

# Characterization of bifunctional PtSn/H[Al]ZSM5 catalysts: a comparison between two impregnation strategies

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## Abstract

Bifunctional monometallic Pt/H[Al]ZSM5, Sn/H[Al]ZSM5 and bimetallic PtSn/H[Al]ZSM5 catalysts were prepared and characterized by means of XPS, TEM and toluene hydrogenation. For the bimetallic samples, co-impregnation of both metals and sequential impregnation (where Sn was added to monometallic Pt catalysts) were used with two tin atomic fractions,  $X_{\text{Sn}} = 0.46$  and  $0.28$ . Based on XPS data, it was found that the surface composition of the Pt–Sn bimetallic catalysts depends on the impregnation method employed: in the co-impregnated samples alloys form between both metals, while in the sequentially impregnated catalysts no alloy formation occurs but both Pt and Sn are easily reduced. Also, TEM analysis showed that the co-impregnated samples have similar particle sizes as the monometallic Pt catalysts, but that the particles in the sequentially impregnated samples are of larger sizes, closer to those seen in monometallic Sn catalysts. It is suggested here that while in the former case the particle size is not affected by the formation of Pt–Sn alloys, in the latter the tin covers the Pt species, and therefore increases the overall particle size. Finally, it was found that some hydrogenating activity could be detected with the co-impregnated catalysts but not with the sequentially impregnated samples, even though the latter had only a small fraction of atomic tin. In general, the results obtained in this study show a significant variation in catalytic properties with the method of preparation used for these bifunctional PtSn/H[Al]ZSM5 catalysts.

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**Keywords:** Pt–Sn catalysts; Bifunctional catalysts; XPS; TEM; Toluene hydrogenation

## 1. Introduction

Heterogeneous catalysis is a field with immense technological importance, being the backbone of a variety of large-scale processes in the petroleum and chemical industries [1]. The success of catalysis relies on the ability of the catalysts to modify the kinetics of the chemical system being catalyzed [2]. To improve their efficiency, the active phase of heterogeneous catalysts are generally dispersed onto high surface-area materials. This is typically the case with metals, which are often supported on highly porous silico-alumina oxides. Those catalysts are commonly prepared by impregnation, in which the oxide carrier is contacted with a solution of a salt or other soluble compound of the desired metal [1]. Nev-

ertheless, other synthetic methods have been advanced over the years, and it has been shown that the performance of the catalyst depends in great part on the way it is made. In this report, we explore the effect of varying preparation methods on the physical properties of zeolite-supported Pt–Sn bimetallic catalysts. A great interest has been developed over the last decades on the possible specificity associated with bimetallic catalysts. Indeed, the incorporation of a second metal to catalysts has proven to often provide additional catalytic stability, selectivity and/or activity [3,4]. The effects of a second metallic component can be very specific, and depend, among other factors, on the nature of the metals dispersed over the support surface, the method employed to prepare the catalyst, the atomic ratio between the two metals, and the type of reaction catalyzed [5]. In the case of catalytic reforming, where saturated hydrocarbons from crude oil are converted to higher octane-number isomers [6], particular attention has

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been placed on the use of Pt–Re [7] and Pt–Sn [8] bimetallic systems. The improvement of the properties of the platinum phase in these catalysts can be traced back to the formation of alloys, which can lead to a reduction in size of the Pt-supported particles (although, as it will be shown here, this depends on the method used to prepare such catalysts), and with that to lower coke formation and higher selectivity towards the desirable products [9]. Pt–Sn alloys formation has been reported on  $\text{Al}_2\text{O}_3$  [10–13],  $\text{SiO}_2$  [9,14,15], carbon black [16,17] and H-mordenite [18] supports, to mention a few.

Another interesting application for these Pt–Sn bimetallic catalysts is in the synthesis of fine chemicals. For instance, we in a previous work have found that PtSn/H[Al]ZSM5 catalysts prepared by co-impregnation of both metals show significant improvements in selectivity towards methyl isobutyl ketone (MIBK) synthesis from acetone [19]. However, a systematic design of better bimetallic catalysts for the manufacturing of specific chemicals is still difficult, in great part because the exact nature of these systems is still unknown [14]. For one, platinum and tin are known to form several intermetallic compounds with different stoichiometries [18], and tin can also exist in three oxidation states: Sn(0), Sn(II) and Sn(IV) [20]. It has been found that the methodology followed in the preparation of Pt–Sn catalysts may lead to different metallic phases, and, therefore such methodology plays an important role in determining the nature of the solid and its catalytic performance [12,15,16,21]. In one study, Coloma et al. contrasted the properties of several catalysts supported over carbon black, prepared by both co- and sequential impregnations, and found the presence of tin in both metallic and oxidized states in the reduced catalysts with different relative amounts depending on the preparation method [16]. In a second report, Chantaraviton et al. found that co-impregnation of the  $\text{Al}_2\text{O}_3$  support with small amounts of tin facilitates high Pt dispersions, while sequential impregnation of the support with Sn first followed by Pt leads to much lower Pt dispersion [12]. The use of anchoring-type controlled surface reaction techniques to prepare PtSn/ $\text{SiO}_2$  catalysts can also ensure an intimate contact of the base metal with the second metal.

As the few examples mentioned above indicate, extensive work has already been carried out on the characterization of Pt–Sn bimetallic catalysts supported on amorphous high-surface area materials. However, much less research has been performed on Pt–Sn catalysts based on zeolites [18,22]. The use of zeolites such as the well-known ZSM5 family may be highly desirable for the production of catalysts to be used in the fine chemical synthesis, because their well-defined porous sizes can be used to obtain additional shape selectivity [23,24]. Giving the uncertainties still outstanding with respect to the nature and performance of Pt–Sn catalysts supported over such crystalline aluminosilicates, we in this work set to characterize several bifunctional PtSn/H[Al]ZSM5 catalysts prepared by two different methods, co-impregnation and sequential impregnation, in order to compare their surface characteristics and catalytic

behavior, and, in this way, complement our previous results on the reactivity of the PtSn/H[Al]ZSM5 co-impregnated system [19,25]. Different characterization techniques were used here, namely, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and toluene hydrogenation reactivity studies. Interesting correlations were found between the preparation method used and both the nature of the resulting metal particles and their catalytic activity. These are discussed below.

## 2. Experimental

Four bifunctional catalysts were prepared in these studies using a zeolite of the Mobil Five (MFI) type (Si/Al=15) as support, two monometallic catalysts (0.5%Pt/H[Al]ZSM5 and 1.0%Sn/H[Al]ZSM5) by using an exchange-impregnation and excess volume method, a bimetallic PtSn/H[Al]ZSM5 catalyst ( $X_{\text{Sn}}=0.46$ ) by using a simultaneous exchange-impregnation (co-impregnation *CI*) method, and another bimetallic PtSn/H[Al]ZSM5 catalyst ( $X_{\text{Sn}}=0.28$ ) by using a sequential exchange-impregnation method (*SI*), where the desired quantity of Sn was added to a previously reduced Pt/H[Al]ZSM5. The metallic precursors used to prepare the catalysts were  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ .

These catalysts, once calcinated under a flow of dry air for 6 h (Pt/H[Al]ZSM5 at 300 °C [26], Sn/H[Al]ZSM5 and PtSn/H[Al]ZSM5 at 500 °C [27]) and reduced under hydrogen atmosphere for another 6 h (all at 500 °C), were characterized by means of XPS and TEM. The XPS analysis was carried out in a VG Scientific X-ray photoelectron spectrometer (ESCALAB 220i-XL) equipped with a dual anode Al/Mg X-ray source. The reduction treatment was carried out in situ by heating the fresh samples under a hydrogen flow at 500 °C for 2 h to avoid any contact with air. The spectra of the reduced catalysts were taken immediately afterwards by transfer to a vacuum ( $10^{-8}$  to  $10^{-11}$  mbar) environment without exposure to air. The binding energy values of the XPS signals were calibrated by using the Si 2p peak at 102.9 eV as reference [28]. The TEM pictures of the external surface of the catalysts were acquired in a JEOL electron microscope (JEM-1220), operated at 120 kV. The samples for this analysis were first prepared in a suspension with 30% of ethanol, and the mixture then ultrasonicated for 5 min until the suspension was homogeneous. Afterwards, one drop of this mixture was placed over a copper grid previously covered with colloidal carbon for use in the TEM. Finally, the catalytic activity for the hydrogenation of toluene of all the bifunctional monometallic and bimetallic samples made in this study was estimated at 110 °C and under atmosphere pressure, using a  $P(\text{H}_2)/P(\text{toluene})=4$  and a weight-hour-space-velocity (WHSV) =  $21.5 \text{ h}^{-1}$ . The reactor effluents were injected in line into a HP-5890 chromatograph equipped with a 25 m OV-101 column and a flame ionization detector (FID).

### 3. Results and discussion

#### 3.1. Toluene hydrogenation

Taken advantage of the fact that the catalytic hydrogenation of toluene is sensitive to both the density of metallic centers and the nature of the supported phase [29], a correlation was obtained here between the hydrogenating activity of our four different catalysts, normalized per gram of platinum extrapolated at zero time ( $AH_0$ ), and the population of metallic centers present in the solid samples. The comparative reactivity studies were also aimed to evidence possible changes in activity due to either electronic or geometric effects in these catalysts caused by the addition of the second metal and by the type of preparation method employed.

Table 1 summarizes both the basic physico-chemical characteristics of the catalysts and their hydrogenation activity. According to these results, a remarkable difference in  $AH_0$  is seen between the monometallic Pt/H[Al]ZSM5 and bimetallic PtSn/H[Al]ZSM5 samples. In addition, observable differences are also detected between the two bimetallic catalysts depending on the type of impregnation strategy employed. In particular, the PtSn/H[Al]ZSM5 *CI* ( $X_{Sn} = 0.46$ ) catalyst shows a decrease in activity of about a factor of seven compared to that of the monometallic sample ( $X_{Sn} = 0.00$ ), but the PtSn/H[Al]ZSM5 *SI* ( $X_{Sn} = 0.28$ ) catalyst does not show any activity at all. These observations may be explained as due to one or more of the following reasons: (a) an important decrease in Pt dispersion; (b) an electronic synergy between Pt and Sn; and/or (c) a geometric effect, by which Pt particles are covered by Sn species. In order to resolve this question, the reactivity studies were complemented with characterization effort using XPS and TEM, as discussed below. It is worth mentioning that these catalysts were also tested for the synthesis of methyl isobutyl ketone (MIBK) from acetone. A decrease in the hydrogenating activity and a corresponding improvement in selectivity towards MIBK was found with the PtSn/H[Al]ZSM5 *CI* sample compared to that of Pt/H[Al]ZSM5 [18]. For the case of the Pt–Sn *SI* bimetallic catalysts, a good selectivity toward MIBK was observed, superior to the one measured with the Pt–Sn *CI* catalysts. However, the former sample showed poor stability.

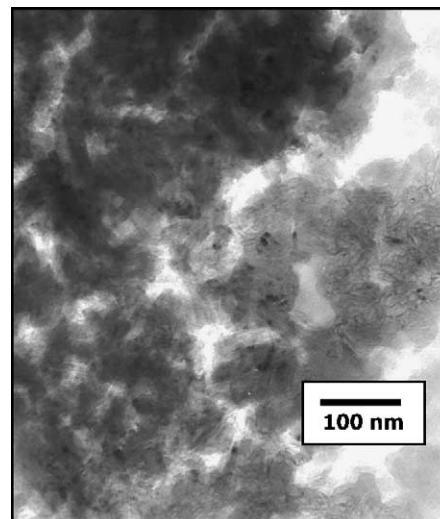


Fig. 1. TEM micrograph of the PtSn/H[Al]ZSM5 *CI* catalyst.

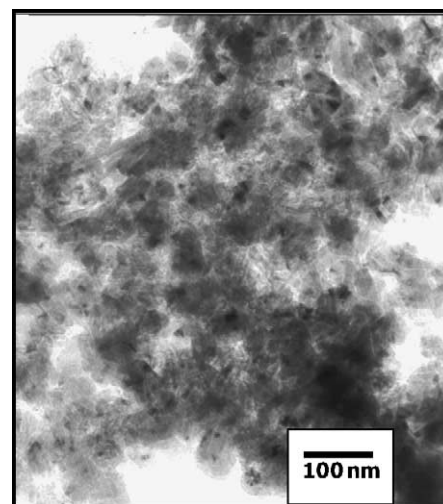


Fig. 2. TEM micrograph of the PtSn/H[Al]ZSM5 *SI* catalyst.

#### 3.2. TEM analysis

Figs. 1 and 2 show the micrographs of the external surface of the Pt–Sn *CI* and *SI* bimetallic catalysts, respectively. An approximate dispersion value was calculated

Table 1

Physico-chemical properties and activity towards toluene hydrogenation for Pt–Sn-supported catalysts studied in this work

Catalyst	Pt (%) exp.	Sn (%) exp.	$X_{Sn}$	SSA <sup>a</sup> (m <sup>2</sup> /g)	$AH_0^b$ (mmol/h g <sub>Pt</sub> )
H[Al]ZSM5	–	–	–	380	–
0.50% Pt/H[Al]ZSM5	0.47	–	0.00	375	3600
0.50% Pt-0.30% Sn/H[Al]ZSM5 ( <i>CI</i> )	0.49	0.26	0.46	373	670
0.50% Pt-0.20% Sn/H[Al]ZSM5 ( <i>SI</i> )	0.42	0.10	0.28	370	0
1.0% Sn/H[Al]ZSM5	–	0.80	1.00	375	0

<sup>a</sup> Specific surface area.

<sup>b</sup> Hydrogenation activity per gram of Pt, extrapolated at zero time.

Table 2  
Metal dispersion ( $D$ ) in the catalysts studied in this work, as determined by TEM

Catalyst	$D$ (%)
0.50% Pt/H[Al]ZSM5	13.5
0.50% Pt-0.30% Sn/H[Al]ZSM5 ( <i>CI</i> )	13.0
0.50% Pt-0.20% Sn/H[Al]ZSM5 ( <i>SI</i> )	8.40
1.0% Sn/H[Al]ZSM5	7.90

from these figures following a procedure described elsewhere [30,31]; the results obtained for the monometallic Pt/H[Al]ZSM5 and Sn/H[Al]ZSM5 and bimetallic PtSn/H[Al]ZSM5 catalysts are reported in Table 2. It was found that while the monometallic Pt/H[Al]ZSM5 and bimetallic PtSn/H[Al]ZSM5 *CI* catalysts have similar dispersion values (ca. 14%), the PtSn/H[Al]ZSM5 *SI* catalyst displays a significantly lower dispersion (ca. 8%), comparable to that of the Sn/H[Al]ZSM5 catalyst. Clearly, the method employed for the impregnation of the metals on the support affects the final dispersion in the bimetallic samples.

When combining these results with those obtained above from activity studies on toluene hydrogenation, it becomes clear that the changes in  $AH_0$  can be ascribed to two different reasons depending on the strategy used to prepare the bimetallic catalysts. For the PtSn/H[Al]ZSM5 *CI* catalyst, it appears that it is an electronic effect that induces a decrease in hydrogenating activity, because the dispersion of the metallic phase remains unchanged compared to that of the monometallic platinum. In contrast, the PtSn/H[Al]ZSM5 *SI* catalyst may be affected by a change in the geometry of the catalytic site, or at least by a combination of both geometric and electronic effects, since there is a clear increase in particle size (which is directly related to the dispersion of the metallic phase). It can be suggested that the tin deposited sequentially covers the Pt phase, a phenomena that could explain the decrease in dispersion value and, with that, the loss in catalytic activity.

### 3.3. XPS analysis

Further characterization of our catalytic samples was carried out by XPS in order to obtain information about the oxidation states of the metal phases (Pt and/or Sn) on the surface. The Al2p, Pt4f and Sn3d XPS spectra obtained for the support and for the monometallic and bimetallic catalysts (*CI* and *SI*) are shown in Figs. 3 and 4, respectively, and the measured binding energies of the Al2p, Pt4f<sub>7/2</sub> and Sn3d<sub>5/2</sub> levels are reported in Table 3 after deconvolution of the spectra.

Fig. 3a, which shows the XPS spectrum of the support, displays one signal at 74.5 eV corresponding to the Al2p signal of the zeolite, but additional Pt4f signals are seen for the metal-supported catalysts, as seen in Fig. 3b–d. In the case of the monometallic Pt catalyst (Fig. 3b) it was found that, in spite of the large Al2p peak, two overlapping signals could be detected at 70.9 and 72.2 eV, corresponding to Pt<sup>0</sup> and PtO<sub>ads</sub> species, respectively [32]. Moreover, third signal is identified in the XPS spectra of the bimetallic PtSn/H[Al]ZSM5

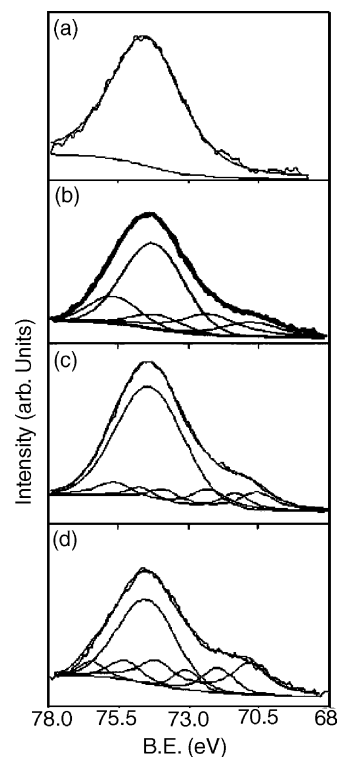


Fig. 3. Al2p–Pt4f XPS spectra for the support and for the catalysts used in this study (a) H[Al]ZSM5, (b) Pt/H[Al]ZSM5, (c) PtSn/H[Al]ZSM5 *CI*, (d) PtSn/H[Al]ZSM5 *SI*.

catalysts, indicating that the presence of tin in the catalysts affects the electronic environment of the platinum. Indeed, three XPS peaks are observed for the PtSn/H[Al]ZSM5 *CI* sample (Fig. 3c), centered at 70.4, 71.3 and 72.3 eV binding

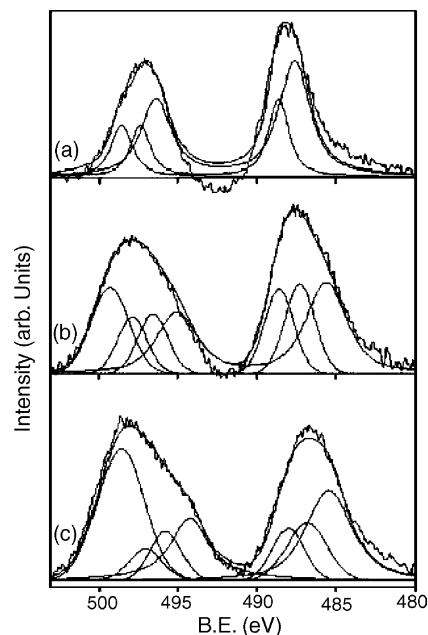


Fig. 4. Sn3d XPS spectra for the catalysts used in this work. (a) Sn/H[Al]ZSM5, (b) PtSn/H[Al]ZSM5 *CI*, (c) PtSn/H[Al]ZSM5 *SI*.

Table 3  
XPS binding energies for the Si2p, Al2p, Pt4f<sub>7/2</sub> and Sn3d<sub>5/2</sub> measured for all catalysts studied in this work

Catalyst	Si2p	Al2p	Pt4f <sub>7/2</sub>	Sn3d <sub>5/2</sub>
H[Al]ZSM5	102.9	74.5	–	–
0.50% Pt/H[Al]ZSM5	102.9	74.5	70.9–72.2	–
0.50% Pt-0.30% Sn/H[Al]ZSM5 (CI)	102.9	74.5	70.4–71.3–72.3	485.7–487.3–488.5
0.50% Pt-0.20% Sn/H[Al]ZSM5 (SI)	102.9	74.5	70.8–72.1–73.1	485.1–486.6–487.7
1.0% Sn/H[Al]ZSM5	102.9	74.5	–	487.6–488.6

All values are reported in eV, and reference to a value of Si2p = 102.9 eV.

energies. The last two can be attributed to Pt<sup>0</sup> and PtO<sub>ads</sub> species, respectively, and were also found in the monometallic catalyst. The first, however, appears at lower binding energies than what would be expected for platinum metal (Pt<sup>0</sup>), an observation that suggests that the platinum in this bimetallic catalyst may gain some electronic density from tin; a similar behavior has been reported previously for PtSn/Al<sub>2</sub>O<sub>3</sub> catalysts [10,11,13]. The opposite effect, i.e., a loss of electronic density, was found in the tin XPS region of this catalyst (see discussion below). Rodriguez et al. in their XPS studies of alloys, have reported similar electronic perturbations in systems with two metals, one with an almost fully occupied valence band and another with a valence band more than half empty. In these cases, the formation of a metal–metal bond generally leads to a gain in electron density by the element initially having the larger fraction of empty states in its valence band [3]. In our case, the alloy formation may involve a net Sn → Pt charge transfer, since in the Pt–Sn combination platinum is the metal with the largest electron affinity [20]. Finally, in the spectrum of the PtSn/H[Al]ZSM5 SI (Fig. 3d) catalyst, the Pt4f XPS signals are centered at 70.8, 72.1 and 73.1 eV; the first two correspond to the Pt<sup>0</sup> and PtO<sub>ads</sub> species identified before, while the latter can be assigned to PtO [32].

Fig. 4 shows the Sn3d XPS region for the monometallic Sn/H[Al]ZSM5 (Fig. 4a) and bimetallic PtSn/H[Al]ZSM5 (4b and 4c for CI and SI, respectively) catalysts. It should first be mentioned that, in all these spectra, the appearance of the signal at high binding energies is caused by the Auger signal of the structural Na in the zeolite. Nevertheless, the tin signals are still clearly discernible. For the monometallic sample, two signals can be observed at 487.6 and 488.6 binding energies, corresponding to SnO and/or SnO<sub>2</sub>. Unfortunately, discrimination between SnO and SnO<sub>2</sub> is not possible by means of the XPS studies alone [16]; the only solid conclusion from these data is that tin exists exclusively in oxidized form. This is so even though these samples were treated under hydrogen atmosphere at 500 °C for 6 h before their XPS analysis. This means that the reduction of the tin to Sn<sup>0</sup> is quite difficult over H[Al]ZSM5 supports [19], perhaps because of a strong interaction between the aluminum and tin atoms. This effect is also seen with pure Al<sub>2</sub>O<sub>3</sub>, as reported by Balakrishnan and Schwank [13], but not with SiO<sub>2</sub> or carbon black [16,27]. In the XPS spectra for the PtSn/H[Al]ZSM5 CI catalyst (Fig. 4b), Sn3d peaks were found at 485.7, 487.3 and 488.5 eV binding energies. The last two correspond to oxidized tin (SnO and/or SnO<sub>2</sub>), but the first can now be at-

tributed to Sn<sup>0</sup>, even though it can be seen that this signal is shifted toward higher binding energies than those reported by Coloma et al. [16] and Aksoyul et al. [17]. As stated above, such displacement suggests that there may be some electron transfer from tin to platinum. It is apparent that a Pt–Sn alloy is formed in this catalyst, an observation that explains the results obtained before in terms of the effect of changes in electronic properties on activity and particle size. The formation of a Pt<sub>3</sub>Sn alloy in this CI catalyst was corroborated by Mössbauer Spectroscopy (results not shown).

The Sn3d XPS data for the bimetallic PtSn/H[Al]ZSM5 SI catalyst are shown in Fig. 4c. In this case, three peaks were obtained (after deconvolution of the main signal) at 485.1, 486.6 and 487.7 eV, attributed to Sn<sup>0</sup> and SnO and/or SnO<sub>2</sub>, respectively. Note that the value of the Sn<sup>0</sup> peak here is quite close to that reported in the past [16,27]. The combined analysis of the Sn3d and Pt4f XPS data indicates that in this sample the Sn is reduced and the Pt is oxidized, but that they do not form any alloys, and that a geometric effect may dominate the catalytic behavior, as supported by the TEM results. Therefore, we suggest that in the Pt–Sn SI sample the Sn may cover some of the Pt particles, inhibiting their reduction (the reason for the identification of oxidized Pt species) and increasing their overall size. The tin metal, on the other hand, is expected to be exposed, and therefore easy to reduce.

#### 4. Conclusions

In this study it was shown that changes in impregnation strategy during the preparation of Pt–Sn bimetallic catalysts on zeolites lead to pronounced changes in the properties of the resulting samples. Significant variations in their catalytic behavior were observed toward toluene hydrogenation, indicative of a decrease in the number of active centers in both types of bimetallic catalyst. Nevertheless, a higher proportion of site blocking was obtained by sequential impregnation (SI), where no hydrogenating activity was found. TEM and XPS analysis of these samples provided evidence for the relative role of electronic and/or geometric effect on the performance of the catalysts depending on the strategy followed in their preparation. An electronic effect is observed in the co-impregnated catalyst (CI) (for a X<sub>Sn</sub> ≤ 0.46), with the formation of an alloy, as evidenced by XPS: there is a charge transfer from Sn to Pt. On the other hand, a geometric effect appears to dominate in the sequentially impregnated

bimetallic catalyst ( $X_{\text{Sn}} \leq 0.28$ ). There, it seems that Sn covers some of the Pt particles, blocking their reduction and increasing the overall particle size.

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