Influence of H_2 on the oxygen-assisted dehydrogenation of ethane over Al_2O_3-supported Pt-Sn catalysts

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Abstract

The oxygen-assisted dehydrogenation of ethane at 650 ºC shows that adding Sn to the Pt catalyst results in increased conversion and selectivity to ethylene. Even the smallest amount of tin (0.16 wt%) has a significant effect. The addition of tin also increases the stability of the Pt/Al_2O_3 catalyst, in particular it reduces the amount of carbon or carbonaceous species. Adding hydrogen to the feed had a remarkable effect on the selectivity, but the conversion of ethane was almost unaffected for Pt-Sn catalysts. The selectivity to ethylene increased substantially and the selectivity to CO/CO_2 decreased even for the smallest amount of tin used. Unexpected values for the selectivity to other compounds were also observed, in particular for the selectivity to acetylene. The importance of possible Pt-Sn alloys or the necessity of contact between Pt and Sn was studied using a physical mixture of Pt/Al_2O_3 and Sn/Al_2O_3. However, almost the same effect was obtained by using the physical mixture as with the co-impregnated sample, i.e. the Pt-Sn catalysts

Keywords: Ethane; Ethylene; Oxygen-assisted dehydrogenation; Pt-Sn catalysts
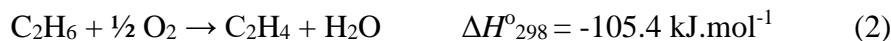
1. Introduction

Light olefins are important intermediates in many chemical processes and homogeneous steam cracking carried out in large units is the main process for synthesis of lower olefins:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad \Delta H^o_{298} = + 136.4 \text{ kJ.mol}^{-1} \qquad (1)$$

In order to shift the equilibrium towards the formation of ethylene and hydrogen, the reaction must be carried out at high temperatures (above 1000 K) [1].

Oxygen-assisted dehydrogenation (ODH) of C_2-C_4 alkanes has been proposed as an interesting alternative for the production of the corresponding olefins [2]. It offers several advantages such as short contact time, adiabatic operation and smaller reactor volumes and it could possibly also be carried out in smaller units [3].

Depending on the process conditions, oxidative dehydrogenation of ethane (or C_3-C_4 alkanes) may give high yields of olefins, high yields of olefins + synthesis gas or high yields of synthesis gas [3], [4], [5].

$$C_2H_6 + \tfrac{1}{2} O_2 \rightarrow C_2H_4 + H_2O \qquad \Delta H^o_{298} = -105.4 \text{ kJ.mol}^{-1} \qquad (2)$$

$$C_2H_6 + O_2 \rightarrow 2 CO + 3 H_2 \qquad \Delta H^o_{298} = -137.0 \text{ kJ.mol}^{-1} \qquad (3)$$

Oxidative dehydrogenation of ethane can be carried out at lower temperatures than used in present steam crackers and it shifts the reaction from being endothermic Eq. (1) to exothermic Eq (2). It has been reported that oxidative dehydrogenation of ethane may give ethylene yields

comparable of steam cracking. The addition of oxygen at elevated temperatures has also the ability to largely reduce the amount of coke formed during the process.

In the same way as for steam cracking, a reduction in the residence time will also for oxidative dehydrogenation lead to a decrease of unwanted side reactions, while the reactor and catalyst can be maintained at elevated temperatures. The short contact time reactors for oxidative dehydrogenation have been pioneered in particular by Schmidt and co-workers [6], [7].

Besides the addition of oxygen to eliminate the thermodynamic limitations, hydrogen might be added as well. This increases the complexity of the whole process even further, but it seems to have a significant positive effect on the ethylene selectivity whereas the ethane conversion seems hardly affected [8], [9]. The effects of hydrogen are manifold, both directly and indirectly. The direct influence can be seen in shifts of equilibria like the ones given in (1), (4) and (5):

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad \Delta H^o_{298} = + 175.0 \ kJ.mol^{-1} \qquad (4)$$

$$C_2H_6 + H_2 \rightarrow 2 \ CH_4 \qquad \Delta H^o_{298} = + 136.4 \ kJ.mol^{-1} \qquad (5)$$

Hydrogen limits the dehydrogenation reactions towards ethylene and acetylene and increases the selectivity towards methane [4], [8], [10]. Although this does not seem to be positive for the ethylene selectivity, additional hydrogen also limits polymerization reactions of ethylene and acetylene, either by lowering the concentration of these olefins or by hydrogenolysis and cracking of larger hydrocarbons. At the same time hydrogen has the ability to hydrogenate coke and coke-like species, such as partially or fully dehydrogenated and adsorbed C_1, C_2 and

C$_3$ derivatives, which in turn limits problems arising from coking and fouling. Secondly, hydrogen can react with either oxygen to form water or oxygenates like aldehydes and ketones to form alcohols and in turn olefins and water which decreases the oxygen concentration in the gas feed.

The ODE process can be run either as a gas phase reaction similar to steam cracking, i.e. at elevated temperatures and short residence times, or as a catalytic reaction at either short or long contact times, depending on the operation temperature [2]. Due to the complexity of oxygen-assisted dehydrogenation reactions, the development of catalytic systems for this particular type of reaction has become just as wide and complex as its purpose, namely finding a catalytic system that resists both coking and total combustion while maintaining a high conversion of reactants and a reasonable yield of the desired products. The majority of the catalysts are based on metal oxides, either modified alkaline earth metal oxides or transition metal oxides [3]. Rare earth metal oxides, perovskites, noble metal catalysts and zeolites are amongst the other types of catalysts for oxygen-assisted dehydrogenation.

In oxidative dehydrogenation of ethane (ODE), homogeneous gas phase reactions are important [11]. However, it has been shown that, depending on the operation conditions, the product selectivities are to a large extent determined by the catalyst [3]. One of the promising catalytic systems for the oxygen-assisted dehydrogenation of ethane is a system based on tin promoted platinum catalysts. For reasons that are not completely understood, the addition of tin as a promoter element to platinum-based catalytic systems has a large effect on both conversion level and selectivity. There are at least three generally accepted models describing the role of tin: The geometric or ensemble effect and the electronic or ligand effect are the two major models for tin promotion. Atom displacements over very short distances, causing

expansion of the lattice parameters of the platinum particles, are also seen as a third possible cause for the role of metallic tin in Pt-Sn alloys [10]. NiO based materials have also been reported to be effective catalysts for oxidative dehydrogenation of ethane [12]. Sn has been added to NiO catalysts and the resulting catalysts are highly efficient [13].

The aim of this work has been to gain more insight in the role of tin on the performance of Al_2O_3-supported Pt-Sn catalysts for the ODE reaction, and for this purpose multiple catalysts were synthesized with an increasing loading of tin. Furthermore the influence of the addition of hydrogen to the feed gas and the total metal loading in the reactor were investigated.

2. Experimental

2.1 Catalyst preparation

A series of $PtSn/\gamma-A_2O_3$ catalysts was prepared by means of incipient wetness impregnation with a constant nominal loading of 1 wt% Pt and increasing loadings of Sn, ranging from 0.16 – 2.5 wt% (Sn/Pt molar ratios from 0.25 – 4). The alumina support was dried for 4 h at 573 K under vacuum (~10 mbar) and kept under static vacuum while cooling down to room temperature. The support was then impregnated via a septum with a solution containing the appropriate amounts of $H_2PtCl_6.6H_2O$ (Sigma-Aldrich) and $SnCl_2.2H_2O$ (99.99+%; Sigma-Aldrich) dissolved in 0.1 M hydrochloric acid, until the wetness point was reached. The freshly prepared catalyst was left under static vacuum overnight in order to let the solution in the pores equilibrate and distribute the platinum and tin more evenly throughout the support. The vacuum was slowly removed to avoid the solution leaving the pores, and the catalyst was dried at 393 K in air for 4 h. The monometallic catalysts were prepared in a similar way by using only one of either precursors and for the blank support only 0.1 M hydrochloric acid was used as the impregnation solution. Since the as-prepared catalysts were slightly

hygroscopic and attracted moisture from the air, an additional drying step of 4 h at 393 K was performed prior to calcination in air at 773 K for 6 h.

A summary of the catalysts is given in Table 1.

Table 1. Volumetric chemisorption of CO and H_2 at 308 K of the PtSn/γ-Al_2O_3 catalysts. γ-Al_2O_3 (Sasol): BET: 200 m^2/g, pore volume: 0.52 ml/g

	Loading (wt%)[a]			CO chem.	H_2 chem.
Name	Pt	Sn	Sn/Pt (at/at)[a]	$(cm^3 \cdot g_{cat}^{-1})$	$(cm^3 \cdot g_{cat}^{-1})$
Al_2O_3	-	-	-	0.162 ± 0.005	n.d.[b]
Sn	-	2.5	-	0.524 ± 0.006	n.d.[b]
Pt	1.0	-	-	1.056 ± 0.013	0.369 ± 0.012
PtSn0.25	1.0	0.16	0.25	0.941 ± 0.013	0.356 ± 0.065
PtSn0.33	1.0	0.21	0.33	0.937 ± 0.014	0.365 ± 0.010
PtSn0.50	1.0	0.32	0.51	0.871 ± 0.008	0.337 ± 0.015
PtSn1.00	1.0	0.64	1.02	0.852 ± 0.019	0.295 ± 0.013
PtSn1.50	1.0	0.94	1.51	0.688 ± 0.010	0.278 ± 0.010
PtSn2.00	1.0	1.3	2.00	0.640 ± 0.010	0.272 ± 0.007
PtSn4.00	1.0	2.5	4.01	0.346 ± 0.008	0.171 ± 0.007

[a] Nominal values [14]. [b] n.d.= not detected

2..2 Chemisorption

Volumetric chemisorption with H_2 as well as CO was carried out at 308 K using a Micromeritics ASAP 2020 set-up. Prior to the analysis, approximately 100 – 150 mg of sample was dried for 30 min under vacuum at 393 K and subsequently reduced in hydrogen

for 30 min at 873 K. After the first adsorption isotherm (i.e. the sum of the reversible and irreversible adsorption isotherms) was collected in the range of 75 – 200 mmHg, the sample was evacuated for 30 minutes and a new adsorption isotherm was measured (the reversible adsorption isotherm). The difference between the two isotherms was used to obtain the chemisorbed amount of either gas.

2.3 Transmission electron microscopy (TEM)

The particle size distribution of a few selected catalysts was determined in a JEOL 2010F electron microscope operating at 200 keV and equipped with a X-MAX Silicon Drift Energy Dispersive X-ray Detector. The catalysts were characterized either in their freshly reduced state (at 873 K for 30 min) or after 11 h on stream under ODE conditions.

2.4 Catalytic testing

The calcined catalysts were tested for short-contact time oxygen-assisted dehydrogenation of ethane (ODE) in a plug flow quartz reactor with an inner diameter of 6 mm. (Figure 1). The dehydrogenation set-up (Figure 1) consisted of four analogue Bronkhorst mass-flow controllers for ethane (99.995%), nitrogen (99.999%), hydrogen (99.999%) and synthetic air (99.999%), an electric tubular furnace, a cold trap for removal of water and other high-boiling components, and an Agilent 6890N online gas chromatograph (GC). The GC was equipped with a HP-PLOT 19095P-M25 capillary column (Agilent) and flame ionisation detector for the detection of all hydrocarbons, and a packed 100/120 Carbosieve S-II column (Supelco) and thermoconductivity detector for the remaining compounds. In this way over 25 different compounds could be identified at concentrations down to sub-ppm levels.

The main products, independent of reaction conditions and the type of catalyst, were always methane, ethylene, carbon monoxide, carbon dioxide and water. In most of the cases also significant amounts of acetylene, C_3 hydrocarbons (mainly propane and propylene), C_4 hydrocarbons (mainly butane, 1-butene and 1,3-butadiene) and benzene were detected.
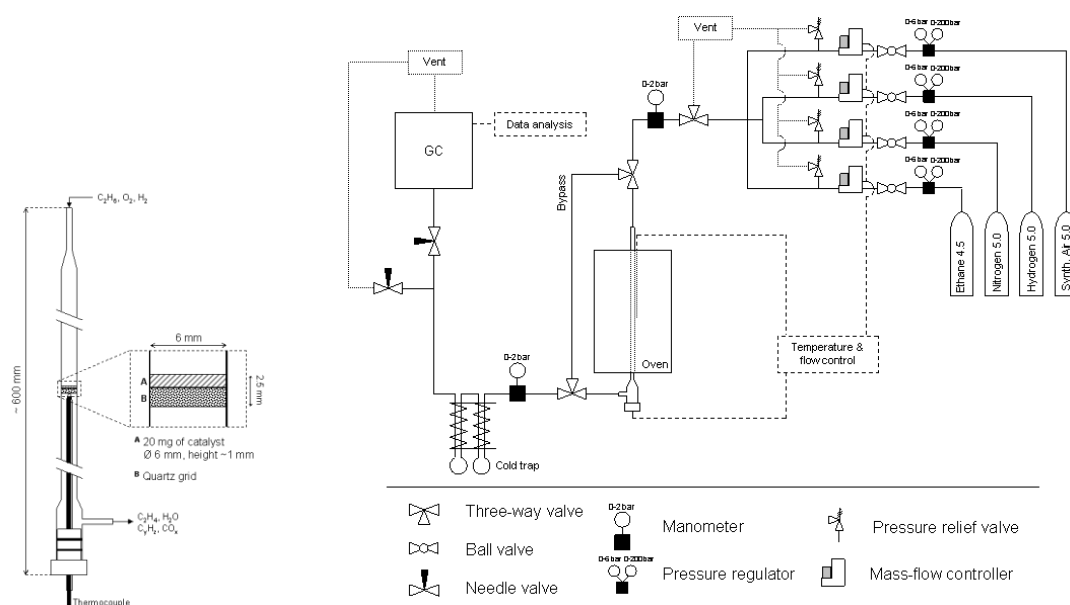

Figure 1. Schematic representation of the ODE set-up and of the ODE plug flow reactor.

3. Results and Discussion

3.1 Characterization by CO and H_2 chemisorption

The CO and H_2 chemisorption data for the Pt-Sn catalysts used in this work are summarized in Table 1. The given metal loadings and atomic Sn/Pt ratios are nominal values and have not been verified experimentally. Small deviations are therefore to be expected, but since high-grade chemicals were used to synthesize these catalysts by incipient wetness impregnation, it was assumed that those deviations were within the 5% error margin.

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It is evident from the results given in Table 1 that the adsorption of CO and H_2 decreases with increasing tin loading. With the assumption of stoichiometric 1:1 adsorption of CO on platinum and after subtraction of CO adsorption on the alumina support, it was calculated that the Pt/Al_2O_3 catalyst had a dispersion close to 80%. However, for the Pt-Sn catalysts this calculation could not be performed, since it was not clear to what extent tin was contributing to the decrease in adsorption of both CO and H_2.

The most logical reason for the decrease in adsorption of both CO and H_2 is a decrease in the total number of platinum surface atoms due to partial covering of platinum by tin or tin oxide. The chemisorption experiments were performed on reduced catalysts and for that reason the presence of metallic tin and Pt-Sn alloys cannot be excluded. In the case of alloy formation also the electronic effect should be considered as a plausible cause for the decrease in adsorption as shown in Table 1. In this case increasing amounts of tin would decrease the heat of adsorption until chemisorption would become an activated process [15]. Chemisorption at temperatures as low as 308 K might thereby be restricted to those Pt atoms not directly in contact with metallic tin. An increase in the average platinum particle size would decrease the surface-to-volume ratio and in turn decrease the amount of adsorption sites. However, a reasonable explanation for the formation of increasingly larger Pt particles with increasing tin loading is not included, since it seems unlikely that tin is causing this increase [16].

The data in Table 1 indicate that the addition of tin has a slightly larger effect on CO adsorption than on H_2 adsorption. When combined with the assumption that the reduced Pt-Sn catalysts are not altered by the adsorbing gas at 308 K, this could indicate that CO and H_2 chemisorb at different adsorption sites and that tin is not randomly and homogeneously

distributed over the Pt surface, thereby affecting the CO adsorption sites to a greater extent than the H_2 adsorption sites.

Pt-Sn alloys seem to be sensitive to the gas atmosphere and the fact that surface enrichment and surface oxidation processes could determine the surface structure of the alloys to a significant extent. It is therefore not likely that the chemisorption data obtained at 308 K in the presence of low pressure CO or H_2 gas, is resembling the catalytic data obtained at 923 K in the presence of oxygen, water, hydrocarbons and coke precursors. Nevertheless, the chemisorption data showed that the addition of tin had a noticeable effect on the adsorption of CO and hydrogen, suggesting that platinum and tin were located in close proximity from each other. This intimacy between the two metals is probably also present at elevated temperatures prior to catalytic testing, but the question remains to what extent the switch from inert nitrogen gas to the feed gas will affect this close contact.

3.2 Characterization by TEM

In order to get more insight in the morphology of the Pt and Pt-Sn catalysts, TEM analysis was used to estimate the particle size distribution for three freshly reduced and passivated catalysts (Figure 2). The TEM analysis showed that the platinum (and tin) particles were well-dispersed over the alumina support, independent of the type of catalyst and tin loading. The average platinum particle size in the monometallic catalyst was between 1.0 and 1.5 nm, which is in good agreement with the results from the CO chemisorption, showing a dispersion of around 80%. The addition of tin did not seem to influence the average particle size, since the average diameter remained less than 2.0 nm. However, the size distribution broadened slightly with the addition of more tin, as becomes evident from the tail in the histogram in

Figure 2C. A detailed STEM-EDX study on similar catalysts has been presented previously [14].
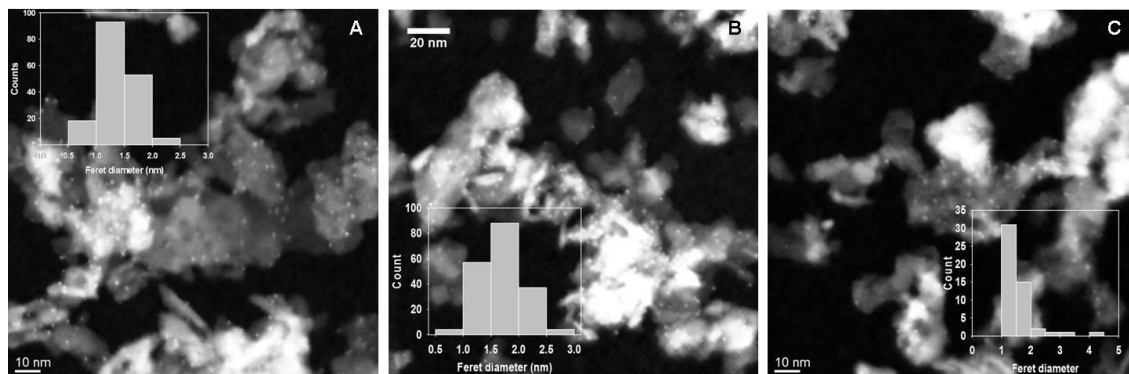

Figure 2. High-Angle Annular Dark-Field (HAADF) images of three freshly reduced catalysts. A) Pt, B) PtSn1.00, and C) PtSn4.00. The particle size distribution of each catalyst shows that the addition of tin has no significant effect on the average particle size of the fresh catalysts.

3.3 Oxygen-assisted dehydrogenation of ethane (ODE) at incomplete conversion of oxygen

The oxygen-assisted dehydrogenation of ethane (ODE) was performed with either diluted or non-diluted Pt-Sn catalysts. In order to obtain oxygen conversion levels below 98%, the oxygen-assisted dehydrogenation of ethane was performed with Pt-Sn catalysts that were diluted ten times with HCl-treated γ-Al$_2$O$_3$. These catalysts were tested in either the absence or presence of hydrogen in order to gain more insight in the benefits of the addition of hydrogen to the feed compared to previous studies at very short contact times in monolithic structures[9].
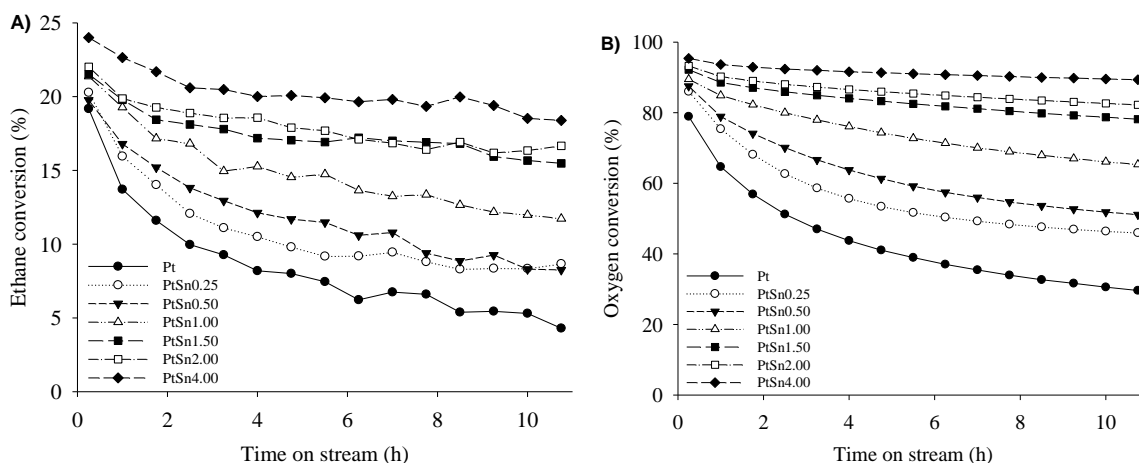
Figure 3. Conversion of ethane A) and of oxygen B) as a function of time on stream and loading of Sn _without additional H$_2$_ added to the feed. Loading of Pt is constant and equal to 0.1 wt%. (10 times dilution of the catalysts in Table 1). Conditions: 923 K, 1 bar, total flow = 1000 ml, min^{-1} with C$_2$H$_6$: O$_2$ = 2:1.

3.3.1 ODE in the absence of additional hydrogen

Figure 3 shows the conversion of ethane and oxygen as function of time on stream and the tin loading. It becomes clear from Figure 3 that the addition of even the smallest amount of tin (PtSn0.25; 0.16 wt% Sn) had a significant effect on the conversion of both reactants. In addition to the increased conversion levels, also the catalyst's stability was improved.

Besides the increase in conversion and stability with increasing tin loading, also the selectivities of the main products were largely affected. The initial selectivity towards ethylene increased significantly with increasing tin loading as shown on Figure 4. The selectivity to CO$_2$ decreased with increasing amount of tin after a short initial period and also with time on stream. For CO the selectivity deceased with increasing amount of tin for the first two hours on stream, and then become constant within the time interval studied except for the Pt catalyst where the selectivity to CO decreased with time on stream.The selectivities

towards acetylene (Figure 4), methane and water (not shown) were only slightly affected although the selectivities increased with the addition of tin.
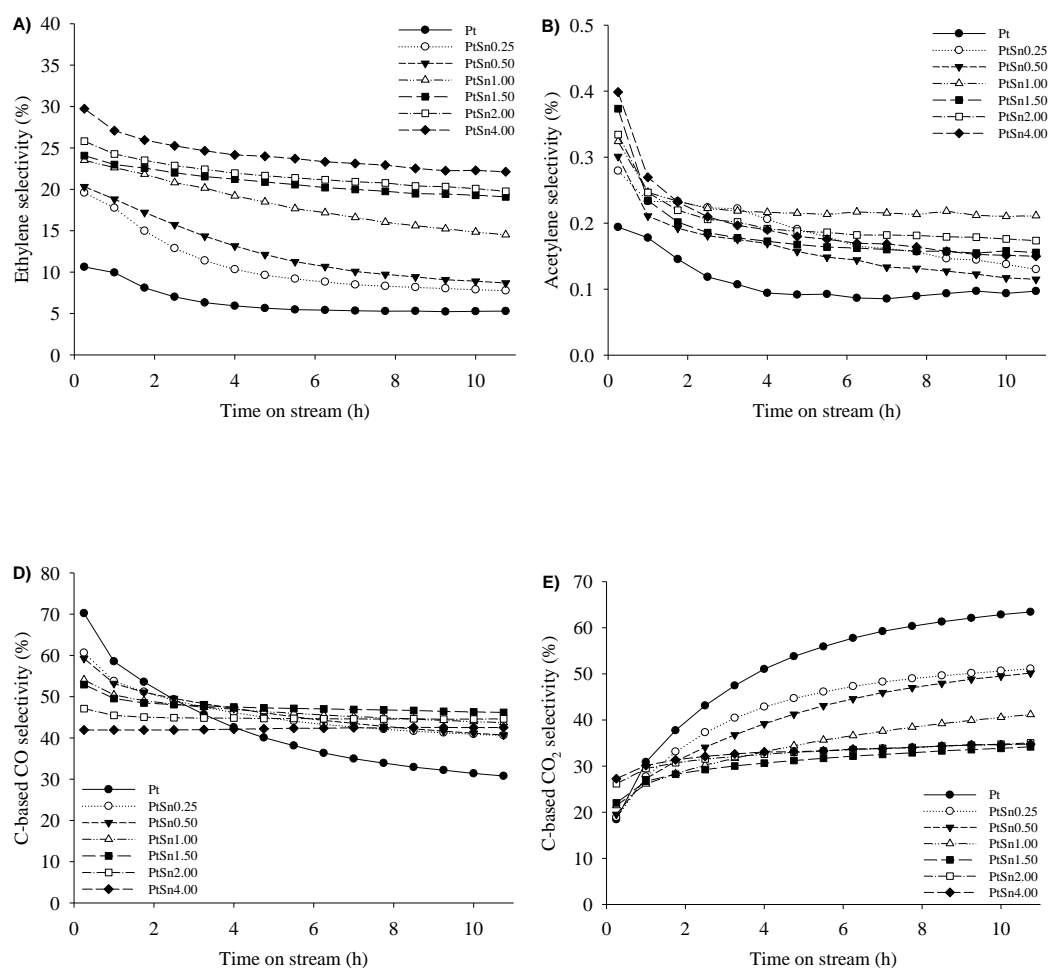

Figure 4. Selectivity of ethylene, acetylene, carbon monoxide and carbon dioxide as a function of time on stream and loading of Sn without additional H_2 added to the feed. Loading of Pt is constant and equal to 0.1 wt%. (10 times dilution of the catalysts in Table 1). Conditions: 923 K, 1 bar, total flow = 1000 ml, min^{-1} with C_2H_6 : O_2 = 2:1.

Without addition of tin the Pt/Al_2O_3 catalyst suffered from severe deactivation in the conversion of both ethane and oxygen (Figure 3). The formation of coke and sintering of platinum are the two most likely causes for the observed deactivation. Coke formation during

hydrocarbon conversion reactions over Pt-based catalysts is a well-known phenomenon resulting in the decrease of the total number of accessible active sites [16-19].

The addition of tin increased the stability of the Pt/Al$_2$O$_3$ catalyst significantly, as observed by the trends of both the conversion and the selectivities with time on stream (Figure 4) which suggests that tin either prevents the platinum from sintering or alters the coke formation to such an extent that it no longer blocks the active sites. The statement that the presence of coke and other large carbonaceous species might play a key role in the observed deactivation is further supported by a visual comparison between the catalysts after 11 h time on stream. Whereas the monometallic Pt catalyst turned completely black due to carbon build-up on the catalyst, the PtSn4.00 catalyst remained practically clear from these carbonaceous species.

It should be noted that unsaturated hydrocarbons, like ethylene and acetylene, are likely precursors for coke formation on Pt-based catalysts, especially in the absence of additional hydrogen that otherwise would prevent total dehydrogenation of these hydrocarbons [20-22].

Due to the moderate to high conversion levels of ethane and oxygen, both readsorption and further conversion of products as well as the presence of possible temperature gradients need to be considered, which at the same time contributes to the complexity of data interpretation. The higher stability of Sn-promoted catalysts might be linked to a reduction in the amount of coke formed during the ODE reaction. Prevention of coke formation might occur due to the lowered affinity of the Pt-Sn catalysts towards coke precursors, but oxidation and reduction of formed coke species might occur as well. Segregation of Sn to the surface of Pt could inhibit the formation of coke due to the decrease of the ensemble size.

Besides oxidation, hydrogenation of adsorbed coke species is possible and would account for both the increase in ethylene selectivity and decrease in H_2 selectivity. The increase in the production of saturated C_3 and C_4 hydrocarbons (data not shown here) seems to support this increased hydrogenation, although the decrease in ethane concentration, i.e. the increased carbon conversion, is contradicting this for the very same reason.

3.3.2. ODE in the presence of additional hydrogen

It has been shown previously that the addition of hydrogen to the feed significantly increases the selectivities toward ethylene and water, especially for the tin-promoted catalysts[9]. It was stated [23] that tin promoted the selective oxidation of hydrogen and that this exothermic reaction locally increased the temperature enough to promote the gas phase dehydrogenation of ethane to ethylene. This selective oxidation also decreased the oxygen concentration in the gas stream, resulting in decreased selectivities toward CO and CO_2. Since the conversion of oxygen was always complete, except from a small by-pass effect [23], no conclusive statements could be made about the effects of tin on the selectivities of the oxygen-containing products. In order to get a better understanding of the role of tin and hydrogen in the oxygen-assisted dehydrogenation of ethane, the experiments as discussed in the previous paragraph, were repeated with addition of sufficient H_2 to obtain an initial H_2/O_2 ratio of 2, i.e. the stoichiometric ratio for the formation of water.
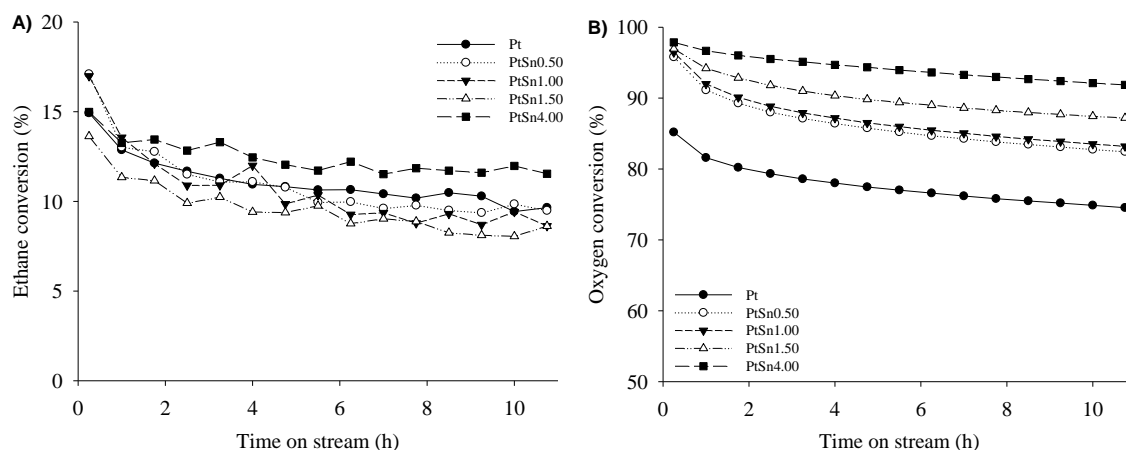
Figure 5. Conversion of ethane and oxygen as a function of time on stream and loading of Sn with additional H_2 added to the feed. Loading of Pt is constant and equal to 0.1 wt%. (10 times dilution of the catalysts in Table 1). Conditions: 923 K, 1 bar, total flow = 1000 ml, min^{-1} with C_2H_6 : H_2 : O_2 = 2:2:1.

When comparing Figure 5 with Figure 3, it becomes immediately clear that the addition of hydrogen almost nullified the promotional effects of tin in the conversion of ethane and that this negative influence is largest for the catalysts with the highest tin loadings. Even the unpromoted Pt catalyst was affected by the addition of hydrogen to the feed, since the initial ethane conversion dropped from 19.2% to 14.9%. This decrease in activity might be partially explained by hydrogenation of formerly dehydrogenated products like ethylene and acetylene. However, a shift in the hydrogenation-dehydrogenation equilibrium between ethane and ethylene/acetylene alone cannot account for the larger decrease with increasing tin loading. It seems from Figure 5 that the conversion of ethane becomes independent of the tin loading, or more generally, independent of the type of Pt-based catalyst (unpromoted or promoted). This suggests that the initial step or steps in the conversion of ethane have become nearly independent of the total catalytic surface area, i.e. the molar C_2H_6/Pt_{surf} ratio, and the type of metal surface, i.e. pure Pt or bimetallic Pt-Sn. It does even suggest that the first step or steps

towards conversion have become activated processes, thereby becoming dependent on the ethane concentration in the feed gas. This would imply that hydrogen plays an important role in reducing the adsorption of ethane onto the platinum surface. However, due to the high reaction temperature (923 K), it does not seem very likely that the additional hydrogen is competing with ethane for adsorption sites on the platinum surface, since H_2 already desorbs at much lower temperatures as shown by the work from Delbecq *et al.* [22]. Other compounds that increase in concentration due to the addition of hydrogen to the system, like water, are more likely to fulfil this role of adsorption on the Pt surface [24].

The hypothesis that the dehydrogenation of ethane is hindered by the addition of hydrogen and that the increase of oxygen conversion is mainly leading to the formation of water, is supported by the gas phase experiment. The addition of H_2 decreased the gas phase ethane conversion from around 0.5% to < 0.1%, whereas the O_2 conversion increased from 2.5% to 8.5%. The O-selectivity towards H_2O increased from approx. 60% to 99.9+%.

Besides the decrease in ethane conversion, diminishing the promotional effects of tin, the addition of hydrogen seems to stabilize the catalyst's performance as becomes clear from the product distribution as function of time on stream (Figure 6). Secondly, with the exception of acetylene, tin seems to have a significant influence on the product distribution, in particular on the selectivity towards ethylene, CO, CO_2 and water. Even relatively small amounts of tin, i.e. 0.32 wt% (PtSn0.50), have a significant effect on the product distribution, suggesting that tin is altering some of the most active sites on these Pt-based catalysts. About the nature of these sites can only be speculated at this stage, but the fact that the carbon selectivities towards ethylene and CO show roughly the opposite trends as function of time and tin-

loading, suggests that these two products are closely related in the overall reaction mechanism.
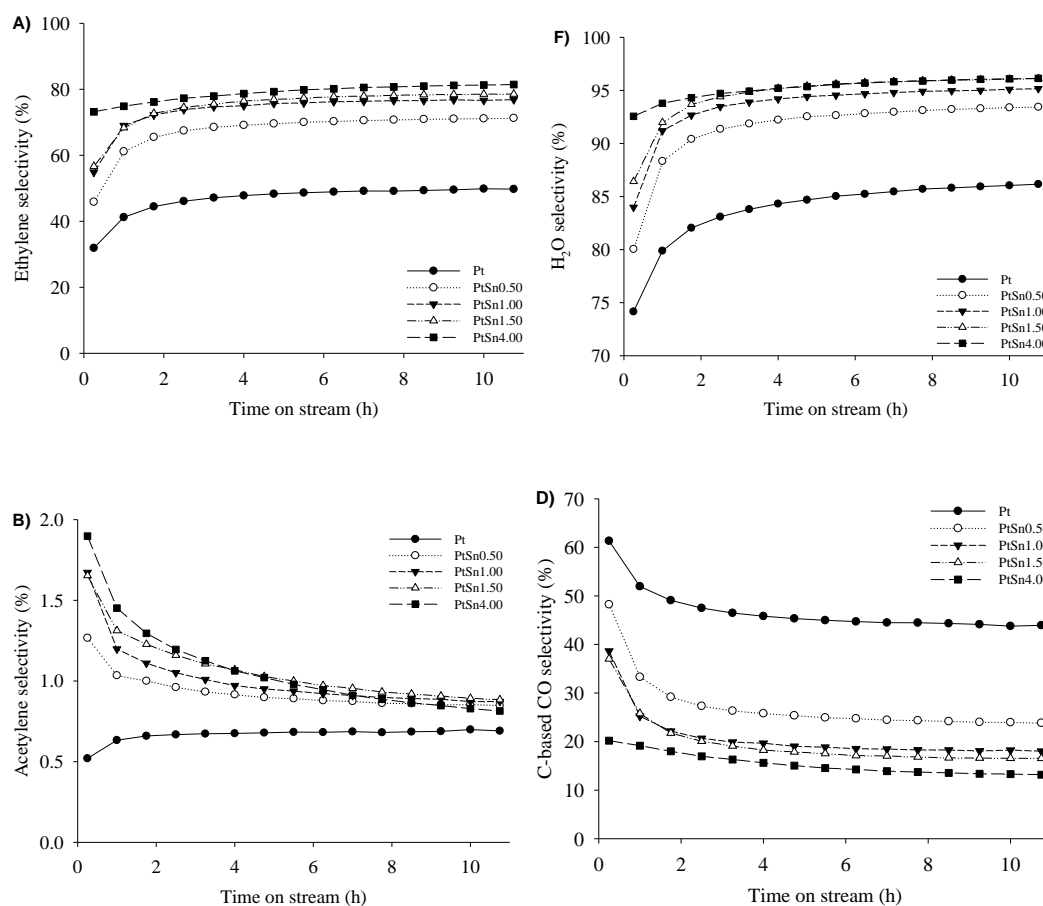

Figure 6. Selectivities of ethylene, water, acetylene and carbon monoxide as a function of time on stream and loading of Sn <u>with</u> additional H_2 added to the feed. Loading of Pt is constant and equal to 0.1 wt%. (10 times dilution of the catalysts in Table 1). Conditions: 923 K, 1 bar, total flow = 1000 ml, min^{-1} with $C_2H_6 : H_2 : O_2 = 2:2:1$.

As discussed previously, deactivation of Pt-based catalysts can be caused by both coke formation and sintering. In the absence of H_2, sintering could not be excluded as a possible deactivation mechanism, since the deactivation rate seemed to be dependent on the tin loading. But with the addition of H_2 the deactivation seemed to have become nearly

independent of the type of catalyst, suggesting that tin is not playing a major role in stabilizing the Pt particles on the alumina support. This lack of particle stabilization by tin has also been observed by de Graaf *et al.* [16].

Coke formation on the other hand can be affected by both tin and hydrogen, and hydrogenation of coke is a plausible explanation for the lower degree of deactivation with increasing tin loading. This is partially supported by the visual comparison of the catalysts after 11 h on stream with hydrogen added to the feed. All catalysts showed the same degree of coking, supporting the statement that the near-identical trends in the deactivation in Figures 5 and 6 are most likely caused by the formation of coke and other large carbonaceous species. But it also suggests that this is independent of the presence and loading of tin under these conditions. Although this implies that the previous statement about the influence of tin on the overall coke formation and removal cannot be correct, it should be kept in mind that the addition of significant amounts of hydrogen to the feed gas, consequently changing the product distribution, might also alter the oxidation state, location and role of tin dramatically.

From a visual observation of the spent catalysts it becomes evident that hydrogen is indeed lowering the build-up of coke on the surface, either by hydrogenation of coke species or by blocking the formation of those same coke precursors.

For the runs without hydrogen added to the feed, the only source of H_2 for hydrogenation of coke is ethane, and since the addition of tin increased the conversion of ethane, also the hydrogenation of coke species was promoted, based on the statements made about the likeliness of coke hydrogenation. In combination with the decreasing H_2 selectivity with increasing tin loading, this suggests that tin-promoted catalysts are more susceptible and

reactive towards hydrogen, resulting in a higher conversion of H_2, more coke hydrogenation and thus a higher catalytic stability. This also holds for the ODE reaction in the presence of additional hydrogen.

Since hydrogen is both a reactant and a product when hydrogen is added to the feed, it is not possible to calculate the H_2 selectivity, as no distinction can be made between the unreacted H_2 and the H_2 produced from ethane. Instead, the ratio of H_2 in the product stream and the H_2 in the feed can provide information about the net production or net consumption of hydrogen by the catalyst. Figure 7 shows that all catalysts consumed more hydrogen than they produced, since the $H_{2,out}/H_{2,in}$ ratio was always lower than 1. Furthermore, the hydrogen consumption increased with increasing tin loading, i.e. a lower $H_{2,out}/H_{2,in}$ ratio, which confirmed the higher susceptibility and reactivity of tin towards hydrogen.
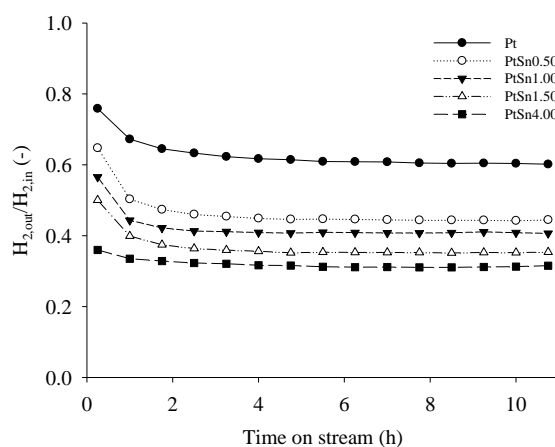

Figure 7. The normalized H_2 concentration in the product stream as function of time on stream and Sn loading when H_2 is added to the feed. Conditions as in Figure 6.

Based on these findings it is very plausible that tin undergoes a continuous oxidation-reduction cycle, consuming H_2 and producing H_2O. This type of cyclic behaviour in which the oxidation state of tin changes continuously between 0, 2+ and 4+ has been proposed earlier

for the H_2-assisted dechlorination of chlorinated hydrocarbons [25]. In a similar way, tin has been suggested to serve as an oxygen or hydroxyl donor in liquid phase oxidation reactions [26-28], oxidizing adsorbed species to form alcohols, aldehydes, carboxylic acids, CO and CO_2.

Based on the present results and the additional literature, it is plausible to assume that for the reactions leading to the increased consumption of H_2 and the higher selectivity towards H_2O when more tin is added to the Pt/Al_2O_3 catalyst, one or both of the following mechanisms are taking place during the ODE reaction in the presence of additional hydrogen:

The most direct way to convert H_2 to H_2O is by a continuous oxidation-reduction cycle with tin as the catalyst. In the presence of oxygen or water, (metallic) tin is readily oxidized to SnO, SnO_2 or any type of hydroxide or oxide hydroxide. These can in turn be reduced by H_2 to form water and one of the reduced tin species, closing the oxidation-reduction cycle. Especially in the vicinity of Pt, adsorbed hydrogen atoms are capable of reducing nearby tin oxides. In the case that tin is acting as a reservoir of OH_{ads} species, adsorbed hydrocarbons on nearby Pt might be oxidized to alcohols or aldehydes. The additional hydrogen on the Pt surface might prevent both the full oxidation of hydrocarbons towards CO and CO_2 by hydrogenating unsaturated C-C and C-O bonds, as well as the probability for dissociative adsorption of ethane on the Pt surface. In addition, hydrogen is needed to replenish the amount of OH_{ads}, since both SnO and SnO_2 on their own are rather poor hydrocarbon oxidation catalysts [29]. In the case ethanol is formed by the oxidation of ethane, dehydration to ethylene and water is very likely, since ethanol readily decomposes at temperatures above 550 K, especially in the presence of metal oxides [30]. An increase in tin loading in combination with excess hydrogen in the gas phase might well result in a higher concentration

of oxygenates on the catalyst's surface, in particular those of ethanol and acetaldehyde, which in turn decompose to ethylene and water, explaining the increased selectivity towards both products at a catalyst-independent ethane conversion rate.

These two mechanisms are also likely to occur in the absence of additional hydrogen, but with the significant difference that the reaction steps that are highly dependent on the hydrogen concentration become suppressed by the lack of sufficient hydrogen. Based on the proposed mechanisms for the ODE reaction in the presence of sufficient hydrogen, it is possible to deduce the effects that a lack of hydrogen would have on the reaction mechanism.

From a comparison between the hydrogen selectivity without additional hydrogen in the feed and the $H_{2,out}/H_{2,in}$ ratio in Figure 7 for the monometallic Pt catalyst it becomes clear that the addition of hydrogen also has a significant influence on platinum itself and not only on tin and its oxides. In the absence of hydrogen the Pt catalyst is producing molecular hydrogen during the whole process of 11 h time on stream, but when hydrogen is added to the feed gas, the monometallic catalyst becomes a net consumer of hydrogen in the same time span. This implies that the addition of hydrogen to the Pt catalyst altered the surface chemistry to such an extent that it opened up different reaction pathways, generating the need for more hydrogen, resulting in a net consumption, and leading to an increase in the selectivities towards ethylene and water.

3.3.3 Physical mixture of Pt/Al$_2$O$_3$ and Sn/Al$_2$O$_3$

In Figure 8 the selectivity to ethylene for the physical mixture of Pt/Al$_2$O$_3$ and Sn/Al$_2$O$_3$ is compared with the coimpregnated PtSn/Al$_2$O$_3$ catalyst. Even though the physical mixture does not have the same performance as the coimpregnated PtSn catalyst within the first 11 h

time on stream, it becomes clear that the performance of both tin-containing catalysts is significantly different from the monometallic catalyst and that the differences between the two tin-containing catalysts are getting smaller with time.

The physical mixture had initially a nearly identical performance as the diluted Pt catalyst, suggesting that the additional tin initially had little effect on the Pt. It should be kept in mind
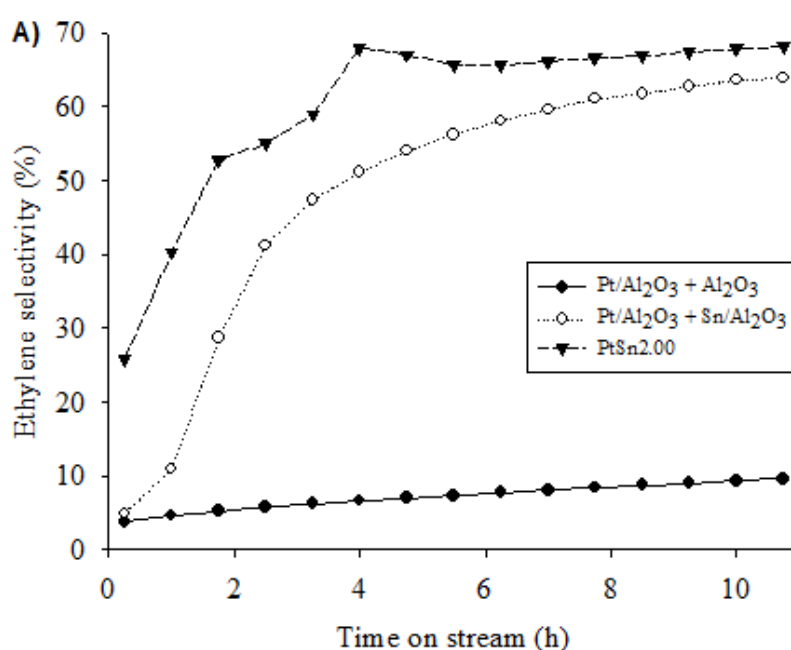

Figure 8 Selectivity to ethylene for the monometallic catalyst, the physical mixture and the coimpregnated catalyst. Conditions: 923 K, total flow = 1000 ml/min, C_2H_6:H_2:O_2=2:2:1. Pt loading = 1.0 wt% (98+% conversion of O_2).

that the platinum and tin in the physical mixture initially were spatially separated and that there were no alumina particles that supported both elements. Nevertheless, after only a few h on stream, the physical mixture had converted to a catalyst similar to the coimpregnated PtSn catalyst.

The catalytic activity in the ODE reaction has been ascribed solely to the activity of platinum or tin-promoted platinum. However, the fact that a physical mixture of Pt/Al_2O_3 and Sn/Al_2O_3 can have a similar performance as a coimpregnated catalyst raises the question whether it might be possible that tin itself is catalytically active in the ODE reaction. The Sn/Al_2O_3 catalyst was therefore compared to both the gas phase activity and the catalysts described above. It was shown that Sn/Al_2O_3 showed some catalytic activity on its own, with an ethane conversion of 0.7 – 0.8% (gas phase: < 0.1%) and an oxygen conversion of 16% (gas phase: 8.5%). Although these conversions were significantly larger than the gas phase activity, they were still rather small in comparison to the catalysts containing platinum. It could therefore be concluded that it is indeed the platinum that is responsible for the observed activity in the ODE reactions, and that tin is merely altering the performance of Pt.

Another reason for the changing performance of the physical mixture might be that one of the metals becomes mobile under these rather harsh catalytic conditions, resulting in redistribution of metals and ultimately in bringing the metals in closer contact with each other, creating a catalyst similar to the coimpregnated one. It has be shown that Pt on alumina sinters in the presence of oxygen and unsaturated hydrocarbons [31], but based on the different deactivation rates for the physical mixture and the diluted Pt catalyst, sintering of platinum seems not very likely here, since this would have resulted in similar deactivation rates. An increased mobility of tin moieties seems therefore to be the most likely explanation for the changing performance of the physical mixture.

4. Conclusions

All experiments were carried out at 923 K with a constant ethane-to-oxygen ratio of 2, a total gas flow of 1000 mL.min^{-1} and 20 mg of catalyst. It was found that for diluted catalysts in the

absence of additional hydrogen the tin loading had a significant effect on the conversions of ethane and oxygen and the selectivities towards ethylene, CO, CO_2 and hydrogen. The addition of tin reduced the amount of coke that was formed during ODE, which could be the main reason for the increased catalytic stability as function of tin loading.

When hydrogen was added to the feed gas the promotional effects of tin on the ethane conversion and the catalytic stability diminished nearly completely, whereas the differences in product selectivity became only slightly less dependent on the tin loading. The addition of hydrogen resulted in significantly higher selectivities towards water and hydrocarbons at the expense of the formation of CO, CO_2 and coke.

It seems that tin and hydrogen have to some extent similar promotional effects on the catalytic performance of a Pt/Al_2O_3 catalyst, resulting in a higher selectivity towards ethylene and reducing the formation of coke and other large carbonaceous compounds. The improved catalytic stability was most likely due to a lower degree of coke formation on the catalyst surface, but it remained unclear whether it was either the rate of coke formation or the rate of coke removal that was affected most.

A non-diluted physical mixture of a monometallic Pt/Al_2O_3 catalyst and a monometallic Sn/Al_2O_3 catalyst was compared with a coimpregnated Pt-Sn catalyst with the same nominal metal loadings. It was found that the physical mixture initially performed similarly to the monometallic Pt catalyst, but after only a few hours time on stream its performance became similar, but not identical, to the coimpregnated Pt-Sn catalyst. Combined with the lack of evidence for sintering of platinum, this suggested that the tin was mobile under ODE conditions, creating bimetallic Pt-Sn particles similar to the coimpregnated sample.

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