Characterization and activity of Pt–Sn / Al_2O_3 catalysts of different preparation: coimpregnation and new Pt–Sn precursor

C. Kappenstein, M. Saouabe, M. Guérin, P. Marecot

LACCO, URA CNRS 350, Faculté des Sciences,
40 Avenue du Recteur Pineau, 86000 Poitiers, France

I. Uszkurat [1] and Z. Paál

Institute of Isotopes of the Hungarian Academy of Sciences,
PO Box 77, Budapest, H-1525 Hungary

Received 5 September 1994; accepted 15 November 1994

A new bimetallic Pt–Sn compound $[Pt(NH_3)_4][SnCl_6]$ has been used as precursor for the preparation of supported Pt–Sn/Al_2O_3 catalysts. A comparison of a dried sample with that prepared by coimpregnation displays different behaviour in TPR, chemisorption. The initial catalytic activity properties were checked in the reactions of cyclohexane dehydrogenation and cyclopentane ring opening, while *n*-hexane skeletal reactions were used to probe the quasi-steady-state activity. The catalyst prepared via the Pt–Sn complex precursors exhibited somewhat lower specific activity. This fact, together with enhanced olefin formation from *n*-hexane was taken as an indication of lower amount of contiguous Pt atoms and some electronic interaction between Pt and Sn in that catalyst.

Keywords: catalyst preparation; alumina supported platinum–tin catalysts; coimpregnation; bimetallic precursor; TPR; cyclohexane dehydrogenation; cyclopentane ring opening; *n*-hexane skeletal reactions

1. Introduction

Despite their industrial importance, the structure of Pt–Sn reforming catalysts is still under debate as far as the valence state of tin and the nature of the active centres are concerned [1]. Burch [2] claims that no proper alloy of Pt and Sn is formed, the small amounts of Sn(0) being present as a solid solution in Pt. Lieske and Völter, on the other hand [3] argue for the presence of a minor part of tin as a Pt–Sn alloy. Both authors point to the presence of Sn(II) species stabilised by the

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[1] On leave from Fachhochschule Ostfriesland, D-26723 Emden, Germany.

alumina and for their interaction with the reduced Pt–Sn(0) particles. The modified catalytic properties of Pt–Sn catalysts have been attributed to electronic modification of Pt to give electron-rich platinum species [4]. On the other hand, Sachtler and co-workers regard the effect of added Sn as a purely geometric one, Sn dividing the contiguous surface of Pt into smaller ensembles consisting of 1–3 Pt atoms [5].

To examine the question from another point of view, different preparation procedures were used resulting in different interactions between platinum and tin. Apart from conventional coimpregnation or successive impregnation techniques using H_2PtCl_6 and $SnCl_4$ or $SnCl_2$ [3,6–8], we can extract from most recent literature: (i) incipient wetness technique with acetone as a solvent [9–11]; (ii) the use of $Pt(NH_3)_4(OH)_2$ and tin tartrate [10]; (iii) formation of bimetallic $[PtCl_2(SnCl_3)_2]^{2-}$ complexes [12]; (iv) coprecipitation of $SnCl_4$ and $Al(NO_3)_3$ with NH_3 followed by H_2PtCl_6 impregnation [13]; (v) solvated metal atom dispersion (SMAD) technique [14]; (vi) surface reaction of hydrogen adsorbed on Pt with SnR_4 [15–18]; (vii) impregnation with $[Pt(SnCl_3)_5]^{3-}$ on alumina [19].

A comparison between coimpregnation and successive impregnation [20,21] has shown that the use of bimetallic $[PtCl_2(SnCl_3)_2]^{2-}$ complexes led to higher amounts of Pt–Sn alloys and higher reduction of tin. The alloy displays very low activities for cyclohexane dehydrogenation or cyclopentane hydrogenolysis whereas Pt ensembles exhibit higher catalytic activity. Electronic interaction by tin in the subsurface layer of exposed Pt surface was also claimed [22].

Recently, we have prepared a new platinum–tin compound $[Pt(NH_3)_4][SnCl_6]$ [23] and the single crystal structure analysis revealed a NaCl type lattice with complex Pt cations and Sn anions but without direct Pt–Sn interaction. In this paper we present a comparison between a Pt–Sn/Al_2O_3 catalyst prepared from the same precursors of the new compound and another catalyst prepared by the more conventional coimpregnation technique. Characterization of the catalyst is reported together with results of both "structure-sensitive" and "structure-insensitive" [24] hydrocarbon test reactions.

2. Experimental

2.1. PREPARATION OF THE SAMPLES

Support. A cubic γ-alumina from Rhone Poulenc (GFS-400) with surface area of 210 $m^2\ g^{-1}$ and pore volume of 0.64 $cm^3\ g^{-1}$ was used. The cylindrical pellets were ground and sieved, the fraction between 0.1 and 0.25 mm selected, then washed with water, dried at 373 K, calcined in air flow (4 h; 803 K) and finally reduced in H_2 flow (4 h; 803 K) before use.

Conventional preparation. Coimpregnation (sample T): the support (4 g) is wetted with the minimum of water to cover it and impregnated with a mixture of

12 cm^3 H_2PtCl_6 (0.00854 mol ℓ^{-1}) in water and 6 cm^3 of $SnCl_4 \cdot 5H_2O$ (0.0171 mol ℓ^{-1}, dissolved in 0.100 mol ℓ^{-1} HCl). After drying in sand bath under stirring, the impregnated alumina is left overnight at 393 K in an oven.

Bimetallic precursor. Wetness impregnation (sample N): The new bimetallic precursor was produced in the pores of the alumina. This was done by a two-step impregnation procedure. For 4 g support, the first step involved 2.56 cm^3 of $Pt(NH_3)_4Cl_2 \cdot H_2O$ solution (0.040 mol ℓ^{-1}) and the second step 2.56 cm^3 of $SnCl_4 \cdot 5H_2O$ solution (0.040 mol ℓ^{-1}) in 0.35 mol ℓ^{-1} HCl. After each step, the sample is dried in a rotovapor apparatus at 353 K for 2 h and finally overnight at 393 K in an oven.

Analytical results after drying (from the Laboratoire Central d'Analyse du CNRS) in mass %: exp. (calc.):
sample T: Pt 0.52 (0.50), Sn 0.24 (0.30);
sample N: Pt 0.48 (0.50), Sn 0.31 (0.30).

2.2. CHARACTERIZATION

TPR. The temperature programmed reduction curves were obtained from 400 mg sample by using a continuous flow apparatus (1% H_2 in Ar; 14 cm^3 min^{-1}) with a temperature ramp of 4 K min^{-1}.

Platinum dispersion. The accessibility of platinum was determined by hydrogen chemisorption (HC) using pressure measurements; the reduced sample (0.5–1.0 g) is pretreated under 100 kPa hydrogen (773 K; 2 h), then evacuated ($\sim 10^{-5}$ kPa) and cooled at room temperature. A further titration with oxygen gave a second value (OT). In the case of dried sample reduced at 573 K, the values of repeated OT and hydrogen titration (HT) were used, both giving identical results.

2.3. CATALYTIC MEASUREMENTS

Initial activity. The dried sample was reduced under Ar + 1% H_2 flow (4 K min^{-1} up to 773 K), then reactivated before test (H_2: 773 K; 2 h). Two catalytic reactions were carried out in a dynamic flow reactor: ring opening of cyclopentane and dehydrogenation of cyclohexane. The former reaction was studied on 50 mg catalysts at 563 K with a mixture of cyclopentane (10 kPa; 2 cm^3 liquid h^{-1}) and hydrogen (90 kPa; 79 cm^3 min^{-1}). The products were separated with a 3 m Squalane on Spherosil column and analysed with a flame ionisation detector (Intersmat IGC 120 1B chromatograph). Only *n*-pentane was detected in our conditions. Dehydrogenation of cyclohexane was investigated on 20 mg sample treated as above. The reaction was performed at 543 K with cyclohexane (3 kPa; 2 cm^3 h^{-1} liquid) and hydrogen 97 kPa; 6 ℓ h^{-1}). The separation column was a 3 m Reoplex 400 on Chromosorb. For both reactions, the initial activities were obtained by extrapolation of the linear part of the reactant consumption as a function of time.

Quasi-steady-state activity was probed with the skeletal reactions of *n*-hexane, measured in a closed circulation loop [25,26]. Results obtained at constant hydrogen/hydrocarbon ratio (1.33 : 16 kPa), at a constant sampling time of 5 min and at different temperatures between 573 and 663 K are presented here. The catalysts (70 mg) have been placed into the reactor after drying at 393 K and were pretreated in situ in circulating hydrogen of a pressure of 16 kPa at 573 K applying a cold trap cooled by liquid nitrogen in order to remove any water formed during reduction [27]. A fused silica column (50 m) coated with CP-Sil 50 served for analysis.

3. Results and discussion

The surface state of the two samples after preparation and drying are clearly different, as indicated by the different TPR curves (fig. 1) with a single sharp peak profile for sample T and a bumpy profile for sample N. The H/Pt ratios are 3.5 (calc. 2.0) and 4.8 (calc. 4.0) for the N and T samples, respectively, showing thus a deeper tin reduction for the sample with the bimetallic precursor. The calculated H/Pt ratios imply no change of the oxidation state of platinum in the precursor during the drying step; this most likely hypothesis is in agreement with previous EXAFS results for Pt(IV) [28] and with unpublished EXAFS data for Pt(II). The chemisorption data defined as the platinum accessibility gave much lower values for sample N (4% HC; 8% OT) than for sample T (28% HC; 40% OT). The dispersion of the dried samples (reduced with a ramp of 20 K min^{-1} up to 573 K) was 33% for sample N and 70% for sample T.

The difference between samples N and T may reveal deeper Pt–Sn interaction or larger crystallite size for sample N. The latter assumption had to be discarded on

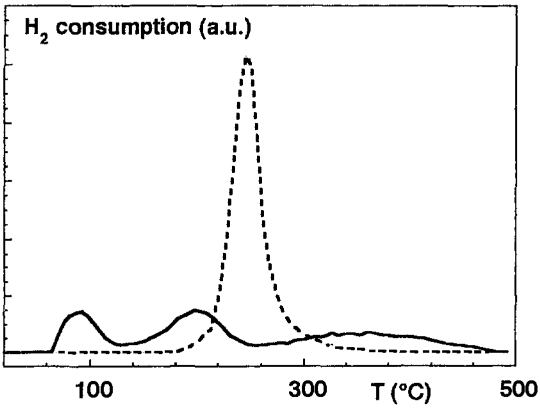

Fig. 1. TPR curves for dried Pt–Sn catalysts (the data are on the same scale). Full line: sample N prepared with Pt–Sn complex precursors; dashed line: sample T prepared with coimpregnation technique.

the basis of microscopic examination. XPS results with catalysts of similar preparation but higher metal loading show an enrichment of Sn on the surface [29]. We believe it is justified to think that the preparation method N brings more Sn to the surface in this case, too.

The *initial activity* of the samples T and N have been compared in the reactions of cyclohexane dehydrogenation which is a structure-insensitive process [24] and in the structure-sensitive skeletal reactions of cyclopentane ring opening [30] (table 1). The higher initial activity of catalyst T is obvious in both processes. The difference in the conversion is about one order of magnitude, but the *intrinsic* activity of catalyst T is higher by a factor of about 1.5 only in both reactions. The former fact confirms the presence of more Sn on the surface while the latter observation points to a lower intrinsic activity of surface Pt atoms and this can be attributed to either geometric reasons (dilution of Pt) or to an electronic interaction between Sn and Pt.

The *quasi-steady-state activity* of the dried and in situ reduced samples was probed with *n*-hexane [31] at different temperatures. The differences between the specific activities of samples T and N corresponded to the differences in dispersion (table 2). The apparent activation energies for the disappearance of *n*-hexane are low and exhibit the same values for both samples, namely 25 kJ mol^{-1} (table 3).

The two catalytic results are not directly comparable but can probe the catalytic properties from different aspects. The single pass reactor with rather low amounts of catalyst gave lower initial conversions for cyclohexane and cyclopentane; the closed loop with longer contact times, in turn, gave rise to higher conversions with *n*-hexane. In addition, a lower amount of sorbed hydrocarbons must have been present in the initial state than in the closed loop after 5 min of contact time, where the catalysts became covered with unsaturated hydrocarbon residues [32] formed by recirculating the unsaturated products (hexenes).

The rate of formation of individual products is shown in figs. 2 and 3 (expressed per mass Pt). Apart from generally higher rates with catalyst T, hardly any differences are seen at the lowest temperature of investigation (i.e., 573 K). More pronounced differences appear at higher temperatures. Catalyst T exhibits relatively high hydrogenolysis activity, fragments being the most abundant prod-

Table 1
Initial catalytic activity for cyclohexane and cyclopentane conversions (per cent conversions are given in parentheses)

Sample	Turnover frequency [a] (h^{-1})	
	cyclohexane dehydr. 543 K	cyclopentane ring opening 563 K
N	2450 (0.64%)	490 (0.1%)
T	4600 (8.5%)	770 (1.3%)

[a] Dispersion values determined by hydrogen chemisorption were used.

Table 2
Overall specific activities for *n*-hexane transformation at different temperatures (mol h^{-1} (g Pt)$^{-1}$) (per cent conversions related to the highest temperature are given in parentheses)

Sample	Temperature (K)				
	573	603	633	663	693
N	0.26	0.34	0.38	0.46	0.70 (18%)
T	0.32	0.44	0.53	0.63	0.84 (24%)

ucts from 633 K upwards. Its aromatization ability – as compared with the products of other nondegradative reactions – is also higher than that of sample N. Of this latter class of products, the formation of methylcyclopentane prevails with both catalysts, isomerization being relatively low. The ability of catalyst N to dehydrogenate *n*-hexane to hexenes is outstanding at 693 K and the corresponding rates are higher than for sample T from 603 K on. Table 3 gives the corresponding activation energies for the three reactions displaying an increasing rate versus temperature. Both samples show the same E_a for hydrogenolysis reaction (37 and 40 kJ mol^{-1}) and for benzene formation (49 kJ mol^{-1}), despite different rates. This can be related to the same type but different amount of active centres. On the other hand, for the formation of olefin, the activation energies are higher but different for sample N (150 kJ mol^{-1}) and sample T (128 kJ mol^{-1}), thus pointing to different reaction sites (vide infra).

Probing the catalysts by well-known model reactants may also give at least the fingerprint-like indications on the distribution of surface active states. Experiments with alloy catalysts showed that dehydrogenation of propane to propene requires single-atom sites [33] while three-atom ensembles have been proposed for aromatization of *n*-hexane [34]. The multiplet theory [35] assumes such ensembles for cyclohexane dehydrogenation, too. Hydrogenolysis requires a few contiguous Pt atoms [36]. C_5-cyclic reactions are only possible in the presence of surface hydrogen and we proposed that they involve at least two-atom sites [31,37]. These considerations were used to explain the differences between two Pt-black samples [38], and the overall initial activity differences seem to be in agreement with the above geometric considerations.

As for the quasi-steady-state activity, the surface of both catalysts was shown

Table 3
Apparent activation energies for the disappearance of *n*-hexane as well as for the formation of different products from *n*-hexane (estimated standard deviations are given in parentheses)

Sample	Activation energy (kJ mol^{-1})			
	reaction rate	fragments	olefin	benzene
N	25 (2)	37 (3)	150 (4)	49 (1)
T	25 (4)	40 (1)	128 (9)	49 (1)

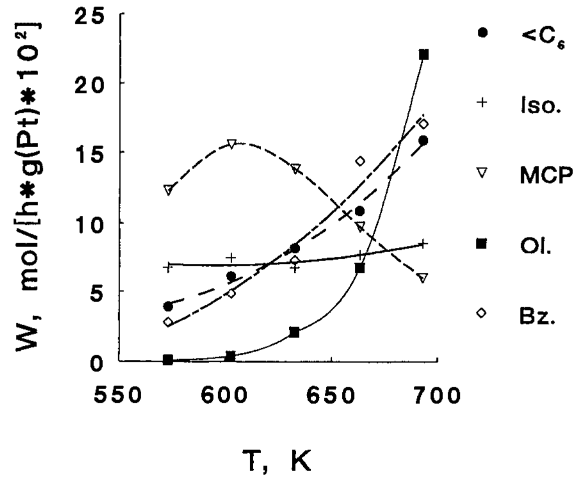

Fig. 2. Specific rate of formation of the products from *n*-hexane reactions for sample N.

to be largely covered by hydrogen at 573 K [31,39]. The product distributions are, therefore, rather similar. No particular promotion or suppression of any product by hydrogen is observed under these conditions on catalysts of different preparation. The fact that methylcyclopentane is a favored product, indicates a moderate abundance of hydrogen in the whole temperature range [37,39] which is not sufficient to produce more isomers. These consist of exclusively 2- and 3-methylpentane pointing to the predominant C_5-cyclic isomerization pathway [30]. A gradual hydrogen depletion of the surface at higher temperature [31,37,39] explains the decreasing amounts of both methylcyclopentane and skeletal isomers.

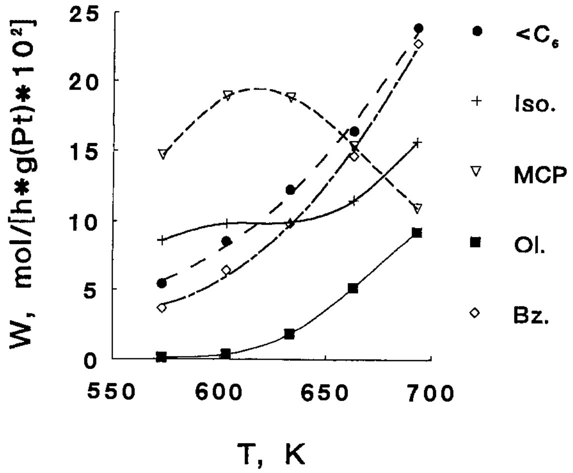

Fig. 3. Specific rate of formation of the products from *n*-hexane reactions for sample T.

The peculiarities of the two catalysts manifest themselves most pronouncedly at the highest reaction temperature. Hydrogenolysis becomes the most favored reaction over catalyst T (benzene being the second most abundant product), whereas the drop of yields of C_5-cyclic reactions is concomitant with enhanced olefin formation over catalyst N. This points to the presence of higher amount of contiguous Pt atoms in sample T than in sample N. The lower overall activities are in agreement with a higher amount of Sn dispersed on the surface of catalyst N and the catalytic probing demonstrates also that this Sn brings about a finer distribution of Pt in the catalyst prepared via the Pt–Sn complex precursor and that this state is preserved even under the conditions of catalytic reactions. No geometric reason can be given for the higher activation energy of dehydrogenation to hexenes on sample N since this reaction requires single-atom sites on both catalysts. Here a more pronounced electronic interaction between Pt and Sn can be assumed.

The present results support the view [40] that a well-selected combination of physical characterization methods with the use of probe reactions is indispensable for the proper characterization of catalyst surfaces.

Acknowledgement

This work has been carried out in the framework of Centre National de la Recherche Scientifique (CNRS)–Hungarian Academy of Sciences (HAS) cooperation (No. 4.2).

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