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The state of Tin on Pt–Sn/Nb_2O_5 catalysts

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Abstract

The effect of tin addition on niobia supported catalysts was studied and compared to the properties of alumina supported bimetallic Pt–Sn catalysts. The catalyst surfaces were probed by methylcyclopentane conversion, showing that both the presence of Sn and the reduction of the support caused a decrease in hydrogenolysis activity, favoring the ring enlargement reaction. The thermodynamics of reduction of these systems, evaluated by following the reduction step (temperature programmed reduction — TPR) with a differential scanning calorimeter (DSC), and irreversible H_2 and CO uptakes, allowed to conclude that a Pt–Sn alloy is formed on niobia supported catalysts. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Pt–Sn catalysts; TPR; DSC; Niobia

1. Introduction

Dehydrogenation of long chain alkanes is usually performed with alumina supported bimetallic catalysts such as Pt–Sn/Al_2O_3. Recently, an alternative Pt/Nb_2O_5 catalyst has been studied in hydrocarbon conversions (1–2). The initial results for *n*-heptane dehydrogenation on this catalyst displayed a higher selectivity towards the formation of olefins as compared to the ones obtained with conventional catalysts. Besides, the formation of aromatics and light products was minimized. These effects have been associated to the low acidity of calcined niobia and to an ensemble effect promoted by niobia reduced species on the platinum surface (strong metal support interaction — SMSI).

In this work, the effect of tin addition on niobia supported catalysts was studied and compared to the properties of alumina supported bimetallic Pt–Sn catalysts. The catalyst surfaces were probed by methylcyclopentane hydrogenolysis. The thermodynamics of reduction of these systems was evaluated by following the reduction step (temperature programmed reduction — TPR) with a differential scanning calorimeter (DSC). The adsorption properties of Pt and Pt–Sn catalysts were evaluated by irreversible H_2 and CO chemisorption.

2. Experimental

2.1. Preparation of catalysts

The catalysts were prepared by incipient wetness, using a commercial γ-Al_2O_3 (Harshaw Al3996, BET area: 200 m^2/g) and Nb_2O_5 (BET area: 80 m^2/g) as supports. Nb_2O_5 was obtained by calcination of niobic acid (CBMM, HY340/AD929) in air at 500°C for 2 h.

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Table 1
DSC–TPR of Pt catalysts

Catalysts	Composition (wt.%)		Energy change (10^{-1} Kcal/g metal)
	Pt	Sn	
Pt/Nb_2O_5	0.9	–	7.7
Pt/Al_2O_3	0.9	–	8.2
$Pt–Sn/Nb_2O_5$ (1:1)	0.9	0.95	11.9
$Pt–Sn/Nb_2O_5$ (1:2)	0.9	1.9	11.0
$Pt–Sn/Al_2O_3$	0.9	0.82	6.9

The monometallic catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of H_2PtCl_6 (Reagen), and $SnCl_2$ (Analar), followed by drying at 393 K for 16 h and calcination in air at 500°C for 2 h.

The bimetallic catalysts were obtained by impregnation of the supported tin catalysts by an aqueous solution of H_2PtCl_6. Then, they were dried at 120°C for 16 h and calcined in air at 500°C for 2 h. The platinum content was close to 1%, and the Sn content was varied between 1 and 2% (Table 1).

2.2. MCP hydrogenolysis

MCP hydrogenolysis was carried out at 10^5 Pa and 300°C. All the experiments were conducted with an MCP/H_2 (1:10.5) mixture. The space velocity was $30\,h^{-1}$ and mass of the samples were adequate to keep the conversions below 10%. The products were analyzed by a gas chromatograph equipped with a polypropyleneglycol on Chromosorb *W* packed column and a flame ionization detector. The selectivities to *n*-hexane, 2-methyl-pentane, 3-methyl-pentane, benzene and cyclohexane were calculated accordingly to the ratio between the molar amount of methylcyclopentane converted to a certain product and the total molar amount of methylcyclopentane converted.

2.3. Differential scanning calorimetry

The differential scanning calorimetry experiments were performed in a Thermal Analysis Station TA100-Rigaku. The calcined catalyst samples (15–20 mg) were dehydrated at 120°C for 30 min, under an Ar flow, before being submitted to a reducing gas consisting of a 1.0% H_2 in Ar stream. The flow rate was $30\,cm^3$/min, and the temperature was raised up to 500°C at a heating rate of 10°C/min.

2.4. H_2 and CO chemisorption

Carbon monoxide and hydrogen uptakes were obtained using an automatic adsorption system (ASAP 2900, Micromeritics). After reduction at 300 or 500°C under H_2 flow, the samples were evacuated at 10^{-6} Torr for 30 min at the reduction temperature and cooled to room temperature. Irreversible uptakes were obtained from the total and reversible adsorption isotherms.

3. Results

3.1. TPR–DSC

The energy change profiles obtained during the TPR/DSC experiments are shown in Figs. 1–5. The

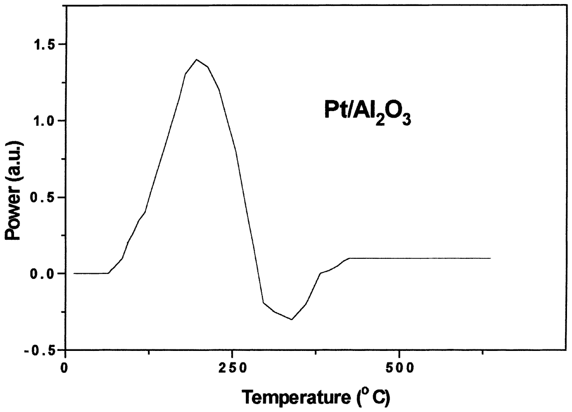

Fig. 1. DSC–TPR profile for Pt/Al_2O_3.

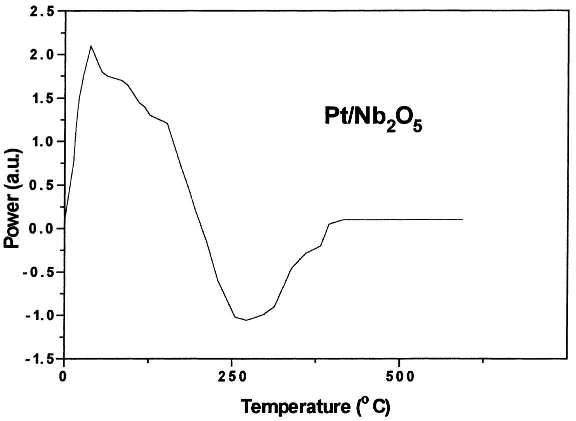

Fig. 2. DSC–TPR profile for Pt/Nb_2O_5.

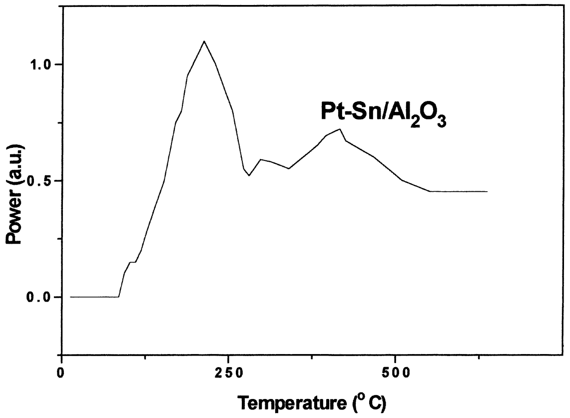

Fig. 3. DSC–TPR profile for Pt–Sn/Al_2O_3.

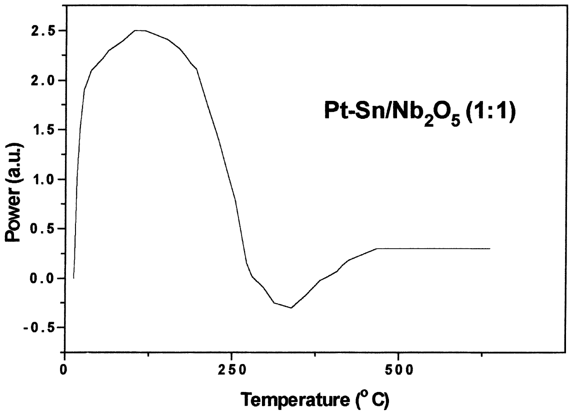

Fig. 4. DSC–TPR profile for Pt–Sn/Nb_2O_5 (1:1).

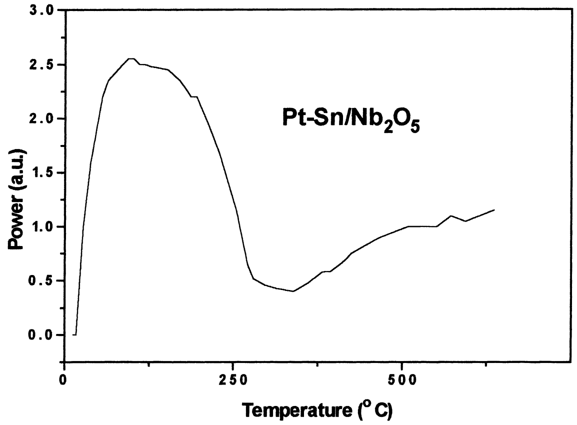

Fig. 5. DSC–TPR profile for Pt–Sn/Nb_2O_5 (1:2).

Pt/Al_2O_3profile presented only one exothermic peak, corresponding to platinum reduction, followed by an endothermic peak, which can be ascribed to the desorption of hydrogen adsorbed on reduced platinum. The profile obtained for Pt/Nb_2O_5 catalyst showed a broad peak of reduction beginning at room temperature, followed by an endothermic process after the metal reduction.

Pt–Sn/Al_2O_3 catalyst presented a first peak similar to the one presented by Pt/Al_2O_3, but its behavior was distinct at higher temperatures, showing two additional peaks. The niobia supported bimetallic catalysts presented broad peaks of reduction, starting at room temperature, which probably represents several simultaneous reduction processes. Moreover, Pt–Sn/Nb_2O_5 (1:2) presented an exothermic step at higher temperatures.

A quantitative analysis can be made by the integration of DSC profiles, and the calculation of energy changes of the reduction process. Table 1 displays these values, with the negative peaks of hydrogen desorption taken in account.

The monometallic platinum catalysts displayed similar energy change values (around 8 kcal/gmetal). The alumina supported bimetallic catalyst showed a slightly lower value, that is, less exothermic during the reduction step. On the contrary, the reduction process of niobia supported bimetallic catalysts was more exothermic, with an increase of 50% as compared to the heat released by Pt/Nb_2O_5.

Table 2
CO and H_2 chemisorption on Pt catalysts

Catalysts	CO (μmols/gcat)[a]	H_2 (μmols/gcat)[b]	CO/H_2
Pt/Nb_2O_5 red. 573 K	15.6	8.4	1.9
Pt/Nb_2O_5 red. 773 K	3.0	1.8	1.7
Pt/Al_2O_3 red. 773 K	35.2	17.1	2.0
$Pt–Sn/Al_2O_3$ red. 773 K	28.2	12.1	2.3
$Pt–Sn/Nb_2O_5$ (1:1) red. 573 K	23.1	5.5	4.2
$Pt–Sn/Nb_2O_5$ (1:1) red. 773 K	13.1	2.0	6.5
$Pt–Sn/Nb_2O_5$ (1:2) red. 573 K	18.6	8.3	2.2
$Pt–Sn/Nb_2O_5$ (1:2) red. 773 K	11.1	1.6	6.9

[a] Amount of CO irreversibly chemisorbed.
[b] Amount of H_2 irreversibly chemisorbed.

3.2. H_2 and CO chemisorption

Table 2 displays the results for CO and H_2 chemisorption for the several catalysts. The addition of $Sn–Pt/Al_2O_3$ catalysts caused a reduction of CO and H_2 uptakes as compared to Pt/Al_2O_3 catalysts. For Pt/Nb_2O_5 catalysts, the reduction at high temperatures caused also a decrease in the capacity of adsorption. $Pt–Sn/Nb_2O_5$ catalysts presented high CO/H_2 ratios, mainly after reduction at 500°C.

3.3. MCP conversion

Table 3 presents the turnover frequencies (TOF) for the two parallel reactions obtained in the MCP reaction, the hydrogenolysis producing hexanes (2-methyl-pentane, 3-methyl-pentane and *n*-hexane) and the ring enlargement producing cyclo-hexane and benzene.

The TOF values related to benzene production were very similar for all the catalysts. Thus, this route seems to fit in the insensitive structure concept proposed by Boudart [3]. On the contrary, the TOF values for hydrogenolysis were quite different. The addition of tin on Pt/Al_2O_3 catalyst produced a decrease in the ability to break C–C bonds, but this inhibition was more pronounced on niobia catalyst after higher temperature of reduction. The specific activity for the bimetallic system supported on niobia was about 2000 times lower than on Pt/Al_2O_3 catalyst. In fact, the hydrogenolysis of hydrocarbons are well-known in the literature as sensitive structure reactions and this was confirmed here.

Table 4 shows the product distribution obtained in the MCP reaction. The alumina supported catalysts presented similar results since the selectivity towards hexane was the main route and its distribution was also close to the statistical ratios. The production of light hydrocarbons and ring enlargement compounds was very small.

On the other hand, benzene was the main product obtained on niobia supported catalysts reduced

Table 3
Turnover frequencies values for hydrogenolysis and ring enlargement of methylcyclopentane

Catalysts	TOF - hydrogenolysis 10^4 (s^{-1})[a]	TOF - benzene 10^4 (s^{-1})[b]
Pt/Al_2O_3	1505	30
$Pt–Sn/Al_2O3$	677	27
Pt/Nb_2O_5 LTR[c]	65	13
Pt/Nb_2O_5 HTR[d]	7	23
$Pt–Sn/Nb_2O_5$ HTR	0.7	8

[a] Hydrogenolysis of the ring producing hexanes.
[b] Ring enlargement represented by the benzene production.
[c] Low temperature of reduction — 300°C.
[d] High temperature of reduction — 500°C.

Table 4
Product distribution in MCP reaction (%)[a]

Catalysts	C_1–C_5	2MP	3MP	n-C_6	Hydrogenolysis[b]	Cyclohexane	Benzene
Pt/Al_2O_3	2.6	37.0	26.6	32.0	98.2	–	1.8
$Pt–Sn/Al_2O_3$	6.0	33.4	27.0	30.0	96.4	–	3.6
Pt/Nb_2O_5 red. 300°C	13.3	25.0	28.0	15.0	81.3	4.8	13.9
Pt/Nb_2O_5 red. 500°C	2.9	6.3	4.5	8.0	21.7	7.6	70.7
$Pt–Sn/Nb_2O_5$ red. 300°C	6.1	4.1	7.0	7.0	24.2	3.8	72.0
$Pt–Sn/Nb_2O_5$ red. 500°C	2.7	1.5	2.7	3.0	9.9	4.1	86.0

[a] Isoconversion: 8–10%.
[b] Total amount of hydrogenolysis products: $C_1 - C_5$+hexanes.

at higher temperatures. Noteworthy, at this temperature, cyclohexane is easily dehydrogenated to benzene on platinum catalysts [1] The sum of ring enlargement products was more than 75% and the inhibition to hydrogenolysis was drastic. One can also include the $Pt–Sn/Nb_2O_5$ catalyst reduced at lower temperature inside this catalytic behavior. However, the monometallic catalyst supported on niobia reduced at 300°C presented an intermediate behavior producing benzene and cyclohexane, but hydrogenolysis was the main route. In fact, this catalyst produced the larger amount of light hydrocarbons which suggests the existence of large metallic ensembles on the surface and this points out to heterogeneous particles size distribution on this catalyst.

4. Discussion

Niobia and alumina supported catalysts presented different temperature zones of reduction of the metallic phase as described by TPR–DSC profiles. These results are in agreement to previous analysis shown elsewhere [1,4]. In fact, surface PtO_xCl_y species were observed on alumina supported catalysts while PtO_2 was the main species observed on niobia by UV–Vis spectra [1,4]. Lietz et al. [5] and Lieske et al.[6] showed that chlorine bonded to platinum oxide precursors presented higher temperature of reduction than PtO_2. The existence of different metallic precursors were clearly evidenced in a comparison involving the profiles of the monometallic Pt/Al_2O_3 and Pt/Nb_2O_5 catalysts.

However, the main reason to perform the TPR–DSC analysis was the investigation of bimetallic catalysts. The characterization of Pt–Sn catalysts are largely described in the literature [7–10] and the alloy formation on the surface has been a controversial task. Several in situ experiments under XRD [9], Mössbauer [7] and XPS analysis [8] have detected Pt–Sn alloys on $Pt–Sn/Al_2O_3$ and $Pt–Sn/SiO_2$ catalysts. On the other hand, some authors claim to a promoter effect of Sn^{+2} and its interaction with platinum and alumina [10]. This contradiction is related to distinct preparation methods and to the easy oxidation of surface Pt–Sn alloys even in the contact with very low oxygen concentrations, possibly present in the analysis chambers. The main advantage of the TPR–DSC technique is to be carried out at the same conditions of the catalytic pre-treatment, atmospheric pressure, dynamic reactor and the same gas used in the reduction before the catalytic reactions. Moreover, Sachtler and Van Santen [11] pointed out to Pt–Sn alloys as an example of exothermic alloy type. Thus, one can expect an increment in the energy change during the reduction of Pt–Sn catalysts with further alloy formation and this cannot be observed by traditional TPR–TCD experiments. In addition, the single reduction of tin oxide is endothermic and this allows us to get an unsuspicious analysis about the alloy formation. The results described in Table 1 indicate the existence of Pt–Sn alloys on niobia catalysts. On the other hand, the decreasing observed in the heat of reduction for $Pt–Sn/Al_2O_3$ catalyst as compared to monometallic catalyst is related to the endothermic reduction of tin and the alloy formation could not be evidenced.

In spite of the clear distinction observed between the heat of reduction for the bimetallic catalysts, the absolute values described in the Table 1 must be seen carefully. Rejai and Gonzalez [12] have shown that the thermal conductivity next to the catalyst surface is changed due to the hydrogen uptake and the generation of water, and this can alter the measurement of the enthalpy of reduction. However, the same authors [12] have presented a comparison of these resultant energies for Pt–Ru catalysts, since the analysis conditions were kept the same for all the samples.

Anomalous high CO/H_2 ratios observed for the Pt–Sn/Nb_2O_5 catalysts are in agreement with the presence of Pt–Sn alloys as described by Verbeek et al. [13]. In fact, the ensemble effect produced in the Pt–Sn particles caused a higher inhibition of dissociative adsorption of hydrogen than single CO adsorption. Thus, even ratios as high as 6 or 8 are reported in the literature for bulk Pt–Sn alloys [13].

The high exothermicity and the CO/H_2 ratios observed for Pt–Sn/Nb_2O_5 catalysts cannot be ascribed to the production of partially reduced NbO_x species during the catalyst activation. If the niobia reduction is influencing these parameters, one would observe similar changes in the Pt/Nb_2O_5 catalyst. In this case, the main niobia effect is to provide a higher mobility for the metallic phase than alumina support. Thus, bimetallic Pt–Sn interaction seems to be more important than SMSI effect on Pt–Sn/Nb_2O_5 catalysts.

The addition of Sn–Pt/Al_2O_3 showed some dilution of platinum surface atoms by Sn as observed by the decrease of the turnover frequency of MCP hydrogenolysis. However, the distribution of C_6 isomers has not changed significantly, with both catalysts presenting a non-selective distribution. This result is consistent with chemisorption results, which indicated the presence of small metallic particles on alumina surface.

In the case of niobia supported catalysts, MCP ring enlargement was as important as hydrogenolysis, with the formation of cyclohexane, which was rapidly dehydrogenated to benzene. The TOF results for this route indicated this is a facile reaction, which demands small ensembles or even isolated sites to occur. This way, the high selectivity to benzene and cyclohexane noticed for niobia supported catalysts can be attributed to a strong inhibition of the hydrogenolysis route.

The MCP isomerization reaction to cyclohexane is mostly promoted by acid sites [14]. However, other isomerization reactions normally catalyzed by acid sites are also carried out on metallic sites [15,16]. Meriaudeau et al. [17] observed the formation of MCP and benzene from *n*-hexane on a Pt/SiO_2catalysts, which indicates the interconversion of those molecules on metallic sites. In fact, previous results indicate niobia present less and weaker acid sites than alumina [2]. However, the TOF for benzene was not altered in the conditions the reaction was carried out. This result suggests that all reactions occurred on metallic sites. Clarke et al. [18] showed that for Pt/TiO_2 , H_2 partial pressure has a strong influence on MCP conversion, specially on SMSI conditions. At low H_2/MCP ratio values (∼1) the selectivity for benzene reaches 80% at 260°C and increases with temperature. The increase in H_2 concentration favored the hydrogenolysis route. The results are explained in function of the metallic phase, due to an increase of the electronic density of platinum, with no mention to acidity of the support.

The analysis of C_6 isomers formation for the Pt/Nb_2O_5 catalyst reduced at low temperature was difficult, as the total hydrogenolysis leading to light hydrocarbons competed with the aromatization. Nevertheless, it is possible to assume a relatively heterogeneous particle size distribution for this catalyst, due to the following reasons: (a) the occurrence of successive hydrogenolysis is less common for well dispersed platinum systems for the conversion range employed, additionally, the chemisorption results showed the platinum particles are larger on niobia than on alumina; (b) the decrease on hydrogenolysis TOF and the formation of cyclohexane and benzene are significant, what is expected for small ensembles, or for diluted ensembles formed by a premature beginning of SMSI behavior.

The increase on the reduction temperature for Pt/Nb_2O_5 catalyst caused the typical decrease on hydrogenolysis activity already reported by another SMSI systems [19]. The results fit the geometric model, in which the metallic particles are covered by sub-oxide species formed by support reduction. This intense dilution moved the reaction toward the cyclic ring enlargement and benzene production. For the Pt–Sn/Nb_2O_5 catalyst reduced at 300°C, the result was equivalent to Pt/Nb_2O_5 catalyst reduced at 500°C, that is, although the presence of tin inhibits the SMSI behavior as shown before [1], the bimetallic interaction causes a strong dilution effect even for low temperature of reduction. This catalyst also showed a high CO/H_2 ratio, typical of Pt–Sn alloys, even for this low temperature reduction, which is characteristic of metal–metal interaction.

The reduction of Pt–Sn/Nb_2O_5 at 500°C intensified the trends of dilution observed after reduction at 300°C, with a higher selectivity for benzene formation. Thus, the formation of Pt–Sn alloy seems to be more intense in this reduction condition.

5. Conclusions

The presence of Sn and the reduction of the support caused a decrease in MCP hydrogenolyisis activity, favoring the ring enlargement reaction. After reduction, Pt–Sn/Nb_2O_5 catalysts presented a bimetallic Pt–Sn interaction that was more important than the SMSI effect, with the formation of an exothermic alloy, as evidenced by the DSC–TPR experiments and CO and H_2 adsorption measurements.

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