these almost to the values found for the support. Reduction of tin oxides to tin again causes a decrease. Furthermore, it is evident that the higher the tin content, the larger the decrease in surface area is for the calcined catalyst (D10 - D17).

The effect is quite small until 2%w tin; at higher concentrations the decrease becomes substantial.

A difference can be observed between the catalysts prepared by dry impregnation with and without addition of acid. The data on D10.b and D1.b, which have the same tin content, indicate that the decrease of the surface area is smaller in the latter case. X-ray diffraction has shown this catalyst to have larger SnO_2 particles. These will stay in larger pores. Smaller SnO_2 particles fit into the smaller pores and have a stronger effect on the surface area by blocking these pores. The amorphous particles which are formed during drying are voluminous and most likely contain some chloride and water. They are able to block also larger pores.

The drop in surface area after reduction must be due to a more effective blockage of pores by the larger tin crystallites formed by coalescence.

The F catalysts show a much increased pore volume and pore radius at more or less constant surface area. Tin seems to have the effect of rearranging the aerosil particles to a more open structure. The G catalysts exhibit this effect only at low tin concentrations. At higher tin contents blockage of the pores by tin compounds counteracts this effect.

A striking difference between the D catalysts and the aerosil catalysts is the occurrence of micropores (< 2.5 diameter) in the latter group. This is particularly noticeable at low tin concentrations and with the G catalysts with its smaller primary particles.

The mordenites have a completely different structure, being crystalline and consisting of cages with small apertures of about 0.7 nm diameter. During synthesis some Al^{3+} can dissolve, but this does not necessarily change the structure, as was discussed before.

2.3.3 Reactions of tin under reducing or oxidizing conditions

The calcined catalyst precursor contains tin(IV) in an oxidic form. Since reduction is necessary to activate the catalyst, the reduction of calcined SnO_2/silica has been investigated. Another problem area studied is oxidation of Sn/silica because this oxidation can occur during aldol condensation, water, aldehydes or oxygen present as contaminant in the feed acting as oxidizing agents. SnO_2 is stable under non-reducing conditions. Only at higher temperatures it will lose some oxygen. SnO is a metastable solid phase; this compound is stable only in the gas phase at 1000 ^{o}C and higher. The solid slowly disproportionates to Sn^{o} and Sn^{4+} at temperatures up to 300 ^{o}C (182, 183, 184), but the reaction becomes fairly fast above 500 ^{o}C (185, 188).

The metastability of Sn^{2+} is confirmed by the reduction and oxidation behaviour of SnO_2 and metallic tin, respectively. Oxidation of metallic tin in air does result in SnO below 200 ^{o}C. At temperatures between 200 and 400 ^{o}C SnO_2 is formed by disproportionation of the intermediate SnO, not by further oxidation of SnO. Temperature-programmed oxidation showed that oxidation of SnO starts at 440 ^{o}C, and that the reaction is not complete until at least 700^{o}C because of the low rate of diffusion of oxygen through the SnO/SnO_2 product layer. Small tin particles are oxidized completely at substantially lower temperatures however(about 400 ^{o}C); similarly small SnO particles are oxidized too at such lower temperatures, viz. 380 ^{o}C (185).

Reduction of SnO_2 initially yields SnO and is followed by disproportionation at temperatures below 400 ^{o}C. Since the disproportionation is extremely slow at temperatures lower than 175 ^{o}C, SnO is not reduced in this temperature region. Water retards the reduction of SnO_2: a few percent of water in hydrogen at 450 ^{o}C even suffices to stop the reduction completely. On the other hand, 3% water in nitrogen did not oxidize metallic tin (7, 186). Particle size has much influence on the effect of water during reduction of SnO_2 because this reaction product must diffuse out of the particle, which controls the rate of reduction. The different regions in the reduction of the catalyst observed by Swift (7) can be explained in this way.

The above reactions were studied by means of thermogravimetric analysis. This method was rather difficult to apply in this study because of the low tin content of the samples and the slow or incomplete desorption of water from the carrier. The results are therefore compared with those obtained by subjecting the support to the same treatments as the catalysts or the catalyst precursors. The data on the TGA reduction experiments are given in table 2.3.4 and figure 2.3.7; for the oxidation experiments reference is made to table 2.3.5 and figure 2.3.8, and data on the reduction in the reaction apparatus are shown in table 2.3.6 and figure 2.3.9.

The calcined catalyst precursor contains tin only in the form of tin(IV)oxide (see 2.3.4). It was therefore expected that a loss of weight would occur during reduction which is in accordance with two oxygen atoms per atom tin. However, isothermal reduction of the catalyst in T.G.A. apparatus at 450^{o}C was accompanied by a larger weight decrease, in spite of prior drying under N_2 to constant weight (in about 16 h). The larger decrease observed is not well understood; it might be due to loss of water retained in the SnO_2 structure or to reduction of $SnCl_2$, which according to X-ray fluorescence is sometimes present in the catalysts even after calcination. The difference between the

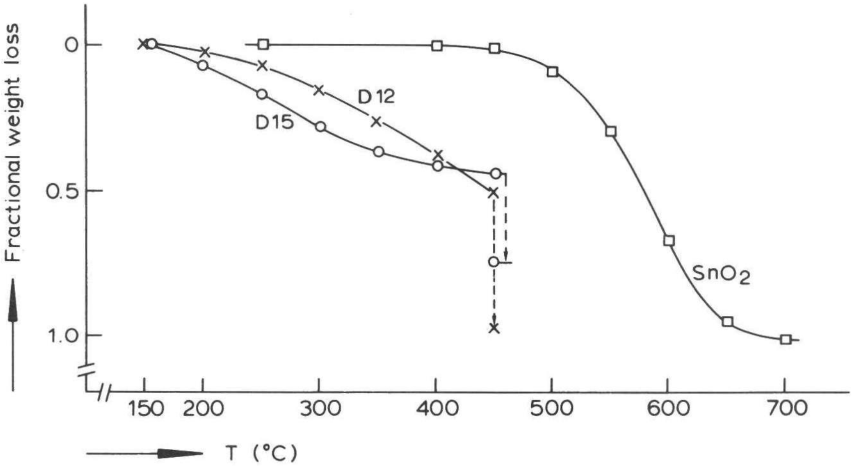


Figure 2.3.7 Reduction of tin on silica catalysts and SnO_2 *(fractional weight loss = 1 when* SnO_2 *is completely reduced to Sn). D12:3.74w%Sn, D15: 0.98w%Sn.*

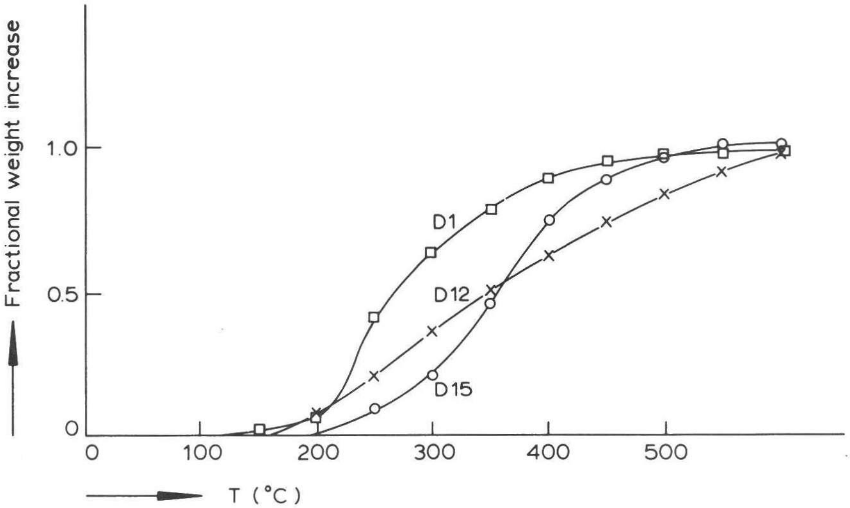


Figure 2.3.8 Air oxidation of tin on silica catalysts (fractional weight increase = 1 after complete oxidation of Sn to SnO_2*) D1:7.3w%Sn, D12: 3.74w%Sn, D15: 0.98w%Sn*

Tabel 2.3.4 Reduction of calcined catalysts with hydrogen.

a) isothermal at 450 °C, until constant weight (about 16h)

catalyst	D1	D2	D12	support D
tin content (w%)	7.3	3.6	3.74	0
theoretical decrease (%)*	1.97	0.97	1.01	-
observed decrease (%)	2.69**	1.41**	1.14**	0.25

b) temperature-programmed, 10 °C.min, 25 - 450 °C and kept at that temperature for 2.5h.

catalyst	D12	D15	support D	SnO_2
tin content (w%)	3.74	0.98	0	
theoretical decrease (%)*	1.01	0.26	-	21.23
observed decrease (%)***	1.01**	0.22**	0.56	21.86

* two oxygen atoms per tin atom

** corrected for the weight decrease of the support

*** from 150 °C on.

Table 2.3.5 Temperature-programmed oxidation of reduced tin on silicagel catalysts (150 - 600 °C, in dried air).

catalyst	D1	D3	D10	D12	D15	D16
tin content (w%)	7.3	3.6	7.5	3.74	0.98	0.51
theoretical increase (%)*	1.97	0.97	2.02	1.01	0.26	0.14
observed increase (%)	1.92	0.89	2.41	0.97	0.26	0.16

* two oxygen atoms per tin atom.

Table 2.3.6 Isothermal reduction of silicagel-based catalysts in a tubular reactor.
Conditions: 450 ^{o}C; H_2; 250 ml.min^{-1}.

catalyst	w%Sn	initial water partial pressure * (kPa)	$P_{H_2O(in)}$/w%Sn	water formed (w% of catalyst)	
				theoretical	observed**
D3	3.6	2.46	0.68	1.09	0.92
D9	1.8	0.90	0.50	0.55	0.51
D10	7.5	5.39	0.72	2.28	2.23
D11	6.36	2.67	0.42	1.93	1.38
D12	3.74	1.91	0.51	1.13	1.02
D13	2.65	1.43	0.54	0.80	0.68
D14	2.00	1.47	0.23	0.61	0.30
D15	0.98	0.32	0.18	0.16	0.05
D17	0.45	0.02	0.05	0.14	0.01

* in sample taken after 30 sec.

** calculation is by integration of the curve (P_{H_2O} - t) with P_{H_2O} after 30 sec. as starting value.

actual and the theoretical weight decrease is particularly apparent for material prepared by dry impregnation without addition of acid (D1 and D3). From the temperature - programmed reduction experiments it can be concluded that reduction of bulk SnO_2 cannot be detected below 450^{o}C (figure 2.3.7). However, the particles of the sample tested here were large, viz. in the range of 1 to 10 µm. By contrast, reduction of the SnO_2 in the catalyst starts at 150 ^{o}C. The catalyst with a small amount of tin (D15, 0.98w%Sn) shows two regions of reduction. From 150 to 450 ^{o}C nearly half the decrease in weight takes place; further reduction occurs at 450 ^{o}C, but only very slowly. The total weight loss does not reach the theoretical value for reduction to metallic tin even after 2.5h. A catalyst containing more tin (D12; 2.7w%) shows only a single reduction region from 150 ^{o}C onwards. Reduction is complete after 2.5h at 450 ^{o}C.

The following reactions can be expected during reduction.
Large crystallites of SnO_2 resulting from precipitation during impregnation are reduced to metallic tin.
Surface tin compounds, which after calcination have the form silica=$Sn(OH)_2$ (163), will lose their hydroxyl groups. A tin(II) surface compound is thus formed which appears to be stable seeing the relatively high stability of tin(II)oxide mentioned above. Further reduction to give single tin(0) atoms appears unlikely.
Furthermore, molecularly dispersed $SnO_2.H_2O$ is present on the surface as a result of hydrolysis of tin ions attached to the surface (187). It is quite mobile at higher temperatures and may form agglomerates which are subsequently reduced to metallic tin. Part of it may react with surface hydroxyl groups to give more tin(II) surface compounds.
The assumption of these reactions and of the two tin compounds formed in the catalyst explains the observed results. Catalysts with a low tin content will contain relatively large amounts of the surface groups. The observed two-step reduction is explained as an initial dehydration at low temperature to silica=SnO, which is reduced to silica=Sn at a higher temperature.
The more difficult and less complete reduction of these catalysts may be caused by the presence of large crystallites of SnO_2 in catalysts with low tin contents, as is shown by X-ray diffraction. Catalysts with higher tin contents contain much greater proportions of crystalline SnO_2.
The larger weight decrease caused by reduction of this compound obscures the two steps in the reduction of the surface compound which is also present.

The reactions described above are also in line with the observations made during isothermal reduction at $450^{o}C$ in the reactor. This reduction proceeds very rapidly during the first 10-15 minutes (see figure 2.3.9). The initial water concentration, after 30 seconds, is not proportional to the tin content (table 2.3.6).
Furthermore, the expected and actually measured amounts of water show a deviation which increases relatively with decreasing tin content.
It is assumed therefore that dehydration (and reduction) of the silica=$Sn(OH)_2$ groups occurs very fast, within the first 30 seconds. Less water is observed in that case, when starting the measurements after part of the dehydration and reduction has already taken place. The effect will be the strongest for the lower tin contents.

Temperature-programmed oxidation of reduced catalysts showed oxidation to start at lower temperatures as the tin content is higher. A catalyst with a high tin

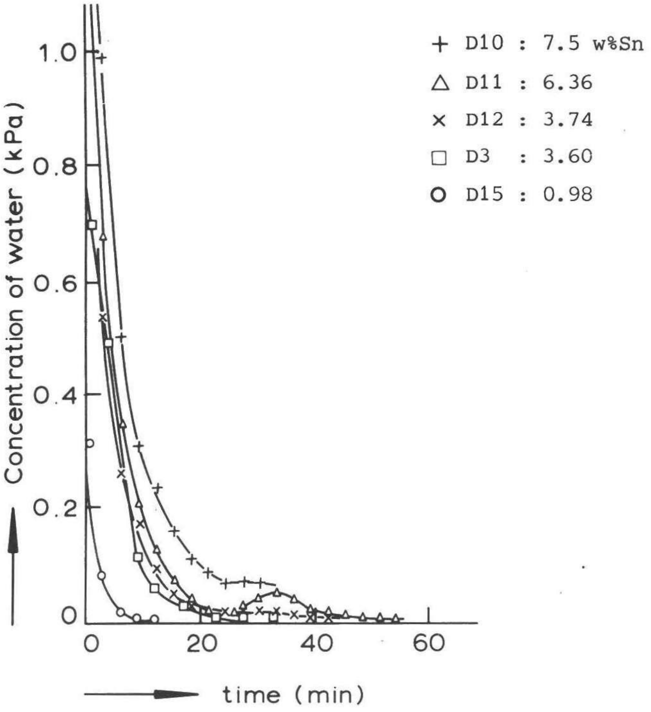


Figure 2.3.9 Concentration of water in the product gas during reduction. Conditions: hydrogen flow 250 ml.min^{-1}; 450^{o}C.

content (D1, 7.3w%) started to oxidize at 100^{o}C and showed a maximum rate at 230^{o}C, but oxidation was still incomplete even at 600^{o}C. The oxidation curve for a catalyst with a high tin content apparently is dominated by the slow oxidation of metallic tin. The curve observed for a catalyst with low tin content (e.g. D15, 0.98w%Sn) indicates oxidation of a tin compound which is relatively stable at oxidizing conditions and for which oxidation is not subject to diffusion limitation. The compound presumably is the tin(II) bound on the surface, discussed before, which is present in relatively large amounts at low tin contents. The oxidation of this tin(II) finally leads to the formation of silica=Sn(OH)$_2$ groups because water is always present.

Some DSC measurements performed with catalyst D1 showed a melting point for the metallic tin phase at 220 - 225 ^{o}C, which is about 10 ^{o}C lower than the normal melting point of tin (231.9 ^{o}C). This difference is believed to be caused by the fine dispersion of the tin.

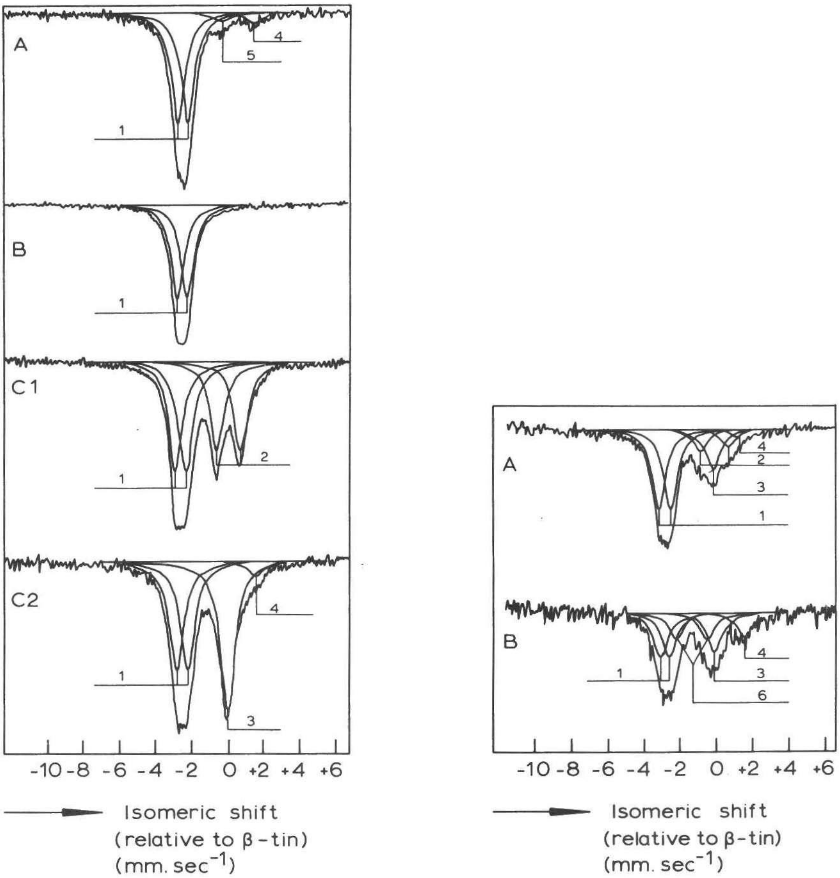
It was furthermore observed that the total heat of melting was 3 times smaller than would be expected from the tin content of the catalyst. This indicates that only part of the tin is present in a crystalline metallic form.

2.3.4 Catalyst analysis by Moessbauer spectroscopy

Moessbauer spectroscopy is a valuable tool for investigation of the electronic state of tin and its surroundings, but most information in literature is available only on compounds in a bulk phase. The influence of the occurrence of surface compounds and single atoms is much less known. Gol'danskii discusses some effects (189); broadening of the quadrupole splitting is to be expected. There are reports on tin chemisorbed on a silicagel surface (187, 190). In this case the strongly adsorbed tin(II) was brought on to the silica surface by ion exchange. Tin(IV) was formed from it by hydrolysis and subsequent oxidation; it was bound with weak Van der Waals forces only, in the form $SnO_2.nH_2O$, and showed a high surface mobility.

In the present work the recorded spectra were interpreted by dissecting them mathematically into separate peaks for the most likely compounds with the known isomeric shifts and quadrupole splitting. The data used are based on Gol'danskii et al (191). The procedure used generally gives good spectra for compounds in large concentrations but reveals small amounts of compounds only when they are not obscured by the larger peaks. The deviations from the peak forms of pure compounds observed in this work (table 2.3.7) are therefore not only caused by structural factors, as very small clusters, crystallites or surface adsorbates, but also by compounds that are difficult to determine because they are present in relatively small quantities. Their peaks coincide almost fully with the major peaks and influence their form.

Two catalysts were investigated, D1 and D3, both prepared by dry impregnation without addition of acid. Their tin content was 7.3 and 3.6 w% respectively. Figure 2.3.10a gives the spectra for catalysts D1 at different stages of preparation. After drying (D1.a) only small amounts of tin(II) are left; most of it has been converted to SnO_2. The calcined catalyst (D1.b) contains only SnO_2. Conditions for the reduction, 400 ^{o}C during 1h, under a small hydrogen flow, were such that complete reduction was not obtained. The sample was exposed to air after the reduction because means of blanketing with N_2 were not yet available. Evidently, the catalyst batch was not homogeneous. The color of the reduced catalyst varied from dark grey to brown and nearly white. Separate spectra were run on the brown and the grey particles.



(2.3.10.a) *(2.3.10.b)*

Figure 2.3.10 Moessbauer spectra of tin on silicagel catalysts.

a. catalyst D1(7.3w%Sn), A dried after impregnation
B calcined
C reduced: two fractions, one of which contains less tin and has a brown color (C1), the other contains more tin (about 10 times) and has a grey color (C2)
b. catalyst D3 (3.6w%Sn), A reduced and exposed to air,
B reduced and kept under nitrogen

Peaks are due to: 1 :SnO_2*, 2:β-tin, 3 :SnO, 4 :*$SnCl_2$*, 5 and 6 :unknown tin compounds*

Table 2.3.7 Isomeric shift and quadrupole splitting for the Moessbauer spectra; given in literature (191, 192), and those used in selecting the best fit for the measured spectra.

sample	tin compound	IS relative to β-tin ($mm.sec^{-1}$)	QS ($mm.sec^{-1}$)
literature data for pure crystalline compounds,			
	$SnCl_2$	+1.59	0
	$SnSiO_2$ (192)	+0.30	2.00
	SnO	+0.12	1.50
	β-Sn	0	0
	α-Sn	-0.55	0
	$SnCl_4$	-1.80	0
	SnO_2	-2.65	0.45
values used for analysis of the spectra,			
D1a	SnO_2	-2.44	0.56
	?	-0.23	0
	$SnCl_2$	+1.53	0
D1.b	SnO_2	-2.65	0.39
D2.c(brown)	SnO_2	-2.52	0.63
	SnO	+0.16	1.34
D1.c(grey)	SnO_2	-2.50	0.61
	β-Sn	0	0
	$SnCl_2$	+1.59	0
D3.c(exposed to air)	SnO_2	-2.54	0.62
	β-Sn	+0.07	0
	SnO	+0.13	1.49
	$SnCl_2$	1.36	0
D3.c(kept under nitrogen)	SnO_2	-2.65	0.45
	?	-1.22	1.69
	β-Sn	0	0
	$SnCl_2$	1.59	0

The former contained much SnO_2 and β-Sn was not detectable, the latter contained mainly SnO_2 and β-Sn, and only very small amounts of SnO. Intensities of the spectra showed that the grey particles had a much higher tin content than the brown fraction. Therefore, SnO is formed in relatively large amounts at low tin content and resists further reduction. It is not just the intermediate for the formation of β-tin because otherwise both samples should have had the same spectrum.
Figure 2.3.10b shows the spectra for catalyst D3 reduced under the same conditions mentioned above. One batch was exposed to the air and another was kept under nitrogen. The spectra show that this batch still contained some $SnCl_2$. The sample which was exposed to air contains SnO_2, β-tin and SnO. The sample kept under nitrogen showed SnO_2 and β-tin but no SnO. However, an unknown compound is present which has a negative shift relative to β-tin and a large quadrupole splitting. It is likely that the observed phenomena are due to the presence of a strongly attached surface tin(II) compound. In such strong interaction some of the electrons can be further removed from the tin atom. The interaction is weakened during exposure to the air, e.g. by the action of water.
Summarizing, it is likely that in the reduced state the catalyst contains tin(0) in the form of β-tin, and some tin(II). The latter is present in relatively larger amounts when the tin content of the catalyst is low. It is furthermore resistant to further reduction because of its attachment to the silicagel surface.

2.4 Concluding remarks

The various methods of catalyst preparation discussed in this chapter give quite different results for the attainable tin content as well as for the tin distribution. This applies to the distribution over each individual particle and over the catalyst batch as a whole. Use of impregnants with a high reactivity results in small tin losses during impregnation but also in a poor tin distribution. The reverse holds for impregnants of low but still sufficient reactivity.

Impregnation with $SnCl_4$ corresponds to the latter case, giving a very even distribution but at the expense of large tin losses: a considerable excess of $SnCl_4$ must be applied and favourable conditions such as the presence of water and a high temperature. Optimal catalysts are obtained when applying dry impregnation of silicagel with an aqueous $SnCl_2$ solution acidified with hydrochloric acid: $SnCl_4$ is formed during drying. $SnCl_4$ is probably more reactive towards silica powder, but then a somewhat less attractive tin distribution is obtained.

An example of an impregnation at too high a reactivity is DBDMT: it reacts so readily with the silicagel surface that most of the tin is deposited near the outer surface of the particle because the rate of diffusion through the pores of the support is much lower than the rate of reaction.

Summarizing, the following phenomena occur during the various steps of catalyst preparation:

Impregnation

- Sn^{2+} is exchanged with Na^+; reactions between tin(II) hydroxides and chlorides and hydroxyl groups do not occur.
- $SnCl_4$ reacts slowly with surface hydroxyl groups.
- DBDMT reacts very fast, two surface hydroxyl groups reacting per molecule to a maximum OH-conversion of about 40% for silicagel (about 1.0 group per nm^2).
- Water and oxygen cause the formation of tin(II) and tin(IV) precipitates. Any precipitate present in the solution accumulates at or near the outer surface of the particles. Precipitates formed inside the particles are generally finely dispersed. Higher concentrations of impregnants give more and finer precipitate inside the particles.

Drying

- Large proportions of $SnCl_4$ are formed under the influence of oxygen and chloride ions, mainly from precipitates, when impregnating with $SnCl_2$.
- Since $SnCl_4$ reacts rather slowly with two surface hydroxyl groups it can diffuse through the pores during drying and even evaporate partially. The maximum amount of hydroxyl groups on silicagel reactive towards $SnCl_4$ is 1.0 group per nm^2 at the conditions used. Silica powder reacts more readily.
- Sn-Cl bonds are further hydrolyzed to SnOH bonds.

Calcination

- The tin compounds in precipitates lose Cl^- and water and oxidize further to SnO_2.
- Weakly adsorbed tin is oxidized and diffuses over the surface; crystallites of SnO_2 may be formed from this source too.
- Strongly adsorbed tin loses adsorbed water and residual chloride.

Reduction

- SnO_2 is reduced to metallic tin, which then coalesces to larger globules of molten tin; β-tin is formed after cooling.
- Strongly adsorbed tin(IV) loses its hydroxyl groups by reduction, the tin(II) formed is even more strongly attached to the surface.

3 CATALYST PERFORMANCE

3.1 Experimental

In this chapter the experimental study of the activity, selectivity, deactivation and regeneration of the Sn/SiO_2 catalysts for gas-phase aldol condensation is discussed. A simplified flow diagram of the equipment used in this work is shown in figure 3.1.1.

Freshly distilled ethanal was fed from cooled vessel ③ to evaporator ⑥ by means of pump ⑤. A gas stream acting as diluent for the reactant (H_2 or N_2) was introduced into the evaporator to ensure smooth evaporation; gas flows were stabilized by flow controllers ① and measured with flowmeters ②. Whenever necessary other liquids, e.g. water, could also be introduced into the equipment by similar means. Piston pumps having a maximum capacity of 45 $ml.h^{-1}$ were installed. Liquid flows were checked with calibrated burettes ④ and flow pulsations in the liquid flows damped by a pressure valve and a membrane. In addition, surge tank ⑦ was installed just upstream of reactor ⑧ to smooth out possible flow and concentration fluctuations still further.
In part of the experiments an alternative feed system was used in which ethanal was heated to 65^oC in a closed vessel. Since at this temperature the vapour pressure of ethanal is about 300 KPa, the vapour can be fed directly into the system by way of a heated flow controller.
Gases were purified before use. Hydrogen was led over a Pd/Al_2O_3 catalyst to remove oxygen and dried over molecular sieves. Nitrogen was first dried and then passed over finely dispersed Cu on silica to remove oxygen. Gas flow measurement ② was either by rotameters or by determining the pressure drop over calibrated capillaries by means of differential pressure indicators, i.e. U tubes filled with silicone oil. The gas flow was checked in each run by means of a calibrated soap film meter.
Reactor ⑧, a stainless steel tube of 3-10 ml and 8 mm internal diameter with sintered metal filters at both ends, was provided with Swagelok connections to facilitate installation after a catalyst change. It was heated by a tubular furnace which could be opened lengthwise for easy access. The temperature was

kept constant by means of an Eurotherm thyristor controller to within 0.5^{o}C during each run.

Analysis of reactor feed and product was done by on-line gas chromatograph ⑨ samples being taken directly from the gas stream with a sample loop and injected into the gas chromatograph by a pneumatic valve.

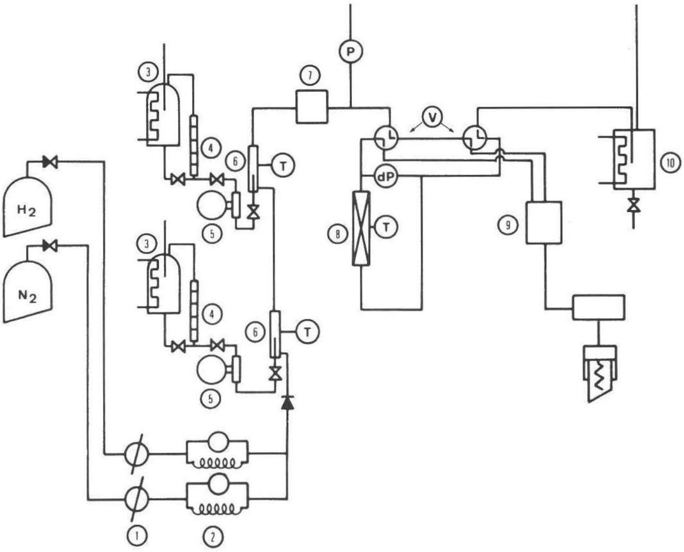


Figure 3.1.1 Equipment for gas-phase aldol condensation

Legend: ① flow controller , ② flow measurement, ③ cooled feed vessel, ④ burette for measuring liquid flow, ⑤ pump, ⑥ evaporator, ⑦ surge tank, ⑧ reactor, ⑨ gas chromatographic analysis, ⑩ condensor, Ⓟ and (dP) pressure and differential pressure indication, Ⓣ temperature control, Ⓥ four way valve

The product gas was passed through water-cooled condensor ⑩ and the non-condensable compounds vented. A vapour trap cooled to -60^{o}C was sometimes added for complete liquid recovery. Construction materials used were brass in the gas section; parts of the system in contact with aldehyde were made of stainless steel, PTFE or ethylene-propylene rubber.

The operation was semi-automatic, which implies that set points were adjusted manually and that after a certain time samples were taken and the analysis started under automatic control. Safety was ensured by installing pressure, temperature and flow control devices; if a pre-set maximum or sometimes minimum allowable value for a given parameter was exceeded, automatic shut-down of the apparatus followed. This made it possible to run the apparatus unattended for long periods of time.

The gas chromatograph used for on-line analysis contained a column (1 m long, 2 mm internal diameter) filled with Porapak QS, mesh size 120-150. The column temperature was 165°C and the carrier gas hydrogen at a flow rate of 32.5 ml.min^{-1}. Detection was by thermal conductivity. The GC was used to determine the concentrations of ethanal, water and butenal in the product. Off-line analyses were carried out with another gas chromatograph equipped with a column filled with 3% SE-30 on Chromosorb W, acid-washed and DMCS-treated, mesh size 100-120. The column was 3 m long and had an internal diameter of 2 mm. The column temperature was maintained at 175°C; the carrier, hydrogen, was passed through at a flow of 25 ml.min^{-1}. Detection was by flame ionisation. This GC was used mainly to analyze for higher-boiling products.

GC-MS was used for qualitative analysis of the products, the conditions being: SP 2250 column, 3 m length, temperature-programmed from 20°C through 210°C at a rate of 8°C.min^{-1}. The catalysts used were analyzed to determine changes in tin content by neutron activation, crystallinity and crystallite size of the metallic tin by X-ray diffraction, and structure by BET analysis, as has been described in 2.2.3.

The feed rate is characterized as the reciprocal molar hourly space velocity (in g cat.h.mol^{-1}), which is measure of the residence time. The density of the catalyst in the reactor was about 0.3 g.ml^{-1}; the reactor usually contained between 1 and 5 g.

Conversion and selectivity were calculated directly from the ethanal, butenal and water concentration in a single sample taken from the gas stream after the reactor. As will be shown in 3.4, nearly all the by-products are formed by condensation of three and four ethanal molecules. It was therefore possible to derive relations for conversion and selectivity based on only those three values (see appendix I).
The following relations apply:

$$\xi = \left[(1-S_F)B_r + (1+S_F)H_r\right] / \left[E_r + (1-S_F)B_r + (1+S_F)H_r\right]$$

and

$$S = 200B_r / \left[(1-S_F)B_r + (1+S_F)H_r\right] \quad (\%)$$

in which E_r, B_r and H_r are the measured concentrations of ethanal, butenal and water after the reactor respectively. S_F is a constant dependent on the ratio of by-products formed by condensation of three and four ethanal molecules; its value is almost constant and taken as 0.45 in our calculations.

Observed values of conversion and selectivity for consecutive samples sometimes showed unexpected and unsystematic differences up to 15% relative. Attempts to improve this by changing the feed system were unsuccessful and the reason could not be traced. It was therefore decided to determine conversion and selectivity by averaging the results of a number of samples taken successively.

Comparison of the results thus obtained with values for conversion and selectivity obtained with measured concentrations for ethanal and butenal before and after the reactor generally showed deviations less than 1% when the average was taken over a series of measurements. Larger deviations were found during the first hours of a run, when the conversion is high and for experiments at temperatures higher than 350°C.

3.2 Preliminary tests and calculations

A general impression of catalyst performance follows from figure 3.2.1, in which results of exploratory tests on some catalysts under different conditions are shown. It is at once apparent that the catalysts deactivate, especially during the first 20 run hours. The rate of deactivation does not depend much on the type of catalyst and the tin content at the reaction conditions applied.

It was reported that the type of diluent influences the deactivation; hydrogen was to be preferred (8). Some preliminary tests showed this to be the case. The use of nitrogen as diluent caused a twice higher deactivation rate compared to hydrogen.

As standard catalyst activation procedure was used reduction at 450°C under hydrogen, 250 $ml.min^{-1}$, during 30 minutes, or till no water could be detected in the outcoming gas stream anymore. We observed, however, already optimum conversion and selectivity after 15 minutes reduction, even for catalyst with a high tin content. This indicates that formation of the active sites is relatively fast (c.f. 2.3.3 and figures 1.3 and 2.1.3).

For comparison of the activity of the different catalysts the conversion after 40 h was chosen. The rate of deactivation is slow after 40 h operation, and this conversion was well reproducible. For activity tests, the reactor was operated close to the differential region. Figure 3.2.2 gives the results for a

catalyst, D2, tested over a wide range of conditions, to establish favourable reaction conditions.
Usual test conditions chosen were: ethanal partial pressure = 10 kPa, $W/F = 5$ g cat.h.mol^{-1}, and a temperature of 523 K (250^{o}C).
Plug flow reactor behaviour is assured because the $L/d_{particle}$ ratio was at least 80 and the $d_{reactor}/d_{particle}$ ratio about 10 (195). Moreover it was ascertained that the reaction rate is not controlled by diffusion; this was done as outlined below.

Several criteria are available for testing for pore diffusion limitation of the reaction rate in a porous catalyst. Most authors apply the Damköhler number for mass transport for this purpose. When diffusion limitation is absent the following relation holds for a reaction in which a volume change does not occur (193, 194, 195):

$$Dam_M = \frac{r' * d_{particle}}{4 * C_0 * D_{eff}} < 1$$

For the most unfavourable case we may assume Knudsen diffusion throughout the particle, as most pores are smaller than 100 nm. For ethanal the effective Knudsen diffusion constant is about $2.2 * 10^{-6}$ m^2.s^{-1}.
Calculations show Dam_M to be smaller than 0.1 at $P_{ethanal} = 10$ kPa and 523 K, and at a conversion of 10%. This points to the absence of diffusion limitation. In the above calculation the reaction was taken to be first order in ethanal.

An experimental check was also made. Two catalyst samples from the same batch but differing in particle size (1.0-0.6 and 0.6-0.3 mm) were tested (see figure 3.2.3). The ageing characteristics appear to be the same, so the ethanal conversion after 40 hours can be used as a measure of catalyst activity at different conditions. The experimental results confirm the assumption made on theoretical grounds that pore diffusion does not control the rate of the reaction.
In view of the absence of pure diffusion limitation it is unlikely that mass transfer from gas to solid influences the process rate. This was confirmed by calculations.
Temperature effects can also be neglected because the heat produced by the reaction is too small to cause non-isothermal reactor behaviour. The rise in temperature observed at the beginning of a run over a fresh catalyst, which amounted to 2-3^{o}C, disappeared within 3 minutes. It is ascribed to strongly exothermic adsorption of the reactants.

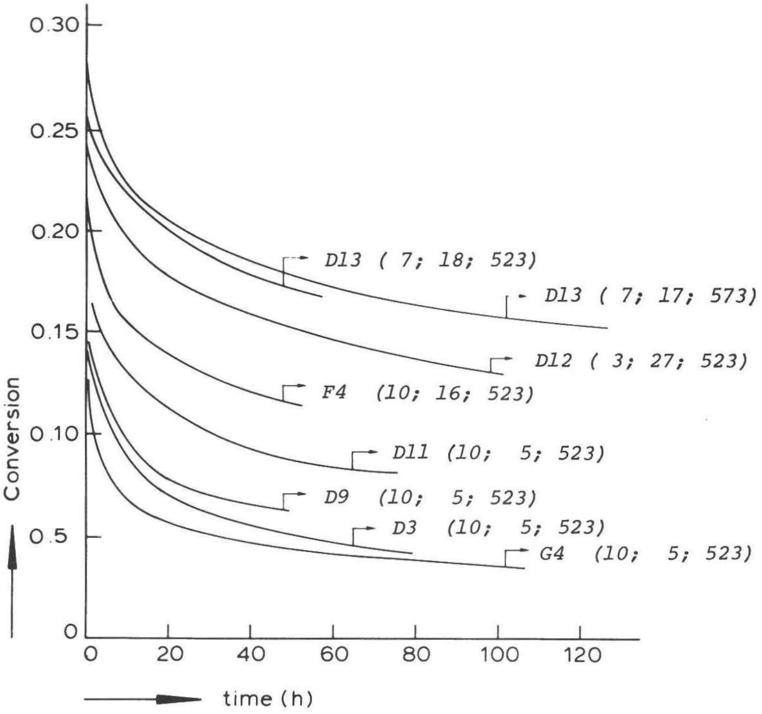


Figure 3.2.1 Behaviour of catalysts during test runs at different conditions Legend: catalyst code ($P_{feed,ethanal}$ in kPa, W/F in g cat.h.mol^{-1}, T in K)

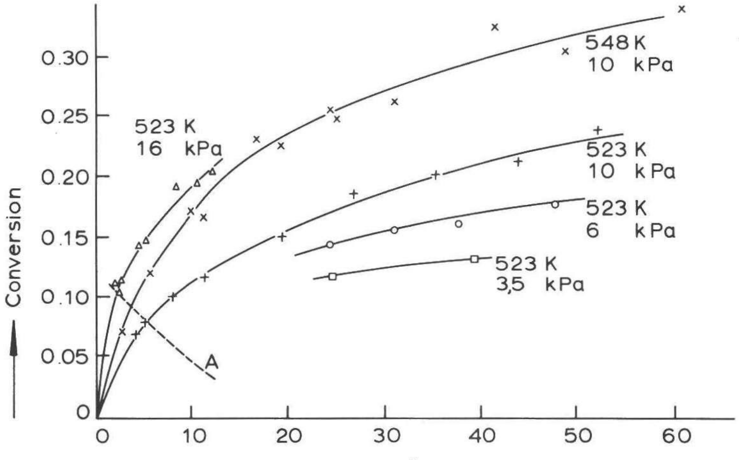
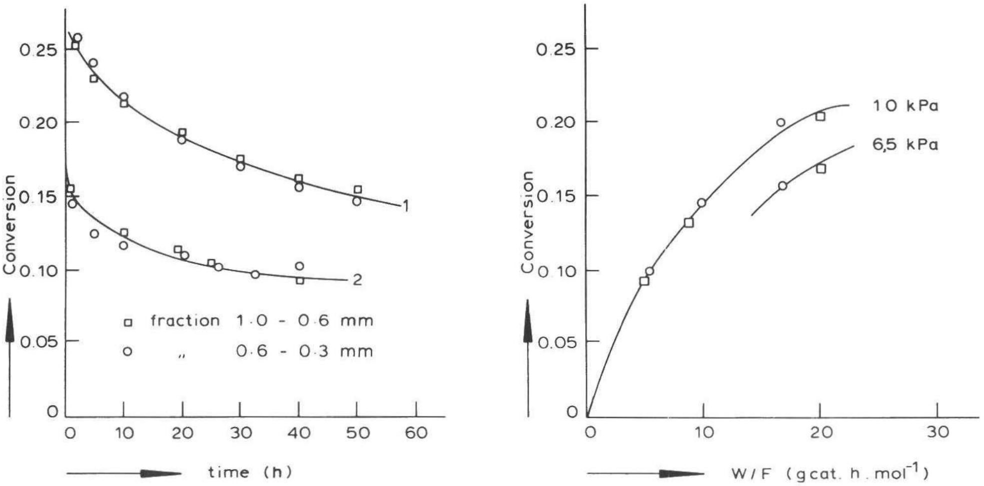


Figure 3.2.2 Activity for catalyst D2 at different conditions after 40 hours operation. Below the dotted line A the reactor is operated differentially.



(3.2.3.a) (3.2.3.b)

Figure 3.2.3 Comparison of two sieve fractions of catalyst D12 to investigate the influence of diffusion on the reaction rate

T 523 K

a. Condition 1: $P_{ethanal}$ *= 8.2 kPa, W/F = 14.1 g cat.h.mol*$^{-1}$

" 2: $P_{ethanal}$ *= 10 kPa, W/F = 5 g cat.h.mol*$^{-1}$

b. Conversion after 40 h operation

3.3 Catalyst activity

3.3.1 Influence of method of preparation

Various methods have been applied to prepare catalysts based on silicagel D. Figure 3.3.1 shows the activity as percentage of the conversion obtained with the most active catalyst plotted against the tin content expressed as tin atoms per unit of surface area. For the purpose of the discussion it is assumed that at a given set of conditions the conversion depends only on the concentration of active tin on the surface.

It follows from the data that the support has a distinct activity for aldol condensation. This is caused by impurities, especially Na^+. However, the activity of silicagel D is much below that of the least active Sn/SiO_2 catalyst (see table 3.3.1a).

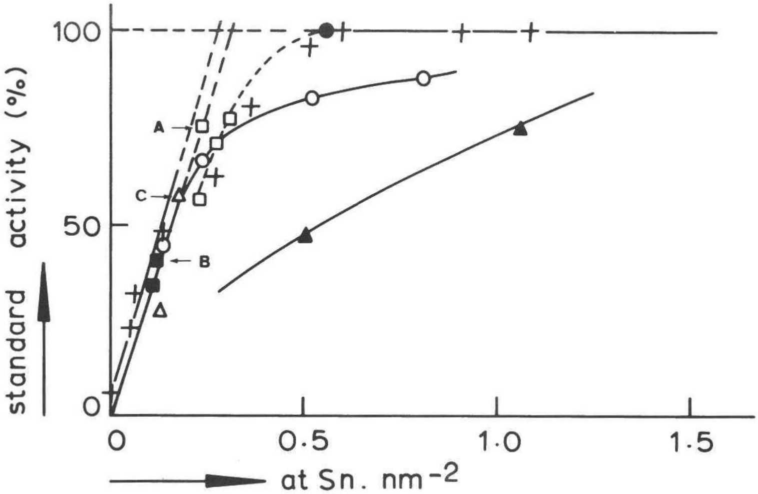


Figure 3.3.1 Comparison of the relative activities obtained by different preparation methods with silicagel D as support.
Legend: ▲ *dry impregnation no acid added,* + *dry impregnation with acid added,* □ *wet impregnation with aqueous* $SnCl_2$ *(A; D9),* ○ *with DBDMT in hexane,* ■ *with* $SnCl_4$ *in hexane (B; treated with water vapour),* △ *with* $SnCl_4$ *in gas phase (C; treated with water vapour),* ● *with* $SnCl_4$ *in liquid phase*

TABLE 3.3.1 Standard activities of catalysts, prepared by different methods (see 2.2.2). Experimental conditions: $P_{ethanal}$ = 10 kPa, W/F = 5 g cat.h.mol^{-1}, T = 523 K.

a. Support, and catalysts prepared by dry impregnation with acid added.

catalyst	w% Sn	at Sn.nm^{-2}	% of activity of D11**
support D*	0	0	6
D17	0.45	0.06	24
D15	0.98	0.13	47
D14	2.00	0.27	63
D11	6.36	0.91	100

* contains 800 ppm Na

** maximum activity observed with D-type catalysts

The highest activity is reached by dry impregnation with added acid (HCl). This method gives the maximal activity at a tin coverage of 0.6 nm^{-2} (4.4 w% tin); addition of more tin does not result in higher activity.
Because of the high Cl/Sn ratio of the solution much $SnCl_4$ is formed during drying which apparently reacts fairly effectively with the surface. This causes a good tin distribution but also a large tin loss during drying (cf. 2.3).

Dry impregnation without added acid gives a much lower Cl/Sn ratio and larger amounts of precipitate. The tin distribution is not very good although only a minor tin loss is observed. The activity of these catalysts is clearly below that of catalysts made with added acid, at the same tin content. Large proportions of tin are inactive from low tin contents onwards, the maximal activity not being reached until a tin density of 1.6-1.7 nm^{-2} (∿ 11 w% tin), the optimal tin content claimed by Swift et al (8) who applied this method of preparation.

Catalysts prepared by wet impregnation with aqueous $SnCl_2$ solution have activities similar to those prepared by dry impregnation with added acid, but contain less inactive tin at the same tin content. This inactive tin is most likely caused by the formation of a precipitate by tin (IV) hydrolysis. Any precipitate of tin (II) formed could be dissolved and is washed out in this preparation method. That inactivity is related to precipitate formation is shown by the results on catalyst D9 which has been prepared with a solution that had been in contact with air for a much shorter time. This catalyst showed an even better activity relative to its tin content which is caused by the relatively lower amount of tin (IV) precipitate formed (table 3.3.1b).

TABLE 3.3.1b Catalysts prepared by wet impregnation with aqueous $SnCl_2$

catalyst	w% Sn	at $Sn.nm^{-2}$	% of maximum observed activity
D7	1.70	0.23	57
D9	1.79	0.24	75 (large part of preparation under N_2)

The D catalysts made by wet impregnation with aqueous $SnCl_2$ solution do not contain as much Na^+ as the other D catalysts. Therefore this impurity does not contribute significantly to the activity. If this is taken into account D9 is seen to come close to the optimal activity-tin relation.

Apparently, ion exchange of Na^+ with Sn^{2+} leads to a good tin distribution and high activity, i.e. about 75% of the maximum. This activity is of course dependent of the initial sodium content of the support.

The catalysts prepared with $SnCl_4$ dissolved in hexane have low tin contents and a consequent low activity. However, they come close to the optimal activity/tin relation, which means that a good tin dispersion is obtained (cf. 2.4). Pretreatment with water prior to calcination resulted in a slightly higher tin content, but a substantially higher activity (catalyst D23(4)) (table 3.3.1c). It is concluded that water reacts with the adsorbed $SnCl_4$, possibly by hydrolysis of the Sn-Cl bond, which results in immobilization of the tin and a stronger interaction with neighbouring hydroxyl groups via hydrogen bonding.
This favourable effect of pretreatment with water is observed even more clearly with the catalysts prepared by interaction with $SnCl_4$ vapour: such pretreatment gives a 50% higher tin content but a 100% higher activity. This type of catalyst (D25(4)) also comes close to the optimal activity line.
The catalyst prepared by dry impregnation with liquid $SnCl_4$ which was also pretreated with water, shows the maximal activity at a relatively low tin content.

TABLE 3.3.1c Catalysts prepared by impregnation with $SnCl_4$, without (2) and with (4) treatment with water vapour previous to calcination.

catalyst	w% Sn	at $Sn.nm^{-2}$	% of maximum observed activity
$SnCl_4$ dissolved in hexane			
D23(2)	0.77	0.10	34
D23(4)	0.80	0.11	42
$SnCl_4$ in vapour phase			
D25(2)	0.92	0.12	28
D25(4)	1.30	0.18	58

Catalysts prepared with DBDMT already deviate from the optimal activity/tin content line at low tin concentration. During preparation the DBDMT reacts so strongly with the support that the surface coverage of tin at the outside of the catalyst particle becomes very high. This is clearly too high for the support to be stable, and large amounts of inactive tin are formed by agglomeration. A large surplus of tin is therefore needed to obtain a catalyst with an activity approaching the maximum. Further treatment of the impregnated catalyst does not influence this phenomenon much: direct reduction or calcination or a heat treatment under nitrogen (see 2.3) in fact gave a catalyst with approximately the same activity (deviation $\leq$ 2% relative).

3.3.2 Influence of the support

In this section, the activities of various catalysts based on silica powder expressed as ξ_{40} are compared with those of the catalysts prepared from silicagel D by dry impregnation with added acid.
The silica powders contain only a minor amount of Na^+ compared to the silicas ($\leq$ 40 ppm). Although they show some activity initially, the conversion is virtually zero after 40 hours. When this is taken into account, the data indicate that the activity/tin relation for the silica powder catalysts having low tin contents is the same as for the silicagel catalysts. This means that tin is equally effective on all types of silica supports examined. However, the activity/tin dependency at higher tin concentrations is different for the various supports. The S catalysts, which were prepared by the same procedure as the D series, viz. wet impregnation with acid added, reach a lower activity maximum than the other catalysts. It is again observed that a large surplus of tin must be added to reach the maximal activity.
At high tin content the activity/tin curve of S catalysts is less steep than for the D catalysts, which indicates a higher mobility of the tin over the surface, causing tin agglomerations and therefore lower activity.
The F and G type catalysts were prepared in a somewhat different way. Here, too, the interaction of $SnCl_4$ with the support surface plays an important role (cf. 2.3). In particular with the G catalysts, which require a small surplus tin content to attain maximal activity, this indicates that the tin becomes firmly attached to the support and that the mobility of the tin over the surface is small.
The data, see figure 3.3.2, show that the activity of the tin is independent of the type of silica used but also that the supports examined show distinct differences in the maximum content of active tin. The theoretical amount of tin needed to reach the maximal activity can be found by extending the observed active tin/activity relations to 100% of the maximum activity.
(The numerical data are given in table 3.3.2.)

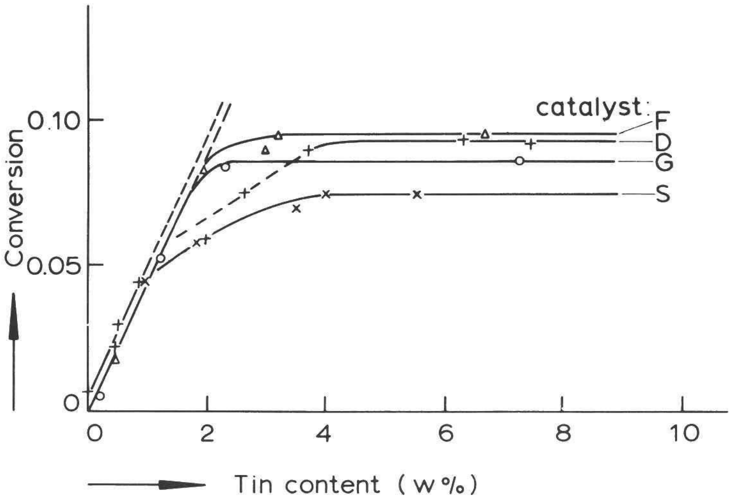


Figure 3.3.2 Relation between ethanal conversion and tin content for different supports. All catalysts prepared with aqueous $SnCl_2$ *solution, acid added. Conditions:* $P_{ethanal} = 10$ *kPa,* $W/F = 5$ *g cat.h.mol*$^{-1}$*,* $T = 523$ *K, conversion is after 40 hours' operation.*

TABLE 3.3.2 Amounts of tin needed to reach maximum activity for the various supports.

support	specific surface area ($m^2.g^{-1}$)	tin concentration needed for maximum activity (A)		(B)	
		w% Sn	at $Sn.nm^{-2}$	w% Sn	at $Sn.nm^{-2}$
S	101	1.8	0.92	4.0	2.10
F	130	2.2	0.92	3.5	1.50
G	326	2.0	0.35	2.5	0.44
D	380	2.0	0.27	4.5	0.64

(A) by extrapolation of line of optimum activity versus tin content

(B) observed

It is evident that the D catalyst can hold much less active tin per unit surface area than the low-surface silica powder catalysts (F and S). This can be attributed to the differences in surface structure between the silicagel and silica powder discussed before (2.1). More surprisingly, there is a distinct difference between the G and F based catalysts, although both are based on silica powder and were prepared in exactly the same way. A difference between S and the two other silica powder supports (F and G) is that quite a large tin surplus is needed with S catalysts to obtain maximum activity, such as is also the case for silicagel D.

In 2.3 it was argued that the formation of $SnCl_4$ during the drying step is essential for optimum dispersion of the tin. The literature indicates that $SnCl_4$ usually reacts with two hydroxyl groups, but dependent on the density of these groups a reaction with one or three groups is feasible. Furthermore, not all hydroxyl groups will react, depending on the type of silica involved (161, 162, 163). Type and number of hydroxyl groups therefore determine the distribution and the mobility of the chemisorbed tin species formed on the surface when preparing Sn/SiO_2 catalysts. This explains the differences observed for the various supports. More research, in particular concerning the reactivity of the different surface groups with $SnCl_4$, is needed to gain more precise insight.

Impregnation of the mordenites did not give catalysts useful for aldol condensation. Even at higher temperatures low conversions (< 0.05) were observed and the catalysts deactivated quite rapidly. The selectivity for the reaction was also low (< 70%).

3.4 Selectivity

3.4.1 By-products

Product composition has been investigated during various runs under different reaction conditions. To this end the gas stream was led through a vapour trap kept at -60°C. The condensate separated in two layers; the lower consisted of water with a few percent organic products and the top layer contained most of the organic products. Samples from the latter layer have been analyzed by GC-MS.
Figure 3.4.1 shows a typical example of a chromatogram.

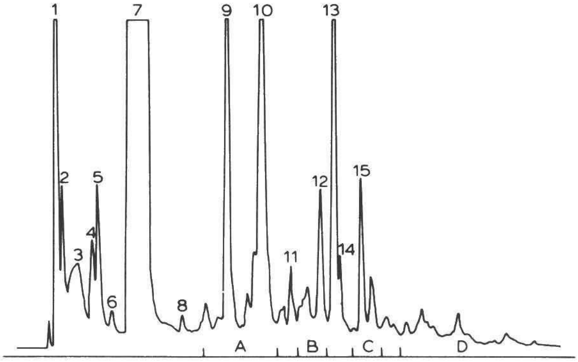


Figure 3.4.1 GC-MS chromatogram of aldol condensation products of ethanal
Reaction conditions: 523 K, 16 kPa, 20 g cat.h.mol^{-1}
Analysis conditions: SP 2250 column, 3 m length, temperature-programmed from 20^{o}*C to 210*^{o}*C, 8*^{o}*C.min*$^{-1}$

1	*ethanal*	*6*	*benzene*	*11*	*paraldehyde derivative*
2	*methylacetate*	*7*	*2-butenal*	*12*	*cyclic octatrienal*
3	*water*	*8*	*paraldehyde*	*13*	*o-tolualdehyde*
4	*3-butenal*	*9*	*2-vinyl - 2-butenal*	*14*	*p-tolualdehyde*
5	*ethylacetate*	*10*	*2,4-hexadienal*	*15*	*2,4,6-octatrienal*
A	*hexadienal isomers*			*C*	*linear octatrienal isomers*
B	*cyclic and branched octatrienal isomers*			*D*	*decatetrenal isomers*

The bulk of the sample consists of 2-butenal, the desired product, and some 3-butenal which is actually not a by-product. At differential reactor conditions ($\xi \leq 0.10$) by-products constitute less than 5% of the product, but with increasing conversion by-product formation increases (figure 3.4.4).

More than 90% of the by-products are formed by aldol condensation of the primary product butenal: hexadienals, octatrienals and tolualdehydes are formed in this manner. Esters formed by Cannizzaro reactions and polymerization products, paraldehyde and derivatives of butenal, are formed in minor amounts. Another minor group of by-products is formed by disintegration of reactants and products: methane, carbon monoxide, propylene and benzene. The first three (hardly 1% of the products, even at 300^{o}C) do not condense at -60^{o}C and are detected only during on-line analysis of the product stream.

In addition, traces of hydrogenated products, such as hexanal and butanal, are sometimes found.

The data in table 3.4.1 show that with increasing conversion relatively larger amounts of 2,4-hexadienal and especially o-tolualdehyde are formed. The importance of another by-product, 2-vinyl-2-butenal, decreases somewhat. Further aldol condensation is of course to be expected because the desired product 2-butenal contains a carbonyl group as well as an α-hydrogen atom. An analysis of by-products is given by Losse (18) for the liquid-phase process and by Rozenberg (101, 196) for the gas phase process. The same range of products is found. Figure 3.4.2 gives a scheme for the likely aldol condensation routes. Other addition reactions are included in the figure since such reactions may occur easily with unsaturated and conjugated aldehydes such as 2-butenal. Among them is the Knoevenagel addition in which an active methylene compound reacts with a carbonyl group:

$$CH_3CHO + CH_3CHCHCHO \longrightarrow CH_3CHCHCHCHCHO + H_2O$$

The aldol condensation is actually a special case of this reaction.

TABLE 3.4.1 Principal by-products (in % of the 2,4-hexadienal concentration)

Experimental conditions and results:				
T (K)	523	523	573	
$P_{ethanal}$ (kPa)	8	16	10	
W/F (g cat.h.mol^{-1})	10	20	15	
Catalyst	D2	D3	D12	
Conversion (40 h)	0.16	0.19	0.19	(average)
Selectivity (%)	93	85	80	(average)
By-product contents:				
2,4-hexadienal	100	100	100	
3,5/2,5-isomers	28	1	-	
2-vinyl-2-butenal	94	26	20	
2,4,6-octatrienal	13	4	0.3	
n-isomers	4	-	-	
cyclic isomers	10	3	0.3	
branched isomers	2	0.5	-	
o-tolualdehyde	5	50	90	
p-tolualdehyde	1	0.5	-	

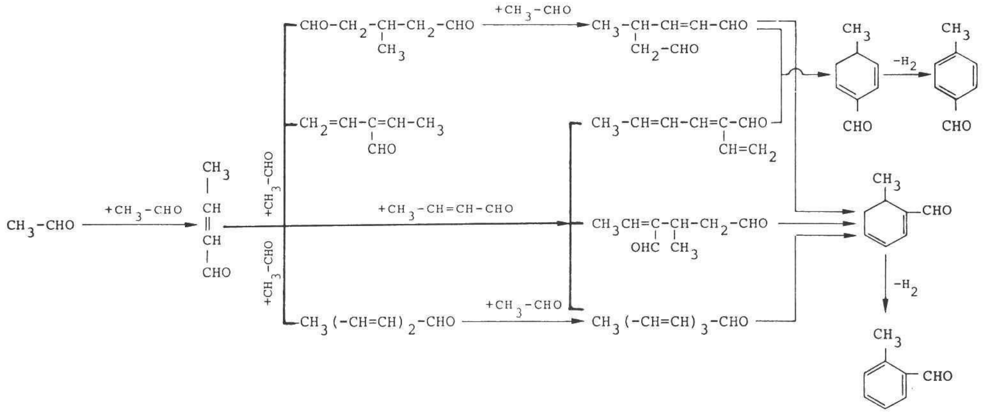
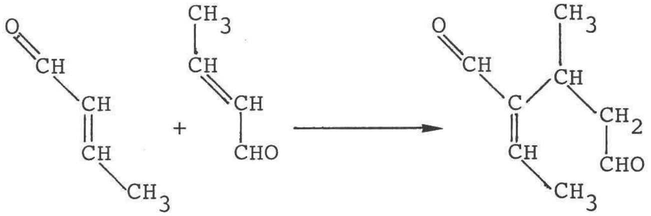


Figure 3.4.2 Reaction network in gas phase aldol condensation of ethanal

Another relevant reaction is the Michael addition. It is a 1,4-addition of a carbanion to an α,β-unsaturated carbonyl compound:



The longer carbon chain and highly unsaturated aliphatic aldol products are easily subject to such internal reactions, which have been reported for the products of ethanal and acetone (197,198,205). Dehydrogenation of the cyclic products formed gives rise to tolualdehydes. This reaction is quite fast as can be concluded from the relatively high proportion of tolualdehyde formed compared to octatrienal isomers. The reaction of 2-butenal to tolualdehydes is well-known (see table 1.3.4). Inspection of the changes in Gibbs free energy of the various reactions (c.f. figure 3.4.3)
shows that the formation of the by-products is favourable from a thermodynamic point of view. Tolualdehydes are clearly favoured over the octatrienals.

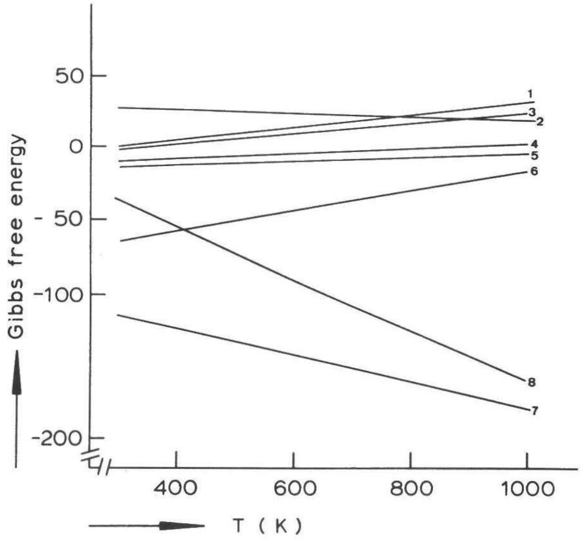


Figure 3.4.3 Gibbs free energies of reaction for some important reactions

1 2 ethanal $\rightleftharpoons$ 2-butenal + water

2 2-butenal $\rightleftharpoons$ 3-butenal

3 butenal + ethanal $\rightleftharpoons$ hexadienal + water

4 hexadienal + ethanal $\rightleftharpoons$ octatrienal + water

5 2 butenal $\rightleftharpoons$ octatrienal + water

6 2 butenal $\rightleftharpoons$ cyclooctadienal + water

7 2 butenal $\rightleftharpoons$ tolualdehyde + water + H_2

8 butenal $\rightleftharpoons$ propene + CO

The formation of polymeric products is often catalyzed by acids; for instance, strong acid sites on heterogeneous catalysts are known to produce large amounts of these products (46, 48). The small amount formed during our experiments points to low catalyst acidity.

Carbon monoxide, methane and propene are formed by pyrolysis of ethanal and butenal. The decomposition of ethanal starts already at 200°C, but substantial conversions require much higher temperatures (199, 200). Decarbonylation of unsaturated products proceeds more readily, especially over acid catalysts, but here too higher temperatures (>350°C) are necessary to give appreciable conversions (46, 107). Ketones are not present in the products. Especially strongly basic solids are known to convert aldehydes to these (45, 118, 128), but the Sn/SiO_2 catalysts studied here do not contain such strongly basic sites apparently.

3.4.2 Influence of reaction conditions

The selectivity towards aldol condensation is very high when using tin on silica catalysts, only minor amounts of other products being formed. The selectivity to butenal depends on the process conditions. A selectivity of 95% is attainable at 250°C when the ethanal partial pressure is 10 kPa or lower and when the conversion is kept below 0.15. Higher temperatures, higher conversions and a higher ethanal partial pressure cause the selectivity to decrease substantially.

Because of the continuous deactivation of the catalysts it is impossible to establish the relation between conversion and selectivity systematically. One has to work with changing values of conversion and selectivity as they occur during a run with a catalyst. Plots of selectivity against conversion were found useful in establishing the effects of process conditions on selectivity.

The *type of support* and the *tin concentration* have little or no influence on the selectivity, as follows from figures 3.4.4a and b.
At conversions below 0.15 the average selectivity is generally higher than 95%, but appreciable random fluctuations occur which are presumably due to the age of the catalysts which does change the relation conversion-selectivity, and to the differences in values for individual consecutive samples, as mentioned before. The figures show a gradual increase in selectivity as the conversion is lower, which is due to decreased formation of higher-boiling products by successive aldol condensation.

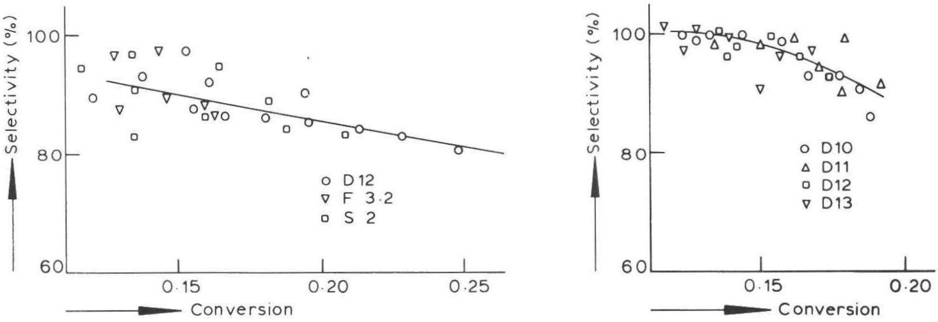
Table 3.4.2 shows data on the selectivity as a function of conversion for some runs at varying *ethanal partial pressure* and *space velocity*. These results show that the relationships between the three variables is complex. At low conversion, i.e. when the concentration of the primary product butenal is low, an increase of the partial pressure of ethanal leads to higher selectivity, presumably because of competition between ethanal and butenal in the adsorption on active sites of the catalyst. At high conversions to butenal, however, an increase in ethanal partial pressure leads to lower selectivity (figure 3.4.5). This is due to an increased probability of successive aldol condensation between ethanal and butenal.

Figure 3.4.6 shows that higher *temperatures* result in lower selectivity. When plotting the logarithm of the conversion to by-products against the reciprocal temperature (300-380°C) a straight line is obtained from which an apparent activation energy for successive aldol condensation of about 23 kJ.mol^{-1} can be derived.

TABLE 3.4.2 Average values of the selectivity at certain levels of conversion, at different process conditions (at 523 K)

$P_{ethanal}$ (kPa)	W/F (g cat.h.mol^{-1})	ξ = 0.200	0.150	0.120
		(selectivity in %)		
10	5	-	100	100
8.2	16	90	97	99
6.0	15	87	95	100
4.0	28	85	95	98
3.4	25	80	90	-

Influence of the process period has been observed too. One would expect the selectivity during a run to increase with time because of the decreasing conversion by which the chances of successive aldol condensation of butenal or between ethanal and butenal are reduced. This seems to be the case at moderate reaction conditions, such as were applied when obtaining the data of figures 3.4.5 and 3.4.6. However, a decrease in selectivity with decreasing conversion was observed in several runs, particularly when working at conditions during which the deactivation rate was very low, e.g. a high ethanal partial pressure and a very short residence time, when the conversion is low (cf. figure 3.4.8). The effect seems to be present in most runs but is generally obscured by the much greater effect of increasing selectivity with decreasing conversion and its consequent lower probability for successive aldol condensation.



(3.4.4.a) *(3.4.4.b)*

Figure 3.4.4 Selectivity versus conversion

a. for several of catalysts with different supports

conditions: $P_{ethanal} = 8$ *kPa,* $W/F = 15$ *g cat.h.mol*$^{-1}$*,* $T = 523$ *K*

(D12, 3.74 w% Sn; F3.2, 3.06 w% Sn; S2, 3.50 w% Sn)

b. for various tin contents

conditions: $P_{ethanal} = 10$ *kPa,* $W/F = 5$ *g cat.h.mol*$^{-1}$*,* $T = 523$ *K*

(D12, 7.5 w% Sn; D11, 6.4 w% Sn; D12, 3.74 w% Sn; D13, 2.65 w% Sn)

The initial increase of the selectivity shown in figure 3.4.8 is then caused by rapid deactivation of large surface concentrations of active sites.
The subsequent decrease is more difficult to explain.
In literature a model is suggested to explain such decreasing selectivity with increasing catalyst age (201, 202, 203). It is based on the concept of mass diffusion influence on the selectivity for catalysts with macro- and micropores proposed by Carberry (204).

Ferraiolo c.s. assume the aldol condensation of ethanal catalyzed by a silica-alumina to be of the type:

$$A \rightarrow B \rightarrow C$$

C is a product which is assumed to poison the active sites. The reaction presumably takes place only in the smaller pores, which are inkbottle-shaped.

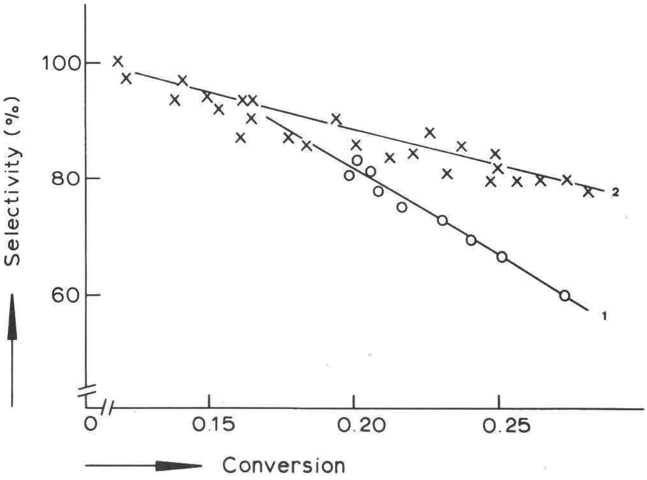


Figure 3.4.5 Selectivity versus conversion for different conditions, at higher conversions

conditions: 1: $P_{ethanal}$ *= 25 kPa, W/F = 15 g cat.h.mol*$^{-1}$*, T = 523 K*

2: $P_{ethanal}$ *= 8.2 kPa, W/F = 16 g cat.h.mol*$^{-1}$*, T = 523 K*

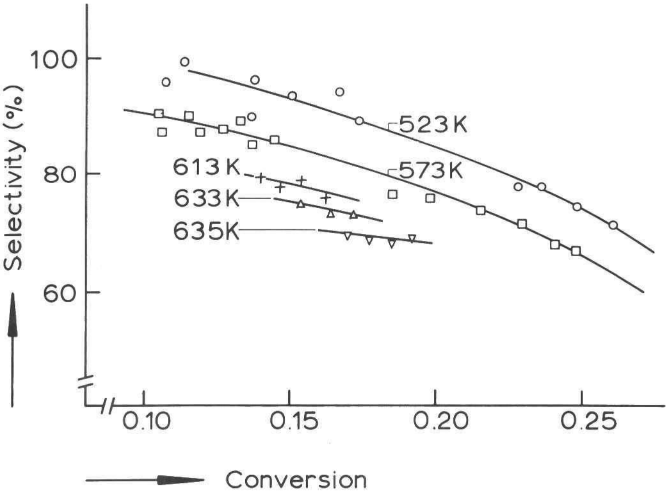


Figure 3.4.6 Selectivity versus conversion at different temperatures

Conditions: $P_{ethanal}$ *= 10 kPa, W/F = 8 g cat.h.mol*$^{-1}$

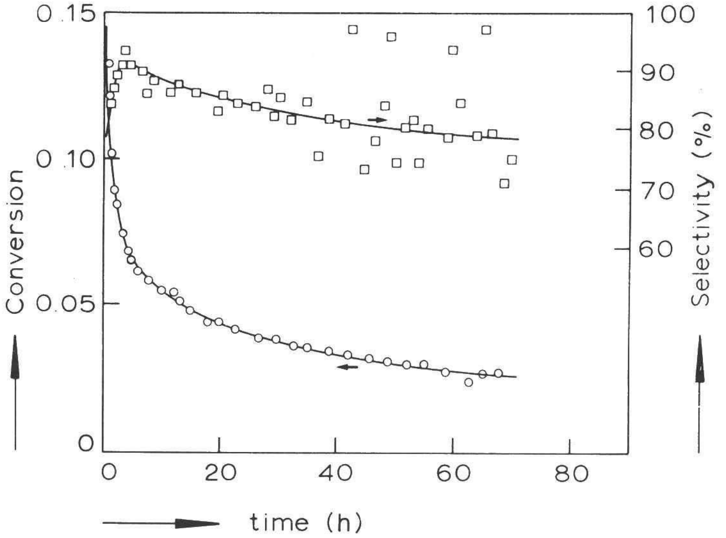


Figure 3.4.7 Selectivity and conversion versus time, with reaction conditions under which the decrease of the selectivity in time is clearly visible
Conditions: catalyst D15, $P_{ethanal} = 20$ *kPa,* $W/F = 2.5$ *g cat.h.mol*$^{-1}$*,*
$T = 523$ *K*

The ratio of the Thiele moduli in micro- and macropores dictates the selectivity. Poisoning of the surface starts at the pore mouth of the micropore, and moves inwards during reaction as a sharp front. The result is an average longer diffusion path and an increase in Thiele modulus. The more tapered the pore, the stronger this effect on the selectivity is. Although Ferraiolo's explanation is an elegant one, their experimental evidence is not very convincing. The silica-alumina catalyst used by these authors is known to catalyze also polycondensation because of its acidity. This is not a consecutive reaction but a parallel one.

Comparison with our findings is further hampered by the large differences in experimental conditions. Ferraiolo et al work with undiluted ethanal in the gas phase, obtaining an initial conversion of 0.500 at 70% selectivity on a fresh catalyst. However, in their experiments, the selectivity is very low already, and decreases rapidly; at a conversion of 0.100 the selectivity declines from 20% to 8% with a 5% decrease in activity, relative. Nevertheless, such a model seems a likely candidate explanation of the decrease in selectivity. In our case, the product poisoning the active sites because of its low volatility is probably the result of several condensation steps. Its formation and the resulting decrease in selectivity will therefore be rather slow, as we have observed.

In summary, the relation between selectivity and process conditions is very complex and requires further investigation.

3.5 Catalyst deactivation

3.5.1 Influence of reaction conditions

Catalyst deactivation was observed throughout every run, the longest of which lasted 350 hours, but the rate of deactivation was not constant. During the first half hour of a run very rapid deactivation was observed, but also very high conversions, up to 60%. The selectivity is, however, very low then, the first minutes often even under 10%. A period of rapid deactivation follows (15 - 25 hours); subsequently, the deactivation rate decreases to become fairly low. The activity versus time curves are almost parallel in this region of slow deactivation for the various catalysts at varying reaction conditions, provided that the temperature is the same (cf. figure 3.2.1). In general the decrease of activity at a given temperature depends only on the duration of the run. The tin content of the catalyst, the residence time and the conversion have virtually no influence within wide ranges. The above behaviour is illustrated in table 3.5.1.

The F and S type catalysts deactivate slightly faster in the region of slow deactivation. Since these catalysts contain less Na^+ and Al^{3+} than the D catalysts, this may indicate that these impurities do not cause the deactivation. Rather, the small difference between the supports may be due to differences in specific surface area: if the amount of deactivating substance is the same, its effect on catalysts with smaller surface area is expected to be greater, if other surface properties are equal.

More extreme process variables do affect the rate of deactivation, as follows from figure 3.5.1. A higher partial pressure and a longer residence time cause faster activity decline. According to figure 3.5.2, a higher temperature increases the deactivation in the region of slow deactivation. It is possible to estimate an apparent energy of activation for the slow deactivation; a value of 35-40 kJmol^{-1} was found when using data on rates of deactivation obtained between 70 and 80 run hours.

TABLE 3.5.1 Absolute drop in activity for various catalysts after 5, 15 and 40 hours

catalyst	ξ_{5h}	$\Delta\xi_{5-8h}$	ξ_{15h}	$\Delta\xi_{15-18h}$	ξ_{40h}	$\Delta\xi_{40-45h}$
D10^a	0.153	0.011	0.122	0.005	0.092	0.003
D12^a	0.140	0.010	0.116	0.005	0.090	0.002
D14^a	0.103	0.010	0.079	0.004	0.059	0.002
D15^a	0.074	0.009	0.053	0.003	0.044	0.002
D12^b	0.230	0.011	0.202	0.005	0.165	0.004
F2^a	0.138	0.012	0.108	0.006	0.083	0.004
F3.2^a	0.143	0.012	0.115	0.005	0.090	0.004
S2^a	0.127	0.010	0.109	0.006	0.082	0.005
S4^a	0.084	0.007	0.069	0.004	0.053	0.003

Conditions: a. $P_{ethanal}$ = 10 kPa, W/F = 5 g cat.h.mol^{-1}, T = 523 K
b. $P_{ethanal}$ =8.7 kPa, W/F =15 g cat.h.mol^{-1}, T = 523 K

When raising the temperature by about 50°C, at otherwise unchanged conditions, the conversion of ethanal increases as expected. When the temperature was returned to its original value after 1-2 hours, it took up to 10 hours for the activity to go down to the level found before the period at higher temperature. The same observation was made after flushing of the catalyst bed with inert gas without reactant being present; the conversion is increased appreciably afterwards which indicates that deactivation is, at least in part, a reversible phenomenon. Relatively strong adsorption of reaction products combined with the possibility of further aldol condensation of these strongly adsorbed intermediates are therefore among the causes of deactivation. These products desorb partially during a short period of higher temperature or flushing of the catalyst, which makes deactivated sites active again. The processes involved in reactivation and deactivation are rather slow, as is shown in figure 3.5.3. It can take some hours to reach a stationary value of conversion after a change in conditions.

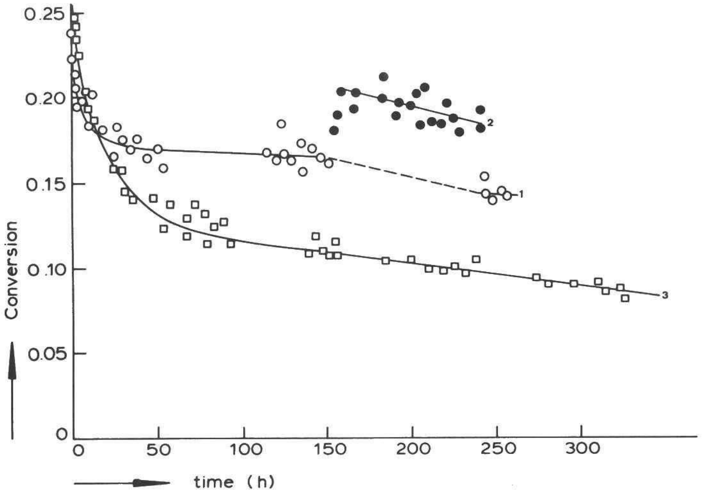


Figure 3.5.1 Catalyst activity decline at different reaction conditions

Catalyst:D12

Conditions: 1. $P_{ethanal}$ = 3.4 kPa, W/F = 26.7 g cat.h.mol^{-1}, T = 523 K

2. as 1. , T = 573 K

3. $P_{ethanal}$ = 8.2 kPa, W/F = 14.1 g cat.h.mol^{-1}, T = 523 K

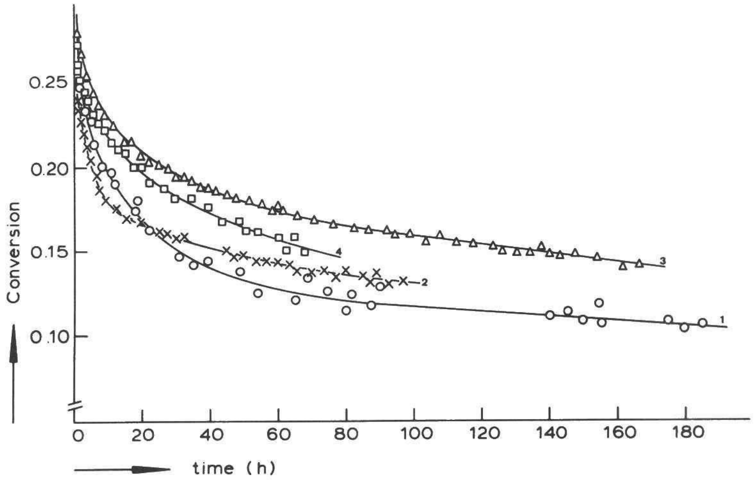


Figure 3.5.2 Catalyst activity decline at different reaction temperatures

Catalyst D13

Conditions: $P_{ethanal}$ = 7 kPa, W/F = 16 g cat.h.mol^{-1}

Legend: 1, 523 K; 2, 547 K; 3, 573 K; 4, 623 K

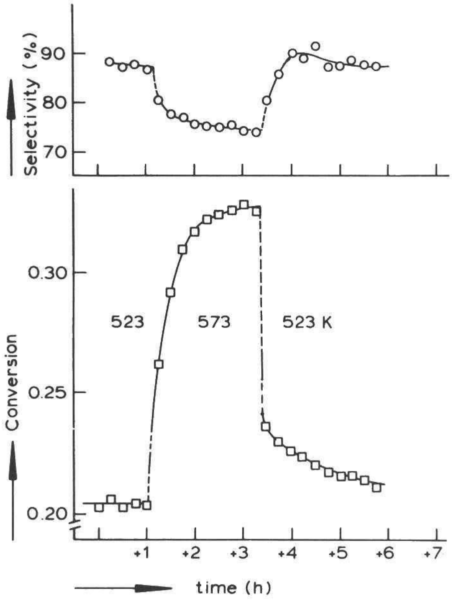


Figure 3.5.3 Change in conversion and selectivity after a change in reaction conditions
Conditions: catalyst D12, $P_{ethanal}$ = 10 kPa, W/F = 20 g cat.h.mol^{-1}
Change in temperature from 523 K to 573 K and back after some hours.

Furthermore, we observed that catalyst deactivation became twice as fast when hydrogen was replaced by nitrogen, or mixtures with less than about 50% hydrogen. A sufficiently high partial pressure of hydrogen is apparently needed. This has been reported in literature (7, 8) and was there tentatively ascribed to oxidation of active sites which is hindered by hydrogen.

3.5.2 Changes in the catalyst during reaction

According to the results of BET measurements the texture of the catalyst changes during the reaction, see table 3.5.2, the decrease in specific surface area observed appears to be proportional to the duration of the run and is most pronounced for the D and G catalysts. The decrease in pore volume makes it evident that pores have become blocked, particularly the smaller ones. The F catalysts contain micropores when fresh, but none after reaction. The data on

the G catalysts show that the mean pore diameter increases during the reaction, which is caused by selective blockage of smaller pores. This is not seen for the D catalysts, but these contain pores of rather uniform size when fresh, which makes a change in pore size unlikely.
It is unlikely that a change in the texture of the support causes the observed changes in surface area and pore volume. An indication is that the support is quite stable under the conditions applied in catalyst preparation, which are much more severe than the reaction conditions as regards the temperature. It is therefore concluded that deposit formation is the main cause of the changes in catalyst texture occuring during processing.

TABLE 3.5.2 Texture parameters of the catalysts before and after reaction. Unless stated otherwise, catalysts were used 50 - 70 hours (.b, after calcination; .c, after reduction; .d, after reaction).

Catalyst	S_{spec} $m^2.g^{-1}$	V_{pores} $cm^3.g^{-1}$	R_{pores} at dV/d(logR)max	$R_{pore, mean}$ nm
D1.c	328	1.11	7.0	6.8
D1.d *(150h)*	239	0.57	6.5	6.5
D2.d1	244	0.71	6.2	6.1
(170 h) (twice regenerated)				
D2.d2 *(80h)*	277	0.71	6.5	6.0
D6.b	387	1.12	7.0	7.6
D6.d	341	0.98	6.5	7.4
D15.b	379			
D15.d1 *(22h)*	378	1.15	6.5	6.3
D15.d3 *(100h)*	343	1.05	7.0	6.3
F3.2.c	125	1.40	38.0	26.9
F3.2.d	119	1.50	38.0	-
F4.b	127	1.63	38.0	24.7
F4.d	130	1.63	37.0	23.5
G4.c	312	1.52	22.5	13.2
G4.d	241	1.49	20.0	16.5
G6.c	280	1.38	18.5	10.8
G6.d	181	1.22	20.0	14.2

The deposits, which have a low volatility at the reaction temperature or are strongly adsorbed, are formed evenly throughout a catalyst particle. The amount of deposit increases from the front end to the outlet of the reactor, as follows from the colour of the particles which changes from almost white via brown to deep black in the same direction. This is further confirmation that the deposits are mainly caused by compounds formed by subsequent condensation of primary and even secondary reaction products.

The coke formation can be followed by the weight increase of the catalyst. The percentage of deposit formed on the catalysts generally ranges from 5 to 20 w%, depending on conversion reached, type of support and the duration of a run (up to 350 hours).

The coke formation is clearly proportional to the activity of the catalyst as is shown in table 3.5.3a. The activity is related to the conversion over the catalyst after 40 hours.

TABLE 3.5.3 Weight increase of the catalysts during reaction caused by deposit formation (conditions: $P_{ethanal} = 10$ kPa, $W/F = 5$ g cat.h.mol^{-1}, $T = 523$ K).

a. influence of the activity of the catalyst

catalyst	w% Sn	ξ_{40}	t (h)	weight increase (%)
D12	3.74	0.090	42	6.9
D13	2.65	0.075	44	6.0
D15.d2	0.98	0.044	38	3.9
D11	6.36	0.094	70	9.6
D14	2.00	0.059	73	5.6
D17	0.45	0.022	71	2.0

With increasing time more coke is formed, but at a decreasing rate. The coke deposit is formed most rapidly in the beginning of the operation of a catalyst, see table 3.5.3b. This is caused by the very high activity of the catalyst at the start and the resulting high conversion.

TABLE 3.5.3b Influence of the duration of a run

catalyst	w% Sn	ξ_{40}	t (h)	weight increase (%)
D15.d1	0.98	0.044	22	3.4
D15.d2	0.98	0.044	38	3.9
D15.d3	0.98	0.044	100	5.1

The method of preparation and type of support have also much influence on the amount of deposit formed. Catalysts prepared from silicagel by dry impregnation with acid added show the largest coke deposits. The influence of the operation time is furthermore strongest for this type of catalyst. Catalysts prepared with aqueous $SnCl_2$ solutions and no acid added show relatively lower coke deposits, and the silicagel-based catalysts prepared with solutions that are not acid at all (e.g. $SnCl_4$ and DBDMT in hexane) show the lowest tendency to deposit formation of the silicagel-based catalysts examined. Catalysts prepared from silica powders show even lower deposits (see table 3.5.3c).

TABLE 3.5.3c Influence of preparation and type of support

catalyst	w% Sn	ξ_{40}	t (h)	weight increase (%)	$\Delta W/(\xi_{40} * t) * 10^3$
D14	2.00	0.059	73	5.6	13.0
D7	1.70	0.053	90	4.0	7.9
D24	0.77	0.032	70	1.1	4.8
F3.2	4.40	0.081	92	2.5	3.4
G4	1.80	0.049	100	1.7	2.9

Silicagel gives rise to more deposit formation than silica powders. This may be due to the larger amount of impurities (Na, Al) in the former. Furthermore, acid treatment of the silicagel increases deposit formation substantially. This indicates that acid sites cause most of deposit formation, viz. by catalyzing polymerization. Since these sites become blocked soon by the products, deposit formation is highest on fresh catalysts. The silica powders are not affected by the acid solutions used.

Deactivation of the catalysts is virtually independent of the type of support and method of preparation as is reported above. We may conclude, therefore, that there is no direct relationship between total deposit formation and activity decline.

X-ray diffraction measurements showed that reduced catalysts contained large crytallites of β-tin. Surprisingly, the spent catalyst examined showed neither lines of β-tin and SnO_2 nor evidence for the presence of other crystalline species. Only in catalysts with high tin contents weak lines were observed that were due to β-tin; in addition, very weak lines of an unidentified (tin) compound were present (d = 0.307, 0.250, 0.233, 0.193 nm).
Activation analysis showed that loss of tin during reaction or regeneration did not occur.
These results are at variance with reports by Swift et al (7), who observed the formation of SnO_2 during processing of butanal and ascribed the deactivation to oxidation of tin.
Calcination at 450°C of used catalysts did not change the x-ray difraction pattern: SnO_2 was not formed. Reduction with hydrogen at 450°C resulted in the reappearance of sharp but weak β-tin lines. In both cases the unknown compound mentioned above was also observed for catalysts with high tin contents.

3.5.3 Catalyst regeneration

The regeneration method recommended by Swift et al (10) was found to be effective for restoring the activity of deactivated catalysts. The procedure followed was a two-hour treatment with hydrogen at the same conditions as those used for the reduction of a fresh catalyst, viz. 450°C and a hydrogen flow of 250 $ml.min^{-1}$. Small amounts (less than 1% by volume) of water, ethanal, butenal, methane and propene were detected in the reactor off-gas during the first half hour. Tests in a glass reactor showed that a small amount of tar-like material is removed when passing through hydrogen or nitrogen at 450°C. After regeneration the percentage of coke-like deposits on the catalyst has decreased appreciably; for instance, catalyst D12.d2 contained about 20 w% coke after a 245-hour process period and only 5 w% after subsequent regeneration by the method outlined above. Even after several successive regenerations the coke content of the catalyst did not rise much above the percentage found after the first regeneration.

The initial activity of the regenerated catalyst and the rate of deactivation were slightly below those of a fresh catalyst (example in figure 3.5.4). After about 20 hours' processing there was little difference in performance between a fresh and a regenerated catalyst, indicating that long catalyst life is possible if periodic regenerations are carried out.

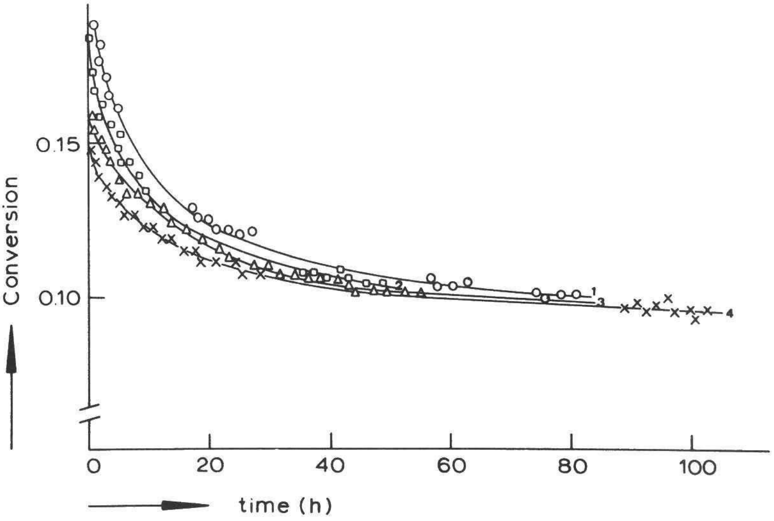


Figure 3.5.4 Catalyst activity decline after several regenerations
Conditions: catalyst D3, $P_{ethanal} = 12.3$ *kPa,* $W/F = 6.7$ *g cat.h.mol*$^{-1}$*,*
$T = 523$ *K*
1, fresh catalyst; 2, 3, 4, catalyst after 1, 2 and 3 regenerations respectively.

The above findings confirm that deactivation is caused by the formation of high-boiling products on the catalyst surface. Most of the reactivation apparently stems from desorption of such condensation products from sites active for aldol condensation.

3.5.4 Influence of water on catalyst deactivation

Because the equilibrium conversion of the aldol condensation of ethanal to butenal and water is not much higher than the observed conversions (cf. figure 5.2.1) the addition of water will decrease the conversion. Moreover water has been reported to be one of the possible causes of catalyst deactivation, tentatively attributed to oxidation of active tin (7). However, when investigating the kinetics of the reaction, a pronounced beneficial effect of water on the stability of Sn/SiO_2 catalysts was noted. Figure 3.5.5 gives an example of the effects observed: although the conversion of ethanal decreases, deactivation is slowed down appreciably over the entire run. Its

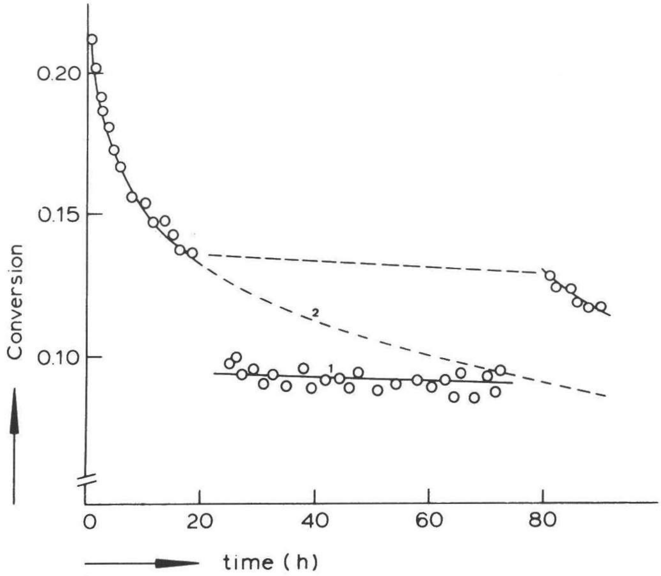


Figure 3.5.5 Catalyst activity decline and the influence of water.
Conditions: catalyst D13, $P_{ethanal} = 7.2$ *kPa,* $W/F = 14.8$ *g cat.h.mol*$^{-1}$*,*
$T = 523$ *K*

1, water added, $P_{H_2O}/P_{ethanal} = 0.12$*; 2, without addition of water*

rate goes up again as soon as the water supply is discontinued. The much slower deactivation during the first 15-20 hours, i.e. during the period where without the presence of water rapid deactivation occurs, especially at 573 K, is also clearly visible in figure 3.5.6. The overall result is that the productivity of the catalyst in extended runs is higher than without added water.

The remaining slow deactivation rate depends on the ratio of water to ethanal. The relation between the rate of deactivation, selectivity and the ethanal/water ratio is given in table 3.5.4. Evidently, water not only slows down deactivation but it also helps in attaining high selectivities, presumably by decreasing the extent to which subsequent aldol condensation of butenal occurs. Overall mass balance data indicate high selectivities even at relatively high conversions and high ethanal partial pressures; for instance, at a water/ethanal ratio of 0.25 the selectivity was higher than 95% when the ethanal conversion was between 15 and 20%. The selectivity increases still

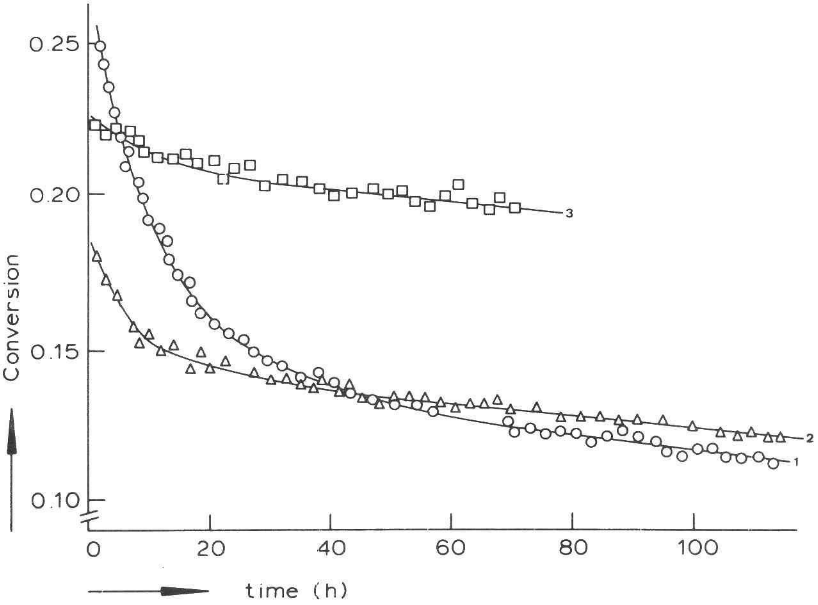


Figure 3.5.6 Influence of water on the catalyst activity decline.
Conditions: catalyst D11,
1 $P_{ethanal}$ *= 10 kPa, W/F = 15 g cat.h.mol*$^{-1}$*, T = 523 K, no water added*
2 $P_{ethanal}$ *= 19.3 kPa, W/F = 17.8 g cat.h.mol*$^{-1}$*, T = 523 K,* P_{H_2O}/P_{eth} *= 0.20*
3 $P_{ethanal}$ *= 22.0 kPa, W/F = 15.0 g cat.h.mol*$^{-1}$*, T = 573 K,* P_{H_2O}/P_{eth} *= 0.18*

further when the water/ethanal ratio is raised; concomitantly, deactivation is nearly absent for water/ethanal ratios higher than 0.3 when working at 523 K, even with an ethanal partial pressure of 30 kPa. Other data indicate that the rate of deactivation does not change when hydrogen is replaced by nitrogen as the diluent.

TABLE 3.5.4 Relation of deactivation rate and selectivity to the ratio of the partial pressure of water to the partial pressure of ethanal
Conditions: $P_{ethanal}$ = 30 kPa, W/F = 14 g cat.h.mol^{-1}, T = 523 K

$P_{H_2O}/P_{ethanal}$	$d\xi/dt\,(10^{-3}h^{-1})$	S (%)
0.30	0.033	≃97
0.25	0.080	96
0.23	0.350	92
0.20	1.500	90

Thus, it is concluded that addition of water to the feed permits higher conversions at higher partial pressure of aldehyde in the feed, whilst maintaining nearly quantitative selectivity and avoiding appreciable catalyst deactivation. These beneficial effects of water are very useful when considering a commercial process with Sn/SiO_2 catalysts, as is discussed more extensively in chapter 7.

3.6 Concluding remarks

The main conclusion drawn from the work reported in this chapter is that process conditions exist at which suitably prepared tin on silica catalysts have a high activity and selectivity for the vapour-phase aldol condensation of ethanal, as well as reasonable stability after an initial period of rapid deactivation.

The active tin sites in the catalysts are equally effective on several silica supports, irrespective of the method of preparation. However, the conditions of preparation and the nature of the carrier largely determine the fraction of the tin on the surface that is active and, consequently, the relative activity of the catalysts. A limit concentration of tin was shown to exist, above which the activity of catalysts for a given support cannot be raised any further by using higher tin concentrations. The minimum tin content at which the maximum activity is reached depends on the surface area and the surface structure of the support, presumably on the distribution of surface hydroxyl groups. Mordenite-based catalysts were found to be much less active than Sn/SiO_2 catalysts.

The method of preparation determines the ultimate tin content, the tin dispersion and the ratio between the different tin species on the surface and, consequently, the activity of the catalyst. Methods in which $SnCl_4$ is used or during which $SnCl_4$ is formed give the best results. $SnCl_4$ apparently is not too reactive towards the surface and is distributed evenly over the particle by diffusional transport before it reacts with surface hydroxyl groups to an appreciable extent. Because of the low reactivity a certain excess of $SnCl_4$ is needed to reach the activity maximum; the amount actually needed varies with the type of silica support. Other data indicate that ion exchange of Sn^{2+} with Na^+ can also give active catalysts, depending on the Na^+ content of the silica. The use of a tin compound that reacts very readily with surface hydroxyl groups is not recommended. Much of the tin is then deposited at or near the outer surface of the support particle, which causes excessively high local tin concentrations and consequent agglomeration, thus rendering a large part of the tin inactive.

Tin on silica catalysts are quite selective for aldol condensation reactions, irrespective of the method of preparation applied. When ethanal is used as feed, less than 1% of the products is formed by other types of reaction. Impurities on the silica surface may give rise to polymerization and consequent coke formation; in other respects there is no difference between the silica carriers examined as far as selectivity is concerned. This does not mean that selectivity to 2-butenal is quantitative or almost so, mainly because the primary product may undergo further aldol condensation to heavier products. Still, more than 95% selectivity can be obtained below 250^{o}C, a conversion of 15% or less, an ethanal partial pressure of 10 kPa and a residence time of 15 g cat.h.mol^{-1}.
Deactivation occurs under all reaction conditions. The initial activity of the catalyst is very high; it is even possible to reach equilibrium conversion to 2-butenal. However, the initial selectivity is low and deactivation rapid. The excessive activity is soon lost, the conversion decreasing to half its initial value in about 20 hours, with a simultaneous increase in selectivity to an acceptable level. After that period deactivation is much slower, the conversion decreasing nearly linearly with time by about 0.3% per 10 hours.
Addition of water appreciably retards the successive aldol condensation of primary products, which leads to much more stable catalyst performance and makes it possible to increase the partial pressure of ethanal. Although the conversion is somewhat lower than without water, acceptable conversions and high selectivities are obtainable at very low rates of deactivation.
The instability of the catalyst, particularly in the absence of water, cause difficulties in interpreting catalyst performance, particularly at the conditions envisaged for a commercial process.

4 KINETICS

4.1 Introduction

Kinetic data are often very helpful for a better understanding of a heterogeneously catalyzed reaction, and are indispensible for reactor design. Moreover, more insight into the reaction mechanism may give clues to optimize catalyst performance and process conditions. Accordingly, a preliminary kinetic study was made of the aldol condensation of ethanal over tin on silica catalysts, although it was realized that this would by no means be easy because of the inadequate stability of the catalysts investigated.

Several authors have reported on the kinetics of the gas-phase aldol condensation over various catalysts (16, 44, 49, 50, 97, 202, 205, 206, 207, 208, 209) However, because the rate of deactivation of the catalysts varies widely and since details on catalyst stability are frequently left unreported, most literature data should be used with caution. In analogy with the liquid-phase aldol condensation Malinowski et al (44, 50, 205) have found that the overall order of the reaction depends on the reactivity and the concentration of reactants as well as on the activity of the catalyst. Most other authors did not study the reaction order extensively and usually just assume an order. Exceptions are DelBorghi et al (202), who found a second order in ethanal during the first phase of processing over silica/alumina; after some deactivation the order approached unity. Kawaguchi et al (206) mention first order over a calcined Na_2CO_3 catalyst. As for the activation energy, values reported for ethanal condensation are usually between 42 and 52 $kJ.mol^{-1}$.
Ivanov et al (210) studied the reaction at 365°C between 2-butenal and water, i.e. hydration followed by retro aldol condensation. The reaction proceeds fairly readily at this temperature. The rate of the retro reaction decreased when the water/2-butenal ratio was increased, which points to competitive adsorption of the two reactants. The aldol condensation is also retarded by water according to Fabbri et al, who applied silica/alumina catalysts (99).

The type of mechanism is not discussed extensively in the literature. A mechanism proposed for catalysis on acidic surface hydroxyl groups (46, 47, 48) is of the Langmuir-Hinshelwood type; both reactants must be adsorbed for the reaction to proceed. On the other hand, Malinowski et al state that adsorption occurs by the formation of hydrogen bonds between the α-hydrogen atoms of the reactants and the oxygen atoms coordinated to an adsorbed metal ion on the surface (43, 95). Intermediate formation is said to occur by reaction from the gas-phase or via a physisorbed reactant, a mechanism often called an Eley-Rideal mechanism.

That the gas-phase aldol condensation is an equilibrium reaction like the liquid-phase reaction is evident from the partial conversion reached over all kinds of catalysts at very low space velocities (tables 1.3.1 - 1.3.5) and from results obtained in this study. Fresh catalysts were very active, but even then yields of butenal were never higher than 30%, even at high temperature and a long residence time.
Equilibrium data are scarce, however. Methods are available to calculate the necessary data; these are discussed in appendix II. Table 4.1.1 gives data from the literature and the results for two methods of approximation.

TABLE 4.1.1 Calculated equilibrium conversion data for the gas-phase aldol condensation of ethanal

T (K)	300	400	500	600	700	800
source:						
Malinowski (95)	0.10			0.49		0.68
Nagarajan (97)		0.99	0.98	0.97	0.96	
Ivanov (210)			0.26		0.15	
This work, method a	0.67	0.64	0.62	0.61	0.59	0.58
This work, method b	0.64	0.46	0.36	0.31	0.28	0.25

a method of van Krevelen and Chermin (236)

b method discussed in appendix II

It follows that the equilibrium conversion decreases with increasing temperature, similar to the liquid-phase reaction. The calculated data are not in conflict with our experimental results: the experimental conversions were invariably lower than the calculated values.

4.2 Experimental approach

The definition of the reaction rate used is:

$$r = -d\xi / d(W/F)$$

ξ being the fraction of initial reactant converted and W/F the reciprocal space velocity in g cat.h.mol^{-1}. When the reverse reaction can be neglected the form of the reaction rate equation is:

$$r = k * P^{n}$$

with

$$k = k_0 * (1-G) * \exp(-E_{act}/RT)$$

k being the reaction rate constant, G the degree of deactivation defined as fraction of the initial activity.

Three methods of investigation for kinetic data are available: (i) the integral method, (ii) the differential method and (iii) the initial rate method. Method (i) uses the derivative of the plot of conversion versus residence time. Data are needed over a wide range of conversion, i.e. up to long residence times. Comparison of the integrated reaction rate equation with the conversions found gives the reaction rate constants and the order in the reactants. The method becomes complicated and thus inaccurate when the influence of the products must be incorporated. This situation certainly applies to our case at higher conversions.

Method (ii) assumes the reaction rate to be constant over the reactor, viz. the reactant concentration is considered to be constant. This is so at low conversions and short residence times. The conversion then is linearly proportional to the residence time. For our catalysts this condition is fulfilled in the region below the dotted line A in figure 3.2.2. In this region, however, the measurements often are rather inaccurate because of the low conversion, the small amount of catalyst and large gas flows needed.

Method (iii) is based on conversion data at varying residence times. By means of a fit method the most likely equation is calculated which describes a curve through the data points and the origin. The tangent to this curve at zero residence time is proportional to the reaction rate at zero conversion. This method seemed best for the reaction system studied here; it was assumed that the conversion/residence time relation could be described by:

$$\xi = Const1 * tangh (Const2 * W/F)$$

Precise adjustment of partial pressure and residence time for each point within one experiment proved to be difficult. Variations in these reaction conditions of up to 10% did occur. Corrected conversions were calculated with the aid of the order in ethanal found using the uncorrected points. The results obtained in this way were not at variance with those obtained using the differential method with the same points; see figure 4.2.1 for such a series of experiments. The deviations between the two methods were less than 5%, a deviation also found during repeated measurement of the kinetic values using the initial rate method. Most data were therefore acquired with the differential method.

4.3 Results

Figure 4.3.1 gives the log r versus log P_{eth} plots at 523 and 573 K (250 and 300°C). The observed order is 1.34 ± 0.05 in ethanal at 573 K and 1.05 ± 0.05 at 523 K.

The temperature effect was further investigated by determining the order at different temperatures between 458 and 547 K (table 4.3.1). Although the order shows deviations due to the limited number of initial rate values used, the mean order of 0.98 ± 0.10 is not essentially different from the value found at 523 K. Therefore, the order is assumed to be constant at temperatures below 547 K.

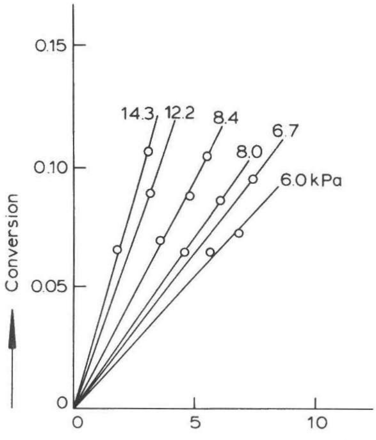


Figure 4.2.1 Determination of reaction rates for various ethanal partial pressures, assuming differential reactor behaviour. Catalyst D13, T = 573 K.

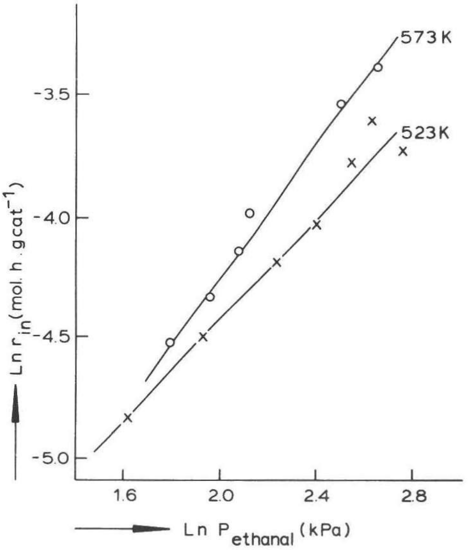


Figure 4.3.1 Determination of the order in ethanal
× *catalyst D3, T = 523 K,* ○ *catalyst D13, T = 573 K*

TABLE 4.3.1 The order in ethanal at different temperatures, catalyst D3, P_{eth} between 4.9 and 12.2 kPa, deactivation 15 h.

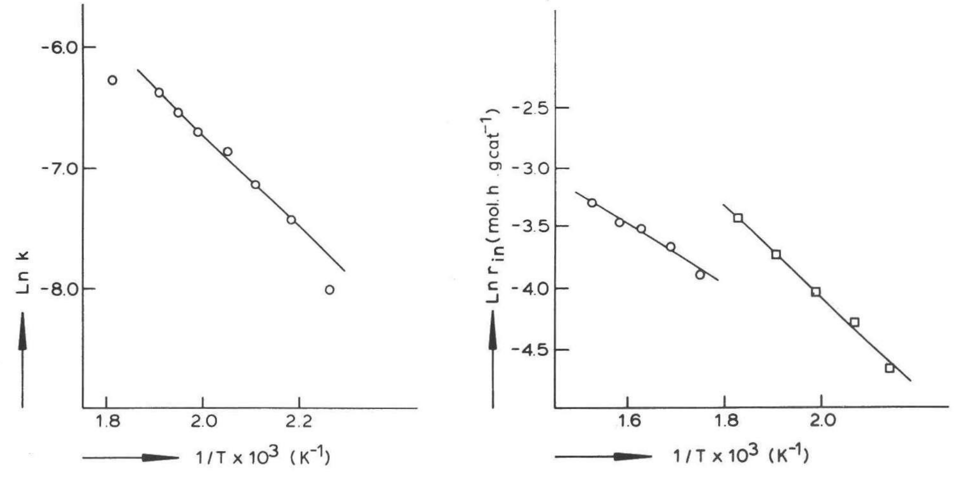
T (K)	n
458	0.94
473	0.88
488	1.12
503	1.08
523	0.91
547	0.94

DelBorghi et al (201, 202, 203) have suggested that the order of the reaction changes as the catalyst deactivates, by the same process by which the selectivity decreases, discussed in 3.4.2. These authors state that the initial order of 2 becomes unity upon aging of the catalyst. Table 4.3.2 gives the results found for an aging tin on silica catalyst. The mean value for the order is again near unity and does not change by catalyst aging. Because the data were obtained with different catalysts the reaction rate constants found differ not only in the degree of deactivation, G, but also in the number of active sites on the fresh catalyst.

TABLE 4.3.2 Values for the order in ethanal and the reaction rate constant, after different time of catalyst deactivation

catalyst	t (h)	n	$k * 10^3$ (mol.h^{-1}.g cat^{-1}.kPa^{-n})
T = 523 K			
D12	2	0.99	2.40
D12	5	1.06	2.02
D12	10	1.02	1.96
D3	15	1.05	1.46
D19	20	1.17	0.82
D12	30	1.01	1.67
D12	60	1.00	1.66
T = 573 K			
D13	4	1.28	1.31
D13	145	1.34	0.96

Figures 4.3.2a and 4.3.2b show Arrhenius plots for the reaction. Because of the change in order in some cases the reaction rate is plotted instead of the reaction rate constant. This was possible when all other conditions were kept constant.



(4.3.2a) *(4.3.2b)*

Figure 4.3.2 Arrhenius plot for the aldol condensation of ethanal

a Catalyst D3

b Catalyst D13 and different periods of deactivation ($T < 547$ K : t_{deact} = 30 h, $T > 547$ K : t_{deact} = 100 h)

Measurements at higher temperature had to cope with a high deactivation rate; therefore, the experiments were generally done over a narrow temperature range. Observed preexponential factors show the marked deactivation of the catalysts at higher temperatures (see table 4.3.3). Apparently, a change in activation energy occurs at the same point where a change in order was observed; the activation energy at temperatures below 547 K is approximately 33 $kJ.mol^{-1}$ whereas at higher temperatures about 21 $kJ.mol^{-1}$ is found. These values are substantially lower than those reported in the literature.
Table 4.3.3 also contains the apparent activation energies for catalyst deactivation and by-product formation (c.f. 3.4.2 and 3.5.1).

The influence of 2-butenal on the conversion of ethanal at different conditions is shown in figures 4.3.3 and 4.3.4. The butenal/ethanal ratio is the important variable. The influence of butenal is confined to low partial pressures where the addition of butenal causes a decrease in conversion; above a butenal/ethanal mole ratio of 0.1 at 523 K further decrease is not observed. The conversion level stabilizes at about 75% of the conversion observed in the absence of butenal in the feed. Furthermore, the order in ethanal does not change by addition of butenal, which indicates that the decrease in conversion

TABLE 4.3.3 Activation energies of reactions occurring during aldol condensation of ethanal over tin on silicagel catalysts

temperature range (^{o}C)	catalyst	deactivation time (h)	E_{act} ($kJ.mol^{-1}$)	preexponential factor
for aldol condensation:				
170 - 275	D3	15	32.9	3.10
190 - 270	D13	30	32.6	4.30
300 - 380	D13	100	20.7	0.08
200 - 250	D2	60	30.9	2.80
250 - 280	D26	20	33.0	
290 - 310	D26	20	22.1	
for by-product formation:				
300 - 380	D10/D11		23.0	
for deactivation:				
250 - 350	D13	>80	37.6	

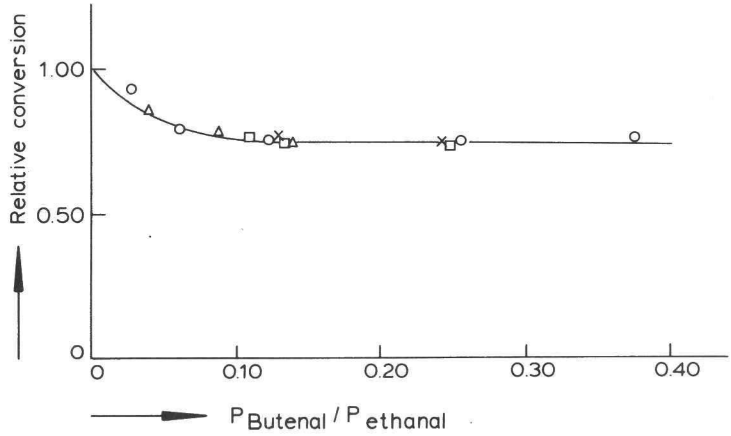


Figure 4.3.3 Dependency of the relative conversion on the ratio of butenal and ethanal pressure, for different pressures of ethanal. Conditions: catalyst D13, T = 523 K, W/F = 10 g cat.h.mol^{-1}, P_{eth} = × :4, □ :6, ○ :8, △ :12 kPa

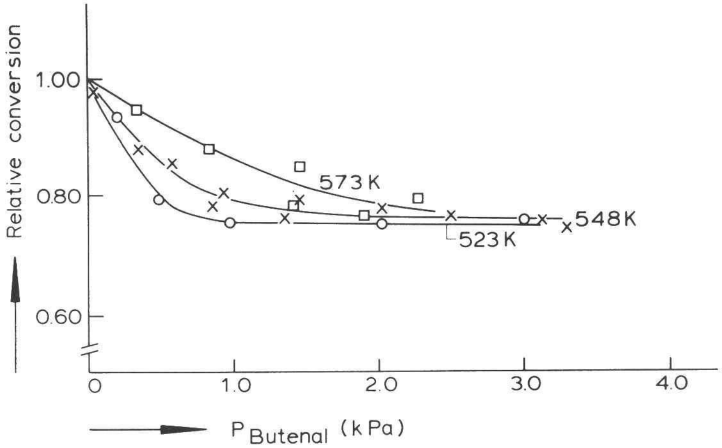


Figure 4.3.4 Dependency of the relative conversion on the partial pressure of butenal at different temperatures. Conditions: catalyst D13; P_{eth} = 8 kPa, W/F = 10 g cat.h.mol^{-1}, T = ○ :523, × :547, □ :573 K

is not caused by a change in reaction mechanism. At higher temperature, the effect of butenal is smaller, although at high butenal concentrations the confinement of the decrease to a level of 75% of the original conversion is observed again.

The influence of water on the conversion is shown in figure 4.3.5. At low water partial pressure its influence increases as the temperature is higher. At high partial pressure the effect of water decreases when the temperature is raised. Comparison with the data obtained at high ethanal partial pressure indicates that the molar ratio water/ethanal is the essential variable, as was found for the influence of butenal (c.f. 3.5.4). In contrast to butenal the decrease of the conversion upon addition of water continues as more water is added.

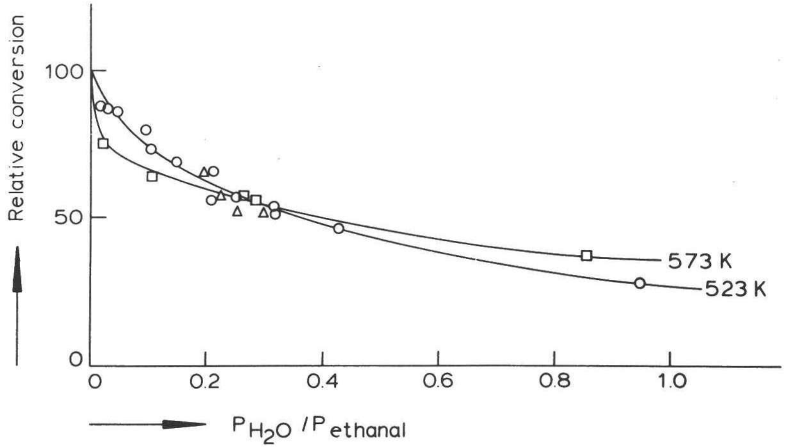


Figure 4.3.5 Dependency of the conversion on the partial pressure of water added; for different temperatures.

Catalyst D13

○ P_{eth} = 7.4 kPa, W/F = 10 g cat.h.mol^{-1}, T = 523 K

□ P_{eth} = 7.8 kPa, W/F = 10 g cat.h.mol^{-1}, T = 573 K

△ P_{eth} = 25-30 kPa, W/F = 15 g cat.h.mol^{-1}, T = 523 K

4.4 Discussion

The results reported in chapter 3 concerning catalyst performance provide the starting point for the discussion on the processes occurring on the surface of the catalyst. The activity is first order in tin, as follows from the linear relation between activity and tin content of the catalyst observed for low tin loads (c.f. figures 3.3.1 and 3.3.2). The data also show that adsorption on the active sites must be strong, particularly for products. The observations leading to this conclusion are: (i) the slow stabilization of conversion after a change in conditions (e.g. figure 3.5.3), (ii) stabilization of the conversion at a lower level with lower ethanal pressure (c.f. figure 3.2.2), (iii) competition of ethanal and butenal which govern the selectivity in part (c.f. table 3.4.2), (iv) deactivation and regeneration are caused for a large part by adsorption and desorption of products.

A relatively large part of the active surface is covered by adsorbed reactant and primary product; the latter leads to further aldol condensation. Moreover, products formed by this multiple aldol condensation tend to eliminate active sites because of their low volatility. The very low turn-over number, <0.05 sec^{-1} after 15 h, is another indication for the limited availability of sites for the reaction.

The first order in ethanal at temperatures under 547 K is in agreement with a mechanism in which one of the reactant molecules is adsorbed very strongly and a second one either adsorbs much less strongly at or near the first one or reacts from the gas phase. The latter step is then rate determining. The fact that the process is first order in tin is yet another indication that the two molecules adsorb on or near a single tin site, if both adsorb before reaction. At higher temperatures, surface coverage by the strongly adsorbed ethanal molecule decreases; surface coverage of both molecules has influence on the rate, according to the increased order.

The low activation energy below 547 K indicates that the second ethanal molecule is indeed adsorbed too. The even lower activation energy at higher temperatures shows the increased participation in the rate determining step of the strongly adsorbed first ethanal molecule.
Water, butenal and the products of further aldol condensation are adsorbed on the same sites. The aldol products probably adsorb in a similar manner as ethanal, and the reactions involving them follow the same mechanism, as is

indicated by the similarity in activation energies for deactivation and by-product formation with that of the aldol condensation of ethanal. The above mechanism is a clear case of competitive adsorption of feed, primary products and by-products.

When water is added to the feed the surface coverage and reaction equilibria are shifted appreciably. Less sites are then available for ethanal and butenal; as a result, the conversion decreases and the selectivity increases. Moreover, the reverse reaction, butenal with water to ethanal, is greatly enhanced. At low water pressure the conversion decreases as the temperature is higher because of a larger reaction rate constant. At high water pressure, however, this decrease is less: lower adsorption of water and butenal cancel the effect of larger reaction rate constants.

Addition of butenal to the feed has a comparable effect on equilibria and surface coverage, more sites being occupied by butenal, which causes the reverse reaction to increase. Concomitantly, the selectivity decreases. Because the adsorption of butenal and water is less with higher temperature the effect decreases with increasing temperature (c.f. figure 4.3.4). The maximum decrease in conversion, about 25%, which is independent of the temperature can be explained by assuming that the increasing reaction of adsorbed water and butenal is the main cause for the decrease in conversion. Only part of the water formed (≃25%) reacts. This is ascribed to adsorption of water on sites which are not in position for reaction; possibly hydroxyl groups which are not close to an active site, formed by tin.

5 ON THE NATURE OF THE ACTIVE SITE FOR THE ALDOL CONDENSATION OVER TIN ON SILICA CATALYSTS

5.1 Catalyst composition

Before embarking on the discussion on the nature of the active site and a possible catalytic mechanism, it is necessary first to review the data on catalyst composition at all stages of preparation reported in chapter 2. It was found that during catalyst preparation surface structures, such as **silica**=$SnCl_2$, are formed by reaction of tin compounds with hydroxyl groups of the silica surface or by ion exchange of Sn^{2+} with Na^+. Hydrolysis and oxidation of the resulting surface compounds then leads to silica=$Sn(OH)_2$ surface groups (162, 163) or to $SnO_2.nH_2O$, the latter only weakly bound to the surface (190). The high mobility of the latter compound is one of the reasons why rather large SnO_2 particles are formed upon calcination. In addition, hydrolysis and oxidation of precipitate formed during impregnation also gives rise to relatively large SnO_2 particles.

It was further found that the catalyst is active for aldol condensation only after reduction. Temperature-programmed and isothermal reduction experiments showed that tin(IV), the only form of tin in the calcined catalyst, is reduced to tin-containing species which are stable to further reduction under the conditions used. The existence after reduction of two different tin species in varying ratio was also established, the ratio depending on the tin content. Moessbauer spectroscopy showed these species to be β-tin and a hitherto unknown stable tin(II) compound (c.f. figure 2.3.10.b, spectrum B, peak 6). The β-tin is formed from the SnO_2 particles; X-ray diffraction indicates that it is present in the form of relatively large crystallites which fit into the larger pores of the silicagel structure. The β-tin was found to react with aldehyde reactant and/or products to an amorphous compound during aldol condensation.

The tin(II) compound shows up as tin(II)oxide in Moessbauer spectroscopy unless the reduced catalyst is kept in very dry conditions. Crystalline tin(II)oxide is not stable under the conditions used here (c.f. 2.3.3). The relatively stable tin(II) ion is most probably formed upon reduction of silica=$Sn(OH)_2$ structures and stabilized through anchoring to the silica surface. It resembles tin(II)silicates: $SnSiO_3$, Sn_2SiO_4, which have been reported to be resistant against reduction at high temperature (212). The tin(II) ion will thus be bound to surface oxygen atoms. Such tin(II) species have also been reported by several other authors (163, 187, 190, 213).

In the subsequent discussion, the above tin(II) surface compound is considered to be the active centre for catalytic gas-phase aldol condensation. Tin(IV) complexes, including bulk tin(IV)oxide, do not qualify because reduction is needed to activate the catalyst.
Earlier, metallic tin has been named as the most likely condidate for the active site on tin/silica catalysts (7, 8). However, observations made during the experiments reported in this thesis contradict this conclusion for the following reasons:
(i) the metallic tin phase in the catalysts has an observed melting range of 220-225^{o}C, as was reported in 2.3.3. One would expect the catalytic activity to change more or less abruptly at the melting range, which is not observed.
(ii) preparation by dry impregnation resulted in a dispersion of smaller SnO_2 crystallites at higher tin contents. Although the tin formed upon reduction agglomerates to some extent, one would expect the metallic tin surface area to increase with increasing tin content, resulting in a higher activity per % weight tin. However, the opposite effect was found.
(iii) the observed tin crystallites had about the same size as the pores of the supports. Therefore, the active surface of the tin crystallites per % tin would decrease with increasing pore size, which would lead to lower activity, which is not observed.
(iv) a maximal activity was found at about 4w% tin, which is equivalent to about 0.5% of the meso-pore volume of the catalyst. One would expect the maximum to occur at a substantially higher tin content.
(v) during aldol condensation metallic tin reacts to an amorphous compound. Catalysts in which metallic tin could no longer be detected were still active for the reaction. If this amorphous compound constituted the active tin compound, an induction period would have been observed. This was not found; on the contrary, a high ethanal conversion was noted early in all runs over a fresh catalyst, indicating a very high initial activity.
(vi) Even after 15 minutes reduction a catalyst with a high tin content, D12, showed optimum activity and selectivity, although reduction of SnO_2 was not complete.

To fortify the hypothesis of tin(II) active sites still further, it is necessary to discuss the nature of the interactions of aldehydes and ketones with oxidic surfaces with and without coordinatively unsaturated polyvalent metal ions. This is the subject of the next section.

5.2 Interaction of aldehydes and ketones with oxidic surfaces

Physisorption of aldehydes and ketones on an oxidic surface with hydroxyl groups, e.g. silicagel and hydrated alumina, occurs by hydrogen bonding of carbonyl groups to the surface hydroxyl groups (47, 48, 214, 215). At low surface coverage of the aldehyde or ketone the carbonyl group may form a hydrogen bond with two vicinal hydroxyl groups (216, 217). This explains the surface coverage dependency of the adsorption enthalpy of ethanal on silicagel reported by Robinson et al (48), which varies from 42 to 67 $kJ.mol^{-1}$.

Chemisorption of aldehydes and ketones is observed on surfaces which contain metal ions functioning as Lewis acid sites. Aldehydes form alkoxy bonds with surface metal ions which are not completely coordinated. Ketones are less reactive and do not chemisorb readily. The reaction has been reported for a wide range of solid compounds, e.g. TiO_2, Cr_2O_3, Al_2O_3 and even SiO_2, if activated at higher temperature and/or in vacuo (214, 218, 219, 220, 221). Chemisorption leads to several (surface) compounds such as carboxylates, enolates, esters and polymers. The product mix strongly depends on the coordination sphere of the ion, the reaction conditions and the presence of other molecules (figure 5.2.1). The formation of carboxylates, esters and alcohols is the gas-phase form of the Cannizzaro or Tsitschenko reaction; the latter is known to be catalyzed by metal alkoxides, in which the metal acts as a Lewis acid, in the liquid phase. On more strongly basic oxides, e.g. MgO, rapid chemisorption of aldehydes on surface oxygens occurs; ethanal and butanal react even at ambient temperature to give carboxylates (222). The reactivity for this reaction increases with increasing carbon chain length and increasing basicity of the catalyst (45, 106, 118, 223). $Ca(OH)_2$ gives large amounts of esters, Ca-orthophosphates hardly any (83).

A related reaction is the formation of ketones from aldehydes, a reaction occurring over several metal oxides and hydroxides, among which are those of tin, and is reported as proceeding via the decomposition of surface carboxylate intermediates. High temperature and availability of water particularly favour the production of ketones (45, 118, 128).

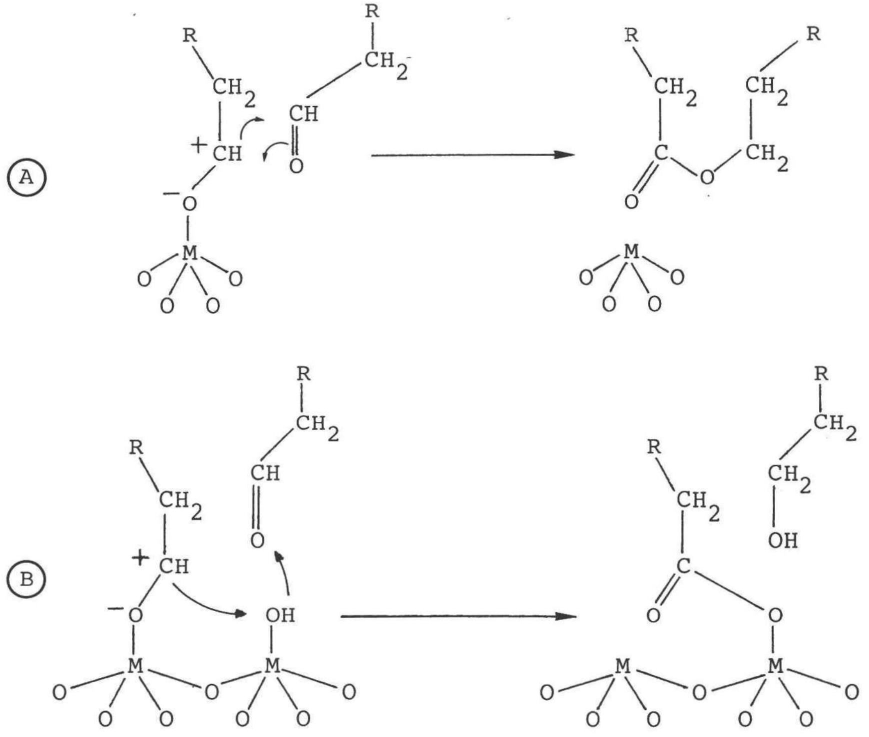


Figure 5.2.1 Reactions of aldehydes on coordinatively unsaturated metal ions on the surface of oxidic materials.
A; ester formation, B; carboxylate and alcohol formation

Aldol condensation may occur on all kinds of oxidic materials (c.f. tables 1.3.1 - 1.3.5). The importance of basic sites for activation described by Malinowski and Minachev is discussed in 1.2. Ketones can be activated for aldol condensation by metal ions acting as Lewis acid sites, as occurs when adsorbing acetone on activated alumina (224). The same mechanism seems also possible for ethanal; in fact, during adsorption on silica-alumina some 2-butenal is formed (225).

Many other authors have reported that solids having clearly acidic characteristics are active for aldol condensation to some extent, although the selectivity is commonly low. Examples are alumina (96, 103, 220), acid-treated silicagel (103), silica-alumina (46, 48) and ZrO_2/SiO_2 (49). However, too high an acidity clearly results in a low selectivity; e.g. highly acid alumina produces only coke from cyclohexanone (226). Furthermore, dehydration of the ZrO_2/SiO_2, by which Zr^{4+} ions are exposed, lowers the yield substantially. Impregnation of such solids with basic compounds, e.g. NaOH, initially only results in increased selectivity towards aldol condensation, without changing the overall catalyst activity. Only after addition of more than a certain amount of base an increase in the overall activity was observed. This indicates that strongly acid sites are first neutralized. New, more basic sites are formed later on, which leads to the conclusion that even with acid oxides the basic sites are very important in the aldol condensation, although the reactions initiated by the acid sites easily dominate the overall activity.

The above phenomena can be summarized as follows:
The surface oxygen atoms of oxidic substances form basic sites, the basicity being influenced by neighbouring cations (c.f. (227)). These sites are certainly capable of initiating aldol condensation by interaction with the α-hydrogen atoms, as discussed earlier, and appear to contribute substantially to the catalytic activity.
Metal ions on the surface of such oxidic solids which are coordinatively unsaturated act as acid sites. They interact with the oxygen atom of the carbonyl group and may initiate several different reactions, depending on the reactivity of the carbonyl group and the acidity of the site.
It is very well possible that the reactants are activated by the acidic and basic sites in combination. Their individual and their relative mutual strength determine the product distribution. In the case of aldehydes and strongly acidic sites the formation of surface compounds and/or polymerization predominates. Both lead to low selectivity for aldol condensation and deactivation of the site. A low acidity favours the aldol condensation of aldehydes. More strongly acid sites are needed to activate ketones for aldol condensation. On the other hand, too strongly basic sites are believed to be unfavourable for the condensation of aldehydes.
Hydroxyl groups present on the surface may adsorb aldehydes and ketones but do not initiate aldol condensation (c.f. 1.2).

5.3 The active centre for aldol condensation

The tin/silica catalysts used in this investigation are more than 99% selective for the aldol condensation reaction: formation of esters, polymeric products and ketones is only of minor importance. Since polymerization is acid-catalyzed and the Cannizzaro reaction leading to esters is initiated by strong bases, it is concluded that the acidity of the catalysts is low and that very strongly basic sites are absent.

Any strongly acidic site present initially is soon deactivated. As was discussed earlier, such acidic sites most likely stem from impurities in the silicagel, e.g. Al^{3+}, or are formed when preparing the catalysts with acid solutions. The relatively large amount of deposits formed on catalysts prepared by dry impregnation with acid added points to the latter possibility.

Surface tin(II) compounds most probably are the active centres. This view is supported by the discussion about the action of oxidic materials as catalysts. The tin(II) ion has the ground state $5s^2 5p^2$. It forms sp^2 hybridization easily. The availability of a donor ligand is known to yield a very stable sp^3 configuration, one empty orbital being filled by the electron pair of the donor ligand, another orbital containing the remaining electron pair (figure 5.3.1). It is probable that the tin atom is anchored to the silicagel surface via one or more hydroxyl groups. Reactants such as $SiCl_4$, $AlCl_3$, BCl_3, $SnCl_4$, $TiCl_4$, $Cu(NH_3)_4^{2+}$ and $CrCl_2O_2$ are probably bound to at most two groups (143, 150, 153, 155, 159, 162). This phenomenon is caused by the small ionic radius of these metal ions, which range from 0.02 nm for B^{3+} to 0.07 nm for Sn^{4+}. The surface hydroxyl groups on a regular surface have a mean distance of about 0.28 nm. On an amorphous silica surface the hydroxyl group coverage is higher; thus the average distance will be smaller.
The radius of the tin(II) ion is much larger than for the above mentioned metal ions, viz. 0.11 nm. Therefore the chances of coordination to three hydroxyl groups are higher. Two of the bonds are valence bonds, Si-O-Sn, the other one is a coordination to the oxygen of Si-OH or possibly a surface siloxane bond.

Earlier the mechanism of the aldol condensation catalysis in the liquid phase and its close similarity expected for a heterogeneously catalyzed aldol condensation has been discussed. Acid and base functions were supposed to be necessary for optimal catalysis of the reaction (c.f. 1.2).

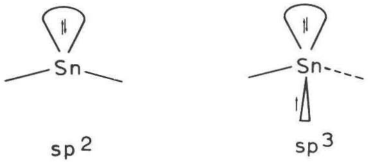


Figure 5.3.1 Hybridization of the tin(II) ion

In the previous paragraph it has been argued that a concerted action of both sites is likely and that too strongly acid or basic sites favour other reactions. The tin(II) compound which is held to be the active species, has a low surface coverage, i.e. 0.3 at.nm^{-2} for silicagel-based catalysts. It is therefore most likely that acid and basic functions are located at a single tin site. The tin ion is the acid site and the coordinated oxygen ions the basic sites. The large distance between the tin ions on the surface prevents reaction of reactant molecules adsorbed on different sites.

A possible way of adsorption is the interaction of the carbonyl group with the tin ion and of the α-protons with one of the surface oxygens (c.f. figure 5.3.2: Ⓐ). This would result in the very strong adsorption and the effective activation found during the kinetic measurements. The second reactant molecule Ⓑ may react directly from the gas phase, but a preceding adsorption is considered necessary to bring the molecule in a better position for the reaction. The adsorption may be on a neighbouring hydroxyl groups, which would cause a relatively long distance to the activated substrate, but it is more likely that it occurs on one of the remaining oxygen ions by its α-proton(s) (figure 5.3.2, configuration 1), or by its carbonyl groups to the hydroxyl group to which the tin is bound (configuration 2). In this way the carbon atoms of both reactant molecules which have to be coupled are within easy reach of each other.

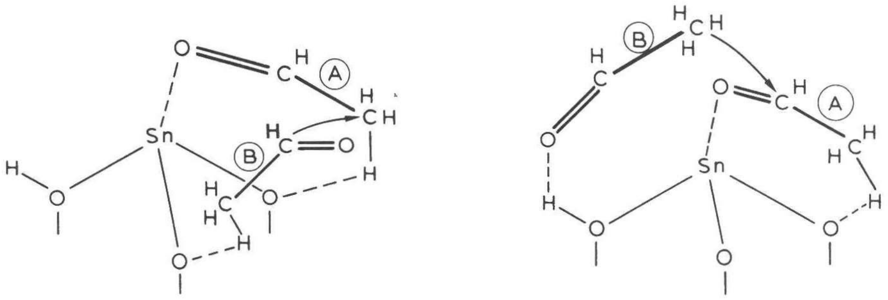


Figure 5.3.2 Modes of adsorption and reaction of reactant molecules. Reactant molecule Ⓐ *adsorbed with α-proton and carbonyl oxygen atom, molecule* Ⓑ *either: 1; with α-proton to an oxygen ion, or 2; with the carbonyl oxygen atom hydrogen-bonded to a hydroxyl group in the coordination sphere of tin (model not to scale).*

6. GAS-PHASE ALDOL CONDENSATION OF n-BUTANAL OVER TIN ON SILICA CATALYSTS

6.1 Introduction

Aldol condensation of butanal followed by hydrogenation of the primary product, 2-ethylhexenal, is of much industrial interest since it is the only feasible route to 2-ethylhexanol, which is applied as a plasticizer compound in about 50% of all soft PVC formulations.
The relevant reactions are:

$$2\ CH_3CH_2CH_2CHO \longrightarrow CH_3CH_2CH_2CHC(C_2H_5)CHO + H_2O$$

$$CH_3CH_2CH_2CHC(C_2H_5)CHO + 2\ H_2 \longrightarrow CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2OH$$

At present, the condensation is carried out industrially in the liquid phase. However, gas-phase aldol condensation is a promising alternative: the tin on silica catalyst of Swift et al (7, 8) is claimed to give a substantially higher yield in n-butanal condensation than earlier heterogeneous catalysts. Moreover, the selectivity was very high, even at high conversions. Therefore, the catalysts developed in the present work were tested for their performance in the gas-phase condensation of n-butanal.

The equilibrium conversion at about 250^{o}C of the reaction to 2-ethylhexenal is probably higher than the analogous reaction for ethanal, as can be seen by comparing the yields in the tables 1.3.1 and 1.3.2. Table 6.1.1 shows the equilibrium conversions for the gas-phase reaction calculated according to the approximation method described in appendix II. It follows that highly active catalysts would be advantageous since these may allow operation at low temperatures where the equilibrium conversion is highest. Experimental data are described in subsequent paragraphs.

TABLE 6.1.1 Calculated equilibrium conversions for the gas-phase aldol condensation of n-butanal.

T (K)		300	400	500	600	700	800
ξ_{eq}	a	0.95	0.85	0.73	0.64	0.57	0.51
	b	0.95	0.85	0.72	0.60	0.54	0.51

a. Method of van Krevelen and Chermin (236)

b. Method discussed in appendix II

6.2 Experimental

The apparatus described in 3.1 for the testing of the ethanal condensation has also been used for n-butanal. Liquid n-butanal, distilled before use, was pumped to the evaporator by means of a low-flow piston pump (figure 3.1.1). The concentration of the feed was varied by adding hydrogen as diluent. About 1 g catalyst prepared by the methods described in chapter 2 was used in each experiment. The concentrations of n-butanal, 2-ethylhexenal and water were determined every 30 minutes by on-line gas-chromatography to allow calculation of conversion and selectivity. The gas-chromatographic column, operated isothermally at 167°C, was filled with a solid compound, Tenax G.C. (AKZO), mesh size 60/80 (3m long, 2mm inside diameter). Hydrogen was applied as carrier gas at a flow of 35 ml.min^{-1}. Detection was by thermal conductivity. GC-MS was used to analyze the products formed. The fresh and used catalysts were examined by neutron activation to determine possible changes in tin content. X-ray diffraction was used to identify crystalline species in the catalysts. These analytical methods are described in 2.2.

Conversion and selectivity for each sample were calculated by the same methods as those applied to ethanal condensation (see 3.1 and appendix I). Here, too, the relation of water formed to 2-ethylhexenal was taken to be a measure of selectivity.
The equations used are:

$$\xi = \left[(1-S_F)\ EH_r + (1+S_F)\ H_r\right] / \left[B_r + (1-S_F)\ EH_r + (1+S_F)\ H_r\right]$$

and

$$S = 200 * EH_r / \left[(1-S_F)\ EH_r + (1+S_F)\ H_r\right] \qquad (\%)$$

B_r, EH_r and H_r are measured concentrations of n-butanal, 2-ethylhexenal and water respectively in the product. In this case, the value 0.5 was taken for S_F. The reproducibility of conversion and selectivity is good, although again a certain amount of unsystematic deviations in the calculated values for successive samples was observed (about 5% relative). Average values for a group of consecutive samples deviated less than 1% from values produced by an overall mole balance based on the concentration of butanal before and after the reaction.

6.3 Catalyst performance

6.3.1 Activity

Figure 6.3.1 shows the activity of the catalysts related to time at several reaction conditions. The data show that the deactivation rates are lower than for the ethanal condensation. The conversion after 40 h was again used as a measure of catalyst activity; numerical data for some catalysts are given in table 6.3.1. When comparing the results for the two reactions, it appears that the order of the activities is the same as for the reaction of ethanal.

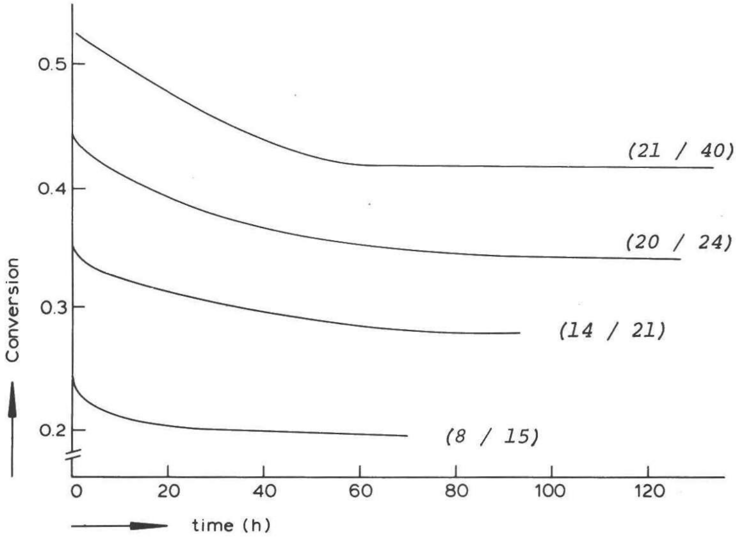


Figure 6.3.1 Activity of tin on silica catalysts for gas-phase aldol condensation of n-butanal.
Catalyst D26; T = 523 K; other conditions, as indicated:
($P_{butanal}$ (kPa) / W/F (g cat.h.mol^{-1}))

TABLE 6.3.1 Activity of tin on silica catalysts for the gas-phase aldol condensation of n-butanal.

Conditions: P_{but} = 8 kPa, W/F = 15 g cat.h.mol^{-1}, T = 523 K

catalyst	w% Sn	ξ_{40h}	% activity relative to catalyst D11 for condensation of butanal	ethanal
D3	3.60	0.092	46	47
D11	0.36	0.201	100	100
D12	3.74	0.189	94	96
D15	0.98	0.105	52	47
D22	5.64	0.181	90	88
D26	4.00	0.184	92	100

Figure 6.3.2 which contains the conversion at different partial pressures and residence times, clearly shows that much higher conversions can be reached with butanal than with ethanal. With the latter feed the yield was never higher than 30% even when using a fresh catalyst and at partial pressures up to 20 kPa. For butanal, on the other hand, conversions up to 50% were reached.

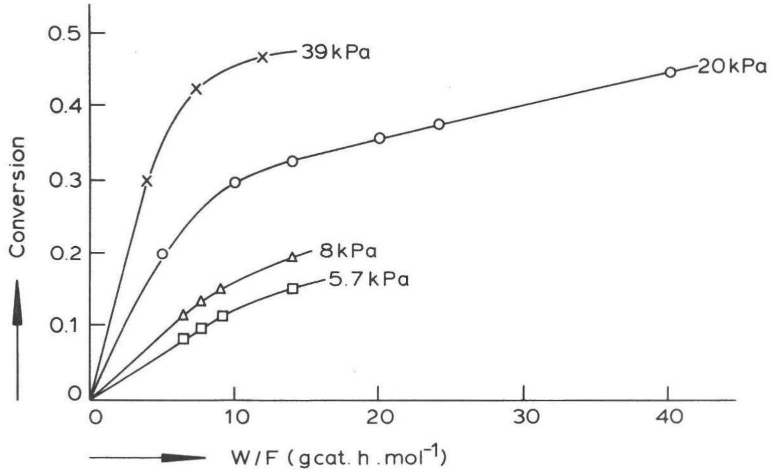


Figure 6.3.2 Plots of conversion against residence time for different partial pressures of n-butanal.
Catalyst D11; T = 523 K

6.3.2 Selectivity

The selectivity of the gas-phase aldol condensation of n-butanal is very high. Even at high butanal partial pressure and high conversion the mean selectivity at 523 K is above 95% in most cases (see table 6.3.2). The lowest selectivity was observed for the lowest partial pressure, which indicates competitive adsorption on the active sites of reactant and product, as was reported for ethanal condensation at lower partial pressures of ethanal (c.f. table 3.4.2).

TABLE 6.3.2 Selectivity of gas-phase aldol condensation of n-butanal

T (K)	P_{but} (kPa)	$\xi_{average}$	run period (h)	selectivity (%)
523	8	0.19	20- 60	92
523	20	0.31	10- 60	98
523	24	0.39	10-120	99
573	20	0.47	20- 60	98

Many products are formed during the condensation reaction; figure 6.3.3 gives an example of the results of a GC-MS analysis. Two isomeric 2-ethylhexenals are formed which differ as regards double bond position; the main component is 2-ethyl-2-hexenal. The other product, 2-ethyl-3-hexenal, was also detected by on-line analysis of the product stream and constitutes up to 5% of the product. The bulk of the by-products (±75%) is formed by further condensation with another butanal molecule to give 2,4-diethyloctadienals. A certain amount of 3-heptene is formed by pyrolysis of 2-ethylhexenal, but this well-known by-product of the gas-phase aldol condensation of butanal is a much smaller fraction (<15%) of the by-products. It is reported to be formed in higher yields at higher temperatures and more acidic catalysts; for instance, the yield of 3-heptene is 6% when reacting n-butanal over Cr_2O_3 at 330°C (107).
A certain amount of ketones is also formed, in contrast to the results obtained with ethanal from which ketones were not formed. Ketone formation appears to increase with increasing chain length of the reactant at the expense of aldol condensation; the same applies to the Cannizzaro reaction (118, 217).
Figure 6.3.4 gives the Gibbs free energies for the reactions leading to the main products calculated by the approximation methods described in appendix II. At the temperatures employed, the formation of the main by-product is thermodynamically equally favourable as the production of 2-ethylhexenal. The high selectivity even at high conversions indicates that the rate of this reaction is much slower than the initial aldol condensation.

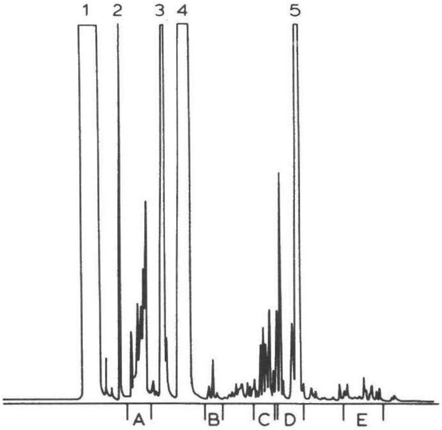


Figure 6.3.3 GC-MS chromatogram of butanal condensation products.
Reaction conditions: 20 kPa; 20 g cat.h.mol^{-1}; 523 K
Analysis conditions: 3m SP2250 column, temperature-programmed from 50 to 280^{o}C at a rate of 8^{o}C.min^{-1}

Legend: 1; n-butanal
2; 3-heptene
3; 2-ethyl-3-hexenal
4; 2-ethyl-2-hexenal
5; 2,4-diethyl-2,4-octadienal
A; ketones
B; undekadienes
C; cyclic trimeres
D; trimeres
E; cyclic tetrameres

6.3.3 Catalyst deactivation

As mentioned before, catalyst deactivation during the reaction with n-butanal proceeds much more slowly than with ethanal. Compared to the latter reaction, a slower but still relatively fast deactivation during the first hour was observed. After 40-80 h the deactivation rate becomes almost constant; this rate is lower by a factor 3-4 than is the case for ethanal condensation.

X-ray diffraction of the spent catalyst showed that, here too, β-tin has disappeared almost completely. Treating the catalyst with hydrogen or air at 450^{o}C had no measurable effect, neither β-tin nor SnO_2 being observed afterwards. This

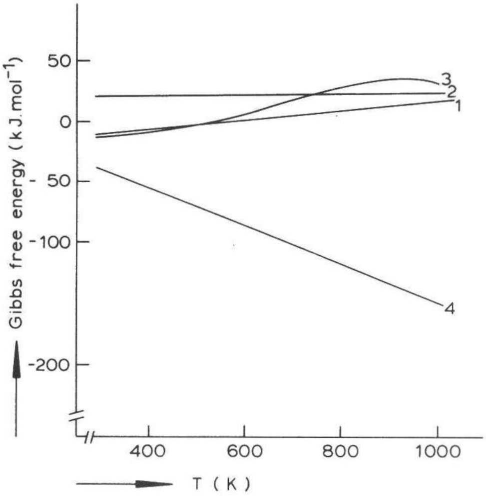


Figure 6.3.4 Gibbs free energy for the reactions:

1. 2 n-butanal $\rightleftharpoons$ *2-ethylhexenal + water*

2. 2-ethyl-2-hexenal $\rightleftharpoons$ *2-ethyl-3-hexenal*

3. ethylhexenal + n-butanal $\rightleftharpoons$ *1,4-diethyloctadienal + water*

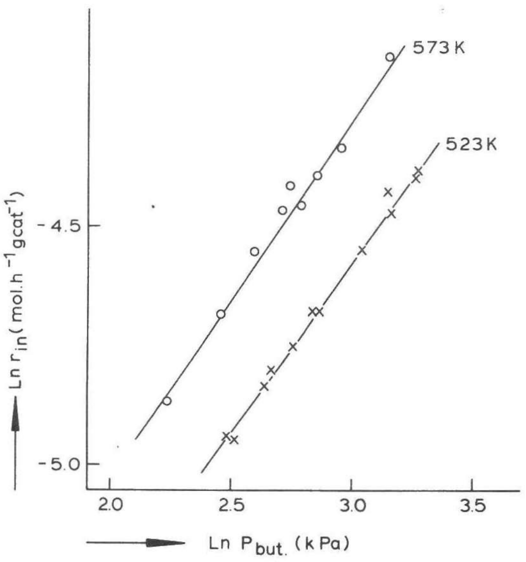
4. ethylhexenal $\rightleftharpoons$ *3-heptene + CO*

is in contrast with the result obtained on the catalyst used in the ethanal condensation where treatment with hydrogen did cause a partial reappearance of β-tin (c.f. 3.2.2). Neutron activation analysis showed that the tin content of the catalysts had not changed.

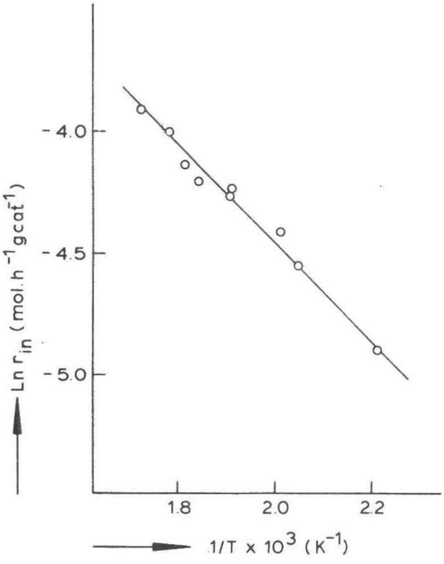
Deposit formation on the catalyst during the reaction is in the same order of magnitude as was observed with ethanal, i.e. between 5 w% for a short experiment and 30 w% for experiments of about 250 h. The deposit formation showed the same dependency on the preparation method. After 60 h catalyst D11, which was prepared by dry impregnation with acid added, had acquired about 50% more deposit than catalyst D26, which was made by reaction with liquid $SnCl_4$. Catalyst behaviour during regeneration was also very similar; for example, a deposit content of 30 w% caused by 250 h reaction was reduced by regeneration to 7 w%. Here, too, a tar-like product was set free. The activity of a regenerated catalyst was virtually equal to the activity of the corresponding fresh catalysts, which is somewhat better than shown by catalyst used for ethanal condensation.

6.4 Kinetics

The kinetic experiments on gas-phase aldol condensation of n-butanal were carried out according to the method described in 4.2.
The order in butanal is about 0.75 (table 6.4.1, figure 6.4.1) and is constant over the temperature range examined, viz. 453-623 K.
Catalyst aging does not affect the order. The activation energy, 16 kJ.mol^{-1}, is also constant over the above temperature range (table 6.4.1, figure 6.4.2). This value is low, even lower than the activation energy found for ethanal condensation. Nevertheless, kinetics and mechanism closely resemble those of the ethanal aldol condensation: competition of reactant and product for active sites influences the selectivity (c.f. table 3.4.2 and 6.3.2) and a large coverage of active sites is again observed. The rate of desorption of products determines the rate to some extent, as evidenced by the low order in butanal.



(6.4.1)



(6.4.2)

Figure 6.4.1 Determination of the order in butanal.

Figure 6.4.2 Arrhenius plot for the gas-phase aldol condensation of butanal.

TABLE 6.4.1 Kinetic data for the gas-phase aldol condensation of n-butanal over tin on silica catalysts.

order in n-butanal

T (K)	catalyst	age (h)	order	$k * 10^3$
523	D16	40	0.73	1.2
523*	D11	80	0.73	3.2
523*	D26	60	0.76	2.8
573	D16	40	0.77	1.4

activation energy

temperature range (K)	catalyst	age (h)	E_{act} (kJ.mol^{-1})	k_0
453 - 583	D26	40	16.0	1.2
473 - 623*	D11	40	15.8	2.0

*based on a limited number of experiments (4-6)

6.5 Conclusions

Catalyst performance and reaction mechanism for ethanal and butanal condensation are quite similar. The butanal condensation, however, produces higher conversions under identical conditions, and the catalyst is much more stable, the deactivation rate being 3-4 times lower for butanal condensation. The selectivity is good, commonly higher than 95%, even at high conversions.

The better selectivity and lower deactivation of the catalyst in the case of butanal condensation are most likely due to the lower reactivity of aldehydes with increasing chain length and branching. Moreover, branching probably decreases the strength of adsorption somewhat and hinders the reactions which influence selectivity and deactivation.

The higher conversion is due, in part, to the more favourable equilibrium conversion. Another reason is the lower rate of catalyst deactivation.

7. PROCESS FEASIBILITY

The preceding chapters have dealt with the preparation of suitable tin on silica catalysts and their performance in relation to the process conditions applied in the aldol condensation of ethanal. Although the experiments were performed in microreactors and in spite of the fact that much remains to be done to develop a catalyst that is entirely satisfactory process-wise, it is concluded that an industrial process may well be feasible. In this chapter a rough outline is given of such a process; it is too early yet to make even a preliminary design study in which all process configurations, reaction and separation conditions, energy requirements and economic aspects are treated in detail.

Reaction conditions and reactor type

Since the cost of the feedstock is one of the major - if not the most important - factor determining product cost, it is a prime requirement that the selectivity of the process must be as high as possible. This is the more important because liquid-phase processes showing selectivities between 90 and 95% are in use. This is one of the reasons why the conditions advocated by Swift (8), viz. a high partial pressure of ethanal and long residence times leading to a relatively high conversion (45-50%) but a selectivity of only 75-80% (c.f. table 7.1) are not acceptable. Moreover, at these conditions the catalyst deactivates very rapidly, which necessitates frequent regeneration.
Although lower partial pressures and relatively short residence times result in a much improved selectivity (see table 7.1) combined with reasonably slow deactivation, operation at a low partial pressure of ethanal and at about 15% conversion is not very attractive since much energy is required to separate the products from unconverted ethanal and for recycling the unconverted feed. Although definite proof cannot yet be offered, it is believed that operation with a feed stream containing sufficient water to retard catalyst deactivation is to be preferred. Higher ethanal partial pressures can then be applied and the amount of hydrogen added to the feed may be reduced. The effects of omitting hydrogen entirely from the feed should be studied; if conditions can be found where hydrogen is superfluous these may well be more favourable. For the purpose of

this discussion, however, it is assumed that addition of hydrogen is a necessity. The combined presence of water and hydrogen then results in selectivities that are at least as high as those obtained in liquid-phase processes, whilst deactivation is so slow that process periods between regeneration of about 1000 hours can be attained if the reactor inlet temperature is adjusted periodically to offset the effects of deactivation. The exact quantity of water to be added to the feed should be established with more certainty, the more so because of the effect of water addition on process energy requirements.

Operation with a feed stream containing hydrogen and water, and ethanal conversions of not more than about 25% have the additional advantage that an adiabatic fixed-bed reactor can be applied. As is shown in appendix 2, the heat of reaction is about -10 kJ/mole, which implies that the adiabatic temperature rise over the reactor is limited to but a few degrees centigrade at the conditions envisaged.
As for the catalyst, the advantages of high activity, stability and ease of regeneration have been discussed in much detail in the preceding chapters. Another aspect that is important process-wise is its mechanical strength. It was found that catalysts containing silica powders as the support are extremely weak mechanically unless a hydrothermal treatment is applied (c.f. support S). The silicagel-based catalysts are more stable. Nevertheless, it is very necessary to optimize the catalyst in terms of mechanical stability. As far as the most suitable method of preparation is concerned, the most promising method appears to be dry impregnation with an acidified solution of $SnCl_2$; the $SnCl_4$ evaporating during catalyst preparation can be recovered. Still, the relation between method of preparation and mechanical strength may lead to the selection of a different method.

Process system

Figure 7.1 shows how the process might be carried out industrially. Fresh ethanal is added to a recycle stream consisting of hydrogen, water vapour and ethanal, heated by heat exchange with the reactor effluent (not shown in the figure) and by a furnace, and fed to the reactor section at $250^{\circ}C$. Two adiabatic fixed-bed reactors are provided to enable the operation to be continuous in spite of the periodic catalyst regeneration required. After heat exchange and cooling most of the butenal, mixed with water and unconverted ethanal, condenses, separated in ④ and is then fed to distillation column ⑥. The uncondensed components are passed to scrubber ⑤ where the remaining products with some ethanal are removed by washing with water. This solution is also fed to column ⑥; the effluent

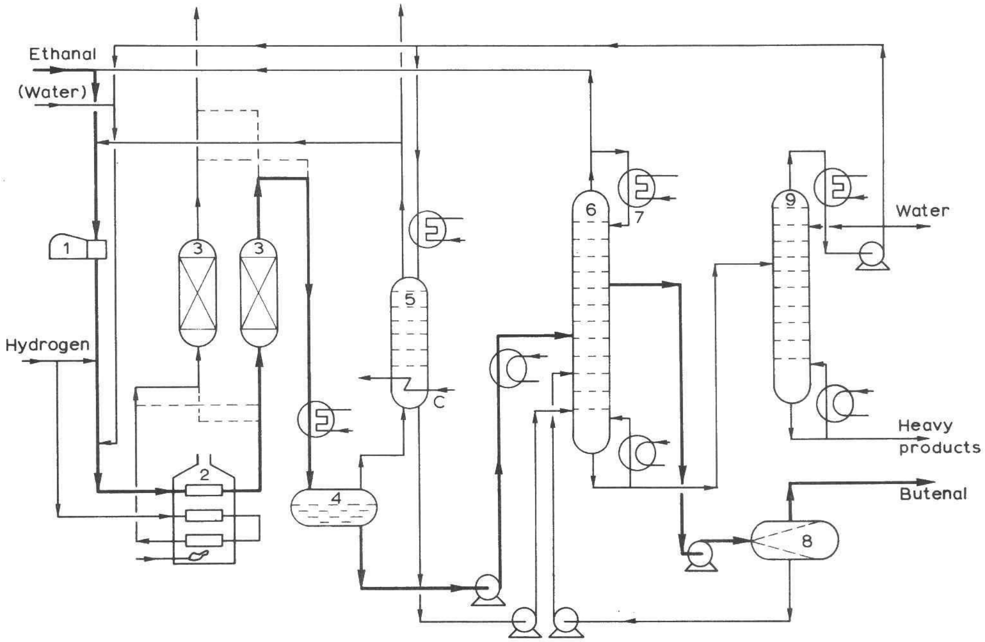


Figure 7.1 Process design for gas-phase aldol condensation of ethanal to butenal. Legend: ① *compressor,* ② *furnace,* ③ *packed bed catalytic reactors,* ④ *gas-liquid separator,* ⑤ *scrubber,* ⑥ *distillation tower (ethanal, butenal),* ⑦ *sub-zero cooling for ethanal reflux (necessary when working at atmospheric pressure),* ⑧ *liquid-liquid separator,* ⑨ *distillation tower (water)*

TABLE 7.1 Process data for the gas-phase aldol-condensation processes

Type of process	T (°C)	$P_{reactant}$ (kPa)	P_{H_2O} (kPa)	LHSV	Diluent	Average conversion	Lowest conversion	Selectivity (%)	Time between regeneration	Annual production per ton catalyst (ton)
for ethanal										
Swift et al (8)	250	40	-	0.5	H_2	0.48	-	78	-	-
proposed, without water	250	10	-	1.0	H_2	0.15	0.10	96	250	2600
proposed, with water	250	30	7.5	1.0	H_2/N_2	0.17	0.15	96	350	3000
						0.16	0.13	97	550	2700
	300	30	7.5	1.0	H_2/N_2	0.20	0.15	95	850	3500
for butanal										
Swift et al (8,9)	250	45	-	0.5	H_2	0.64	-	97	>400	-
proposed	250	20	-	0.64	H_2	0.37	0.30	96	1300	4500

containing hydrogen, water and ethanal is recycled to the reactor section. Column ⑥ produces ethanal as the top product, which is also recycled. A butenal/water cut is drawn off at some intermediate position in the form of an azeotrope (84°C; 24.8% vol water). Upon cooling this mixture separates into two liquid layers in separator ⑧ ; the top layer is technical butenal with 9.6 vol % water. If necessary, it must be purified further by distillation in a subsequent column (not shown). The lower layer from separator ⑧ consists of water and 15.6 vol % butenal; it is returned to column ⑥ . The bottom product of column ⑥ is further separated into water for recycle and heavy ends.
Most of the gas from scrubber ⑤ and nearly all the water can be recycled; small amounts must be vented because CO and methane, by-products from the thermal or catalytic decomposition of ethanal, may accumulate in the gas, and because contaminants in the water recycle stream. However, it is expected that the amount of aqueous effluent to be treated is relatively small. The heavy products obtained as bottoms in column ⑥ contain usefull products as hexadienal and tolualdehyde or/and can be used as fuel.

Comparison with liquid-phase processes

It is not yet possible to compare the proposed gas-phase process with existing liquid-phase processes. Qualitatively it can be said that the gas-phase reactor system is less energy consuming than the liquid phase reactor, where very large recycle streams are needed as well as cooling to about 25°C, which requires low-temperature coolants. In the gas phase process this is not needed if column ⑥ is operated under a pressure somewhat above atmospheric; then, here too cooling water can be used to condense ethanal. However, more energy is needed for the evaporation of the relatively large amounts of water recycling in the gas phase process.
The consumption of catalyst and auxiliary chemicals in the gas-phase process is much less costly than in liquid-phase operation, although the tin on silica catalyst is more expensive than the alkali catalyst normally used in liquid-phase aldol condensation. The cost of effluent treatment for the latter process is, however, expected to be much higher.
If butanal is the desired product it may be possible to hydrogenate the butanal intermediate in the same or in a second reactor downstream of the aldol-condensation reactor. Catalysts have been described which give conversions approaching 100% at selectivities close to 100% (237, 238, 239). The effects on the hydrogenation function of the large amounts of water needed to stabilize the tin on silica catalyst is, however, not known.

In conclusion, the gas-phase aldol condensation process described in this thesis is a potentially attractive alternative for conventional liquid-phase processing.

Much further work remains to be done to establish the feasibility of the heterogeneously catalyzed gas-phase process.

SUMMARY

The rising prices of crude oil and chemical feedstocks derived from it have led to an increased interest in biomass as a raw material for industrial organic chemicals. One of the potential routes for the production of several chemicals that are now based on ethene and propene employs aldol-condensation reactions; notably of ethanal.

In present processes homogeneously catalyzed liquid-phase aldol condensation is applied. In principle, however, heterogeneously catalyzed gas/solid processes offer advantages, particularly as regards better reactor control, reduced catalyst consumption and diminished production of waste water. Literature data indicate that tin on silica catalysts offer good perspectives in respect of stability as well as selectivity. Therefore, this thesis describes an investigation into the preparation and the action of these catalysts and the search for the optimal process conditions for the aldol condensation of ethanal to 2-butenal. Results are also given on the condensation of n-butanal to 2-ethylhexenal.

The method of preparation and the type of support have much influence on catalyst activity but not on selectivity and stability, as far as silica supports such as silicagel and aerosil are concerned. Very poor catalysts were obtained from a mordenite support.
Impregnation of silicagel with aquous $SnCl_2$ solutions acidified with hydrochloric acid produces the best results for tin distribution and activity. During drying of the impregnated support $SnCl_4$ is formed, which reacts with surface hydroxyl groups of the silica. The higher temperature applied during drying apparently favours the reaction. Direct reaction with dissolved or gaseous $SnCl_4$ at room temperature leads to low tin loads and a consequent low activity. When the impregnating solution is not acidified ion exchange occurs between Sn^{2+} and Na^+, which is commonly present in silicagel as an impurity. This also leads to an even tin distribution and high activity.
The use of tin compounds that are very reactive towards the surface hydroxyl groups, such as dibutyldimethoxytin, gives unsatisfactory results. At the periphery of the support particles a very high tin concentration is then

obtained, which causes agglomeration of the tin, with adverse effects on catalyst activity.
The behaviour of the aerosils differs from that of silicagel: aerosils are much more reactive towards $SnCl_4$ and can contain more active tin per unit of surface area. This is seen most clearly with aerosils of low surface area. Differences in surface structure, notably as regards the number and type of hydroxyl groups, are among the probable causes.

It is demonstrated that tin is present in the activated (i.e. reduced) catalyst in two forms: as metallic tin which is molten at reaction conditions and accumulates in the wider pores, and as tin(II) ions that are firmly anchored to the silica surface. Such tin ions bound to oxygen atoms of the surface constitute the active sites of the catalyst. The metal ions and the surrounding oxygen ions act as acid and basic sites, respectively, and together activate the two molecules involved in the reaction.

Kinetic measurements showed the order in ethanal to be 1.0 and the activation energy 33 $kJ.mole^{-1}$ at temperatures below $275^{o}C$. At higher temperatures the order rises to 1.3 whereas the activation energy goes down to 21 $kJ.mole^{-1}$. It is concluded that at the lower temperatures coverage of the active sites by one of the reactant molecules is almost quantitative and that adsorption of the second molecule is rate determining. At higher temperatures coverage by the first reactant molecule decreases causing the surface concentration of both molecules to influence the rate.
The kinetic study of the condensation of butanal indicates the order to be 0.75 and the activation energy 16 $kJ.mole^{-1}$ over the entire temperature range examined, viz. $170\text{-}370^{o}C$. A similar mechanism as found for ethanal is likely, the adsorption of products being stronger, causing adsorption as well as desorption to influence the rate.

The catalysts are very selective for aldol condensation reactions (>99%). Although continuing aldol condensation causes a decrease in the selectivity for desired products, it appears that selectivities above 95% are feasible. The relation between process conditions and selectivity is complex. Selectivity decreases as the temperature and the conversion are higher, but also competition between reactants and products for active sites and changes in reaction conditions in the catalyst particles caused by catalyst aging have much influence.

The formation of heavy products by further aldol condensation of primary products is the main cause of catalyst deactivation. These products block active sites because they do not desorb readily. A large percentage of the sites becomes deactivated soon after the beginning of a run. As processing is continued, the rate of deactivation increases markedly. Regeneration of the catalyst is easily accomplished by treating it with hydrogen at 450°C: the heavy products are then desorbed and condensed materials evaporate. Although 30-50% of the deposits remain on the catalyst its activity is almost fully restored.

Addition of water to the ethanal feed substantially improves the selectivity and reduces the rate of deactivation. The main reaction as well as further aldol condensation are retarded and the equilibrium conversion becomes less favourable. Although the conversion decreases at otherwise unchanged conditions, addition of water is still advantageous because it is possible to apply much higher ethanal partial pressures. Thus, the process conditions can be adjusted in such a way that higher conversions combined with high selectivities can be attained, whilst catalyst deactivation is much reduced.
Similar results were obtained with the aldol condensation of butanal. The lower reactivity of butanal results in a higher selectivity and in slower deactivation of the catalysts.

On the basis of the data obtained in this study a commercial process for the production of butenal by heterogeneously catalyzed gas-phase aldol condensation is believed to be feasible. When water is added to the feed selectivities of more than 95% can be reached at an average conversion of 0.17, when using an ethanal partial pressure of 30 kPa at 250°C. The catalyst must be regenerated every 500 run hours. The addition of water does facilitate product recovery: most of the product stream condenses at 25°C because of the high partial pressures of products and water. The uncondensed gases can be scrubbed with water; the scrubbed gases contain only hydrogen, ethanal and water and can be recycled directly to the reactor.
In view of the above, it is concluded that a further technical and economic evaluation of this process is worthwhile.

SAMENVATTING

De stijgende prijzen van ruwe aardolie en de daaruit bereide grondstoffen voor industriële organische chemicaliën doen de belangstelling voor biomassa als grondstof toenemen. Een voor de productie van een aantal thans op etheen en propeen gebaseerde chemicaliën in aanmerking komende route maakt gebruik van de aldolcondensatie reactie van met name ethanal. In de huidige processen past men de homogeen gekatalyseerde aldolcondensatie in vloeistoffase toe. Vooral vanwege een betere procesbeheersing, verminderd katalysatorverbruik en een slechts geringe productie van afvalwater bieden heterogeen gekatalyseerde gasfaseprocessen in principe voordelen. Uit literatuurgegevens blijkt dat tin op silica katalysatoren zowel qua stabiliteit als selectiviteit goede perspectieven bieden. Deze dissertatie beschrijft dan ook een onderzoek naar bereiding en werking van deze katalysatoren, en naar de optimale procescondities voor de aldolcondensatie van ethanal naar 2-butenal. Ook worden resultaten gegeven voor de condensatie van n-butanal naar 2-ethylhexenal.

De bereidingsmethode en het type drager hebben een grote invloed op de activiteit van de katalysator, niet echter op selectiviteit en stabiliteit, voor zover het de silica dragers silicagel en aerosil betreft. Het gebruik van mordeniet als drager geeft zeer slechte katalysatoren.
Impregnatie van silicagel met waterige oplossingen van $SnCl_2$ aangezuurd met zoutzuur levert de beste resultaten op voor wat tindistributie en activiteit betreft. Tijdens het drogen van de geïmpregneerde drager ontstaat $SnCl_4$, dat reageert met oppervlaktehydroxylgroepen van de silica. De verhoogde temperatuur, bij drogen, speelt hierbij een duidelijke rol. Bij directe reactie met, opgelost of gasvormig, $SnCl_4$ worden bij kamertemperatuur slechts lage tinbeladingen verkregen en dus ook lage activiteiten. Bij gebruik van niet aangezuurde oplossingen van $SnCl_2$ vindt ionenuitwisseling plaats tussen Sn^{2+} en Na^+, dat nagenoeg altijd als verontreiniging in silicagel aanwezig is. Ook dit geeft een goede tindistributie en redelijke activiteit.
Gebruik van tinverbindingen die zeer sterk met de oppervlaktehydroxylgroepen reageren, zoals dibutyldimethoxytin, geeft slechte resultaten. Aan de buitenkant van een katalysatordeeltje ontstaat dan namelijk een zeer hoge tin-

concentratie, waardoor gemakkelijk agglomeratie van het tin optreedt, hetgeen de activiteit ongunstig beïnvloedt.
Het gedrag van de eveneens als drager toegepaste aerosils wijkt af van dat van silicagel: de aerosils blijken veel sterker met $SnCl_4$ te reageren en kunnen per oppervlakte-eenheid meer actief tin bevatten. Dit laatste is het duidelijkst waargenomen voor aerosils met een relatief gering specifiek oppervlak. De verschillen in oppervlaktestruktuur, met name voor zover het aantal en type hydroxylgroepen betreft, is hier waarschijnlijk de oorzaak van.

Aangetoond is dat het tin op de actieve (gereduceerde) katalysator in twee vormen aanwezig is: als onder reactiecondities gesmolten metallisch tin dat zich in de grotere poriën bevindt, en als tin(II) ionen die sterk aan het silica-oppervlak zijn gebonden. Deze aan zuurstofionen van het oppervlak gebonden tinionen vormen de actieve centra van de katalysator. De metaalionen en omringende zuurstofionen fungeren respectievelijk als zure en basische plaatsen, die tezamen zorgen voor activering van beide bij de reactie betrokken reactantmoleculen.

Uit kinetisch onderzoek blijkt dat bij temperaturen beneden 275°C de orde in ethanal 1.0 is en dat de activeringsenergie 33 $kJ.mol^{-1}$ bedraagt. Bij hogere temperatuur wordt respectievelijk 1.3 en 21 $kJ.mol^{-1}$ gevonden. Conclusies zijn dat de bezetting van de actieve plaatsen door één van de reactantmoleculen bij lage temperatuur praktisch kwantitatief is, en dat adsorptie van het tweede molecule snelheidsbepalend is voor de reactie. Bij stijgende temperatuur wordt de bezetting minder en gaat de oppervlakteconcentratie van beide moleculen een rol spelen.
Het kinetisch onderzoek van de butanal condensatie toont een orde van 0.75 in butanal en een activeringsenergie van 16 $kJ.mol^{-1}$ in het gehele onderzochte temperatuurgebied van 170-370°C. Een vergelijkbaar mechanisme als voor ethanal lijkt waarschijnlijk met sterke adsorptie van product, waardoor adsorptie en desorptie de reactiesnelheid bepalen.

De katalysatoren zijn zeer selectief voor aldolcondensatie reacties (>99%). Hoewel verdergaande condensatie de selectiviteit naar gewenst product doet dalen, blijken selectiviteiten hoger dan 95% zeer goed haalbaar. De invloed van de condities op de selectiviteit is gecompliceerd. De selectiviteit daalt bij toenemende temperatuur en toenemende conversie. Maar ook hebben concurrentie van reactanten en producten voor de actieve plaatsen en als gevolg van veroudering van de katalysator veranderende reactie-omstandigheden in de katalysatordeeltjes veel invloed.

De vorming van zware producten ten gevolge van verdergaande condensatie is de hoofdoorzaak van de veroudering van de katalysator. Deze producten blokkeren actieve plaatsen doordat ze nauwelijks desorberen. Een groot percentage van de actieve plaatsen wordt reeds in het begin van de reactie snel gedeactiveerd. Met de duur van het experiment daalt de snelheid van deactivering echter sterk. Regeneratie van de katalysator blijkt eenvoudig mogelijk door de katalysator bij 450°C met waterstof te behandelen waardoor zware producten desorberen en gecondenseerd materiaal verdampt. Hoewel 30-50% van de afzetting achterblijft in de katalysator wordt zodoende de activiteit vrijwel geheel hersteld.

Toevoegen van water aan de ethanalvoeding doet de selectiviteit sterk toenemen en de deactivering afnemen. De hoofdreactie en de verdergaande condensatie worden geremd en de evenwichtsligging wordt ongunstiger. Hoewel daardoor de conversie onder overigens gelijkblijvende omstandigheden daalt, is toevoeging van water toch gunstig omdat met veel hogere partiaaldrukken van ethanal kan worden gewerkt. Zodoende kunnen procescondities worden toegepast, waarbij toch een hogere conversie kan worden behaald met hoge selectiviteit en sterk vertraagde veroudering.
Voor de condensatie van n-butanal worden vergelijkbare resultaten verkregen. De lagere reactiviteit van n-butanal leidt tot hogere selectiviteit en een tragere deactivering van de katalysator.

Een commercieel proces voor de productie van butenal door heterogeen gekatalyseerde aldolcondensatie van ethanal in de gasfase lijkt op basis van de verkregen gegevens goed mogelijk. Bij toevoeging van water kan een selectiviteit van $\geq$95% worden bereikt bij een gemiddelde conversie van 0.17, een ethanal partiaalspanning van 30 kPa en een temperatuur van 250°C. Wel moet de katalysator om de 500 uur geregenereerd worden.
Watertoevoeging blijkt ook de productopwerking te verbeteren: door de relatief hoge partiaalspanningen van de producten condenseert het merendeel bij koeling tot 25°C. Het overblijvende gas bestaat na een waterwas uit waterstof, ethanal en water en kan worden gerecirculeerd naar de reactor.
Op grond van deze gegevens wordt geconcludeerd dat het de moeite waard is dit proces economisch en technisch nader te analyseren.

LIST OF SYMBOLS

B_r	partial pressure of 2-butenal/n-butanal in product stream	(kPa)
C_o	reactant concentration outside catalyst particle	(mol.m^{-3})
D_{eff}	effective diffusion constant	(m^2.sec^{-1})
d	diameter	(m)
E_r	partial pressure of ethanal in product stream	(kPa)
EH_r	partial pressure of 2-ethylhexenal in product stream	(kPa)
F	mole flow	(mol.h^{-1})
G	degree of deactivation (fraction of initial activity)	
H_r	partial pressure of water in product stream	(kPa)
IS	isomeric shift	(mm.sec^{-1})
k	reaction rate constant	(mol.h^{-1}.g cat^{-1}.kPa^{-n})
k_o	preexponential factor	(mol.h^{-1}.g cat^{-1}.kPa^{-n})
L	length of reactor	(m)
n	order of the reaction	
P	partial pressure	(kPa)
QS	quadrupole splitting	(mm.sec^{-1})
R_{pore}	pore radius	(nm)
r	reaction rate	(mol.h^{-1}.g cat^{-1})
r'	reaction rate	(mol.sec^{-1}.m^{-3})
S	selectivity (% of reactant converted)	
S_F	constant dependent on ratio of by-products	
S_{BET}	specific surface area	(m^2.g^{-1})
T	temperature	(K/^{o}C)
t	time	(h)
V_{pore}	specific pore volume	(cm^3.g^{-1})
W	catalyst weight	(g)
y	ratio of by-products	
ξ	conversion (fraction of initial amount of reactant)	

Catalyst codes

(see further table 2.2.1)

A,D	hydrogenic silicagel
F,G,S	pyrogenic silica powder (aerosils)
K,M	mordenites
.a	after impregnation and drying step
.b	after calcination step
.c	after reduction step
.d	after use in the reaction

REFERENCES

1 *Chem.Eng.* 1978, 85(27/2), 63.
2 *Chem.Age* 1977, (29/7), 16.
3 E.J. Wickson, H.P. Dengler; *Hydroc.Process* 1972, 51(11), 69-75.
4 F.A. Lowenheim, M.K. Moran; Faith, Keys and Clark's Industrial Chemicals, 4th ed. 1975. *(Wiley)*
5 M.A. Stadherr, D.F. Rudd; *Chem.Eng.Sc.* 1978, 33(7), 923-33.
6 H.E. Swift, J.E. Bozik; *J.Cat.* 1968, 12, 5-14.
7 H.E. Swift, J.E. Bozik, F.E. Massoth; *J.Cat.* 1969, 15, 407-16.
8 H.E. Swift (Gulf); U.S. pat. 3.542.878 (1970).
9 J.E. Bozik, H.E. Swift (Gulf); U.S. pat. 3.636.157 (1972).
10 S.W. Chun, F.E. Massoth, H.G. McIlvried (Gulf), U.S. pat. 3.948.991 (1976).
11 A.T. Nielsen, W.J. Houlihan; Organic Reactions, vol.6, 1968. *(Wiley)*
12 H.M. Stanley, G. Minkoff (Brit.Dist.); Brit. pat. 537.672 (1940).
13 A. Hann, A. Lapworth; *J.Chem.Soc.* 1904, 85, 46.
14 V. Franzen; *Chem.Ztg.* 1956, 80, 446-9.
15 A.A. Frost, R.G. Pearson; Kinetics and Mechanisms, 2nd ed. (1961).*(Wiley)*
16 R. Inoue, A. Ichikawa, K. Furukawa; *Kôgyô Kag.Zasski* 1957, 60, 33-37.
17 R.P. Bell; The Proton in Chemistry, 2nd ed. (1973).
18 A. Losse, F. Wolf, J. Muecke; *Fresenius' Z.Anal.Chem.* 1967, 232(3), 180-93.
19 V.S. Markevich; *Zh.Uses.Khim.Obshchest.* 1972, 17(2), 231-2.
20 L.P. Koshechkina, A.A. Yasnikov; *Ukr.Khim.Zh.* 1974, 40(9), 948-57.
21 K. Snyama, T. Nakanishi; *Agric.Biol.* 1978, 42(3), 507-13.
22 M. Iwata, S. Emato; *Bull.Chem.Soc.Jpn.* 1976, 49(5), 1369-74.
22a D. Walther, E. Dinjus; *Z.Anorg.Allg.Chem.* 1978, 440, 22-30.
23 H. Horiuchi, A. Hemmi; *Ekime, Daigaku Kiyo, Shizen Kagaku, C.Shirizu* 1972, 7(1), 1-4, *(CA80; 59112t)*.
24 D.A. Phipps; *Inorg.Chem.Acta* 1978, 27(2), L103-4.
25 K. Irie, K. Watanabe; *Chem.Lett.(Tokyo)* 1978, (5), 539-40.
26 H. Nozaki, K. Oshima, K. Takai, S. Ozawa; *Chem.Lett.(Tokyo)* 1979, (4), 379-80.
27 K. Maruoka, S. Hashimoto, Y. Kitagawa; *J.Am.Chem.Soc.* 1977, 99(23), 7705-7.
28 N. Yoshino, H. Akutsu; *Nippon Kagaka Kaishi* 1978, (5), 742-7.
29 P. Fellmann, J.E. Dubois; *Tetrahedon* 1978, 34(9), 1349-57.
30 J. Hanuise, R.R. Smolders; *Ing.Chim.(Brussels)* 1978, 60(288-289), 55-66.
31 K.K. Heng, R.A.J. Smith; *Tetrahedron* 1979, 35(3), 425-35.
32 H. Reiff; *Neuere Method.Praep.Org.Chem.* 1970, 6, 42-60.
33 R.A. Keimsch, W.E. Weesner (Monsanto); U.S. pat. 3.148.218, (1964).
34 C. Roming (Esso); U.S. pat. 3.153.673, (1964).
35 W.J. Porter, R.N. Watts, L.V. Robbins (Esso Res.); U.S. pat. 3.272.873, (1966).
36 C.S. Elliot (ICI); Brit. pat. 1.302.374, (1973).
37 K.A. Alekseeva, et.al.(6); *Khim.Promst.(Moscow)* 1976, (11), 811-3.
38 V.B. Del'nik, et.al.(7); S.U. pat. 667.540 (1976), (CA91:123397w).
39 K.A. Alekseeva, et.al.(4); *Neftep.Nepktektrim (Moscow)* 1977, (5), 28-9, *(CA88:6267f)*.
40 I.I. Ioffe, S.Z. Roginskii; *Zhur.Fiz.Khim.* 1957, 31, 612-625.

41 L. Beranek, M. Kraus; Comprehensive Chemical Kinetics (1978), vol.20, 263-266. *(Elsevier)*

42 S. Malinowski, H. Jedrzejewski, S. Basinski; *Rocznik Chem.* 1956, 30, 1129-38.

43 S. Malinowski, S. Basinski, S. Szczepanska, W. Kiewlicz; *Proc.Intern. Congr.Cat.3rd,* 1964, 1, 441-7.

44 W. Kiewlicz, S. Malinowski; *Bull.Acad.Pol.Sci., Ser.Sci.Chim.* 1969, 17(5), 259-62.

45 Kh.M. Minachev, O.K. Atal'yan, M.A. Markov; *Izv.Akad.Nauk.USSR, Ser.Khim.* 1978, (12), 2731-7.

46 C. Hugueny, L. de Morgues, Y. Trambouze, M. Prettre; *Bull.Soc.Chim.France* 1965, (2), 497-501.

47 R.P. Young, N. Sheppard; *J.Cat.* 1967, (7), 223-33.

48 E. Robinson, R.A. Ross; *J.Chem.Soc.,A* 1968, (9), 2137-41.

49 A.D. Makarov, G.K. Boreskov, V.A. Dzis'ko; *Kin.Cat.(USSR)* 1961, 2(1), 84-93.

50 S. Malinowski, S. Basinski, S. Szczepanska; *Intern.Chem.Eng.* 1965, (5), 426-428.

51 S. Malinowski, B. Zielinski; *Bull.Ac.Pol.Sci.Ser.Sci.Chim.* 1972, 20(11-12), 1015-9.

52 A.J. van Roosmalen; Ph.D.Thesis, Amsterdam 1980.

53 L. Alhéritière (Usines de Melle); U.S. pat. 2.489.608 (1949).

54 W.E. Heinz, A.F. MacLean (Celanese); U.S. pat. 3.077.500 (1963).

55 (Melle-Bezons); Fr. pat. 2.058.532 (1971).

56 (I.G. Farbe); Brit. pat. 298.349 (1927).

57 H.M. Guinot, L. Alhéritière (Usines de Melle); Fr. pat. 942.081 (1942).

58 F.J. Metzger (Air Reduction); U.S. pat. 2.376.070 (1943).

59 D.C. Hull (Eastman Kodak); U.S. pat. 2.468.710 (1944).

60 D.C. Hull (Air Reduction); U.S. pat. 2.428.846 (1943).

61 (BASF); Brit. pat. 660.972 (1951).

62 (Usines de Melle); Brit. pat. 761.203 (1956).

63 H.M.E. Guinot (Usines de Melle); U.S. pat. 2.096.637 (1935).

64 (Usines de Melle); Brit. pat. 579.047 (1940).

65 (Consort.f.Electrochem); Belg. pat. 452.221 (1943).

66 L. Alhéritière (Usines de Melle); U.S. pat. (1945).

67 M.L. Deem, K.CH. Stueben (U.C.); U.S. pat. 4.101.586 (1976).

68 P. Mimoun, Do Thao, I. Seree de Roch (Inst.Francais du Pétroles); Fr. pat. 2.287.434 (1976).

69 H.J. Hagemeyer (Eastman Kodak); U.S. pat. 2.639.295 (1953).

70 R.M. Cole (Chemical Elaborations); U.S. pat. 2.545.261 (1951).

71 F.A. Biribauer, C.S. Carlson, C.E. Morell (St.Oil); U.S. pat. 2.684.385 (1954).

72 H.J. Hagemeyer, H.M. Wright (Eastman Kodak); Brit. pat. 922.826 (1963).

73 (Celanese); Brit. pat. 833.666 (1955).

74 P. Mastagli, G.V. Durr; *Bull.Soc.Chim.France* 1955, 268-72.

75 (Chiso); Jap. pat.appl. 78.039.407 (1978).

76 E.N. Martinez, J.A. Lafraya, I.G. Blanco; Span. pat. 466.470 (1978).

77 R.M. Watts, W.J. Porter, J.A. Wingate, J.A. Hanau (Esso); Fr. pat. 1.344.591 (1963).

78 W.J. Porter, J.A. Wingate, J.A. Hanau (Esso Res.); U.S. pat. 3.248.428 (1966).

79 A. Hoffmann; Germ. pat. 229.678 (1909).

80 R. Leopold, B. Schacke (I.G. Farbe); Germ. pat. 591.316 (1934).

81 H.S. Mc.Allister, E.F. Ballard (De Bataafsche Petr.); Brit. pat. 502.450 (1939).

82 P. Godet (Usines de Melle); U.S. pat. 2.889.369 (1956).

83 F.M. Scheidt; *J.Cat.* 1964, 3(4), 372-8.

84 P. Sabatier, G. Gaudion; *Compt.Rendu* 1918, 166, 632-6.

85 Th. Odinga (Elektr.werk Lonza); Swiss pat. 87.758 (1920).

86 H. Adkins, K. Folkers, M. Kinsey; *J.Am.Chem.Soc.* 1931, 53, 2714-20.

87 M.Ya. Kagan, G.D. Lyubarskü, O. Podurovskaya; *Bull.Ac.Sci.USSR.Classe Sci. Chim.* 1947, 173-81.

88 W.M. Quattlebaum, W.J. Toussaint, J.T. Dunn; *J.Am.Chem.Soc.* 1947, 69, 593-9.

89 H.F.A. Topsøe, A. Nielsen (Stockholms Superfosfat Fabr.); Swed. pat. 124.737 (1949).

90 H.E. Jones, E.E. Stahly, B.B. Corson; *J.Am.Chem.Soc.* 1949, 71, 1822-8.

91 H.A. Mottern, V.F. Mistretta (St.Oil, Delaware); U.S. pat. 2.530.987 (1950).

92 R. Nodzu, S. Kunichika; *J.Chem.Soc.Jap., Ind.Chem.Sect.* 1954, 57, 914-6.

93 J.F. Gabbett (Escambia); U.S. pat. 2.810.760 (1957).

94 A.A. Baladin, N.P. Sokolova; *Izvest.Ak.Nauk.SSSR.Otdel.Khim.Nauk.* 1959, 949-50, *(CA54:1279f)*.

95 S. Malinowski, J. Jedrzejewska, S. Basinski; *Chim.Ind.* 1961, 85, 885-96.

96 Z. Czarny; *Chem.Stosowana, Ser.A.* 1963, 7(4), 609-19.

97 V. Nagarajan, N.R. Kuloor; *Indian J.Techn.* 1966, 4, 46-54.

98 J.A. Paine, L.D. Hinson (Celanese); U.S. pat. 3.450.769 (1965).

99 G. Fabbri, G. Lodi; *Ann.Chim.(Roma)* 1968, 58(5), 546-50.

100 V. Macho (Vyzkumny Ustov pro Petrochemin); Ger. pat. 2.023.512 (1969).

101 Yu.A. Gorin, N.A. Rozenberg; *Zh.Prikl.Klim.(Leningrad)* 1970, 43(10), 2301-8.

102 W.Th. Reichle (U.C.); Deutsches Offen. 2.705.857 (1977).

103 M. Marczewski, S. Malinowski; *Bull.Ac.Pol.Sci.Ser.Sci.Chim.* 1976, 24(1), 1-5.

104 K. Hoshiai; *J.Chem.Soc.Japan* 1953, 56, 381-3.

105 A. Rothaus (BASF); Ger. pat. 943.406 (1956).

106 Ya.I. Isakov, Kh.M. Minachev, N.Ya. Usachev; *Izv.Akad.Nauk.SSSR, Ser.Khim.* 1972, (5), 1175-7.

107 V.I. Komarewsky, T.H. Kritchevsky; *J.Am.Chem.Soc.* 1943, 65, 547-8.

108 L.V. Robbins, W.J. Porter (Esso); U.S. pat. 3.361.828 (1962).

109 V. Macho, M. Polievka, Fr. Gregor; Czech. pat. 122.761 (1965).

110 Yu.T. Hwang, W.A. Krever, W.J. Sanduer (Union Oil Calif.); U.S. pat. 3.301.912 (1965).

111 J. Fox, D.A. Lawton, L.E. Cooper, M.L. Sutcliffe (Distillers); Ger. pat. 1.232.942 (1967).

112 V. Macho, M. Polievka, M. Filadelfyova; Czech. pat. 162.295 (1969).

113 (Shell); Dutch pat.appl. 70.14.622 (1970).

114 Y. Watanabe, Y. Matsuzuma, A. Izumi, Y. Mizutani;
- *J.Cat.* 1975, 40(1), 76-85.
- (Tokuyaura Soda), Jap. pat. 77.15.576 (1977).

115 A.A. Shammarova Kh.R. Rustamov; *Deposited Doc. 1976, VINITI* 2370-76, *(CA:108004f)*.

116 Y. Mizutami, A. Izumi, Y. Watanabe (Tokuyama Soda); Jap. pat. 77.46.922.

117 W.J. Porter, E.B. Ellerbe (Esso); U.S. pat. 3.153.068 (1960).

118 F. Wolf, A. Losse, J. Muecke; *J.Prakt.Chem.* 1971, 313(1), 145-52.

119 J. Wiemann, L. Martineau, J. Tiquet; *Compt.Rendu* 1955, 241, 807-8.

120 A. Losse, J. Wilke, Fr. Wolf; *Chem.Tech.(Berlin)* 1968, 20(7), 422-5.

121 H.O. Mottern (Stand.Oil); U.S. pat. 2.549.508 (1951).

122 T.C. Snapp, A.E. Blood, H.J. Hagemeyer (Eastman Kodak); U.S. pat. 3.701.798 (1972).

123 T. Ichikawa, T. Kamio; *Yaki Gasei Kagaku Kyokaishi* 1962, 20, 56-61, *(CA56:11433a)*.

124 I. Ichikawa; *Rept.Govt.Chem.Ind.Res.Inst.Tokyo,* 1954, 40, 387-90.

125 S. Malinowski, W. Kiewlicz, E. Soltys; *Bull.Soc.Chim.France* 1963, 30, 439-44.

126 W. Droste, F. Obenaus; *Mon.Hefte Chem.* 1973, 104, 485-95.

127 A. Nissen, G. Heilen (BASF); Deutsches Offenl. 2.625.541 (1977).

128 T. Isoshima; *Bull. Inst.Chem.Res.Kyoto Univ.* 1954, 32, 168-78.

129 T. Miyake, K. Noguchi, K. Imamura (Asahi); Deutsches Offenl. 2.746.177 (1978).

130 G.K. Boreskov; Preparation of Catalysts, ed. B. Delmon, (1976), pp 224-250. *(Elsevier)*

131 L.A.M. Hermans, J.W. Geus; Symp.pap. Scientific bases for the preparation of heterogeneous catalysts, sec.int.Symp., Louvain-la-Neuve, 1978, pp B2.1-16.

132 V.B. Fenelov, A.V. Neimark, L.I. Kleifets, A.A. Samakhov; *As (131)*, pp C2.1-10.

133 B. Delmon, M. Houalla; *As (131)*, pp E1.1-26.

134 N.K. Bebris, A.V. Kiselev, Yu. Nikitin; *Coll.J.USSR* 1967, 29, 244-8.

135 N.K. Bebris, A.V. Kiselev, Yu.S. Nikitin; *Coll.J.USSR* 1978, 40(1), 6-11.

136 R.M. Barrer, J.Chr. Trombe; *J.Chem.Soc., Far.Trans I* 1978, 74(11), 2786-806.

137 J.R. Kiovsky, W.J. Gayette, Th.M. Natermann; *J.Cat.* 1978, 52(1), 25-31.

138 S. Vishnoi; *Chem.Ind.Dev.* 1977, 11(50), 15-26.

139 B. Coughlan, W.M. Carroll, Th.C. Kelly; *Chem.Ind.* 1978, (10), 167-8.

140 A.J. van Roosmalen, J.C. Mol; *J.Phys.Chem.* 1978, 82, 2748-51.

141 A.J. van Roosmalen, J.C. Mol; *J.Phys.Chem.* 1979, 83, 2485.

142 G.E. Berendsen, L. de Galan; *J.Liq.Chromatogr.* 1978, 1, 403.

143 D. Barby; Charact.Powder Surf., ed. G.P. Parfitt, K.S.W. Sing, 1976, pp 353-425. *(Ac.Press)*

144 H.P. Boehm, G. Kämpf; *Z.Physik.Chem.(N.F.)* 1960, 23, 257-66.

145 S.A. Mitchell; *Chem.Ind.* 1966, 924-33.

146 C. Okkerse; Physical and chemical aspects of adsorbents and catalysts, ed. B.G. Linsen, 1970, pp 213-264. *(Ac.Press)*

147 A.V. Kiselev, V.I. Lygin; Infrared Spectra of Surface Compounds, 1975, pp 75-122. *(Wiley)*

148 B.E. Wagner, J.N. Helbert, E.H. Poindexter; *Surf.Sci.* 1977, 67, 251-68.

149 J.H. de Boer, J.M. Vleeskens; *Proc.Koninkl.Ned.Acad.Wet.* 1958, B61, 2-11.

150 J.B. Peri, A.L. Hensley; *J.Phys.Chem.* 1968, 72(8), 2926-33.

151 J.A. Hockey; *Chem.Ind.* 1965, (2), 57-63.

152 J.A. Hockey, B.A. Pethica; *Frans.Far.Soc.* 1961, 57, 2247-62.

153 H.P. Boehm, M. Schneider, F. Arendt; *Z.Anorg.Allgem.Chem.* 1963, 320, 43-53.

154 A.P. Dushina, V.B. Aleskovskii, L.V. Ponomareva; *Zh.Prikl.Khim. (Leningrad)* 1977, 50(9), 1949-50.

155 R.L. Burwell; *Chem.Tech.* 1974, 4(6), 370-7.

156 Fr. Janowski, W. Heyer; *Z.Chem.* 1979, 19(1), 1-11.

157 R.L. Burwell, R.G. Pearson, G.L. Haller; *Inorg.Chem.* 1965, 4, 1123-8.

158 B. Horvath, J. Strutz, R. Moeseler, E.G. Horvath; *Z.Anorg.Allg.Chem.* 1979, 449, 5-24.

159 H.L. Krauss, D. Naumann; *Z.Anorg.Allg.Chem.* 1977, 430, 23-37.

160 V. Hronsky, M. Rakos, J. Belak; *Czech.J.Phys.* 1978, B28(11), 1277-86.

161 S.Ya. Tret'yakov, L.M. Sharygin, Yu.V. Egorov; *Kinet.Katal.* 1976, 17(1), 264.

162 R.R. Rachovskii, S.I. Kol'tsov, V.B. Aleskovii; *Russ.J.Inorg.Chem.* 1970, 15(11), 1646-7.

163 P. Fink, B. Camara, E. Welz, Ph. Dinh Ty; *Z.für Chemie* 1971, 11(12), 473-4.

164 S. Gobom; *Acta Chem.Scand.* 1976, A30, 745-50.

165 A.B. Garrett, R.E. Heiks; *J.Am.Chem.Soc.* 1941, 63(2), 562-7.

166 L.R. Allison, E.J. Hartung, E. Heymann; *J.Phys.Chem.* 1940, 44, 1033-7.

167 R.S. Tobias, Z.Z. Hugus; *J.Phys.Chem.* 1961, 65, 2165-9.

168 V.A. Nazarenko, V.P. Antonovich, E.M. Nevskaya; *Russ.J.Inorg.Chem.* 1971, 16(7), 980-2.

169 J.C.P. Broekhoff; Ph.D.Thesis, Delft, 1969.

170 J.C.P. Broekhoff; Symp.pap. Scientific bases for the preparation of heterogeneous catalysts, 2nd Int.Symp., Louvain-la-Neuve, 1978, pp N2.1-21.

171 Gmelin , Sn:46; C1; 228-229, 244; B; 384-387, 398-399.

172 R. Leboda; *J.Therm.Anal.* 1978, 13(2), 213-22.

173 N.V. Akshinskaya, A.V. Kiselev, Yu.S. Nikitin; *Russ.J.Phys.Chem.* 1963, 37(4), 491-492.

174 M.J.L. van Beem, W.H.J. Stork (Shell); Deutsches Offenl. 2.753.393 (1978).

175 R. Harsono, W.H.J. Stork (Shell); Deutsches Offenl. 2.753.392 (1978).

176 W.G. Schlaffer, C.R. Adams, J.N. Wilson; *J.Phys.Chem.* 1965, 69, 1530-6.

177 B. Imelik, Y. Carteret; *Bull.Soc.Chim.France* 1951, 18, 864-7.

178 S. Kondo, M. Muroya; *Bull.Chem.Soc.Jap.* 1970, 43(8), 2657.

179 M. Muroya, S. Kondo; *Bull.Chem.Soc.Jap.* 1970, 43(10), 3454-6.

180 C. Mougey, J. François-Rossetti, B. Imelik; Proc. 10th Symp.Colston Res.Soc. 1958, 266-94.

181 J. Godon-Renou, J. François-Rossetti, B. Imelik; *Bull.Soc.Chim.France* 1962, 29, 816-22.

182 J.C. Platteeuw; Ph.D.Thesis, Delft, 1953.

183 F.C. Platteeuw, G. Meyer; *Frans.Far.Soc.* 1956, 52, 1066-73.

184 J.D. Donaldson; *Progr.Inorg.Chem.* 1967, 8, 287-356.

185 P. Spinedi, F. Gauzzi; *Annali Chim.* 1957, 47, 1305-15.

186 C.G. Fink, C.L. Mantell; *Trans.Am.Electrochem.Soc.* 1927, 51, 429-44.

187 I.P. Suzdalev, A.S. Plachinda, E.F. Makarov; *Soviet.Phys.-JETP* 1968, 26(5), 897-900.

188 Gmelin ,46 Sn; C1; 42-4, 98-9; B; 347-51.

189 V.I. Goldanski, I.P. Suzdalev; *Russ.Chem.Rev.* 1970, 39(7), 609-25.

190 I.P. Suzdalev, V.I. Gol'danskii, E.F. Makarov; *Soviet Phys.-JETP* 1966, 22, 979.

191 V.I. Gol'danskii, R.H. Herber; Chemical Applications of Moessbauer Spectroscopy, 1968. *(Ac.Press)*

192 A.A. Bekker, A.M. Babeshkin, K.V. Pikholov, A.N. Nesmeyanov; *Vestn.Mosk.Univ.Ser.Khim.* 1967, 22(6), 83-4.

193 P.B. Weisz, C.B. Prater; *Adv.Catal.* 1954, 6, 143-196.

194 D.E. Mears; *Ind.Eng.Chem.Process.Des.Dev.* 1971, 10(4), 541-7.

195 J.B. Butt, V.W. Weekman; *A.I.Ch.E.Symp.Ser.No.143,* 1974, 70, 27-41.

196 N.A. Rozenberg, Yu.A. Gorin, A.V. Koroleva; *J.Appl.Chem.USSR* 1968, 41, 1215-9.

197 J. Wiemann, Sa-Le Thi Thuan, J.M. Conia; *Bull.Soc.Chim.France* 1957, 908-12.

198 J. Wiemann, L. Martineau, J. Tiquet; *Bull.Soc.Chim.France* 1958, 884-5.

199 K.J. Laidler, M.T.H. Liu; *Can.J.Chem.* 1968, 46, 479-90.

200 K.J. Laidler, M.T.H. Liu; *Proc.Roy.Soc.* 1967, A297, 365-75.

201 G. Ferraiolo, D. Beruto; *Ing.Chim.Ital.* 1969, 5(12), 165-70.

202 M. Del Borghi, G. Ferraiolo, M. Giordani; *Ing.Chim.Ital.* 1971, 7(10), 144-9.

203 G. Ferraiolo, A. Peloso, M. Del Borghi; *Ing.Chim.Ital.* 1971, 7(11), 151-5.

204 J.J. Carberry; *Chem.Eng.Sc.* 1962, 17, 675-81.

205 S. Malinowski, S. Basinski; *Bull.Ac.Pol.Sc.Ser.Chim.* 1963, 11(2), 55-61.

206 T. Kawaguchi, S. Hasegawa, S. Kawamata; *Tokyo Gakuchi Daigaku Kiyo* 1970, 22, 47-51 *(CA 74:6853e)*.

207 P. Beltrame; *Gazz.Chim.Ital.* 1960, 90, 239-46.

208 V. Nagarajan; *Ind.J.Techn.* 1971, 9, 380-6.

209 K. Kato, H. Arai, U. Ito; *Adv.Chem.Ser.* 1974, 133, 271-80.

210 V.S. Ivanov, N.M. Maksikowa; *J.Gen.Chem.USSR* 1960, 30(10), 3140-2.

211 H. Weber; *Z.Anorg.Allg.Chem.* 1959, (301), 109-12.

212 Gmelin , 46 , Sn; C2, 347-51.

213 R. Bacaud, P. Bassiere, F. Figueras, J.P. Mathieu; Prep.of Cat., ed. B. Delmon, 1976, 509-23. *(Elsevier)*

214 D.V. Sokol'skii, V.F. Vozdvizhenskii, A.Sh. Kuanyshev, A.V. Kobets; *React.Kin.Cat.Lett.* 1976, 5(2), 163-8.

215 R.P. Young, N. Sheppard; *J.Cat.* 1971, 20, 340-9.

216 S.N.W. Cross, C.H. Rochester; *J.Chem.Soc., Far.Trans.1* 1978, 74(8), 2130-40.

217 D.M. Griffiths, K. Marshall, C.H. Rochester; *J.Chem.Soc., Far.Trans.1* 1974, 70, 400-10.

218 A.V. Kiselev; *Dokl.Akad.Nauk.SSSR* 1956, 106, 1046-9.

219 J. Haber, H. Piekarska, T. Romotowski; *Bull.Ac.Pol.Sc., Ser.Sc.Chim.* 1978, 26(12), 967-74.

220 D.M. Griffiths, C.H. Rochester; *J.Chem.Soc., Far.Trans.1* 1978, 74(2), 403-17.

221 H. Knozinger; *Forschungsber.Wehrtech. (Luft-, Raumfahrt, T.2)* 1976, 53-9.

222 M.J.D. Low, H. Jacobs, N. Takerowa; *Water, Air, Soil Pollut.* 1973, 2(1), 61-73.

223 F. Wolf, A. Losse, J. Muecke; *J.Prakt.Chem.* 1971, 313(1), 137-44.

224 V.A. Kargin, N.A. Plate, I.A. Litvinov; *Vysokom.Sved.* 1961, 3, 1091-99.

225 G. Fabbri, G. Farne; *Atti Ac.Nazl.Lincei, Rend.Sci Fiz.Mat.Nat.* 1966, 40(3), 406-10.

226 P. Ganguly; *Proc.Indian Ac.Sc., Sect.A* 1977, 86A(1), 65-79.

227 K. Tanabe; Solid acids and bases, 1970. *(Ac.Press)*

228 R.C. Reid, T.K. Sherwood; The properties of gases and liquids, 2nd ed. 1966. *(McGraw-Hill)*

229 S.W. Benson; Thermochemical kinetics, 2nd ed. 1976. *(Wiley)*

230 C.J. Dobratz; *Ind.Eng.Chem.* 1941, 33, 759-62.

231 D.R. Stull, E.F. Westrum, G.C. Sinke; The chemical thermodynamics of organic compounds, 1969. *(Wiley)*

232 J. Tjebbes; *Pure Appl.Chem.* 1961, 2, 129-32.

233 J.H.S. Green; *Quart.Rev.* 1961, 15, 125-52.

234 J.D. Cox, G. Pilcher; Thermochemistry of organic and organometallic compounds, 1970. *(Ac.Press)*

235 S.W. Benson, et.al.; *Chem.Rev.* 1969, 69, 279-324.

236 D.W. van Krevelen, H.A.G. Chermin; *Chem.Eng.Sc.* 1951, 1(2), 66-80.

237 K. Hauffe, G. Micus (Hoechst); Ger. pat. 1.075.104 (1960).

238 F. Büttner, X. Gregory (Wacker Chemie); Ger. pat. 1.206.878 (1965).

239 V. Macho; Czech. pat. 131.903 (1969).

APPENDIX I. Derivation of the relations used for calculation of conversion and selectivity

As is discussed in 3.4.1 virtually all by-products are formed by condensation of three and four molecules ethanal. The following reactions are therefore of interest:

(i) 2 ethanal → butenal + water (in code: $2E \rightarrow B + H$)

(ii) butenal + ethanal → hexadienal + water (in code: $B + E \rightarrow F_{(B+H)} + H$)

(iii) 2 butenal → tolualdehyde/octatrienal + water (in code: $2B \rightarrow F_{(B+B)} + H$)

The amount of hydrogen produced in reaction (iii) is neglected. Furthermore, the formation of an octatrienal by reaction of hexadienal and ethanal is incorporated in reaction (iii). The result, formation of a C_8 and 3 water from 4 ethanal, is the same. It is further assumed that the mixture shows ideal gas behaviour.

The following indices are used:

O: refers to molar amounts before reaction

i: refers to molar amounts which would be expected if the condensation is fully selective

r: refers to quantities actually present in the product stream

It is now possible to derive as mole balances:

$$E_O = E_r + 2B_r + 3F_{(B+E)} + 4F_{(B+B)} \tag*{1)}$$

$$B_i = B_r + F_{(B+E)} + 2F_{(B+B)} \tag*{2)}$$

$$H_r = B_i + F_{(B+E)} + F_{(B+B)} = B_r + 2F_{(B+E)} + 3F_{(B+B)} \tag*{3)}$$

The total amount of by-products is:

$$F_r = F_{(B+E)} + F_{(B+B)} \tag*{4)}$$

Combination of these leads to:

$$E_O = E_r + B_r + H_r + F_r \tag*{5)}$$

Because it is not possible to measure the amount of by-products on-line for each single sample, this value must be calculated from the available data. The difference between the actual amount of water and butenal in the product gas, i.e. $H_r - B_r$, is essential; it can be calculated by combination of 2), 3) and 4):

$$H_r - B_r = 2F_{(B+E)} + 3F_{(B+B)} \qquad 6)$$

Furthermore it is necessary to know the ratio between $F_{(B+B)}$ and $F_{(B+E)}$:

$$y = F_{(B+B)} / F_{(B+E)}$$

With this ratio one can derive the amount of by-products formed as:

$$F_r = S_F * H_r - S_F * B_r \qquad 7)$$

with $S_F = (1+y) / (2+3y)$

The fractional conversion and the percentage selectivity are defined as:

$$\xi = 1 - E_r/E_O$$

$$S = 2 * B_r / (E_O - E_r) * 100$$

After insertion with the above equations one finds:

$$\xi = \left[(1-S_F)B_r + (1+S_F)H_r\right] / \left[E_r + (1-S_F)B_r + (1+S_F)H_r\right]$$

and:

$$S = 200 * B_r / \left[(1-S_F)B_r + (1+S_F)H_r\right]$$

To use these equations S_F has to be known for each sample. Since this quantity is unknown it must be estimated. An indication for the extreme can be found, considering that y varies between zero and unity (c.f. table 3.4.1). This leads to a value of S_F in the range 0.4 - 0.5. Since S_F does not vary much, it was taken to be 0.45 for the conditions encountered during the aldol condensation of ethanal.

In an analogous manner the following equations can be derived for the condensation of n-butanal (B) to 2-ethylhexenal (EH):

$$\xi = \left[(1-S_F)EH_r + (1+S_F)H_r\right] / \left[B_r + (1-S_F)EH_r + (1+S_F)H_r\right]$$

and

$$S = 200 * EH_r / \left[(1-S_F)EH_r + (1+S_F)H_r\right]$$

In this case, the value 0.5 was taken for S_F.

APPENDIX II. Approximation of thermodynamic data for the products of gas-phase aldol condensation, to calculate equilibrium conversion and heats of reaction.

The heat of formation of reactants and products must be known to calculate the heat of reaction of the gas-phase aldol condensation of ethanal and n-butanal. Moreover, the Gibbs free energies of formation of the compounds involved in these reactions are required to calculate equilibrium conversions as a function of the temperature. The methods employed are outlined below.

Thermodynamic values for ethanal, n-butanal and water are known (231), but hardly any of butenal and none of 2-ethylhexenal and the products formed by further aldol condensation. Many approximation methods, however, are available for calculating the necessary values, but all show certain shortcomings (228, 229, 230, 235, 236).
For the calculation of ΔG_f one can use either a direct method, in the form of group contribution methods, or via the estimates of ΔH_f, S^0 and $C_p(T)$. Comparison between the results of such calculations and known data, in the literature, showed that approximation via the component values of ΔH_f, S^0 and $C_p(T)$, will lead to acceptable results for ΔG_f if the method of Benson (235) is used in calculating $C_p(T)$ and that of Anderson (228) for S^0. These methods also gave the best agreement between calculated and measured values of ΔH_f for butenal. As data on the conjugational effect of the C=C-C=O group are unavailable, the value for the C=C-C=C group was taken into account. The error introduced in this way cannot be estimated in any way. For comparison, the often used group contribution method van van Krevelen and Chermin was also applied. Here too the conjugational effect of C=C-C=O had to be estimated.

Table II.1 contains the known data on the heat of formation of 2-butenal. A value of $-100\ \mathrm{kJ.mol^{-1}}$ was applied in the calculations because it is the most recent given value and appears the best documented. The standard heat of reaction of the aldol condensation of ethanal found with this value is $-13\ \mathrm{kJ.mol^{-1}}$; the dependence of the heat of reaction on the temperature is shown in table II.2. It should be noted that the approximations involved make it necessary to measure the heat of conversion directly for purposes of reactor design.

The calculated Gibbs free energy of reaction for the aldol condensation of ethanal and n-butanal are given in figures 3.4.3 and 6.3.4 respectively. Tables 4.1.1 and 6.1.1 give the respective calculated equilibrium conversions.

TABLE II.1 Thermochemical data for 2-butenal

		$(kJ.mol^{-1})$		
1)	$\Delta H_{f,298}(l)$	-143.3 ± 0.4	(231, 232, 233)	1961
2)	id	-137.8 ± 1.8	(234)	1970
3)	$\Delta H_{f,298}(g)$	-99.9 ± 1.5	(234)	1970
4)	$\Delta H_{evaporation}$	37.8 ± 0.8	(231)	
5)	$\Delta H_{hydrogenation,298}(g)$	103.6 ± 0.4	(231)	
6)	$\Delta H_{f,298}(g)$ butanal	-203.8	(231)	

ABLE II.2 ΔH_r for the gas-phase aldol condensation of ethanal and n-butanal t different temperatures $(kJ.mol^{-1})$

(K)	300	400	500	600	700	800
thanal condensation	-13	-11	-11	-10	- 9	- 9
ı-butanal condensation	-24	-24	-23	-22	-22	-21

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STELLINGEN

1 Schijnbare autokatalyse tijdens de gasfase aldolcondensatie lijkt beter te verklaren door een initiëel sterk toenemende selectiviteit ten gevolge van vergiftiging van te actieve plaatsen die volgreacties bevorderen of van plaatsen die snelle nevenreacties katalyseren; de methode van conversie bepaling is essentiëel in dit verband.
S.Malinowski ;Chim. Ind. 1961, 85, 892

2 Bij de verklaring van de vorming van een gechloreerd silica oppervlak tijdens de reactie van vluchtige metaalchloriden met silica houden Hair en Hertl ten onrechte geen rekening met het ontstaan van silicium oppervlakteradicalen tijdens de voorbehandeling van de silica op 800°C.
M.L.Hair, W.Hertl ;J.Phys. Chem. 1973, 77, 2070-5

3 In hun beschouwing betreffende de deactivering en selectiviteitsverandering van een silica-alumina katalysator tijdens de gasfase aldolcondensatie van ethanal nemen Ferraiolo en medewerkers ten onrechte mogelijke parallelle reacties van ethanal niet in beschouwing.
G.Ferraiolo,M.DelBorghi,M.Giordani;Quad.Ing.Chim.Ital. 1971,7(10),144-9

4 Het door Badilla-Ohlbaum en medewerkers voorgestelde mechanisme voor de hydrogenering van benzeen over ijzer, waarbij 6 geadsorbeerde waterstofatomen gelijktijdig met 1 geadsorbeerd benzeenmolecule reageren, is niet realistisch; door desorptie van cyclohexaan als snelheidsbepalende stap te nemen kan de gevonden reactiesnelheidsvergelijking beter worden verklaard.
R.Badilla-Ohlbaum,H.J.Neuberg,W.F.Graydon,M.J.Phillips;J.Cat. 1977,47,273-9

5 Bij zeer nauwkeurige kwantitatieve gaschromatografische bepalingen met behulp van warmtegeleidbaarheidsdetectoren mag niet worden uitgegaan van zuiver lineaire verbanden tussen concentratie en detectiesignaal.
D'Ans-Lax, Taschenbuch für Chemiker und Physiker, 1^{er} Band, 3^{e} Auflage
R.T.Wittebrood ; Chromatographia 1972, 5, 454

6 Het op grote schaal toepassen van biomassa als grondstof voor energie en chemicaliën kan voor veel ontwikkelingslanden uitlopen op de tweede sociaal-economische ramp na de oliecrisis.

7 Onderzoek naar verbeterde sigarettenfilters is een typisch voorbeeld van symptoombestrijding bij de aanpak van de vele structurele problemen waarmee de wereld kampt en van de verspilling die daarmee gepaard gaat.
Brits octrooi 2.026.842 en 1.541.235, Duits octrooi 2.902.118/19/20 (allen in 1979 toegekend)

8 Suiker is altijd al dé energiedrager van elk organisme geweest.

9 Registratie van huisdieren door middel van een getatoeëerd nummer als controle en rem op misbruik van dieren, zal de ellende van de dieren enkel vergroten.

10 Het de gehuwde vrouw moeilijk maken haar eigen naam te voeren moet beschouwd worden als een wetsovertreding.
Burgelijk wetboek art. 1.6 ;art 1.9.-1

11 Wetenschap en techniek nemen door eigen nalatigheid in onze samenleving een merkwaardig geïsoleerde positie in.

12 In het algemeen kan worden gesteld dat de gemiddelde bekwaamheid in organisaties omgekeerd evenredig is met de grootte van de organisatie; zie bijvoorbeeld politieke partijen .

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20 november 1980