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# Influence of the Synthesis Method on the Catalytic Behavior of Pt and PtSn/Al<sub>2</sub>O<sub>3</sub> Reforming Catalyst

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Received December 1, 2008. Revised Manuscript Received June 14, 2009

The effect of the synthesis method over the catalytic behavior was investigated in Pt and PtSn catalysts. Catalysts synthesized using the one-step sol–gel method (OSSGM) were compared with those synthesized by conventional impregnation in the *n*-heptane reforming reaction at 500 °C and 1 atm, showing that the one-step sol–gel synthesis enhances both the activity and the resistance to deactivation by coking. The formation of coordinatively unsaturated aluminum (Al<sup>V</sup>) in the materials is promoted by the OSSGM, and it can be related to the increment in both their acidity and their platinum dispersion. Therefore, the bifunctionality of the catalysts, measured as the metal/acid site ratio ( $\Psi$  parameter), was also correlated to the Al<sup>V</sup> species. Higher values of  $\Psi$  implied a higher resistance to deactivation, higher rates of toluene production, and an inhibition of benzene induced by the OSSGM.

## Introduction

Alumina support has important industrial applications in the petroleum industry in reforming and hydrotreating processes.<sup>1</sup> For instance, many important hydrocarbon reactions, such as paraffin cracking and isomerization, are catalyzed by materials with acid properties. The most important naphtha reforming reactions occur through bifunctional catalysis. In this case, the metal function dehydrogenates the saturated hydrocarbons (alkylcyclopentanes or paraffins), producing more reactive olefin compounds. Therefore, the reaction to produce aromatic compounds is bifunctional since it uses both the metal and the acid sites.<sup>2</sup> In the catalytic reforming (CR) processes, platinum is the active component; it is found dispersed on the surface of an aluminum oxide used as support which has its acidity promoted by the addition of chlorine.<sup>3–5</sup> In the late 1960s, the monometallic catalysts were replaced by bimetallic Pt–Re/Al<sub>2</sub>O<sub>3</sub>–Cl catalysts, which were especially promising for low-pressure operation, helping to improve the length of the operation cycles due to a higher coking deactivation resistance, a higher selectivity to aromatic compounds, and a decrease of gas formation. In this context, new trimetallic catalysts have recently appeared in the literature, which are even more selective to isomerized compounds and more resistant to coke deactivation than the bimetallic ones.<sup>7–9</sup>

Alumina has been the subject of research and modified with different cations to produce mixed oxides with improved characteristics for CR.<sup>10–12</sup> For example, Contreras et al.<sup>11</sup> modified alumina with different cations (La<sup>3+</sup>, Zr<sup>4+</sup>, Ti<sup>4+</sup>), and according to their results, the modified support has a strong influence on the catalytic behavior of PtSn particles, particularly on the selectivity and deactivation of the reforming catalysts.

On the other hand, the wet impregnation method has traditionally been used to prepare mono- and bimetallic reforming catalysts. However, their final catalytic properties are strongly dependent on the preparation method employed; therefore, important changes have been observed in the catalytic behavior for the impregnated catalysts, e.g., the order of the metals addition in the case of bimetallic catalysts.<sup>8</sup> It seems necessary to do studies to attempt to improve the catalysts performance employing different methods of synthesis. In this sense, the sol–gel method has been reported as an alternative to produce better catalysts,<sup>13–15</sup> especially the one-step route. The one-step sol–gel method (OSSGM) starts with both the metal and support precursors and then goes all way to the final catalysts in one batch, producing catalysts with well-defined physical properties that increase the homogeneity and purity of the solid, with better microstructural control of the support, well-defined pore size distribution, and higher thermal stability of the catalyst.<sup>13</sup> However, Balakrishnan et al.<sup>14,15</sup> pointed out that the sol–gel method is very complex and requires a great degree

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(1) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of the Catalytic Processes*; McGraw-Hill Chemical Engineering Series: New York, 1979.

(2) Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice*; McGraw-Hill: New York, 1991.

(3) Regalbuto, J. R.; Antos, G. J. Preparation of Reforming Catalysts. In *Catalytic Naphtha Reforming*, 2nd ed.; Antos, G. J., Aitani, A. M., Eds.; Marcel Dekker: New York, 2004; pp 141–198.

(4) Hansel, V. U.S. Patent 2,479,101, 1949.

(5) Hansel, V. U.S. Patent 2,479,110, 1949.

(6) Klusksdahl, H. E. U.S. Patent 3,415,737, 1968.

(7) Fürcht, A.; Tungler, A.; Szabó, S.; Sárkány, A. *Appl. Catal. A: Gen.* **2002**, 226, 155–161.

(8) Carvalho, L. S.; Pieck, C. L.; Rangel, M. C.; Fígoli, N. S.; Grau, J. M.; Reyes, P.; Parera, J. M. *Appl. Catal. A: Gen.* **2004**, 269, 91–103.

(9) Carnevillier, C.; Epron, F.; Marecot, P. *Appl. Catal. A: Gen.* **2004**, 275, 25–33.

(10) Montoya, J. A.; Domínguez, J. M.; Navarrete, J.; Shifter, I.; Viveros, T.; Chadwick, D.; Zheng, K. J. *Sol-Gel Sci. Technol.* **1994**, 2, 431–435.

(11) Contreras, I.; Pérez, G.; Viveros, T. *Int. J. Chem. React. Eng.* **2005**, 3, A32.

(12) Montoya, J. A.; Rodríguez, C.; Shifter, I.; Monzón, A.; Viveros, T. *Stud. Surf. Sci. Catal.* **1994**, 88, 531–536.

(13) Lamber, C. K.; Gonzalez, R. D. *Appl. Catal. A: Gen.* **1998**, 172, 233–239.

(14) Balakrishnan, K.; González, R. D. *J. Catal.* **1993**, 144, 395–413.

(15) Balakrishnan, K.; González, R. D. *Langmuir* **1994**, 10, 2487–2490.

of control of the synthesis parameters; in their studies they obtained Pt/Al<sub>2</sub>O<sub>3</sub> and PtSn/Al<sub>2</sub>O<sub>3</sub> catalysts with higher surface area and metal dispersion using the sol–gel method, which were more resistant to coke deactivation than those conventionally synthesized. They suggested that the large surface area and big pore sizes obtained by the one-step sol–gel method can be responsible for the resistance to deactivation when the catalysts are tested in the *n*-hexane conversion due to prevention of pore blocking. However, some controversial results between the one-step sol–gel and traditional impregnated methods can be found in the literature. For instance, for the impregnation method platinum is present at the surface, whereas for the one-step sol–gel method the particles can be partially buried in the bulk of alumina, leading to the loss of Pt active sites which are not accessible for reactants, losing catalytic activity.<sup>16</sup>

There are other types of sol–gel catalysts that have been used in the catalytic reforming process.<sup>17,18</sup> These studies report the effect of tin on the activity of impregnated platinum, when tin is added to alumina by sol–gel. According to these findings, more active catalysts with lower deactivation are obtained by this procedure (two-step sol–gel method), the behavior being related to the formation of stable tin–aluminates and unreactive PtSn alloys. However, the diversity of ideas, methods, approaches, etc., reflects truly the present situation with the one-step sol–gel method where the experimental results as a function of several parameters lack well-established and generally valid interpretations. Since the literature is still far from being comprehensive, fundamental studies in the structural and surface characteristics of sol–gel catalysts will certainly contribute to the better understanding of the catalytic properties of this type of material. Changes in the coordination of aluminum ions induced by the preparation method can lead to modification of the acidity of the catalyst and finally to improve the catalytic behavior of the catalysts due to a higher interaction between metal and support, as a result of the formation of the mixed oxide during the preparation. Hence, in this work, the use of the OSSGM to improve the catalytic properties of supported platinum and platinum–tin is reported. The effect of the synthesis method on the changes in the coordination spheres of the aluminum, acidity, and catalytic properties of the reforming catalysts was investigated; the catalytic behavior and deactivation of the solids were evaluated in the *n*-heptane reforming at 500 °C and 1 atm. Monometallic Pt/Al<sub>2</sub>O<sub>3</sub> and bimetallic PtSn/Al<sub>2</sub>O<sub>3</sub> catalyst performance prepared via the one-step sol–gel method was compared to that obtained by traditional wet-impregnation samples. A detailed characterization was carried out, using physical adsorption of N<sub>2</sub> at liquid nitrogen temperature, thermogravimetric and thermodifferential analysis (TG-DTA), ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD),<sup>27</sup> AlMAS-nuclear magnetic resonance (NMR), temperature-programmed reduction (TPR), CO chemisorption, and transmission electron microscopy (TEM) measurements.

## Experimental Section

**Catalysts Preparation.** *Method A.* This method was used to prepare alumina to be used as the support for impregnated samples (conventional catalyst). The preparation procedure was based on

the methodology reported by Pérez-Pastenes et al.<sup>19</sup> Aluminum tri-*sec*-butoxide (ATB, Aldrich, 97%) was dissolved in 2-propanol (Baker, 77.8%) with a molar ratio of alcohol:ATB of 1:65. To produce 5 g of Al<sub>2</sub>O<sub>3</sub>, 25 g of the ATB was dissolved in 506 mL of 2-propanol. Then, the temperature of synthesis was lowered to 5 °C under vigorous stirring (400 rpm) and maintained constant at 5 °C. Subsequently, a solution containing enough deionized water and HNO<sub>3</sub> to satisfy the H<sub>2</sub>O:ATB molar ratio and HNO<sub>3</sub>:ATB molar ratio of 20:1 and 0.2:1, respectively, was added at a rate of  $21 \times 10^{-2}$  mL min<sup>-1</sup>. After adding the HNO<sub>3</sub>, the pH of the solution in the synthesis reactor was found to be ca. 4 and the sol formation took a place; subsequently, the obtained gel was aged for 24 h and then dried in a vacuum oven at room temperature. The xerogel obtained was calcined under air at 600 °C for 4 h using a 3 °C min<sup>-1</sup> heating rate. Alumina was impregnated conventionally with a solution of either H<sub>2</sub>PtCl<sub>6</sub> or H<sub>2</sub>PtCl<sub>6</sub> + SnCl<sub>2</sub> to produce mono- and bimetallic catalysts (Pt/Al<sub>2</sub>O<sub>3</sub>-I and PtSn/Al<sub>2</sub>O<sub>3</sub>-I), respectively. All catalysts were designed with 1 wt % of Pt and 0.6 wt % of Sn in the case of bimetallic catalysts, and before reaction, the calcined solid was activated in situ at 500 °C in H<sub>2</sub> flow for 2 h.

*Method B.* One-step sol–gel catalysts were prepared as follows: the solutions containing the metal precursors were prepared, the ATB was dissolved in alcohol (as method A), and the temperature (5 °C) and stirring speed (400 rpm) were reached. For the case of monometallic catalyst, a solution containing 129 mg of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Sigma, 39.2 Pt %) and enough deionized water and HNO<sub>3</sub> to satisfy the H<sub>2</sub>O:ATB and HNO<sub>3</sub>:ATB molar ratios used in method A was prepared. For the bimetallic catalysts, in addition to the platinum precursor, 47 mg of SnCl<sub>2</sub>·2H<sub>2</sub>O (Baker, 98.7%) was dissolved and the (PtCl<sub>2</sub>(SnCl<sub>3</sub>)<sub>2</sub>)<sup>2-</sup> complex<sup>20</sup> was formed (as corroborated by UV–vis spectroscopy). Afterward, those solutions were added to the ATB–alcohol mixture using an adding rate of  $21 \times 10^{-2}$  mL min<sup>-1</sup>, and a colored sol was obtained with a final pH ≈ 4. After 24 h of the aging process, the solvent was removed by drying under vacuum at room temperature and a xerogel solid was obtained. The resulting solid was calcined under air (3 L h<sup>-1</sup>) following the same thermal treatment of method A. Prior to reaction, the calcined solid was activated in situ at 500 °C in H<sub>2</sub> flow for 2 h.

**Catalyst Characterization.** The textural properties (i.e., surface area, pore size distribution) were measured by N<sub>2</sub> adsorption and desorption isotherms at liquid N<sub>2</sub> temperature in an Autosorb-1 Quantachrome equipment, using 100–120 mg of sample. Before analysis, the sample was outgassed in vacuum ( $\sim 1 \times 10^{-5}$  Torr) at 120 °C for 24 h. The total surface areas were obtained using the BET equation, while the pore size distributions were obtained using the BJH desorption procedure.

The thermal stability, weight loss, and thermochemical processes of xerogel samples were determined using an STA 409 EP NETZSCH thermoanalyzer. The TGA-DTA experiments were carried out in a static air environment from 20 to 1000 °C with a heating rate of 10 °C/min.

The total amount and strength of acid sites in the supports were determined by NH<sub>3</sub>-TPD. A 500 mg amount of sample was placed in a quartz tube microreactor, where a 6 L h<sup>-1</sup> helium gas flow was passed over the sample during the thermal treatment. The temperature was raised from room temperature to 500 °C using a 3 °C/min heating rate; it was held at this condition for 1 h and then cooled down to 100 °C. The helium flow was changed to a helium–ammonia mixture gas (NH<sub>3</sub> 5% balanced in He, Praxair). The sample was left in an ammonia flow until the acid sites were saturated (6 L h<sup>-1</sup> for 2 h). Once the excess and physically adsorbed ammonia was removed, the ammonia desorption stage started, increasing the oven temperature from 100 to 500 °C using a heating rate of 10 °C/min in flowing He; the TPD profiles were recorded using a thermal conductivity detector.

(16) Cho, I. H.; Park, S. B.; Cho, S. J.; Ryoo, R. *J. Catal.* **1998**, *173*, 295–303.

(17) Lopez, T.; Asomoza, M.; Gomez, R. *Mater. Lett.* **1994**, *19*, 199–206.

(18) Gomez, R.; Lopez, T.; Bertin, V.; Silva, R.; Salas, P.; Schifter, I. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 847–849.

(19) Pérez-Pastenes, H.; Ochoa-Tapia, A.; Montoya, J. A.; Viveros, T. *J. Sol-Gel Sci. Technol.* **2006**, *37*, 49–56.

(20) Baronetti, G. T.; De Miguel, S. R.; Scelza, O. A.; Fritzler, M. A.; Castro, A. A. *Appl. Catal.* **1985**, *19*, 77–85.

NMR spectroscopy was used to analyze the coordination spheres of <sup>27</sup>Al. Powder samples were studied in a Bruker ASX-300 NMR spectrometer, using a frequency of 78.21 MHz with a spinning speed of 10 kHz. All MAS NMR spectra were recorded after single excitation with a repetition time of 500 ms, and the chemical shifts were referred to aluminum in Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ion. The reducibility of the catalysts was determined by TPR with an ISRI, RIG-100 instrument; typical TPR experiments were carried out from room temperature to 1000 °C with a heating rate of 10 °C/min.

CO pulse chemisorption was used to measure the dispersion of the metallic phase of the catalysts; this CO chemisorption analysis was performed using an ISRI, RIG-100 instrument. Samples were reduced in situ in H<sub>2</sub> flow for 2 h and then cooled to room temperature in a He environment. The sample was saturated by pulses of CO (4.8% of CO balanced in He, Praxair) using a loop volume of 8 μmol; this way, the total amount of CO adsorbed in the samples was recorded using a thermal conductivity detector. Next, the samples were exposed to a He flow (6 L h<sup>-1</sup>) for 30 min to remove the physically adsorbed CO. Afterward, a second isotherm was measured, saturating the samples again with CO pulses. Once both isotherms were known, the chemically CO adsorbed in the monolayer was calculated by subtracting the amount of CO in the second isotherm from the first one. To determine the Pt dispersion, a CO/Pt stoichiometry of 1 was assumed and also that tin does not adsorb CO.

On the other hand, to estimate the average particle size from the results of CO chemisorption, the particles were assumed as spheres. The average particle size, *d*, was calculated from the following equation<sup>21</sup>

$$dD = 10^{21} \frac{M \times 6\rho_{\text{site}}}{\rho_{\text{metal}}N} \quad (1)$$

where *d* is the average particle size (nm), *D* is the dispersion, *M* is the Pt atomic weight,  $\rho_{\text{site}}$  is the Pt surface site density (12.5 Pt atoms/nm<sup>2</sup>),  $\rho_{\text{metal}}$  is the Pt density (21.45 g/cm<sup>3</sup>), and *N* is the Avogadro constant.

The size of the particles and morphology of the surface of the support were also observed using a Carl Zeiss EM-910 transmission electron microscope. To determine their average size, the crystals were considered spherical particles and a statistical method using 100 micrographs was performed for each catalyst. The TEM micrographs were obtained on samples which went through a thermal and reduction treatment (in H<sub>2</sub> flow at 500 °C for 2 h and He flow from 500 °C to room temperature). Samples were crushed to obtain very fine powders and dissolved in ethanol to obtain a cloudy solution. Then, an aliquot of that solution was added to a copper grid covered with an amorphous carbon layer.

The catalytic behavior of the materials was measured using the *n*-heptane (Sigma-Aldrich, 99%) reforming as a test reaction; in these experiments a typical continuous flow glass fixed bed microreactor coupled to a gas chromatograph was employed. The experiments were performed saturating a H<sub>2</sub> flow with the reactant (*n*-heptane) at ~0 °C (H<sub>2</sub>/*n*-heptane ratio equal 60, volumetric flow of 60 cc/min, 100 mg of catalyst, 500 °C, and 1 atm). At these conditions a system free of diffusional effects was assured; before carrying out the reaction all catalyst were activated in situ at 500 °C in H<sub>2</sub> flow for 2 h. During reaction the products were analyzed by gas chromatography, employing a 750 series Gow-Mac equipment, using an SE-30 packed column. The yield of one component was calculated as *C<sub>i</sub>/C<sub>t</sub>*, where *C<sub>i</sub>* is the concentration of product *i* and *C<sub>t</sub>* is the total concentration on stream; the selectivity was calculated as the ratio between the *C<sub>i</sub>/C<sub>j</sub>*, e.g., where *C<sub>i</sub>* is considered

**Table 1. Textural Properties of the Materials after Calcinations at 500 °C<sup>a</sup>**

sample	surface area, m <sup>2</sup> g <sup>-1</sup>	pore volume, cc g <sup>-1</sup>	pore diameter, Å
Pt/Al <sub>2</sub> O <sub>3</sub> -I	240	0.98	163
Pt/Al <sub>2</sub> O <sub>3</sub> -I-T	224	1.07	190
Pt/Al <sub>2</sub> O <sub>3</sub> -SG	337	1.38	164
Pt/Al <sub>2</sub> O <sub>3</sub> -SG-T	357	1.45	162
PtSn/Al <sub>2</sub> O <sub>3</sub> -I	245	0.97	140
PtSn/Al <sub>2</sub> O <sub>3</sub> -I-T	275	1.02	148
PtSn/Al <sub>2</sub> O <sub>3</sub> -SG	243	1.08	174
PtSn/Al <sub>2</sub> O <sub>3</sub> -SG-T	275	1.18	172

<sup>a</sup> I, impregnated catalysts; SG, sol–gel catalysts; T, after treatment at reaction conditions for 3 h without *n*-heptane.

as a desirable compound (toluene in our case) and *C<sub>j</sub>* corresponds to the undesirable compounds (benzene plus light compounds (C<sub>1</sub>–C<sub>4</sub>)).

## Results

The textural properties of the catalysts synthesized are given in Table 1. In this table samples calcined as well as those that after calcination went through a thermal treatment similar to the reaction conditions (60 cc min<sup>-1</sup> of H<sub>2</sub> for 3 h and 500 °C, without *n*-heptane) are shown. BET areas for the materials are between 240 and 357 m<sup>2</sup> g<sup>-1</sup>, even for those that went through the thermal treatment. For all solids, type IV isotherms were obtained with closed hysteresis loops described as type A, characteristic of the mesoporous solids with open cylindrical channels.<sup>22</sup> The total pore volumes lie in the range from 0.98 to 1.45 cm<sup>3</sup> g<sup>-1</sup>. Figure 1 shows the thermochemical behavior of the fresh dried precursors of pure Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>-SG. Only the results of monometallic catalysts are presented because no differences were observed between mono- and bimetallic catalysts. A weight loss of ca. 35% (Figure 1A) can be observed for alumina in the TG experiments in the temperature range from 100 to 400 °C, which coincides with exothermic and endothermic processes being present simultaneously. There is an endothermic signal between 100 and 170 °C, which is attributed to the evaporation of physically adsorbed water and solvent. Then, there is a sharp exothermic signal between 170 and 250 °C, produced by the combustion of residual organic compounds coming from the precursor of the solid, mainly 2-propanol and *sec*-butoxy groups;<sup>10,11,19,23</sup> the small exothermic signals with negligible weight loss at around 400–500 and 850 °C were caused by the structural rearrangement toward  $\gamma$ -alumina and  $\gamma$ - to  $\alpha$ -alumina, respectively.<sup>10,19,23</sup> In fact, the signal at 850 °C is not shown by materials synthesized by the one-step sol–gel method (Figure 1B), which suggests that Pt can be in the structure of alumina or interacting very strongly with the support, hindering its structural transformation.

Figure 2 shows the TPR profiles of both one-step monometallic and bimetallic sol–gel catalysts and the catalyst prepared by impregnation. For both types of catalysts pronounced hydrogen consumption between 200–300 and 350–500 °C can be seen. The hydrogen consumption in these catalysts is characteristic of the reduction of different species of PtO<sub>x</sub>. This reduction pattern has been frequently observed,<sup>24–26</sup> and it seems

(22) de Boer, J. H.; Lippens, B. C. *J. Catal.* **1964**, *3*, 38–43.

(23) Escobar, J.; de los Reyes, J. A.; Viveros, T. *Ind. Eng. Chem. Res.* **2000**, *39*, 666–672.

(24) Mazzieri, V. A.; Grau, J. M.; Yori, J. C.; Vera, C. R.; Pieck, C. L. *Appl. Catal. A: Gen.* **2009**, *354*, 161–168.

(25) Le Normand, F.; Borgna, A.; Garetto, T. F.; Apesteguia, C. R.; Morawek, B. J. *Phys. Chem.* **1996**, *100*, 9068–9076.

(26) Lieske, H.; Lietz, G.; Spindler, H.; Völter, J. *J. Catal.* **1983**, *81*, 8–16.

(21) Scholten, J. J. F.; Pijpers, A. P.; Hustings, A. M. L. *Catal. Rev.-Sci. Eng.* **1985**, *27*, 151–206.



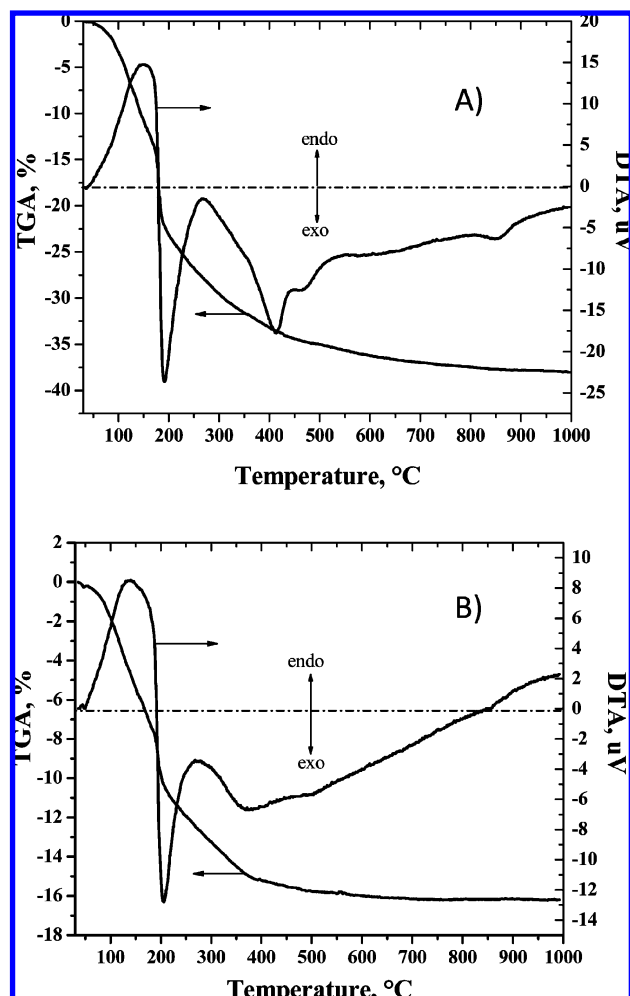


Figure 1. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA): (A)  $\text{Al}_2\text{O}_3$  and (B)  $\text{Pt}/\text{Al}_2\text{O}_3\text{-SG}$ .

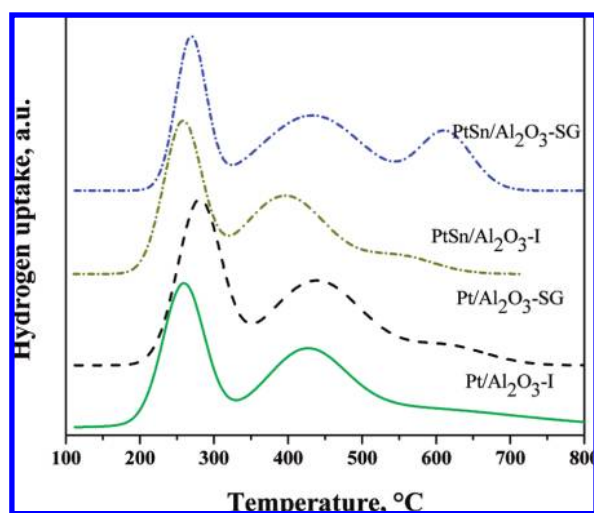


Figure 2. Temperature-programmed reduction (TPR) profiles of Pt and PtSn catalysts.

to be generally accepted that the first peak is due to reduction of the bulk of  $\text{PtO}_x$  weakly interacting with alumina, whereas the second  $\text{H}_2$  consumption band at higher temperature (350–550 °C) is due to the reduction of this species interacting strongly with the support. Several authors have attributed this signal to the reduction of oxy- or more probably hydroxychlorided Pt species strongly interacting with the support.<sup>24–26</sup> It should be noticed that in the above reduction processes the synthesis

method has a small effect; the reduction temperature of the platinum synthesized by the one-step sol–gel method is slightly higher than that observed in the impregnated catalysts. On the other hand, for the bimetallic sol–gel catalyst a third well-defined signal was found between 550 and 650 °C. Finally, from the total  $\text{H}_2$  consumption values of TPR profiles of Figure 2 the H/Pt atomic ratio was calculated and reported in Table 2; it can be seen that higher H/Pt values were obtained for solids synthesized by OSSSM. The H/Pt values shown in Table 2 lie between 1.8 and 2.88. These values were considerably smaller than those needed to reduce Pt oxides species ( $\text{Pt}^{4+}$  to  $\text{Pt}^0$ ), where H/Pt should be 4,<sup>27</sup> or for Pt hydroxide  $[\text{Pt}_2(\text{OH})_4\text{Cl}_2]^{2-}$ -like species in which H/Pt should be 6, according to Le Normand.<sup>25</sup> Thus, quantitative TPR results strongly suggest that our Pt species reduced during TPR experiment are related to  $\text{Pt}^{2+}$ , which upon reduction to  $\text{Pt}^0$  a H/Pt = 2 is observed, since no evidence of the typical signal of reduction of  $\text{Pt}^{4+}$ -like species, which occurs at 95–105 °C,<sup>27</sup> was detected in the TPR profiles.

Table 2 also shows the effect of the synthesis method on the particle size and dispersion of the catalysts. Data of the current metal load obtained by atomic absorption are also given. Small differences between designed and the actual metallic load were found in the materials. According to the CO chemisorption particle sizes between 1.44 and 2.60 nm were found. These results are compared with those obtained from TEM. As can be seen in Table 2, in 3 of the 4 samples TEM results show larger particle sizes than those obtained by CO chemisorption and 1 of the samples shows CO chemisorption particle sizes slightly larger than those from TEM. The actual errors, taking as a basis the smaller particle sizes, are between 9% and 49%. The largest difference is for the monometallic sample prepared by the one step sol–gel procedure. One possible explanation lies in the experimental errors of both techniques and also to the possibility that CO chemisorption is a more sensitive technique than TEM; therefore, the amount of CO adsorbed is large, giving higher dispersions and smaller particle sizes.

In the case of the bimetallic samples, the results are explained considering that conventional TEM is unable to discriminate between Pt and Sn particles and CO does not chemisorb on Sn particles; therefore, some Pt sites are blocked by tin. Consequently, CO chemisorption gives smaller particles than TEM. Table 2 also shows that metal dispersion is also improved by the one-step sol–gel method. Actually, the effect of tin over platinum dispersion becomes apparent; a decrease of ca. 8% in Pt dispersion is observed by the introduction of tin in impregnated samples, and a higher decrease was found for the sol–gel sample (approximately 35%).

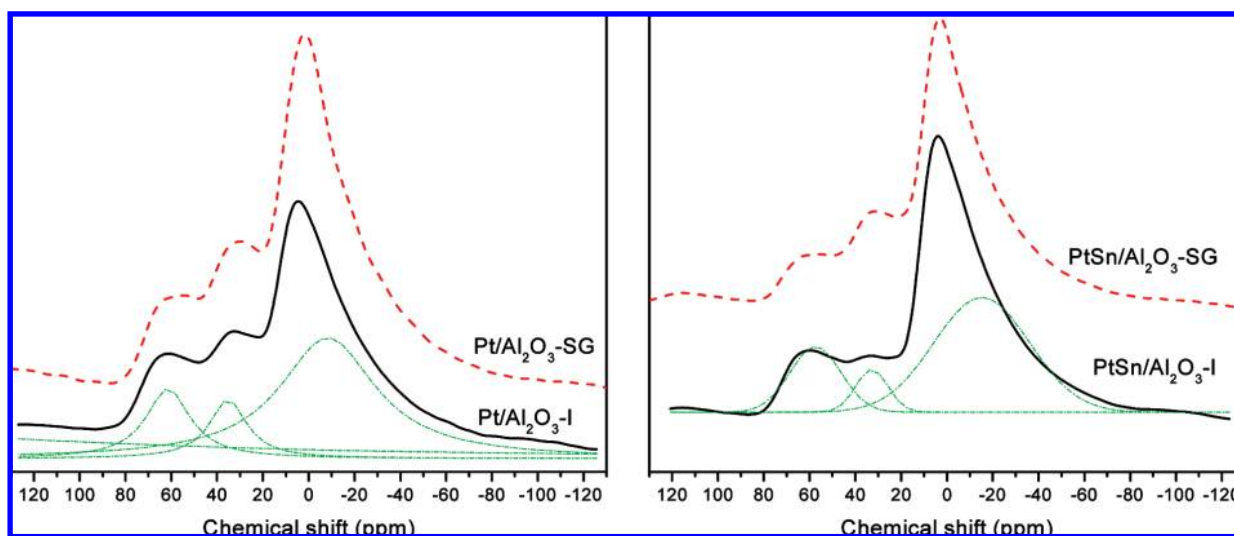
<sup>27</sup>Al MAS NMR spectra of calcined samples are shown in Figure 3. Three resonance signals are present mainly at ~0, 30, and 60 ppm; these signals are assigned to octahedral ( $\text{AlO}_6$ ), pentahedral ( $\text{AlO}_5$ ), and tetrahedral ( $\text{AlO}_4$ ) aluminum. From the quantitative analysis presented in Table 3, it is possible to observe that the amount of aluminum in a pentahedral environment is a function of the synthesis method; it seems that the one-step sol–gel procedure promotes the presence of this aluminum species, since the  $\text{Al}^{\text{V}}/\text{Al}^{\text{IV}}$  site ratio is higher for catalysts synthesized by the one-step sol–gel method (47% and 86% for monometallic and bimetallic catalysts, respectively) than those produced by impregnation. Table 3 also shows that the increase of the  $\text{Al}^{\text{V}}/\text{Al}^{\text{IV}}$  site ratio agrees with the increase of the total acidity of the supports.

(27) Borgna, A.; Le Normand, F.; Garetto, T. F.; Apesteguía, C. R.; Morawek, B. *Catal. Lett.* **1992**, *13*, 175–188.

**Table 2. Metal Loading, Dispersion, and Acidity Properties of the Catalysts**

sample	metallic load, <sup>a</sup> %		particle size, <sup>b</sup> nm		dispersion, <sup>c</sup> %		H/Pt ratio <sup>d</sup>
	Pt	Sn	CO Chem.	TEM	CO Chem.	TEM	TPR
Pt/Al <sub>2</sub> O <sub>3</sub> -I	0.89		2.53	2.30	45	49	2.28
Pt/Al <sub>2</sub> O <sub>3</sub> -SG	0.70		1.47	2.20	77	51	2.88
PtSn/Al <sub>2</sub> O <sub>3</sub> -I	1.07	0.66	2.76	3.01	43	38	1.81
PtSn/Al <sub>2</sub> O <sub>3</sub> -SG	0.72	0.34	2.26	3.00	50	38	2.59

<sup>a</sup> Determined by atomic absorption (AA). <sup>b</sup> Value  $\pm$  experimental error; 5% for CO chemisorption and 8% for TEM measurements. <sup>c</sup> Determined by CO pulse chemisorption assuming a 1:1 CO:Pt stoichiometry. <sup>d</sup> From the H<sub>2</sub> consumption values of TPR profiles.



**Figure 3.** <sup>27</sup>Al MAS NMR spectra for mono- and bimetallic catalysts supported on Al<sub>2</sub>O<sub>3</sub> synthesized by impregnation (solid line) and the sol–gel method (dashed line); the dashed dot line represents the deconvolution data reported in Table 3.

**Table 3. Relative Population of Al Species from Deconvoluted <sup>27</sup>Al MAS NMR**

sample	distribution, %				total acidity	
	tetrahedral Al <sup>IV</sup> ( $\delta$ = 60 ppm)	pentahedral Al <sup>V</sup> ( $\delta$ = 30 ppm)	octahedral Al <sup>VI</sup> ( $\delta$ = 0 ppm)	Al <sup>V</sup> /Al <sup>IV</sup> ratio	$\mu$ mol NH <sub>3</sub> /g	$\mu$ mol NH <sub>3</sub> /m <sup>2</sup> $\times 10^3$
Pt/Al <sub>2</sub> O <sub>3</sub> -I	19.91	15.51	64.57	0.78	0.51	2.28
Pt/Al <sub>2</sub> O <sub>3</sub> -SG	10.35	11.83	77.81	1.15	0.88	2.61
PtSn/Al <sub>2</sub> O <sub>3</sub> -I	12.21	7.07	80.17	0.58	0.59	2.13
PtSn/Al <sub>2</sub> O <sub>3</sub> -SG	21.60	24.0	54.40	1.11	0.57	2.34

The catalytic results are shown in Figure 4 and Table 4. These results show that the catalysts synthesized in the one-step method are more active than those prepared by impregnation. TOF calculations in Table 4 suggest that the intrinsic activity of the platinum catalysts is improved by the OSSGM.

From Figure 4 the effect of the synthesis method over the activity of the supported platinum particles is clear, since even though both catalysts suffered a high deactivation (81% and 51% for impregnation and sol–gel, respectively, see Table 4), the sol–gel catalyst is three times more active. When tin is present we also observe that the OSSGM samples are more resistant to deactivation than the impregnated ones. A 68% initial conversion was obtained for the Pt/Al<sub>2</sub>O<sub>3</sub>-SG catalyst with a residual conversion of 34% after 100 min reaction to give ca. 51% of catalyst deactivation, whereas for the Pt/Al<sub>2</sub>O<sub>3</sub>-impregnated (I) catalyst an initial conversion of 25% and residual conversion of 4.7% were obtained, showing a higher catalyst deactivation (81%). The higher resistance to deactivation was found for the one-step bimetallic PtSn/Al<sub>2</sub>O<sub>3</sub>-SG catalyst (only 36% deactivation after 100 min reaction). From Figure 4B it can also be observed that PtSn/Al<sub>2</sub>O<sub>3</sub>-SG showed a higher initial overall conversion (38%) than PtSn/Al<sub>2</sub>O<sub>3</sub>-I (25%). Impregnated catalysts (Pt/Al<sub>2</sub>O<sub>3</sub>-I and PtSn/Al<sub>2</sub>O<sub>3</sub>-I) showed similar residual conversions (ca. 5%), with only small differences in the slope of the deactivation as a consequence of the presence of tin. The bimetallic PtSn system is particularly

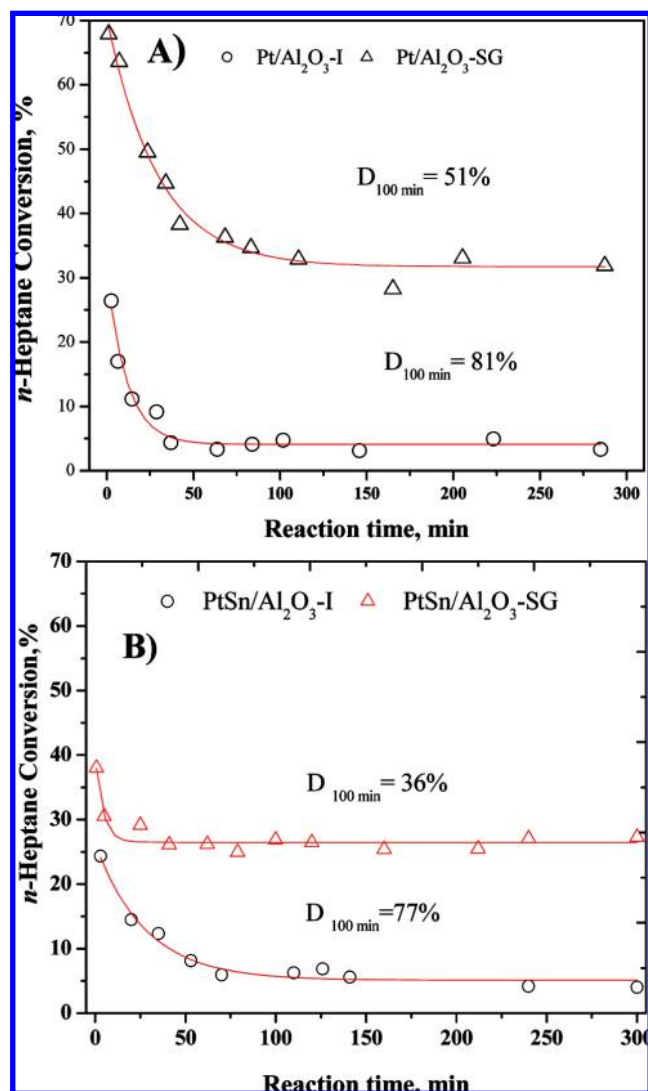
resistant to coke deactivation (Figure 4B); the lower deactivation of PtSn catalysts is in agreement with reports in the literature.<sup>28–33</sup>

The effect of the synthesis method on yield and selectivity is also shown in Table 4. In general, light compounds (C<sub>1</sub>–C<sub>4</sub>), benzene, and toluene were the main reaction products. The yield of toluene is higher than that for the other products for all catalysts. Also, benzene selectivity is more influenced by tin and the synthesis method than toluene selectivity.

## Discussion

This study reports the effect of the synthesis method on the catalytic performance and physicochemical properties of Pt and PtSn catalysts supported on alumina. The one-step sol–gel method employed for the synthesis produced materials with higher activity and higher selectivity that were more resistant to deactivation in the *n*-heptane catalytic reforming, in com-

- (28) Siri, G. J.; Ramallo-López, J. M.; Casella, M. L.; Fierro, J. L. G.; Requejo, F. G.; Ferretti, O. A. *Appl. Catal. A: Gen.* **2005**, 278, 239–249.
- (29) Burch, R. J. *Catal.* **1981**, 71, 348–359.
- (30) Gómez, R.; Bertin, V.; López, T.; Schifter, I.; Ferrat, G. *J. Mol. Catal. A: Chem.* **1996**, 109, 55–66.
- (31) Beltramini, J.; Trimm, D. L. *Appl. Catal.* **1987**, 31, 71–83.
- (32) Arteaga, G. J.; Anderson, J. A.; Becker, S. M.; Rochester, C. H. *J. Catal.* **1999**, 184, 268–279.
- (33) Barbier, J. *Appl. Catal.* **1986**, 23, 225–243.
- (34) Menon, P. G.; Froment, G. F. *Appl. Catal.* **1981**, 1, 31–48.



**Figure 4.** *n*-Heptane conversion profiles: (A) monometallic Pt catalyst and (B) bimetallic PtSn catalyst. The deactivation (*D*) after 100 min on stream is also given.

**Table 4.** Catalytic Behavior of Pt and PtSn Catalysts for the *n*-Heptane Reforming

catalyst	TOF <sup>a</sup> (s <sup>-1</sup> )	<i>D</i> <sup>b</sup> (%)	yield, %			
			C <sub>1</sub> –C <sub>4</sub>	benzene	toluene	toluene selectivity <sup>c</sup>
Pt/Al <sub>2</sub> O <sub>3</sub> -I	204	81	38	20	42	0.72
Pt/Al <sub>2</sub> O <sub>3</sub> -SG	301	51	13	3	84	5.20
PtSn/Al <sub>2</sub> O <sub>3</sub> -I	149	77	28	2	70	2.40
PtSn/Al <sub>2</sub> O <sub>3</sub> -SG	379	36	18	2	80	3.95

<sup>a</sup> Obtained at the beginning of the reaction assuming that all the fresh platinum surface sites are catalytically active. The dispersion, measured with CO chemisorption, and metal loading were used for these calculations. <sup>b</sup> Catalyst deactivation after 100 min on stream and 500 °C. <sup>c</sup> Calculated as toluene/benzene + C<sub>1</sub>–C<sub>4</sub> production ratio.

parison to those obtained via impregnation. The activity is increased for both mono- and bimetallic catalysts if the samples were prepared using the one-step sol–gel method (OSSGM); also, the Al<sup>V</sup>/Al<sup>IV</sup> ratio follows the same trend.

The OSSGM is a very complex process;<sup>14,15</sup> it produces more homogeneous and more stable materials than pure alumina. The better thermal stability of OSSGM materials was corroborated by TG-DTA results, when comparing the thermochemical behavior between the materials with and without platinum and noticing the absence of the DTA signal at around 850 °C for the platinum–alumina sample, which is observed in the alumina

sample. The hindering of the alumina structural rearrangement to corundum could be due to the homogeneous distribution of platinum into the alumina framework as has been observed for other cations.<sup>11</sup>

Therefore, it is reasonable to think that during the preparation of platinum-based catalysts with the OSSGM a homogeneous mixed oxide of platinum and aluminum is formed during the synthesis. This can help to explain the textural properties found in this work. In fact, the physisorption results for the samples that suffered a thermal treatment support the better thermal stability mentioned, since no surface area loss was found. The surface area results reported in this study agree with those shown by Gómez et al.<sup>30</sup> but not with those obtained by Balakrishnan and Gonzalez.<sup>14</sup> Balakrishnan and Gonzalez (1993) report a detailed study where the textural properties depend on the water/ATB ratio, showing that maximum surface areas occur at a water/ATB ratio of 3, which is different than the ratio used in this work (water/ATB = 20).

Regarding the structural results, NMR experiments indicate the formation of Al<sup>V</sup> sites when employing the OSSGM for the synthesis. The increase of Al<sup>V</sup> sites should be related with the formation of defects or disorder in the solid. In fact, the increase of Al<sup>V</sup> sites correlates very well with the increase of the acidity of the solids. According to the NMR results (Figure 3) tin seems to modify preferentially the five-coordinated Al<sup>3+</sup> in impregnated catalysts. In contrast to the result shown for the PtSn/Al<sub>2</sub>O<sub>3</sub>-I, no changes were observed between the NMR spectrum of Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>-I (spectrum not shown). For PtSn/Al<sub>2</sub>O<sub>3</sub>-I, a decrease of the Al<sup>V</sup> sites was observed when Pt and Sn were impregnated to the alumina support (Figure 3 and Table 3), which correlates with the decrease of the support acidity (which seems to be an effect of tin). In the case of the OSSGM catalysts, no significant changes were observed in the Al<sup>V</sup> and Al<sup>IV</sup> site distribution (Table 3) with tin.

As for the acidity properties of materials, it has been shown that tin clearly decreases the acidity of both impregnated and one-step sol–gel catalysts in the same proportion (7% and 10%, respectively). These results agree with those reported by Gómez et al.,<sup>30</sup> who observed a strong decrease of the acidity as a consequence of the cogelation of aluminum tri-*sec*-butoxide and tetrabutyltin.

After the reduction with hydrogen, a high metallic dispersion was found in one-step sol–gel samples as found by both CO chemisorption and TEM. The increment of platinum dispersion with OSSGM agrees with that reported by other authors,<sup>30,35</sup> who explained this increment to the exchange occurring between the hydroxyls and the platinum precursors. Even though for one-step sol–gel catalysts the Pt dispersion is always higher than those obtained by impregnation, they present a higher decay in dispersion from mono- to bimetallic catalysts (Table 2). The decrease of 35% of dispersion (from Pt/Al<sub>2</sub>O<sub>3</sub>-SG to PtSn/Al<sub>2</sub>O<sub>3</sub>-SG) in these catalysts suggests an enhancement in the interaction between Pt and Sn induced by this method. It also appears that the decrease in dispersion in one-step sol gel samples (measured with CO chemisorption) is due to the presence of Pt and Pt–Sn particles that remain in unreduced state, since the samples reduction for the chemisorption experiments takes place at a temperature (500 °C) lower than that needed to reduce the sample completely, as shown by the TPR experiment. According to the TPR experiments, in the PtSn/Al<sub>2</sub>O<sub>3</sub>-SG TPR profile a hydrogen consumption signal above 550 °C is observed. Several authors have suggested that the decrease in dispersion between

(35) Rodríguez-González, V.; Gómez, R.; Moscote-Santilla, M.; Amouroux, J. *J. Sol-Gel Sci. Technol.* **2007**, *42*, 165–171.



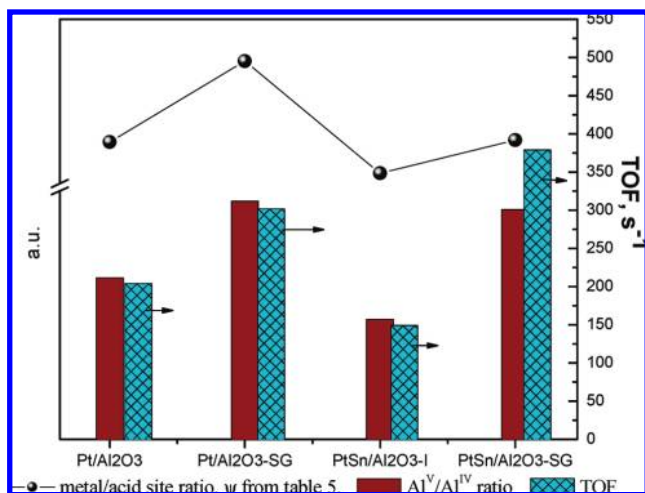


Figure 5. Recap of the main changes induced by the sol-gel method.

Table 5. Metal and Acid Density of the Catalysts

sample	metallic site density, <sup>a</sup> (Pt atoms/m <sup>2</sup> ) × 10 <sup>-15</sup>	acid site density, <sup>b</sup> (site/m <sup>2</sup> ) × 10 <sup>-16</sup>	metal/acid site ratio, $\Psi$
Pt/Al <sub>2</sub> O <sub>3</sub> -I	5.49	1.37	40.07
Pt/Al <sub>2</sub> O <sub>3</sub> -SG	7.85	1.57	49.92
PtSn/Al <sub>2</sub> O <sub>3</sub> -I	4.64	1.28	36.25
PtSn/Al <sub>2</sub> O <sub>3</sub> -SG	5.68	1.41	40.28

<sup>a</sup> Obtained from CO chemisorption. <sup>b</sup> Obtained from TPD-NH<sub>3</sub> analysis.

the sol-gel samples is due to the nonreduced platinum particles due to the metal-support interaction and the Pt-Sn interactions.<sup>8,34,35</sup> On the other hand, the average particle sizes calculated from CO chemisorption were comparable to those obtained with TEM (Table 2); these results suggest that Pt is not encapsulated into alumina as it has been suggested by other authors.<sup>16</sup> The shift to higher temperatures found in the TPR profiles for one-step sol-gel catalysts would indicate the presence of the metal-support interaction already mentioned or changes in the particle size. This change is more pronounced in PtSn catalyst, and the amount of hydrogen consumed in this material is related to the reduction of platinum of very difficult access, which is strongly interacting with the support. The TPR signal for PtSn/Al<sub>2</sub>O<sub>3</sub> should not discard the possibility of reduction of Sn(IV) to Sn(II) or Sn(0) as suggested by Nava et al.<sup>36</sup> and since its reduction has been observed in the temperature range of 200–300 and 380–520 °C, respectively.<sup>8</sup>

Regarding the catalytic performance, several facts are observed: the activity as TOF is higher for OSSGM catalysts than for impregnated ones, especially for monometallic samples; toluene selectivity is also higher for one-step sol-gel samples, and benzene yield although similar for monometallic samples decreases for those catalysts containing tin. The higher activity of sol-gel bimetallic catalysts has been reported by other authors.<sup>30,35</sup> In fact, the main results can be summarized in Figure 5. In this figure TOF, the Al<sup>V</sup>/Al<sup>IV</sup> ratio, and the  $\Psi$  (metal site/acid site) parameter shown in Table 5 are compared for each of the samples prepared. The parameter  $\Psi$  should be understood as a measurement of the bifunctionality of the catalysts, which is improved by the sol-gel synthesis. Our results reveal that the acidity of the support and the changes in the coordination spheres of aluminum have an important role

in the catalytic behavior. In fact, it seems that the  $\Psi$  parameter also has a relationship with the catalysts deactivation and the particle size, high values of  $\Psi$  correlate with lower deactivation and smaller Pt particles, suggesting that small particles are less sensitive to coke formation than larger particles as previously suggested by Beltramini.<sup>37</sup> Moreover, as tin is added, the deactivation decreases and PtSn/Al<sub>2</sub>O<sub>3</sub>-SG present lower deactivation than PtSn/Al<sub>2</sub>O<sub>3</sub>-I. Actually, the effect of tin on catalyst deactivation is widely documented.<sup>28,31–33,37,38</sup> The formation of the coke precursors is inhibited on the PtSn phases because these sites display low activity for transformation of methylcyclopentene (MCPe), which is the key intermediate for coke production.

On the other hand, the observed decrease in benzene production (Table 4) with tin in both the conventional and the sol-gel catalysts corresponds to the decrease in the amount of surface platinum as corroborated by CO chemisorption (Table 2), which suggests benzene production occurs mainly on Pt.<sup>33</sup> Similarly, benzene selectivity is strongly affected by the one-step sol-gel method (Table 4). The changes in selectivity of benzene and toluene can be explained if we keep in mind the metal-support interaction in one-step sol-gel catalysts occurred. This interaction can be connected with the peculiar activity of the metal-support boundary (adlineation) sites suggested by Hayek et al.,<sup>39</sup> where the adlineation of the defect of the support and the metal sites at the surface may be an important factor, which is promoted by the acidity of the support surface.<sup>40</sup> Therefore, platinum in the adlineation sites is electron deficient and has a very strong effect in the selectivity of benzene and toluene. To explain these differences in selectivity it should be considered that both benzene and toluene are absorbed nondissociatively prior to hydrogenation, but toluene is the stronger electron donor of the two; hence, its chemisorption on the metal should be less influenced.

## Conclusions

The effect of the of synthesis method on the physicochemical properties of supported Pt and PtSn reforming catalysts and in turn changes in the catalytic behavior has been studied. As the one-step sol-gel method (OSSGM) was used, there is an increase of the Al<sup>V</sup> species which correlates with the increase of the bifunctionality of the catalysts. In addition, as demonstrated by hydrogen TPR, the OSSGM induces stronger metal-support interactions, creating defects (Al<sup>V</sup>) in the support and consequently enhancing its acidity and metal dispersion due to a better interaction between Pt and these coordinatively unsaturated aluminum species (Al<sup>V</sup>). OSSGM produces not only reforming catalysts with less deactivation but also more selective to toluene, inhibiting benzene production.

**Acknowledgment.** The authors would like to thank the following: CONACyT-Mexico for financial support and CONACyT-Mexico and the Universidad Autónoma de Sinaloa for the scholarship granted to Ignacio Contreras-Andrade. Special thanks are given to Marco A. Vera for the NMR studies.

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(37) Beltramini, J.; Trimm, D. L. *Appl. Catal.* **1987**, *31*, 113–118.

(38) Carvalho, L. S.; Pieck, C. L.; Rangel, M. C.; Fígoli, N. S.; Vera, C. R.; Parera, J. M. *Appl. Catal. A: Gen.* **2004**, *269*, 105–116.

(39) Hakey, K.; Kramer, R.; Paál, Z. *Appl. Catal. A: Gen.* **1997**, *162*, 1–15.

(40) Akubuiro, E. C.; Verykios, X. E. *J. Catal.* **1988**, *113*, 106–119.

(36) Nava, N.; Montoya, A.; Viveros, T. *Mol. Phys.* **2002**, *100*, 3173–3175.