



# Effect of the sequence of impregnation on the activity and sulfur resistance of Pt–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts for the selective hydrogenation of styrene

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## ABSTRACT

The influence of the preparation of bimetallic Pt–Ni catalysts on their activity and sulfur resistance during styrene semi-hydrogenation was studied. The preparation variables assessed were the sequence of impregnation and the kind of nickel precursor used. The catalysts were tested with the styrene hydrogenation reaction and further characterized by ICP, TPR, XPS and pyridine TPD.

All catalysts showed high selectivities to ethylbenzene (>98%). The bimetallic catalysts were more active than monometallic Pt and the following activity order was found: Pt  $\cong$  NiClPt  $\leq$  NiNPt < PtNiCl < PtNiN. After poisoning with 300 ppm of thiophene the following order of sulfur resistance was found: PtNiCl < Pt  $\ll$  PtNiN  $\cong$  NiClPt  $\cong$  NiNPt.

Differences in activity and sulfur resistance between the catalysts were attributed to electronic effects, in turn related to the presence of different electron-rich and electron-deficient surface species of Pt and Ni interacting between themselves and with the support. The bimetallic catalyst with the highest Cl/Pt atomic ratio on the surface (as obtained by XPS) proved to be the most sulfur resistant; this higher poison resistance was rationalized in terms of both steric and electronic effects.

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## 1. Introduction

The reactions of selective hydrogenation of vinylic bonds that keep unaltered the aromatic ring and that proceed through heterogeneous catalysis are of great interest and usefulness for the petrochemical, fine chemistry and specialty chemicals industries.

Benzene, toluene and xylenes, commonly known as the BTX fraction, are useful solvents and intermediate. One important source of BTX in the cracking of different petroleum cuts [1–3]. These streams can have up to 1000 ppm of sulfur compounds, thiophene being among the most common ones [1,2]. These sulfur compounds are the main cause of the loss of activity and selectivity of metal catalysts in several refinery processes [4,5].

In the petrochemical industry gasoline and BTX streams coming from the cracking of petroleum cuts must be purified in order to minimize the concentration of olefins and diolefins. The widespread method of purification is the selective hydrogenation of vinylic compounds, keeping the aromatic rings unaltered [6–8]. The employed catalysts must have a great resistance to different sulfur compounds. A particular type of supported catalysts is that of the highly dispersed bimetallic catalysts, that have

properties clearly different from those of the monometallic catalysts [9]. They have a higher activity and selectivity and a greater resistance to the poisoning by sulfur compounds. Many studies on bimetallic catalysts for selective hydrogenation have been performed using both surface characterization techniques and catalytic activity/selectivity tests [9–11]. The greater part of these studies has involved bimetallic catalysts in reactions of selective hydrogenation of hydrocarbons of low molecular mass.

In recent works our group has studied the effect of the precursor salt and the temperature of reduction on the activity and poison resistance of monometallic catalysts for the selective hydrogenation of styrene [12,13]. The objective of this work is to extend this research to the reaction system of the bimetallic Pt–Ni/ $\gamma$ -alumina catalyst and the model feedstock of styrene contaminated with thiophene. The preparation parameters varied are the kind of nickel precursors and the sequence of impregnation of the metal salts. Properties especially assessed are the activity, selectivity and sulfur resistance.

## 2. Experimental

### 2.1. Catalysts preparation

Bimetallic catalysts were prepared by means of successive impregnations over a previously calcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support

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(Ketjen CK 300,  $S_{\text{BET}} = 224 \text{ m}^2 \text{ g}^{-1}$ ). For the incorporation of the metals to the support a technique of incipient wetness impregnation was used. The point of incipient wetness was detected at the value of  $0.7 \text{ mL g}^{-1}$ . The impregnating solutions were  $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$  (Strem Chemicals, Cat. No. 78-0200, purity > 99.9%) and  $\text{NiCl}_2$  (Merck, CAS: 7718-54-9, purity > 98%). These solutions were acidified to pH = 1 with dropwise addition of HCl. The solutions were used to obtain the monometallic catalysts of Pt and NiCl. A solution acidified to pH = 1 with  $\text{HNO}_3$  containing dissolved  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fluka, Cat. No. 72253, purity > 98.5%) was used to obtain the monometallic NiN catalyst. The concentrations of the solutions were adjusted in order to get loads of ca. 1 wt% of Pt and 2 wt% of Ni on the final catalysts. The monometallic catalysts were dried 24 h in a stove at 383 K, and then they were calcined in dry air for 3 h at 823 K. Finally they were reduced for 1 h at 673 K in a hydrogen stream ( $110 \text{ mL min}^{-1}$  flow rate).

The impregnation of the second metal was performed using a similar procedure and taking the monometallic catalyst as support. The acidic solution of  $\text{H}_2\text{PtCl}_6$  was added to the monometallic catalysts of NiN and NiCl to obtain the catalysts NiNPt and NiClPt, respectively. Similarly, acidic solutions of  $\text{NiCl}_2$  and  $\text{Ni}(\text{NO}_3)_2$  were added to the monometallic Pt catalyst to obtain the catalysts PtNiCl and PtNiN, respectively. The bimetallic catalysts were then dried for 24 h in a stove at 383 K, calcined for 3 h at 823 K and finally reduced for 1 h at 673 K in  $\text{H}_2$  ( $110 \text{ mL min}^{-1}$ ). It was found that the specific surface area of the support was practically not modified by the addition of the different metal precursors or by the subsequent thermal treatment.

## 2.2. Characterization of the catalysts

The Pt and Ni content of the catalysts were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a Perkin Elmer ICP OPTIMA 2100 instrument. The samples were immersed in a dilute solution of sulfuric acid at 363 K before each analysis.

The electronic state of the surface species of Pt and Ni and the atomic ratios of the different elements was determined by X-ray photoelectron spectroscopy (XPS). The analysis was performed in a Multitech UniSpecs equipment with a dual XR-50 Mg/Al X-ray source and a Specs Phoibos 150 hemispherical analyzer working in transmission, fixed analysis (FAT) mode. All the samples were dried at 353 K and they were examined in potassium bromide disks in a concentration ranging 0.5–1% to assure non saturated spectra. The samples were reduced *ex situ* 1 h at 673 K and were then heated in a flow of  $\text{H}_2/\text{Ar}$  (5%, vol/vol) at 673 K for 10 min in the instrument chamber before recording the spectrum. The spectra were obtained with an energy step of 30 eV, using a Mg anode operated at 200 W, and at a total pressure lower than  $2 \times 10^{-8}$  mbar. A careful deconvolution of the spectra was made and the areas under the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peaks to a combination of Lorentzian/Gaussian lines of 30–70% proportions. The binding energy used as a reference was the C 1s 284.6 eV signal. Since there is an interference between the Al 2p and Pt 4f<sub>7/2</sub> binding energies, the peak studied was the Pt 4d<sub>5/2</sub>.

The study of the reducibility of the surface species was performed by temperature programmed reduction (TPR) in an Ohkura TP2002 apparatus equipped with a thermal conductivity detector. The samples were pretreated *in situ* for 30 min in an air stream at 673 K for 30 min. Then they were cooled down to room temperature in an Ar stream. Finally they were reduced with a 5% (vol/vol)  $\text{H}_2$  in Ar stream while heating with a  $10 \text{ K min}^{-1}$  rate to a final value of 1173 K.

The amount and strength of the acid sites of the catalysts were measured by means of temperature programmed desorption of

pyridine. 200 mg of the previously reduced catalyst samples were used. They were first impregnated with an excess of pyridine at room temperature. The excess of pyridine was then evaporated under a fume hood at room temperature until a dry powder was obtained. Then the samples were put in a fixed bed reactor under a constant flow of nitrogen ( $40 \text{ mL min}^{-1}$ ). A first stage of desorption of weakly adsorbed pyridine and stabilization of the sample was performed by heating the sample at 383 K for 1 h. Then the temperature was increased from 383 to 823 K at a heating rate of  $10 \text{ K min}^{-1}$ . The gases issued by the reactor were directly sent to a flame ionization detector (FID) and the signal of the detector was recorded continuously together with the temperature of the sample.

X-ray diffraction (XRD) spectra of the powdered samples were obtained in a Shimadzu XD-1 instrument using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) filtered with Ni, in the  $15^\circ < 2\theta < 85^\circ$  range and at a scan speed of  $1^\circ \text{ min}^{-1}$ . The samples were powdered and reduced *ex situ* under a hydrogen flow. Then they were cooled down to room temperature in nitrogen flow and put into the chamber of the equipment to record the spectrum.

## 2.3. Catalytic tests

The reaction test for assessing the activity, selectivity and sulfur resistance of the prepared catalysts was the selective hydrogenation of styrene. The reaction was performed in a stainless steel, PTFE coated, stirred tank reactor, operated in batch mode, at 353 K, 2 MPa hydrogen pressure and 1200 rpm stirring rate. In each test 0.3 g of the catalyst and 200 mL of a solution of 5% (vol/vol) of styrene (Aldrich, Cat. No. S497-2, purity > 99%) in toluene (Merck, Cat. No. TX0735-44, purity > 99%) were used. n-Decane (Fluka, Cat. No. 30550, purity > 98%) was added as an internal chromatographic standard. In the case of the sulfur resistance tests, 300 ppm of thiophene were also added to the reaction mixture. The PTFE lining of the reactor ensured that no chemical contamination from steel occurred [14]. Reactants and products were analyzed in a gas chromatograph, using a 30 m, J&W INNOWax 19091N-213 capillary column. The runs were carried out in triplicates with a recorded average experimental error of 3%.

## 3. Results and discussion

### 3.1. Catalysts characterization

Table 1 contains the catalyst notation used. The values of mass concentration determined by the ICP technique were 1 wt% of Pt and 2.1 wt% of Ni, with an atomic ratio of Ni/Pt = 7.

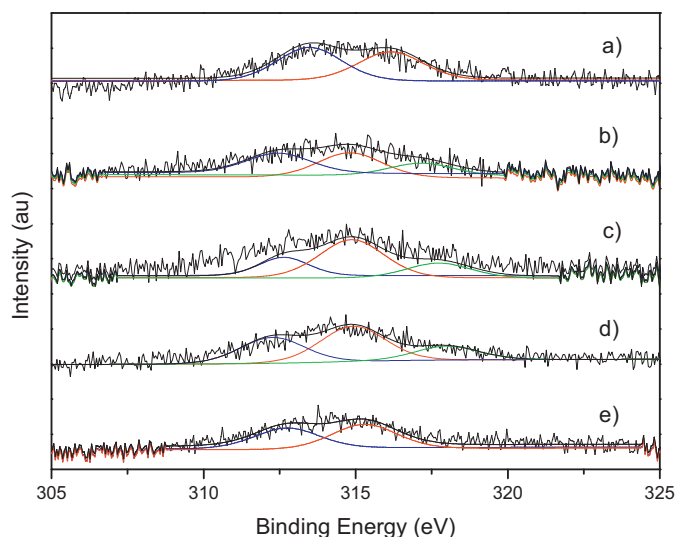
Figs. 1 and 2 contain the XPS spectra of the Pt 4d<sub>5/2</sub> and Ni 2p<sub>3/2</sub> species on the catalysts. The binding energies (BE) were determined by the fitting of the curves. The Pt/Al and Cl/Pt atomic ratios were calculated from the ratio of the corresponding peak areas (see Table 1).

As it can be seen in Fig. 1 all catalysts have the Pt 4d<sub>5/2</sub> peak at low values of binding energy, in the 312.3–313.5 eV range. From literature reports this peak could be attributed to  $\text{Pt}^0$  [15,16]. When comparing the BE of the bimetallic catalysts with those of the monometallic ones, a shift can be seen between 0.8 and 1.4 eV toward lower BE values, indicating the presence of  $\text{Pt}^{\delta-}$  with a higher availability of electrons than  $\text{Pt}^0$ . This could be due to the formation of metallic bonds or alloying, occurring at low temperatures [17,18]. On the other side a second peak with BE between 314.8 and 316.7 eV could be attributed to the presence of complex electrode deficient  $\text{Pt}^{\delta+}$  species, with  $0 < \delta < 2$ , stabilized by the presence of remaining chloride ions [15]. The third peak with BE of  $317.6 \pm 0.4 \text{ eV}$  would indicate the presence of another complex

**Table 1**

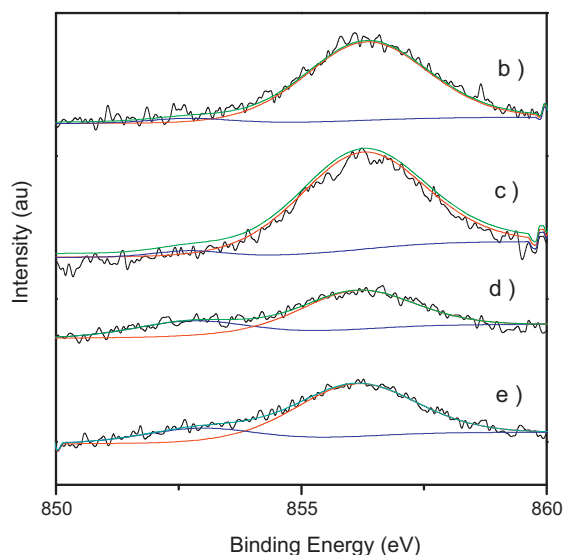
Catalysts naming convention. Pt and Ni binding energies and atomic superficial ratios as determined by XPS.

Catalyst	1st imp <sup>a</sup>	2nd imp <sup>a</sup>	Pt 4d <sub>5/2</sub> BE (eV)		Ni 2p <sub>3/2</sub> BE (eV)			Pt/Al (at/at)	Cl/Pt (at/at)
Pt	Pt	–	313.5 (54%)	316.7 (46%)				0.0035	0.96
NiClPt	Ni	Pt	312.6 (21%)	314.9 (57%)	317.7 (22%)	852.5 (3%)	856.2 (97%)	0.0038	2.49
NiNPt	Ni	Pt	312.4 (35%)	314.8 (43%)	317.2 (22%)	852.7 (4%)	856.3 (96%)	0.0035	2.07
PtNiCl	Pt	Ni	312.3 (35%)	314.9 (47%)	318.0 (18%)	852.7 (28%)	856.1 (72%)	0.0036	1.33
PtNiN	Pt	Ni	312.7 (47%)	315.3 (53%)		852.9 (20%)	856.1 (80%)	0.0039	1.13

NiN: Ni(NO<sub>3</sub>)<sub>2</sub> precursor; NiCl: NiCl<sub>2</sub> precursor.<sup>a</sup> imp = impregnation step.**Fig. 1.** XPS profiles of Pt 4d<sub>5/2</sub>: (a) Pt; (b) NiClPt; (c) NiNPt; (d) PtNiCl and (e) PtNiN.

electrodeficient Pt<sup>δ+</sup> species, Pt<sup>δ+</sup>Cl<sub>x</sub>O<sub>y</sub>, with  $2 < \rho < 4$  [15], formed during the calcination or the subsequent reduction process [16]. In Table 1 it can be seen that the PtNiCl is the catalyst that has species with the highest value of electrodeficiency, 318 eV.

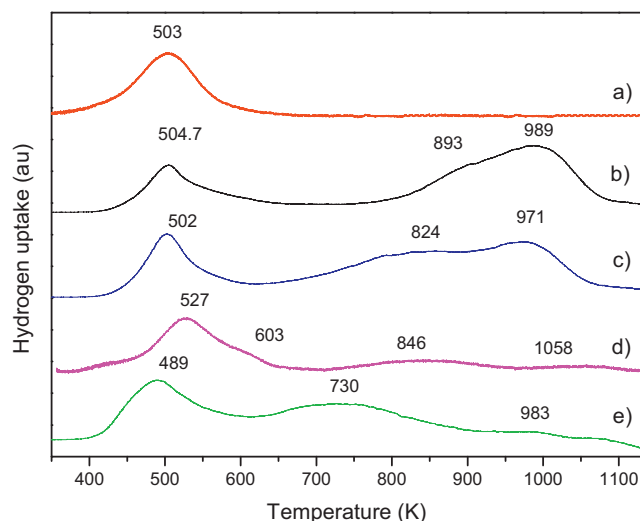
When analyzing the BE region corresponding to the 2p<sub>3/2</sub> spectrum of nickel, it can be seen (Fig. 2) that the bimetallic catalysts have two peaks, the first one at about 852.7 ± 0.2 eV that could be assigned to Ni<sup>0</sup> [15] and another at 856.2 ± 0.1 eV attributed to electrodeficient species of Ni<sup>2+</sup>. According to literature reports the latter could be Ni species strongly interacting with

**Fig. 2.** XPS profiles of Ni 2p<sub>3/2</sub>: (b) NiClPt; (c) NiNPt; (d) PtNiCl and (e) PtNiN.

alumina [15,19,20]. Other authors suggest the presence of species NiO·x(Al<sub>2</sub>O<sub>3</sub>) (0 ≤ x ≤ 1) [21] that would be formed during the thermal treatments. In the case of the bimetallic NiNPt and NiClPt catalysts the signal assigned to Ni<sup>0</sup> is smaller than the signal of the bimetallic catalysts prepared with an inverse order of impregnation, PtNiN and PtNiCl. These would have 20 and 28% completely reduced Ni. This could be due to the way of preparation of these catalysts. The bimetallic catalysts firstly impregnated with Ni were calcined and reduced twice and would have a stronger interaction with the support, thus making the reduction of the Ni species difficult. The bimetallic catalysts have slightly higher Ni 2p<sub>3/2</sub> BE values in comparison to the Ni monometallic catalyst (852.3 eV [19]), possibly because Pt is bonded to Ni through a metal–metal or alloy bond. Since Pt is more electronegative it would have a higher electron density (Pt<sup>δ-</sup>) and Ni would be electrodeficient.

The XPS spectra of the catalysts had a peak at about 198.5 eV that would correspond to Cl 2p<sub>3/2</sub>, and that could be associated to chloride species that were not eliminated during the thermal treatment stages [15]. With respect to the atomic ratios obtained by XPS (Table 1), a similar Pt/Al ratio for all catalysts was found. The catalysts with a higher Cl/Pt ratio are the bimetallic catalysts in which Pt was impregnated the last.

Fig. 3 shows the TPR traces of the calcined Pt mono and bimetallic catalysts. Lieske et al. [22] reported that Pt/Al<sub>2</sub>O<sub>3</sub> prepared from chlorinated precursors should have two peaks in the TPR trace because of two complex surface species that contain chlorides. The peak at 533 K would be related to [Pt<sup>IV</sup>(OH)<sub>x</sub>Cl<sub>y</sub>] and the one at 563 K to [Pt<sup>IV</sup>O<sub>x</sub>Cl<sub>y</sub>]. The formation of these species mainly depends on the temperature of calcination of the catalyst [23]. Reyes et al. [24] have attributed the peak between 420–460 K to the reduction of PtO<sub>2</sub> and the peak at about 600 K to the reduction of PtO<sub>x</sub>Cl<sub>y</sub>. Finally Navarro et al. [25] reported that silica–alumina supported Pt catalysts prepared from H<sub>2</sub>PtCl<sub>6</sub> had a broad reduction peak at

**Fig. 3.** TPR traces of: (a) Pt; (b) NiClPt; (c) NiNPt; (d) PtNiCl and (e) PtNiN catalysts.

300–700 K. They suggested the presence of oxychlorinated species such as  $\text{Pt}(\text{OH})_x\text{Cl}_y$ ,  $\text{PtO}_x\text{Cl}_y$  and  $\text{PtO}_2$ .

With respect to the Ni catalysts supported over alumina, some authors define three different reduction temperature ranges: (I) up to 600 K only the Ni oxides with weak or null interaction with the support (bulk NiO) are reduced; (II) between 600 and 1000 K the reduction of Ni oxides strongly interacting with the support occurs; (III) between 1000 and 1273 K nickel aluminates ( $\text{NiAl}_2\text{O}_4$ ) are reduced [26–29].

According to the surveyed literature the broad peak between 323–673 K in Fig. 3(a)–(c) (Pt, NiClPt and NiNPt TPR plots), could be due to the reduction of oxychlorinated  $\text{Pt}^{\delta+}\text{O}_x\text{Cl}_y$  species. In the case of the bimetallic catalysts in which Pt was impregnated first and Ni second (Fig. 3(d) and (e)) the first peak is broader than the same peak for monometallic Pt. Hence it could correspond to the simultaneous reduction of both Pt and bulk NiO [26,27,29–31]. In the case of PtNiN the first peak can be found at lower temperatures (489 K) indicating that in that catalyst the Pt species are more easily reduced than those found on the monometallic catalyst [18]. In the case of PtNiCl the position of the first peak is shifted to higher temperatures (527 K) suggesting that the Pt particles are harder to reduce (in comparison to the monometallic catalyst). Reduction peaks can also be found at 600–1000 K in the case of the bimetallic catalysts. These peaks could be related to the reduction of NiO in strong interaction with the support [24,29,31,32]. In the case of the bimetallic NiNPt and NiClPt catalysts the position of the peaks is slightly shifted to higher temperatures, indicating that Ni species on these catalysts have a lower reducibility. This could be due to a greater interaction of NiO with other surface species or with the support. It must be recalled that Ni on the NiNPt and NiClPt catalysts suffered a double calcination and reduction treatment.

According to the literature and the temperature of reduction used (673 K), for all the prepared catalysts the broad peak between 300 and 673 K should be related to the reduction of  $\text{PtO}_2$  and the oxychlorinated species  $\text{Pt}^{\delta+}\text{O}_x\text{Cl}_y$  or  $[\text{Pt}^{\text{IV}}(\text{OH})_x\text{Cl}_y]$ . For the PtNiN and PtNiCl bimetallic catalysts it would also be related to the reduction of Ni in weak interaction with the support. The TPR results agree with the XPS results since in all the samples there were  $\text{Pt}^0$ ,  $\text{Pt}^{\delta+}$  and  $\text{Pt}^{\text{IV}}$  oxychlorinated species, while on the surface of the bimetallic PtNiN and PtNiCl catalysts more  $\text{Ni}^0$  was found. Also the fact that the PtNiN has a first peak at low temperatures is in agreement with the higher amount of reduced platinum ( $\text{Pt}^{\delta-}$ ) found in the XPS spectra of the bimetallic catalysts. The lower reducibility of the Ni species on the NiNPt and NiClPt catalysts (shown in Fig. 3(b) and (c)) also agrees well with the lower amount of  $\text{Ni}^0$  species found by XPS.

When a base is adsorbed over an acid surface, strong bonds appear and high temperatures are needed to desorb it. In the case of pyridine the molecules adsorbed over weak acid sites are desorbed at relatively low temperatures and those adsorbed over strong acid sites are desorbed at much higher temperatures. The amount of base desorbed in different temperature ranges is a measure of the distribution of the acid strength. The pyridine TPD traces were thus integrated to give the total amount of weak acid sites (room temperature to 773 K), mild acid sites (773–873 K) and strong acid sites (temperatures higher than 873 K). These acidity values are included in Table 2. A marked difference can be seen between the amount and main kind of acidity for the different catalysts. For example the total acidity of the bimetallic catalysts is 4–27 times the acidity of the monometallic catalyst. In the case of the bimetallic catalysts there is also a great effect of the kind of metal precursor and the order of impregnation on the total acidity and the acid strength distribution. These results agree with those of the distribution of the Pt and Ni electrodeficient species as measured by XPS, since both species would provide Lewis acid sites. It can be seen that catalysts with high total acidity have

**Table 2**  
Pyridine TPD results.

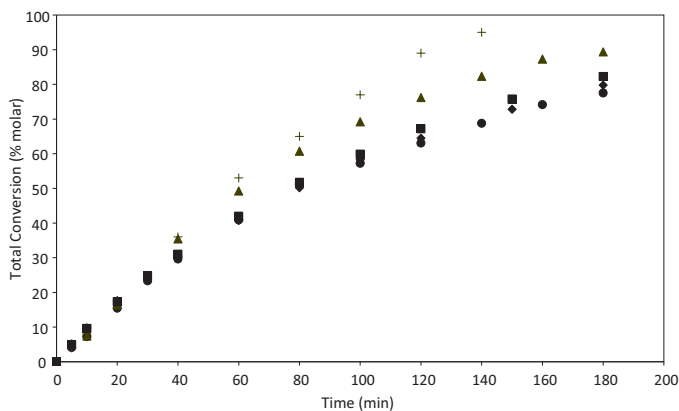
Catalyst	Distribution of acid strength (a. u.)			Total acid concentration (a.u.)
	973–873 K (high)	873–773 K (medium)	373–773 K (low)	
Pt	–	0.23	0.89	1.1
PtNiCl	1.80	5.80	2.10	9.7
PtNiN	3.20	0.84	0.71	4.7
NiClPt	–	2.50	27.00	29.5
NiNPt	0.37	4.50	18.00	22.5

Pt particles close to the surface and have low amounts of  $\text{Ni}^0$ . The values shown in Table 2 suggest the following decreasing order of total acidity:  $\text{NiClPt} > \text{NiNPt} \gg \text{PtNiCl} > \text{PtNiN} > \text{Pt}$ . This is also the order of the superficial Cl/Pt atomic ratio as measured by XPS (shown in Table 1). Carvalho et al. [33] reported that a chlorinated support had 2.9 times more acidity than pure alumina and that the replacement of different kinds of OH groups by Cl produced acid sites of different strength. Chlorine was also thought to displace water molecules coordinated to surface Al atoms of different chemical nature.

The X-ray diffractograms of all catalysts had only three peaks at  $2\theta = 37.7^\circ$ ,  $46.0^\circ$  and  $67.0^\circ$ , corresponding to the structure of  $\gamma\text{-Al}_2\text{O}_3$  [34]. No peak at  $39.9^\circ$  related to the (1 1 1) reflections of  $\text{Pt}^0$  could be found, neither the peaks corresponding to the (2 0 0) planes of  $\text{PtO}_2$  or  $\text{Pt}^{\text{IV}}$  [35–37], or the peaks due to bulk NiO. This was attributed to the small particle size and the relatively high limit of detection of the XRD technique [38]. Heracleous et al. [39] have reported that in catalysts of Ni supported over alumina a minimum Ni mass content of 15% is needed in order to detect the NiO (bulk) diffraction lines at  $2\theta = 43.3^\circ$ ,  $63.0^\circ$ ,  $75.5^\circ$  and  $79.5^\circ$ . Salagre et al. [21] have reported that the low intensity diffraction lines of NiO particles of Ni/ $\text{Al}_2\text{O}_3$  catalysts would only be detected at Ni contents higher than 26.6%. Due to this low sensitivity of the XRD method the Pt and NiO phases cannot be detected in our case.

### 3.2. Catalytic tests

The selectivity found in all the tests performed was higher than 98% (styrene to ethylbenzene). Also no products of hydrogenolysis of thiophene could be detected. Fig. 4 shows the results of total conversion of styrene as a function of time-on-stream for the mono and bimetallic catalysts, in the absence of poisons. It can be seen that all bimetallic catalysts display a higher total conversion than the monometallic catalyst. The most active catalyst is PtNiN and the order of activity found is:  $\text{PtNiN} > \text{PtNiCl} > \text{NiNPt} \geq \text{NiClPt} \cong \text{Pt}$ .



**Fig. 4.** Styrene total conversion as a function of time in the absence of poison. (●) Pt, (◆) NiClPt, (■) NiNPt, (▲) PtNiCl and (+) PtNiN.



**Table 3**

Values of the initial rate of hydrogenation of styrene hydrogenation rate.

Catalyst	Sulfur-free condition		Sulfur-poisoned condition		$\alpha$
	$r_{sf}^0$ (mol L <sup>-1</sup> min <sup>-1</sup> )	$R^2$	$r_{sp}^0$ (mol L <sup>-1</sup> min <sup>-1</sup> )	$R^2$	
Pt	0.27 ± 0.01	0.995	0.14 ± 0.01	0.997	0.49
NiClPt	0.27 ± 0.02	0.988	0.18 ± 0.03	0.970	0.33
NiNPt	0.28 ± 0.02	0.990	0.19 ± 0.02	0.981	0.31
PtNiCl	0.32 ± 0.02	0.996	0.13 ± 0.01	0.998	0.59
PtNiN	0.34 ± 0.01	0.998	0.18 ± 0.01	0.994	0.45

 $\alpha$ : fraction of poisoned sites

Fig. 5 shows the results of total conversion of styrene in the presence of thiophene as a function of time-on-stream. A decrease in total conversion can be seen as a result of the loss of active sites. The activity order is now: NiNPt  $\cong$  NiClPt  $\cong$  PtNiN  $\gg$  Pt > PtNiCl.

In order to compare the sulfur resistance of the catalysts the initial rates of reaction of styrene were determined for the tests with sulfur-free ( $r_{sf}^0$ ) and sulfur-poisoned ( $r_{sp}^0$ ) feed. A kinetic rate model was used that assumed a zero order with respect to styrene that seemed in accord with the conversion patterns found. Table 3 shows the values of the initial reaction rates, as obtained by least squares fitting with the MicroMath Scientist program. As indicated in the experimental section all tests were performed in triplicates. In this sense the error associated to ( $r_{sf}^0$ ) and ( $r_{sp}^0$ ) in Table 3 corresponds to the standard deviation of  $r^0$  as obtained by propagation of the error of the ethylbenzene yield (2–4% error). The values of the coefficient of regression  $R^2$  indicate that the fitting of the model is good in all cases. From the regressed values of the two kinetic constants, the fraction of poisoned sites ( $\alpha$ ) was determined as:  $\alpha = 1 - (r_{sf}^0/r_{sp}^0)$ .

It can be seen (Table 3) that the NiNPt and NiClPt bimetallic catalysts in which Pt was impregnated last, are those with the lowest amount of poisoned sites. According to the other characterization results these catalysts have a low amount of Ni<sup>0</sup> (by XPS and TPR), a high value of the Cl/Pt ratio and the highest amount of total acidity. With a related but opposite trend, the PtNiCl catalyst which has the highest amount of Ni<sup>0</sup> and Pt <sup>$\delta^-$</sup>  species with the highest electronic availability, shows the highest amount of poisoned active sites.

The XPS results indicate that all catalysts have different kinds of platinum species and that those on the surface of the bimetallic catalysts have a higher electronic availability (species with lower BE). During the reaction of hydrogenation the cleavage of the H–H bond is favored by the interaction of the electron-rich d orbitals of the metal with the molecular antibonding orbitals of hydrogen [40]. Since the bimetallic catalysts have a higher amount of available

electrons in the 5d Pt orbital in comparison to monometallic Pt, the cleavage of the H–H bonds would be favored on these catalysts. This would explain the higher activity of the bimetallic Pt–Ni catalysts.

It has also been well established that the mechanism of poisoning of Group VIII metals by sulfur compounds is due to an effect of donation of electrons from the metal to sulfur. Particularly thiophene interacts with the surface of metals in a planar way through the  $\pi$  electrons of the aromatic nucleus (weak  $\eta_5$  bond) [13,41,42]. During the thiophene poisoning tests some of the platinum electrons of the d orbital are shared with the S atom and for this reason the metal would have a lower amount of electrons available for promoting the cleavage of the hydrogen bond. The catalytic activity is thus reduced for all the catalysts after poisoning occurs. In this sense the differences in activity and sulfur resistance between the catalysts could partly be attributed to electronic effects.

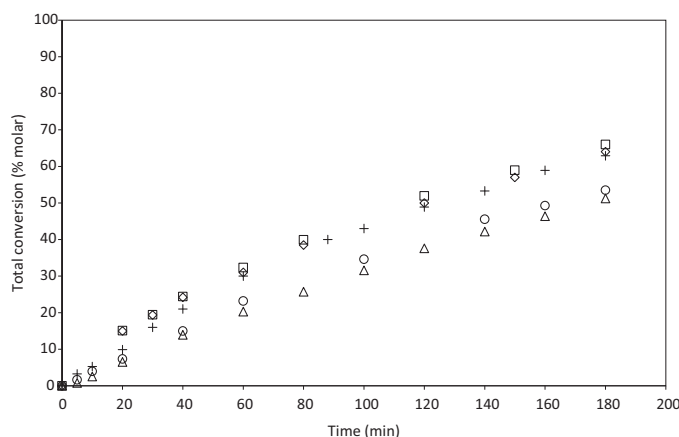
The NiNPt and NiClPt bimetallic catalysts have the highest values of the superficial Cl/Pt atomic ratio (XPS data of Table 1) and are also the most resistant to sulfur poisoning. It is possible that Pt oxychlorinated species prevent the adsorption of thiophene both by a steric hindrance effect (big size of oxychlorinated species) and an electronic one (high electronegativity of chlorine). Bimetallic PtNiCl catalysts turned out to be the least sulfur resistant. This is likely due to its high amount of exposed Ni<sup>0</sup> and the presence of Pt <sup>$\delta^-$</sup>  species with the highest availability of electrons (with BE of 312.3 eV). Both effects would promote a strong adsorption of thiophene and thus an enhanced blocking of active sites.

#### 4. Conclusions

The effect of the sequence of impregnation and of the kind of nickel precursor used was evaluated for a series of bimetallic Pt–Ni catalysts. The properties assessed were the catalytic activity and the sulfur resistance, during the selective hydrogenation of styrene. All the bimetallic catalysts were found to be more active than the Pt monometallic catalyst.

The XPS results point to the presence of different Pt<sup>0</sup>, Pt <sup>$\delta^-$</sup>  and Pt <sup>$\delta^+$</sup> O<sub>x</sub>Cl<sub>y</sub> species. The presence of Pt <sup>$\delta^-$</sup>  species would indicate the formation of a metallic bond or a Pt–Ni alloy. Species of Pt with high availability of electrons were found on the bimetallic catalysts suggesting that an electronic effect would be partly responsible for their higher conversion of styrene, either in the presence or the absence of thiophene. The order of total conversion of styrene in the absence of sulfur was: Pt  $\cong$  NiClPt  $\leq$  NiNPt < PtNiCl < PtNiN. After the poisoning with 300 ppm thiophene the order changed to: PtNiCl < Pt  $\ll$  PtNiN  $\cong$  NiClPt  $\cong$  NiNPt. The bimetallic catalysts prepared by successive impregnation of Ni and Pt had a high surface content of chlorine, a low amount of Ni<sup>0</sup> and a high total acidity. These catalysts were the most sulfur resistant because of steric and electronic effects.

The great poisoning of the PtNiCl bimetallic catalyst would be due to the easy adsorption of the thiophene sulfur atoms over the relatively abundant Ni<sup>0</sup> and Pt <sup>$\delta^-$</sup>  species with high availability of electrons.



**Fig. 5.** Styrene total conversion as a function of time in the presence of poison. (○) Pt, (◇) NiClPt, (□) NiNPt, (△) PtNiCl and (+) PtNiN.

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## References

- [1] L.F. Hatch, S. Matar, *From Hydrocarbon to Petrochemicals*, Gulf Publishing Company, Houston, TX, 1981 (Chapters 3 and 7).
- [2] G. Chauvel, G. Lefebvre, *Petrochemical Processes*, Institut Francais du Pétrole Publications, Paris, 1989 (Chapter 2).
- [3] R. Sadeghbeigi, *Fluid Catalytic Cracking Handbook*, Gulf Publishing Company, Houston, TX, 2000 (Chapters 1 and 10).
- [4] B. Chen, U. Dingerdissen, J.G.E. Krauter, H.G.J. Lansink Rotgerink, K. Möbus, D.J. Ostgard, P. Panster, T.H. Riermeir, S. Seebald, T. Tacke, H. Trauthwein, *Appl. Catal. A: Gen.* 280 (2005) 17–46.
- [5] Á. Mastalir, Z. Király, *J. Catal.* 220 (2003) 372–381.
- [6] A. Molnár, A. Sárkány, M. Varga, *J. Mol. Catal. A: Chem.* 173 (2001) 185–221.
- [7] D.E. Grove, *Platinum Met. Rev.* 47 (1) (2003) 44.
- [8] J. Dunleavy, *Platinum Met. Rev.* 50 (2) (2006) 110.
- [9] D.W. Goodman, *J. Phys. Chem.* 100 (1996) 13090–13112.
- [10] V. Pallassana, M. Neurock, *J. Catal.* 191 (2000) 301–317.
- [11] J.G. Chen, C.A. Menning, M.B. Zellner, *Surf. Sci. Rep.* 63 (2008) 201–254.
- [12] J. Badano, C. Lederhos, M. Quiroga, P. L'Argentièrre, F. Coloma-Pascual, *Quim. Nova* 33 (2010) 48–51.
- [13] J.M. Badano, M. Quiroga, C. Betti, C. Vera, S. Canavese, F. Coloma-Pascual, *Catal. Lett.* 137 (2010) 35–44.
- [14] S. Hu, Y. Chen, *J. Chin. Inst. Chem. Eng.* 29 (1998) 387–396.
- [15] NIST, X-ray Photoelectron Spectroscopy Database NIST Standard Reference Database 20, Version 3.5 (Web Version), National Institute of Standards and Technology, USA, 2007.
- [16] J.C. Serrano-Ruiz, G.W. Huber, M.A. Sánchez-Castillo, J.A. Dumesic, F. Rodríguez-Reinoso, A. Sepúlveda-Escribano, *J. Catal.* 241 (2006) 378–388.
- [17] K.W. Park, J.H. Choi, Y.E. Sung, *J. Phys. Chem. B* 107 (2003) 5851–5856.
- [18] N.H.H. Abu Bakar, M.M. Bettahar, M. Abu Bakar, S. Monteverdi, J. Ismail, M. Alnot, *J. Catal.* 265 (2009) 63–71.
- [19] C.D. Wagner, W.M. Riggs, R.D. Davis, J.F. Moulder, G.E. Muilenberg (Eds.), *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Preirie, MN, 1978.
- [20] P. Castaño, B. Pawelec, J.L.G. Fierro, J.M. Arandes, J. Bilbao, *Fuel* 86 (2007) 2262–2274.
- [21] P. Salagre, J.L.G. Fierro, F. Medina, J.E. Sueiras, *J. Mol. Catal. A: Chem.* 106 (1996) 125–134.
- [22] H. Lieske, G. Liets, H. Spindler, J. Völter, *J. Catal.* 81 (1983) 8–16.
- [23] J. Völter, in: L. Červený (Ed.), *Studies in Surface Science and Catalysis*, vol. 27, Elsevier Science Publishers B.V., Amsterdam, 1986 (Chapter 10).
- [24] P. Reyes, G. Pecchi, M. Morales, J.L.G. Fierro, *Appl. Catal. A: Gen.* 163 (1997) 145–152.
- [25] R.M. Navarro, B. Pawelec, J.M. Trejo, R. Mariscal, J.L.G. Fierro, *J. Catal.* 189 (2000) 184–194.
- [26] P. Kim, H. Kim, J.B. Joo, W. Kim, I.K. Song, J. Yi, *J. Mol. Catal. A: Chem.* 256 (2006) 178–183.
- [27] B.W. Hoffer, A. Dick Van Langeveld, J.P. Janssens, R.L.C. Bonne, C.M. Lok, J.A. Moulijn, *J. Catal.* 192 (2000) 432–440.
- [28] J. Juan-Juan, M.C. Román-Martínez, M.J. Illán-Gómez, *Appl. Catal. A: Gen.* 301 (2006) 9–15.
- [29] Z. Hou, O. Yokota, T. Tanaka, T. Yashima, *Appl. Catal. A: Gen.* 253 (2003) 381–387.
- [30] F. Cardenas-Lizana, S. Gómez-Quero, M.A. Keane, *Appl. Catal. A: Gen.* 334 (2008) 199–206.
- [31] G. Li, L. Hu, J.M. Hill, *Appl. Catal. A: Gen.* 301 (2006) 16–24.
- [32] S. Abelló, D. Verboekend, B. Bridier, J. Pérez-Ramírez, *J. Catal.* 259 (2008) 85–95.
- [33] L.S. Carvalho, C.L. Pieck, M.C. Rangel, N.S. Figoli, C.R. Vera, J.M. Parera, *Appl. Catal. A: Gen.* 269 (2004) 105–116.
- [34] S. Huang, C. Zhang, H. He, *Catal. Today* 139 (2008) 15–23.
- [35] T. Onoe, S. Iwamoto, M. Inoue, *Catal. Commun.* 8 (2007) 701.
- [36] Y.G. Shul, T. Sugiura, T. Tatsumi, H. Tominaga, *Appl. Catal.* 24 (1986) 131–143.
- [37] S.Y. Huang, S.M. Chang, C.T. Yeh, *J. Phys. Chem. B* 110 (2006) 234–239.
- [38] M.M. Telkar, J.M. Nadgeri, C.V. Rode, R.V. Chaudhari, *Appl. Catal. A: Gen.* 295 (2005) 23–30.
- [39] E. Heracleous, A.F. Lee, K. Wilson, A.A. Lemonidou, *J. Catal.* 231 (2005) 159–171.
- [40] D.F. Shriver, P.W. Atkins, C.H. Langford, *Inorganic Chemistry*, 3rd ed., WH Freeman and Co., New York, 1994, p. 258.
- [41] A. Arcoya, X.L. Seoane, L.M. Gómez-Sainero, *Appl. Surf. Sci.* 211 (2003) 341–351.
- [42] P.C. L'Argentièrre, M.G. Cañón, N.S. Figoli, *Appl. Surf. Sci.* 89 (1995) 63–68.