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Surface Characterization of Li-Modified Platinum/Tin Catalysts for Isobutane Dehydrogenation

Mónica L. Casella,† Guillermo J. Siri,†,‡ Gerardo F. Santori,†,‡ and Osmar A. Ferretti*,†,‡

Centro de Investigación y Desarrollo en Procesos Catalíticos (CINDECA) and Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional de La Plata, calle 47 No. 257, CC59, B1900AJK La Plata, Argentina

María Magdalena Ramírez-Corredores

INTEVEP S.A., Catálisis Aplicada, Apdo. 76343, Caracas 1070A, Venezuela

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The superficial properties of different Pt/γ-Al_2O_3 catalysts, modified by the addition of tin and/or lithium, were studied by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, BET, and 2-propanol transformation. The results obtained were correlated with the behavior of the catalysts in applied reactions such as the dehydrogenation of isobutane. To obtain very well defined bimetallic superficial phases, tin was introduced by means of surface organometallic chemistry on metals techniques and the nature of the bimetallic-active sites so obtained was compared with the ones prepared by conventional procedures. XPS measurements indicate that tin is present in both zeroth valent and oxidized states. The addition procedure of both tin and lithium has a marked influence on the characteristics of the surface of the catalysts. The order in which lithium is added generates solids having different properties in relation to texture, dispersion, and catalytic behavior, for both Pt and PtSn systems.

Introduction

Most of the light molecular weight olefins are mainly produced by thermal and catalytic cracking processes but also from catalytic dehydrogenation. The increase in isobutene matches the increment in the demand for methyl *tert*-butyl ether (MTBE), motivated by the necessity of producing reformulated or oxygenated gasoline.[1,2] Platinum-based mono- and bimetallic catalysts supported on γ-Al_2O_3 are broadly used in dehydrogenation processes. The operating conditions imposed by thermodynamics to carry out the catalytic dehydrogenation of paraffins to olefins lead to catalyst deactivation. The process is endothermic, which requires high temperatures, a fact that besides representing a high energy cost, promotes the appearance of undesirable side reactions, such as the formation of carbonaceous deposits and light products. Pt/γ-Al_2O_3 is a very active catalyst for isobutane dehydrogenation, but its drawback is the simultaneous formation of light products. At the same time, deactivation of the catalyst due to carbonaceous deposits is very high. Also, the acidity of the alumina used as support catalyzes the undesirable cracking and isomerization reactions.[3−5] Obviously, a need for selectivity and stability improvement exists.

The addition of tin has an important effect on the selectivity toward the dehydrogenation reaction, at the expense of hydrogenolysis reactions, by decreasing the size of platinum ensembles needed. The addition of tin has also been suggested to improve the stability of the catalytic systems by decreasing the adsorption energy of coke precursors, increasing their mobility so that they can migrate easily to the support. Preparation techniques play a significant role in controlling the type of materials obtained. Surface organometallic chemistry on metals (SOMC/M) leads to well-defined bimetallic catalysts whose active sites have high homogeneity in their nature.[6−13]

On the other hand, improving selectivity also requires inhibiting the acid-catalyzed reactions on the support (isomerization, polymerization). The acid sites of the alumina support may be poisoned by adding alkaline metal ions.[14,15]

The aim of this work is to correlate X-ray photoelectron spectroscopy (XPS) information from different Pt/γ-Al_2O_3 catalysts, modified by the addition of tin and/or lithium, with their behavior in the dehydrogenation of isobutane.

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* Corresponding author: Dr. Osmar A. Ferretti, CINDECA, 47 No. 257, C.C. 59, B1900AJK La Plata, Argentina. Phone: 54-221-421-0711. Fax: 54-221-425-4277. E-mail: ferretti@dalton.quimica.unlp.edu.ar.

† Centro de Investigación y Desarrollo en Procesos Catalíticos (CINDECA), Universidad Nacional de La Plata.

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Table 1. Composition and Methods of Preparation of Studied Catalysts

catalyst	Pt (wt %)	Sn (wt %)	Li (wt %)	method of preparation
Pt	0.96			H_2PtCl_6 aqueous solution on γ-Al_2O_3
$PtLi^B$	0.90		1.0	H_2PtCl_6 aqueous solution on lithium impregnated γ-Al_2O_3
$PtLi^A$	0.96		1.0	LiOH aqueous solution on Pt catalyst
PtSn OM	0.96	0.32		$SnBu_4$ in *n*-C_7 solution (SOMC/M) on Pt catalyst
PtSn OM Li^B	0.90	0.27	1.0	$SnBu_4$ in *n*-C_7 solution (SOMC/M) on $PtLi^B$ catalyst
PtSn OM Li^A	0.96	0.32	1.0	LiOH aqueous solution on PtSn OM catalyst
PtSn SI	0.96	0.27		$SnCl_2$ aqueous solution on Pt catalyst
PtSn SI Li^B	0.90	0.25	1.0	$SnCl_2$ aqueous solution on $PtLi^B$ catalyst
PtSn SI Li^A	0.96	0.27	1.0	LiOH aqueous solution on PtSn SI catalyst

To obtain well-defined bimetallic catalysts, tin was introduced by means of SOMC/M techniques and the bimetallic catalysts so obtained are compared to the conventional ones. Also studied is the influence of the order in which lithium is added on the characteristics of the catalyst.

Experimental Section

A commercial γ-Al_2O_3 (Cyanamid Ketjen) crushed to a size of 60−100 mesh, was used as support. Before impregnation, it was calcined at 823 K for 3 h. A solution of H_2PtCl_6 having a concentration so as to obtain 1% w/w Pt exchanged was added onto the γ-Al_2O_3. The solid was repeatedly washed, dried at 378 K, calcined in air at 773 K, and reduced in flowing H_2 at the same temperature. The monometallic Pt/γ-Al_2O_3 catalyst so obtained was denoted Pt. Bimetallic catalysts were prepared using different deposition techniques of the metallic precursors. Samples designated PtSn SI were prepared introducing platinum first, as H_2PtCl_6, and then tin as $SnCl_2$. The PtSn OM catalyst series was obtained by employing SOMC/M techniques**.** The Pt catalyst was reacted with tetra-*n*-butyltin in *n*-heptane solution under H_2 atmosphere at 363 K. Elimination of all the organic moieties with a reduction treatment under H_2 flow at 773 K gave rise to the bimetallic phase PtSn/γ-Al_2O_3. Lithium was added in two different sequences: In one case (Li^B catalysts) γ-Al_2O_3 was impregnated with an aqueous solution of LiOH, then after drying and calcination, the metallic precursors were added. In the other case (Li^A catalysts), lithium was introduced on the reduced Pt and/or PtSn catalysts. After the reduction step, all the catalysts (monometallic, bimetallic, with and without Li) were washed several times with NH_3 solution (0.1 M) at room temperature, to obtain a chlorine concentration under 0.1% in the resulting solids. Table 1 summarizes the composition and methods of preparation of the different studied catalysts.

Hydrogen chemisorption measurements were performed in pulse dynamic equipment with catharometric detection, considering a stoichiometry of adsorption $H/Pt_s = 1$. The specific surface area (BET method) was determined by N_2 adsorption ($T = 77$ K), using Micromeritics equipment. Micrographs were obtained by using a Philips 505 scanning electron microscope. Samples of 100 mg of γ-Al_2O_3 with and without lithium were tested in the 2-propanol dehydration reaction at atmospheric pressure in a flow reactor. The alcohol was fed to the reactor in a nitrogen stream (30 $cm^3\ min^{-1}$). The reaction temperature ranged between 373 and 673 K. Reaction products were analyzed by gas chromatography, using a 1.2 m column packed with Carbowax 20 M on Chromosorb W and a flame ionization detector. XPS analyses were obtained with the surface analysis system from Leybold-Heraeus (LHS-11) equipped with a Al Kα (1486.6 eV) X-ray source. Prior to analysis, all the samples were reduced under H_2 atmosphere and mounted onto a manipulator which allowed the transfer from the preparation chamber into the analysis chamber without exposure to air. The binding energy (BE) of the C 1s (284.6 eV) peak was taken as an internal standard. Peak intensities were estimated by calculating the integral of each peak after subtraction of the S-shaped background and fitting the experimental peak to a Lorentzian/Gaussian mix of variable proportion.

Catalytic activity for isobutane dehydrogenation was measured in a conventional flow reactor at atmospheric pressure, 823 K, total feed flow of 50 $cm^3\ min^{-1}$, and a H_2/iso-C_4H_{10} ratio of 3. The composition of the feed flow and of the reaction products was analyzed by gas chromatography, using a Carlo Erba Fractovap series 2150 gas chromatograph on line with the reactor. A $^1/_4$ in. o.d. stainless steel column, 6 m in length, packed with tricresyl phosphate on Chromosorb W, operated at 353 K was employed in this work.

Table 2. Textural Properties and Chemisorption Capacity of Studied Supports and Catalysts

sample	S_g ($m^2 \cdot g^{-1}$)	H/Pt at/at
γ-Al_2O_3	185	
Li/γ-Al_2O_3	160	
Pt	185	0.36
$PtLi^B$	195	0.09
$PtLi^A$	160	0.34
PtSn OM	210	0.10
PtSn OM Li^B	205	0.02
PtSn OM Li^A	165	0.13
PtSn SI	200	0.11
PtSn SI Li^B	205	0.04
PtSn SI Li^A	170	0.10

Results and Discussion

The values of the specific surface area (S_g), measured by the BET method, are presented in Table 2. An important decrease in S_g values is observed when lithium is added after the metallic precursors impregnation. This decrease is in the order of 20−30 $m^2\ g^{-1}$ and is similar to that obtained when γ-Al_2O_3 is doped with the same Li amount. When the metallic phase is incorporated on the Li-modified support, the initial S_g value of the support is approximately recovered. This is a fact that can be assigned to the acid media existing during impregnation of H_2PtCl_6 (pH $\approx$ 2), discarding that the loss in the S_g value of Li-modified support could be a result of a sintering process of the γ-Al_2O_3.

Table 2 also shows the results of H_2 chemisorption for some of the catalysts, reported as the hydrogen to platinum atomic ratio (H/Pt). Two effects may be distinguished, that caused by the addition of tin and that by the action of the addition of lithium. When tin is added on Pt catalysts, a large decrease in chemisorption capacity is observed, as has been previously published.[15,16] The effect of lithium is strongly dependent on the way in which it is added. For the Li^B samples, in which lithium is added before the incorporation of the metallic precursors, the total quantity of chemisorbed hydrogen strongly decreased, both for the monometallic as well as for the bimetallic catalysts. The lower dispersion of the metallic phase can be attributed to modifications of the support textural and acid properties.

The changes in support acidity due to the addition of lithium were evident when the activity for 2-propanol dehydration was evaluated. From the expected products, the main yield was propylene (selectivity over 80%) but also small quantities of isopropyl ether and acetone were obtained. In Figure 1 the conversion is shown as a function of temperature, for different supports. A drop in the

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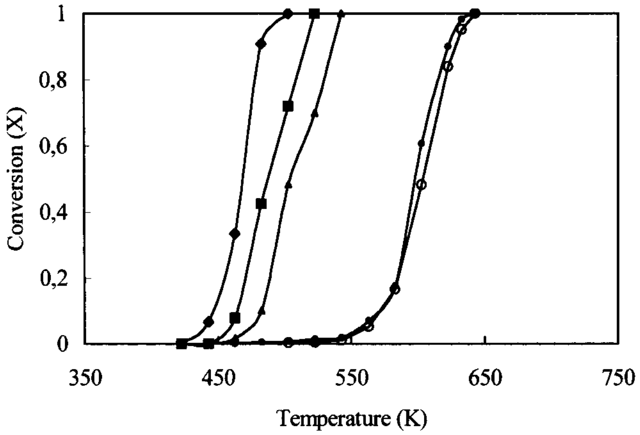

Figure 1. Influence of the reaction temperature (K) on the conversion of 2-propanol for γ-Al_2O_3 and γ-Al_2O_3 modified with different Li contents: (◆) γ-Al_2O_3; (■) 0.1% Li; (▲) 0.3% Li; (●) 1% Li; (○) 2% Li.

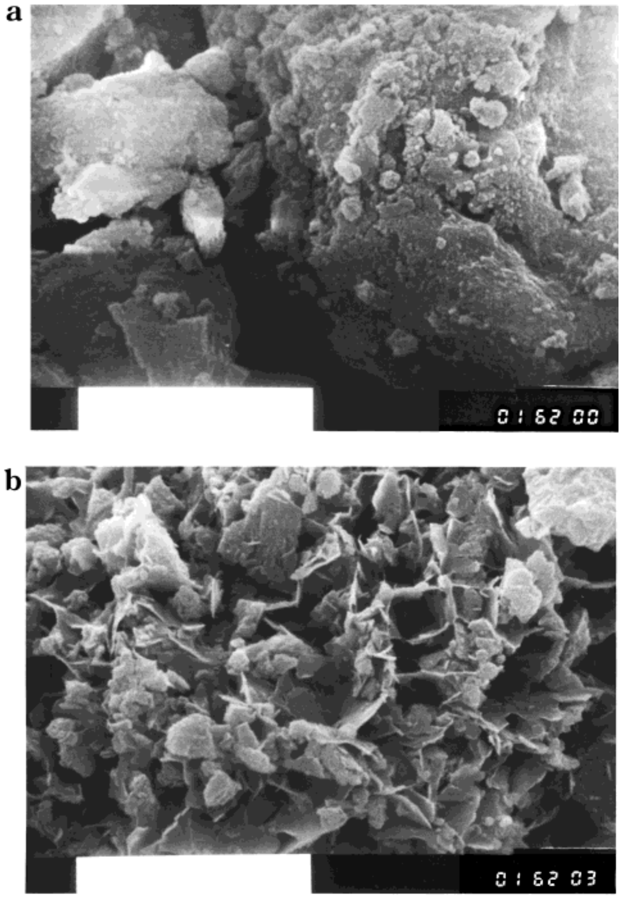

Figure 2. SEM micrographs (scale bar = 1 μm): (a) γ-Al_2O_3; (b) γ-Al_2O_3 modified with 1% Li.

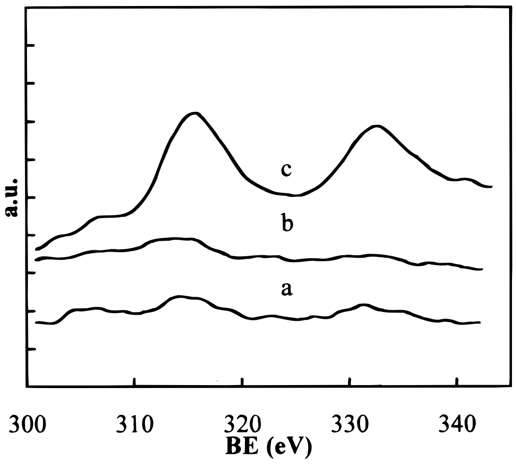

Figure 3. XPS Pt $4d_{5/2}$ region of the following catalysts: (a) Pt; (b) $PtLi^A$; (c) $PtLi^B$.

Table 3. Binding Energies (BE) (eV) for the Studied Catalysts, with Reference C 1s at 284.6 eV (Lithium Content 1% w/w Li)

catalyst	C 1s	Pt $4d_{5/2}$	Al 2p	Sn $3d_{5/2}$	Li 1s
Pt	284.6	314.8	74.4		
$PtLi^A$	284.6	314.1	74.2		54.7
$PtLi^B$	284.6	315.4	74.0		54.2
PtSn OM	284.7	313.6	74.3	484.6 486.5	
PtSn OM Li^A	284.6	313.8	74.1	484.6 486.5	54.5
PtSn OM Li^B	284.7	314.4	74.1	484.6 486.5	54.3
PtSn SI	284.5	313.4	74.1	486.3	
PtSn SI Li^A	284.6	315.6	74.1	486.3	54.3
PtSn SI Li^B	284.6	314.7	74.0	486.2	53.3

dehydrating activity of γ-Al_2O_3 is observed when it is doped with lithium. As shown in Figure 1, for lithium contents higher than 1%, there is no further modification of the dehydrating capacity of the γ-Al_2O_3. For instance, the temperature increases from 465 K for γ-Al_2O_3 to 600 K for Li-doped γ-Al_2O_3 (Li content 1 or 2%) in order to obtain an 2-propanol conversion of 50%.

The scanning electron microscopy (SEM) micrographs of γ-Al_2O_3 and Li-doped γ-Al_2O_3 are presented in Figure 2. As can be seen, the alumina support suffers an important modification in its texture when it is impregnated with lithium, probably due to the melting effect of LiOH whose melting point is 723 K. The catalyst activation temperature is higher than the melting point, so "patches" are generated on the γ-Al_2O_3 surface, as observed in the micrographs.

Figure 3 shows XPS spectra of lithium-modified monometallic catalysts ($PtLi^A$ and $PtLi^B$), in the region of Pt $4d_{5/2}$ (314.6 eV). This secondary line was chosen considering the overlapping of the Pt 4f lines with Al 2p line. The Pt signal of $PtLi^B$ sample is quite more intense than that of the $PtLi^A$ catalyst, giving $(Pt/Al)_{XPS}$ ratios of 0.94 and 0.22, respectively. These results seem to be coherent with the values of dispersion measured by H_2 chemisorption for the same samples as shown in Table 2. Thus, they could be interpreted in terms of the textural modifications of the support, following León's proposals.[17] Most likely, the promoter on the $PtLi^B$ catalysts has not been homogeneously distributed, but instead deposited onto the external surface of the material grains, due to the changes in the textural characteristics observed by SEM, for instance, pore plugging due to the melting of LiOH. The same behavior was obtained for the PtSn bimetallic catalysts modified by the addition of lithium.

Table 3 summarizes the results of binding energies (BE) for the studied catalysts. Although the complexity of these catalytic systems does not allow the extraction of many conclusions, it is observed that for Li-modified catalysts, the BE of Pt $4d_{5/2}$ is shifted from the value corresponding to Pt/γ-Al_2O_3, indicating a modification of the electronic density on platinum atoms.

The addition of tin causes a decrease in the BE of the Pt $4d_{5/2}$, which is more noticeable in those catalysts prepared via SOMC/M. This larger decrease in BE could be associated with an increase in the electronic density

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of the platinum atoms, a very important fact concerning the catalytic behavior of these organometallic systems. The oxidation state of tin and the possibility of alloy formation between Sn and Pt after the reduction step is often a point of controversy and seems to depend on the catalyst preparation method used. The results presented in Table 3 show that the PtSn OM catalyst has two peaks in the region corresponding to Sn $3d_{5/2}$ at 484.6 and 486.5 eV, assigned to Sn(0) and Sn(II,IV), respectively. This fact is not observed in the other bimetallic samples (PtSn SI), for which the Sn $3d_{5/2}$ signal is resolved as a narrow peak centered around 486.3 eV. These results are clearly indicating the influence of the preparation procedure upon the superficial characteristics of the catalysts. As a difference with PtSn/γ-Al_2O_3 catalysts obtained by using conventional techniques, in catalysts prepared via SOMC/M a signal due to Sn(0) can be undoubtedly detected. XPS results for PtSn SI systems are in agreement with data previously published for PtSn/γ-Al_2O_3 catalysts obtained by impregnation with $SnCl_2$ and H_2PtCl_6 ;[18−21] in the cases there presented, the only important peak is that corresponding to ionic tin (486−487 eV). Balakrishnan and Schwank assigned the presence of ionic tin to the existence of a very stable Al,Sn mixed oxide (probably an aluminate).[18] Bacaud et al. studied the same system by Mössbauer spectroscopy and observed large amounts of Sn(II) and Sn(IV) species and an important fraction of isolated platinum, corroborating the lack of specificity of the conventional preparation methods.[22] These conventional preparation procedures lead to detectable quantities of Sn(0) only when using supports such as SiO_2 or C.[18,23]

The deconvolution of the Sn $3d_{5/2}$ peak for the PtSn OM sample showed the contribution of Sn(0) (484.5 eV) and Sn(II,IV) (486.4 eV) species (see Figure 4 and Table 4). The presence of metallic Sn could be taken as an indication that part of the tin is probably forming a PtSn superficial alloy. Five stable alloys are known for PtSn systems: Pt_3Sn, PtSn, Pt_2Sn_3, $PtSn_2$, and $PtSn_4$.[24] For the PtSn OM studied catalyst, and taking into account that the dispersion of the platinum phase is 0.36 as measured by hydrogen chemisorption, the atomic ratio for Sn(0)/$Pt^{superficial}$ would be around 0.4; this would be compatible with an active phase composed of a superficial alloy $PtSn_y$ with $y \cong 0.4$ (i.e., Pt_3Sn) interacting with ionic tin located in the metal−support interphase, as previously proposed for RhSn/SiO_2.[12]

All the prepared catalysts were tested in the isobutane dehydrogenation reaction and the results, measured after 4 h on stream, are gathered in Table 5. Pt/γ-Al_2O_3 presents the highest reaction rate, but a very low selectivity toward isobutene, due to the important contribution of cracking and isomerization reactions. In relation to the catalytic behavior, additional evidence is the influence of the addition procedure employed to incorporate lithium: $PtLi^A$ catalyst shows almost the same level of global activity as the Pt catalyst with an important cracking activity, probably caused by the modification of the electronic properties of platinum atoms introduced by lithium, as observed by XPS. As could be foreseen, the presence of lithium on $PtLi^A$ catalysts provokes a strong diminution of isomerization reactions. On the other hand the $PtLi^B$ sample has a lower global activity than Pt^A, which could be explained in terms of the lower dispersion, measured by H_2 chemisorption (see Table 2). In relation to cracking reactions, $PtLi^B$ shows a similar behavior to the Pt sample, while isomerization reactions are strongly penalized. These results are indicating that the lithium concentration, as chosen from the 2-propanol dehydration reaction, was adequate in order to avoid isomerization reactions.

Whatever the preparation procedure employed (SI or OM), the addition of tin produces a catalytic material having an important selectivity toward isobutene. However, OM samples present higher activity, which can be explained in terms of the specific interaction between Pt and Sn in these PtSn samples derived from the use of SOMC/M techniques. In these materials tin is present in

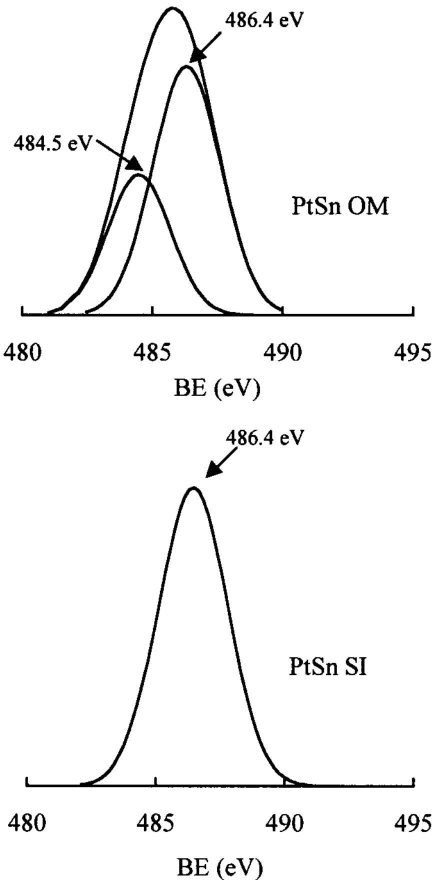

Figure 4. XPS Sn $3d_{5/2}$ region for PtSn bimetallic catalysts.

Table 4. Deconvolution of Sn $3d_{5/2}$ Peak of PtSn OM Catalyst

BE (eV)	species	%
484.6	Sn(0)	34
486.5	Sn(II,IV)	66

Table 5. Results of Catalytic Performance in the Isobutane Dehydrogenation (for Experimental Conditions, See the Text)

catalyst	$S_{cracking}$	$S_{isobutene}$	$S_{isomerization}$	r (mmol·g_{Pt}^{-1}·s^{-1})
Pt	0.20	0.53	0.27	2.5
$PtLi^A$	0.34	0.57	0.10	2.1
$PtLi^B$	0.20	0.75	0.05	1.2
PtSn OM	0.03	0.78	0.19	1.8
PtSn SI	0.04	0.88	0.08	1.0
PtSn OM Li^A	0.00	0.97	0.03	1.7
PtSn OM Li^B	0.01	0.99	0.00	1.0
PtSn SI Li^A	0.00	1.00	0.00	0.5
PtSn SI Li^B	0.05	0.93	0.02	0.3

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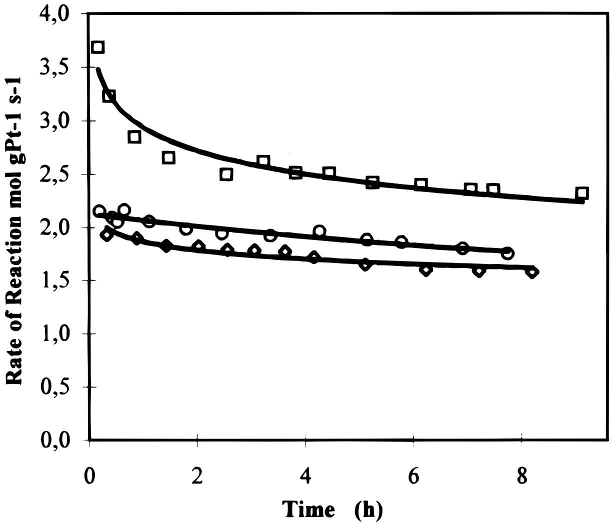

Figure 5. Dehydrogenation activity as a function of time for the following catalysts: (□) Pt; (○) PtSn OM; (◇) PtSn OM Li^A.

both metallic and oxidized states, as determined by XPS. The BE shift indicates a close interaction between platinum and tin species, Sn(0) and Sn (II, IV) leading to bimetallic catalysts (PtSn OM) with better properties (high activity and selectivity to isobutene) than the conventionally prepared catalysts. The selectivity to isomerization products is almost unaffected, indicating that, due to the specificity of SOMC/M techniques, tin might not be modifying the support acidity. Indeed, metal−metal interactions seems to be favored by the SOMC/M methods, inhibiting in this way the "waste" of metal promoter by direct interaction with the support material. Bimetallic catalysts prepared by successive impregnation, on the contrary, present a strong diminution in the isomerization reactions compared to the monometallic catalyst. Obviously then, some of the tin is deposited on the support, blocking its acid sites, during these preparations.

The effect of lithium addition on the bimetallic systems is similar to what was observed for the monometallic catalysts: (i) PtSn Li^B systems present a much stronger inhibition of isomerization reactions than PtSn Li^A systems; in fact, these reactions are almost extinguished. (ii) lithium added after the incorporation of the metallic precursors (PtSn Li^A catalysts) generates a system with a markedly higher activity that PtSn Li^B catalysts.

In Figure 5 the evolution of the catalytic activity is presented as a function of time on stream for the nonpromoted monometallic catalyst (Pt/γ-Al_2O_3), for PtSn OM, and for the system that showed the best global performance (PtSn OM Li^A). As can be observed, the activity decay along the reaction time is more pronounced for Pt/γ-Al_2O_3 than for PtSn OM Li^A catalyst, especially at the beginning of the analysis. The main cause of deactivation for both systems is coke formation, and their different behavior must be assigned to the presence of tin in the multimetallic catalyst. Tin, besides inhibiting the formation of coke due to the blocking of active sites, may be responsible for the diminution of coke rate deposition by means of an electronic effect. In fact the increase of the electronic density on the platinum atoms (observed by XPS) causes the decrease of the interaction between coke precursors and the active site. Figure 5 clearly shows the improvement achieved in the stability of the Pt catalysts when a formulation PtSn OM Li^A is obtained via SOMC/M preparation. This catalyst can be submitted to several sequential cycles of deactivation−regeneration, recovering the same level of initial activity each time.[25] The stability of the PtSn OM catalysts during the cycles of deactivation−regeneration is a very important property, especially taking into account that conventional preparations lead to SnO_2 segregation during the calcination in oxygen (analogous to the regeneration step).[26] Finally, it can be said that two promoters, Sn and Li, are required for high activity, selectivity, and stability in the isobutane dehydrogenation reaction.

Conclusions

On the monometallic platinum catalysts, XPS results indicate that when lithium is added after the metallic precursor ($PtLi^A$ catalyst), a system having an important dispersion is obtained. In this case, platinum presents an important modification in its electronic properties. When lithium is added before the metal precursor compounds, the dispersion of the resulting systems is markedly lower, due to the modification of the textural properties and of the acidity of the support. This lower dispersion is responsible for a lower catalytic activity, for both mono- and bimetallic catalysts (series Li^B).

The addition of tin improves the selectivity toward isobutene, whatever the preparation procedure employed. When tin is selectively deposited on platinum (via SOMC/M), the resulting material exhibits zeroth valent and oxidized states of tin. A close interaction occurs between Pt and Sn species as evidenced by a XPS BE shift. This interaction leads to bimetallic catalysts (PtSn OM) having better properties (selectivity to isobutene and stability) than the conventional ones.

Finally, the presence of both tin (added via SOMC/M) and lithium in the PtSn OM Li^A sample resulted in a catalyst having high activity and stability in the dehydrogenation of isobutane to isobutene, with an almost complete inhibition of undesired reactions (cracking and isomerization).

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