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Propane dehydrogenation over supported platinum catalysts: Effect of tin as a promoter

Odd A. Bariås [1], Anders Holmen, Edd A. Blekkan

Department of Industrial Chemistry, The Norwegian Institute of Technology (NTH), The University of Trondheim, and SINTEF Applied Chemistry, N-7034 Trondheim, Norway

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Abstract

The catalytic dehydrogenation of propane has been studied over Pt and Pt–Sn catalysts supported on γ-Al_2O_3 and SiO_2. Without the promoter Pt shows the same initial specific activity (TOF) on both supports, but deactivates rapidly due to coking. The effect of Sn as a promoter depends on the support. On γ-Al_2O_3 tin interacts with the support and is stabilized in an oxidation state > 0. The result is an increase in Pt dispersion and reduced deactivation without any change in the initial specific activity in dehydrogenation. The selectivity to propene is strongly enhanced by tin, particularly due to blocking or poisoning of acid sites on the support. On SiO_2 the Sn is more readily reduced, and alloy formation is possible. This leads to a similar increase in Pt dispersion and improved catalytic stability, but also to a strong reduction in the specific activity. The change in catalytic stability on both supports is parallelled by a dramatic change in the hydrogen adsorption properties, as seen from the TPD profiles after reduction.

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1. Introduction

Supported bimetallic Pt-based catalysts are important for many hydrocarbon reactions. The promotion by Sn is known to increase the lifetime of these catalysts due to reduced deactivation by coking [1,2]. Most studies dealing with the Pt–Sn system have used reforming reactions as models, and it is not evident that the conclusions drawn are valid for the apparently more simple dehydrogenation system. Extensive characterization work (see e.g. refs. [1,3–6]) has not provided a consensus to the oxidation state of Sn in the reduced catalyst. This paper presents some experimental results from a study of Pt and Pt–Sn catalysts supported on γ-Al_2O_3 or SiO_2 and used in the dehydrogenation of propane.

2. Methods

Pt and Pt–Sn catalysts supported on Al_2O_3 (Kaiser Chemicals versal 250) and SiO_2 (Merck Kieselgel 60) were prepared by incipient wetness impregnation using water as the solvent and the appropriate amounts of salts ($H_2PtCl_6 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$). The bimetallic systems were prepared by sequential impregnation (Sn first) with drying and calcination between the impregnation steps. The SiO_2-based samples were calcined in dry air (550°C, 4.5 hours, whereas the γ-Al_2O_3-based samples were calcined in humid air ($P_{H_2O} = 25$ kPa) at 550°C for 2.5 hours followed

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[1] Present address: ABB Environmental, P.O. Box 6260, Etterstad, N-0603 Oslo, Norway.

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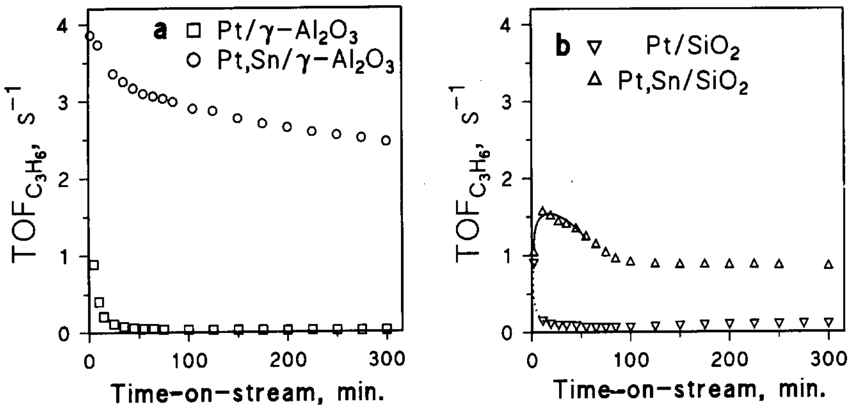

Fig. 1. Activities (TOF) as a function of time-on-stream. Conditions: 519°C, C_3H_8:N_2 = 3:7, WHSV = 10 h^{-1}.

by calcination in dry air at 550°C for 2 hours. The humid air calcination step was introduced to reduce the chlorine content of the γ-Al_2O_3-based catalysts. Details of the preparation procedure are given elsewhere [2].

The catalysts were characterized by TPR, TPD and hydrogen chemisorption using the pulse technique. The dehydrogenation of propane was studied by activity/selectivity measurements at 427–519°C using low propane conversions.

3. Results and discussion

gives some characterization data for the catalysts. The TPR profiles were used to estimate the degree of reduction of Sn, correcting for the hydrogen consumed in reduction of Pt. On the γ-Al_2O_3, the data indicates that Sn was less reduced, whereas on SiO_2 close to complete reduction of Sn was observed. Table 1 also gives data from pulse chemisorption measurements. The hydrogen uptake is increased as a consequence of the Sn addition on both supports. TPD profiles of hydrogen adsorbed during reduction and cooling in flowing H_2 revealed striking differences between the catalysts. All the catalysts show small TPD peaks around 80°C, usually attributed to hydrogen chemisorbed on metallic Pt. The Sn-promoted samples in addition show very large peaks at higher desorption temperatures. The amount of hydrogen desorbed at the high temperatures corresponds to H:Pt ratios of about 4 on PtSn/γ-Al_2O_3 and 8 on PtSn/SiO_2 respectively. For PtSn/γ-Al_2O_3 the peak temperature for this large peak is about 740°C, close to that reported for spillover hydrogen on a γ-Al_2O_3 support [7]. For PtSn/SiO_2 the desorption peak has a maximum around 300°C.

The initial activity of the samples in propane dehydrogenation at 427°C is reported in Table 1. The initial specific activity (TOF) is similar for the unpromoted samples and for the PtSn/γ-Al_2O_3 sample, whereas the PtSn/SiO_2 is about one order of magnitude less active on a Pt site basis at these conditions. As expected, the deactivation patterns were different for the promoted and unpromoted catalysts. Fig. 1 shows the catalyst activities (run-plots) obtained at 519°C. The initial activities show a similar trend, but on the unpromoted samples the deactivation is very rapid and initial values difficult to obtain. In comparison, the PtSn/γ-Al_2O_3 retained 2/3 of its initial activity after 300 minutes on stream. The PtSn/SiO_2 showed an initial increase in the activity which passed through a maximum. A similar effect was also observed at 427°C. This behaviour is probably due to inhibition by strongly adsorbed hydrogen after reduction, as also observed by Rochefort et al. [8] in dehydrogenation reactions. Fig. 2 shows the selectivities to C_1 and C_2 hydrocarbons over the alumina-supported catalysts. On Pt/γ-Al_2O_3 the light products are methane and ethene in about equimolar amounts, the typical

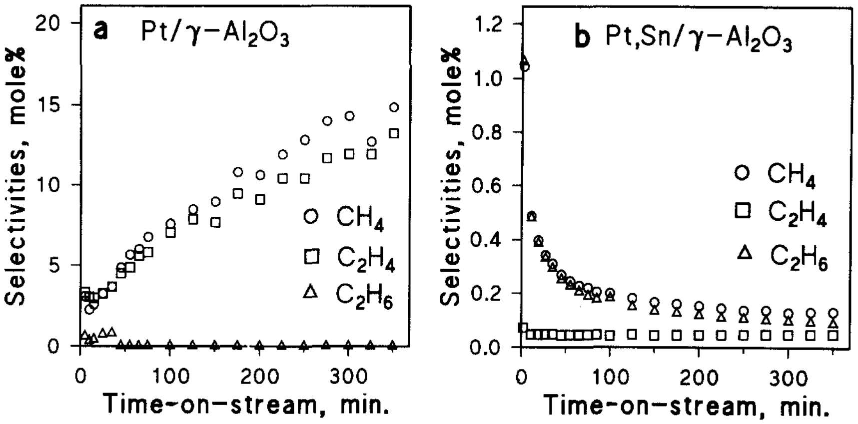

Fig. 2. Selectivities to C_1 and C_2 products over γ-Al_2O_3-supported catalysts. Conditions as given in Fig. 1.

Table 1. Results from characterization and activity testing of the catalysts.

Catalyst	S_{BET} m^2/g	Wt% Pt	Wt% Sn	H:Pt[1]	Red.Sn[2] %	In.act.[3] s^{-1}
Pt/γ-Al_2O_3	180	0,44	-	0,17	-	0,8
PtSn/γ-Al_2O_3	155	0,35	1,26	0,28	25	1,2
Pt/SiO_2	442	0,60	-	0,06	-	0,9
PtSn/SiO_2	417	0,60	1,20	0,13	70	0,1

1. From pulse chemisorption at 298 K.
2. Assuming $SnO_2 \rightarrow Sn$. From TPR (7% H_2 in Ar, 10 K/min) up to 600 °C.
3. Initial TOF of propene formation. Conditions: 427 °C, 0.3 bar C_3H_8, total pressure 1 bar, balance N_2.

products of an acid catalyzed cracking reaction. The selectivity increases with time-on-stream, showing that the metal catalyzed dehydrogenation reaction deactivates much more rapidly than the cracking reaction. With tin present the light products are ethane and methane in equimolar amounts, typical of a metal-catalyzed hydrogenolysis reaction. The selectivity to light products is much lower, and decreases with time, indicating that the hydrogenolysis reaction is inhibited by coke formed on the metal particles to a greater extent than the dehydrogenation reaction. On SiO_2 the selectivity to propene was initially close to 100% both with and without tin present, showing an absence of acid sites capable of catalyzing the cracking reaction.

Our Sn-promoted catalysts fit the general picture [5] of Sn being stabilized in the 2+ state on γ-Al_2O_3, but reduced to metallic Sn and in close contact with Pt (bimetallic clusters) when supported on SiO_2. In both cases the deactivation by coking is strongly reduced, but when metallic Sn is in close contact with the Pt as on SiO_2 the result is also a large loss in the intrinsic activity. On SiO_2 the degree of Sn reduction is higher, a large fraction of the Sn is reduced to the metallic state and possibly in alloy with Pt. In this state Sn exerts a strong negative effect on the intrinsic catalytic activity of Pt. This is in line with the findings of Yarusov et al. [9], who also included a sample of an unsupported PtSn alloy in their investigation. An important effect of tin on alumina is also to block or poison acidic sites on Al_2O_3 leading to cracking.

4. Acknowledgements

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