

## Research Article

# Sulfur Resistance of Pt-W Catalysts

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The sulfur resistance of low-loaded monometallic Pt catalysts and bimetallic Pt-W catalysts during the partial selective hydrogenation of styrene, a model compound of Pygas streams, was studied. The effect of metal impregnation sequence on the activity and selectivity was also evaluated. Catalysts were characterized by ICP, TPR, XRD, and XPS techniques. Catalytic tests with sulfur-free and sulfur-doped feeds were performed. All catalysts showed high selectivities (>98%) to ethylbenzene. Activity differences between the catalysts were mainly attributed to electronic effects due to the presence of different electron-rich species of Pt<sup>0</sup> and electron-deficient species of Pt<sup>δ+</sup>. Pt<sup>0</sup> promotes the cleavage of H<sub>2</sub> while Pt<sup>δ+</sup> the adsorption of styrene. The catalyst successively impregnated with W and Pt (WPt/Al) was more active and sulfur resistant than the catalyst prepared with an inverse impregnation order (PtW/Al). The higher poison resistance of WPt/Al was attributed to both steric and electronic effects.

## 1. Introduction

Catalytic selective hydrogenation reactions are of vital importance in the petrochemical and petroleum refining industries. In refining operations one such important reaction is the selective hydrogenation of pyrolysis gasoline (Pygas). Pygas is a naphtha-range product with a high content of aromatics and olefins that is produced as a byproduct of the production of olefins in the steam cracking units [1]. Due to its high content of aromatics and olefins, pyrolysis gasoline is used as high octane compounds for blending in the gasoline pool or as a highly unsaturated feedstock for the extraction of BTX aromatics. Up to 15% of Pygas compounds are highly reactive, mono- and diolefins that tend to polymerize into gums in vessels, pipelines, and catalysts must therefore be eliminated from the feedstock of the refinery units before its processing [2]. The most widespread method of purification is the selective hydrogenation of vinylic compounds, keeping

the aromatic rings unaltered [3–5]. Styrene is routinely used as a useful laboratory model compound of Pygas to investigate the catalytic performance of metal catalysts. It has two types of unsaturated groups thus needing selective hydrogenation [6], and it is one of the most refractory compounds of these streams [2]. Styrene hydrogenation is also used in the industrial practice as a test reaction for assessing the performance of the hydrogenation catalysts under real conditions [7].

Pygas selective hydrogenation catalysts must have a great resistance to poisoning because Pygas usually contains variable degrees of sulfur and nitrogen compounds. Deactivation by sulfur poisoning of noble metal supported catalysts is especially serious and has been widely studied [8]. Catalyst deactivation can be caused by a decrease in the number of active sites or a change in their nature. As it is well known, sulfur compounds are the most effective poisons for metal catalysts extensively used in petrochemical industries. For

naphtha range feedstocks thiophenic compounds are the most poisonous and therefore thiophene is usually taken as a model compound for sulfur resistance studies [9].

In a previous paper we have evaluated the activity and poisoning of different monometallic alumina supported catalysts [10]. Pd and Pt low-loaded catalysts were the most sulfur resistant and the most active for the selective hydrogenation of styrene to ethylbenzene. Besides it was found that the formation of oxychlorinated species, refractory to reduction, contributed to the sulfur resistance by forming electron deficient metal species forming weaker sulfur-metal bonds. It was also rationalized that chloride species could additionally contribute to sulfur resistance by a steric factor.

Pt catalysts have proved to be active for many selective hydrogenation reactions. The increase in the demand for Pt in many industries such as the petroleum refining and fuel cell ones has led to a drastic increase in the price of the noble metal. This situation is expected to become worse in the next decades. For this reason it is convenient to decrease the load of Pt in industrial catalysts, partly replacing it with cheaper components. This additional components are usually nonnoble metals and the so-called multimetallic not only can have a lower cost but also enhanced properties of selectivity and poison resistance [11, 12]. One family of bimetallic catalysts drawing especial attention is that in which the second component is a transition metal with available electron in the nd level [13]. Pt bimetallic catalysts are used in many processes, the most commonly known being the catalytic reforming of virgin naphtha for the production of high octane gasoline and BTX. Some authors suppose that Pt bonds with the other metals, thus forming alloys of enhanced catalytic properties [14, 15]. It is also stated that the increase in activity and selectivity of the bimetallic systems is a product of the high dispersion of Pt, which is achieved by the dilution effect of the second metal [16]. Other authors claimed that the selectivity of bimetallic catalysts is mainly produced by the "ensemble" effect, the promoter producing the physical isolation of Pt in smaller clusters on the main particle [17]. The word "ensemble" refers to the number of active sites on the surface that are required by a specific reaction. Reactions demanding big ensembles (big number of active sites) can be selectively suppressed by poisoning or when a fraction of the active sites is blocked. Electronic effects on the other hand are related to a redistribution of the charge, as a consequence of the metal-metal bonds. Depending on the nature of the metal-metal and metal-sulfur interactions many phenomena can occur when sulfur reacts over the surface of a bimetallic particle: (a) the formation of bimetallic sulfides is reported for some systems, and these bimetallic sulfides having properties much different from those of the pure monometal sulfides; (b) in other systems the interaction between sulfur and one of the metal is a repulsion type and leads to a weak bimetallic bond and a reduction of the degree of mixing of the metals; (c) bimetallic systems can also be gotten in which one of the metals promotes the reactivity of the second towards sulfur; (d) the case of the formation of bimetallic alloys that produces, as a consequence of an electronic effect, a decrease of the affinity for sulfur of both metals. This last situation is particularly interesting and useful for the

design of thiotolerant catalysts. Thus the understanding of the interaction of sulfur with bimetallic particles is critical for the design of catalysts and process conditions that prevent or decrease the deactivation of the catalyst.

In a recent work [18] we found that the order of impregnation and of the kind of metal precursor salts had a great influence on the activity and sulfur resistance of Pt-Ni catalysts for the gas phase selective hydrogenation of styrene. In this work our attention is now focused on the sulfur resistance of low-loaded mono- and bimetallic catalysts with Pt as the active phase and W as a promoter. The reaction is carried out in the liquid phase in order to obtain a higher reactor throughput. The influence of the metals impregnation sequence on the activity, selectivity, and sulfur resistance is especially studied.

## 2. Experimental

**2.1. Catalysts Preparation.**  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Ketjen CK300 was used as support. This was previously calcined in air at 823 K to stabilize its texture ( $S_{\text{BET}}$ : 224 m<sup>2</sup> g<sup>-1</sup>). Platinum and tungsten mono- and bimetallic catalysts supported over alumina were prepared by the incipient wetness technique. Volume and concentration of the impregnating solutions were adjusted to get 1 wt% Pt and 3.5 wt% W on the final mono- and bimetallic catalysts.

An aqueous acid solution of H<sub>2</sub>PtCl<sub>6</sub> (Strem Chemicals, Cat N°: 78-0200 purity > 99.9%) at pH 1 (with HCl) was used to prepare the platinum monometallic catalyst (sample Pt/Al). The tungsten monometallic catalyst (sample W/Al) was prepared using a phosphotungstic acid solution H<sub>3</sub>PO<sub>4</sub>·12WO<sub>3</sub> (Fluka, Cat N°: 79690 purity > 99.9%). After impregnation the monometallic catalysts were dried 24 h at 373 K and calcined in an air flow at 823 K during 3 or 7 h. They were named Pt/Al and W/Al, respectively. The calcination conditions used for preparing W/Al assured the complete elimination of phosphorus from the catalyst [19, 20].

A portion of W/Al was impregnated with an aqueous acid solution of H<sub>2</sub>PtCl<sub>6</sub> (pH 1 with HCl) to prepare the bimetallic catalyst (WPt/Al). Part of the Pt/Al catalyst batch was impregnated with an acid solution of H<sub>3</sub>PO<sub>4</sub>·12WO<sub>3</sub> to obtain the bimetallic catalyst, PtW/Al. WPt/Al and PtW/Al bimetallic catalysts were both dried and calcined in an air flow at 823 K during 3 (WPt/Al) or 7 h (PtW/Al). Immediately before the catalytic test the catalysts were reduced in a hydrogen stream during 1 h at 673 K.

**2.2. Catalyst Characterization.** The contents of platinum, phosphorus, and tungsten of the catalysts were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) using a Perkin Elmer ICP OPTIMA 2100 instrument.

The dispersion of the metal particles was measured by means of the chemisorption of CO in a pulse apparatus. The samples of the catalysts were first reduced 1 h in hydrogen at 673 K. Then the samples were flushed in nitrogen for 1 h and cooled down to room temperature. Then 0.25 cm<sup>3</sup> pulses of a reducing gas mixture were successively sent to the

TABLE 1: Catalysts naming convention. Data of dispersion ( $D$ ), Pt and W binding energies, and atomic superficial ratios as determined by XPS.

Catalysts	1st imp.	2nd imp.	$D$ (%)	BE (eV)		BE (eV)	Cl/Al	W/Al	Pt/Al
				Pt <sup>0</sup>	Pt 4d <sub>5/2</sub>	W 4f <sub>7/2</sub> W <sup>+6</sup>			
W/Al	W			—	—	35.7	—	0.0161	—
Pt/Al	Pt		37	313.5 (54%)	316.7 (46%)	—	0.0033	—	0.0035
WPt/Al	W	Pt	27	313.7 (51%)	315.9 (49%)	36.0	0.0055	0.0097	0.0029
PtW/Al	Pt	W	17	313.3 (49%)	315.2 (51%)	35.9	0.0022	0.0161	0.0015

reactor. This mixture is comprised of 3.5% (v/v) CO in N<sub>2</sub>. Part of the CO is chemisorbed, and the rest flows from the adsorption cell to a methanator containing a Ni/kieselguhr catalyst. The methanator is fed with a hydrogen stream, and CO is quantitatively transformed into CH<sub>4</sub>. This methane is detected in a flame ionization detector downstream. The amount of CO adsorbed is measured by calculating the amount of methane not reaching the detector.

The electronic state of the surface species on the catalyst was determined by X-ray Photoelectron Spectroscopy (XPS) in a VG-Microtech Multilab equipment, equipped with a MgK<sub>α</sub> (hv: 1253.6 eV) radiation and a pass energy of 50 eV. The analysis pressure during data acquisition was  $5 \times 10^{-7}$  Pa. Samples were treated *in situ* in the presence of a H<sub>2</sub> stream during 1 h at 673 K. 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 peak to a combination of Lorentzian/Gaussian lines of 30–70% proportions. The reference binding energy (BE) was C 1s peak at 284.6 eV. For the quantification, the areas were normalized using the sensitivity factors of each element.

X-ray diffraction (XRD) measurements of powdered samples were obtained using a Shimadzu XD-D1 instrument with a CuK radiation ( $\lambda = 1.5405 \text{ \AA}$ ) in the  $21 < 2\theta < 49^\circ$  at a scan rate of  $0.25^\circ \text{ min}^{-1}$ . Samples were powdered and reduced under a hydrogen flow, the samples were put into the chamber of the equipment, and then the spectrum was acquired.

The reducibility of the surface species on the catalysts was assessed by temperature programmed reduction (TPR), using a Micromeritics AutoChem II instrument equipped with a TCD. Samples were pretreated under an oxygen flow stream at 673 K during 30 min, and then they were cooled down up to room temperature in argon. TPR profiles were obtained increasing the temperature up to 1223 K at a heating rate of  $10 \text{ K min}^{-1}$  in a 5% (v/v) hydrogen : argon stream.

**2.3. Catalytic Tests.** Activity, selectivity, and sulfur resistance of the prepared catalysts were assessed with the test reaction of styrene hydrogenation in the presence of small amounts of thiophene. 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. In some blank tests the reaction was performed in the absence of thiophene. In these poison-free tests the reactor was

loaded with 0.3 g of catalyst and 200 mL of a solution of 5% (v/v) styrene (Aldrich, Cat. N° S497-2, purity > 99%) in toluene (Merck, Cat. N° TX0735-44, purity > 99%) using n-decane (Fluka, Cat. N° 30550, purity > 98%) as an internal chromatographic standard. In the case of the catalytic tests in the presence of sulfur, 300 ppm of thiophene was added to the feed. Catalytic tests were carried out in duplicates. The average experimental error was lower than 5%. Reactants and products were analyzed by gas chromatography using a 30 m, J&W INNOWax 19091N-213 capillary column.

### 3. Results and Discussion

**3.1. Catalysts Characterization.** The values of mass concentration determined by ICP technique were 1 wt% of Pt and 3.5 wt% of W. The W/Pt atomic ratio was equal to 3. On the other hand, no phosphorus was detected by ICP chemical analysis after the calcination and reduction of the prepared catalysts, suggesting that all phosphorus was eliminated from the catalysts. Table 1 shows the dispersion of the samples, as calculated from the CO chemisorption data. As W does not chemisorb CO at room temperature, in the case of the bimetallic catalysts we considered that only the platinum sites were responsible for CO chemisorption, and we assumed a chemisorption stoichiometry H : Pt = 1. The results show that the dispersion of monometallic Pt/Al is 1.4 times higher than that of WPt/Al and twice as high as that of PtW/Al. This indicates that Pt in the monometallic system is more accessible to CO chemisorption. The lower CO adsorption on PtW/Al could be due to an effect of decoration of Pt particles by W species, the latter being not active for CO adsorption [21, 22].

The X-ray diffractograms of all the catalysts presented only the typical signals of the gamma phase of alumina:  $37.7^\circ$ ,  $45.98^\circ$ , and  $66.98^\circ$  [23, 24]. Because of the low concentration of platinum, no peak at  $39.9^\circ$  due to the  $\langle 111 \rangle$  reflections of Pt<sup>0</sup>, neither those corresponding to the  $\langle 200 \rangle$  planes of PtO<sub>2</sub> or Pt<sup>0</sup> could be found [25–27]. For the bimetallic systems the absence of peaks in the region  $20^\circ < 2\theta < 30^\circ$  indicates that there is no tungsten oxide present as a crystalline segregated phase. Segregated monoclinic WO<sub>3</sub> crystallites can be detected by XRD for W surface concentrations higher than the corresponding surface monolayer saturation value ( $4.3 W_{\text{atoms}} \text{ nm}^{-2}$ ) [28]. In our case, the W surface density was lower than the corresponding monolayer value ( $0.64 W_{\text{atoms}} \text{ nm}^{-2}$ ). Because of the small particle size and the

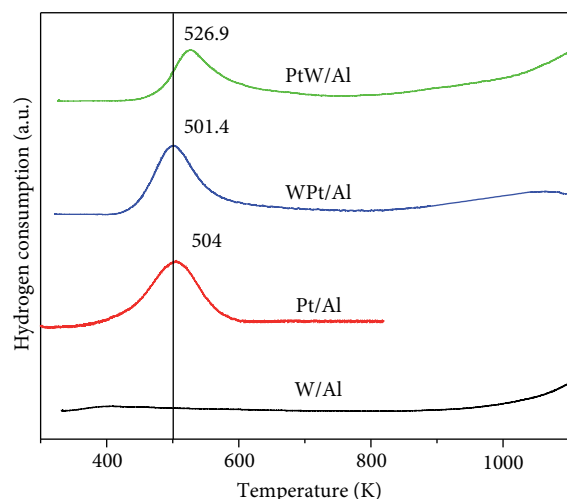


FIGURE 1: TPR traces of the Pt/Al, W/Al, WPt/Al, and PtW/Al samples.

low sensitivity of the XRD method, Pt and  $\text{WO}_x$  crystalline phases cannot be detected in our case.

Figure 1 shows the TPR traces of the calcined Pt and W mono- and bimetallic catalysts. It can be seen that the TPR trace of the Pt monometallic catalyst has a main hydrogen consumption peak at 504 K that can be assigned to the reduction of oxychlorinated  $\text{Pt}^{\delta+}\text{O}_x\text{Cl}_y$  species [29–33]. These particles are agglomerated over the support during the calcination of the catalyst.

For the monometallic W/Al sample the TPR trace shows that the main reduction peak starts at 900 K. The maximum hydrogen consumption occurs at temperatures higher than 1100 K. Several authors have reported that highly dispersed  $\text{WO}_x$ , bound to alumina by strong bonds, had reduction peaks at high temperatures (950–1300 K) [34–36]. Therefore the observed reduction peak can be assigned to the reduction of amorphous  $\text{WO}_x$  species.

Up to 800 K the reduction traces of WPt/Al and PtW/Al bimetallic catalysts (Figure 1) are very similar to the trace of Pt/Al, with a main reduction peak at 501.4 and 526.9 K, respectively, corresponding to the reduction of  $\text{Pt}^{\delta+}\text{O}_x\text{Cl}_y$  species. Comparing these profiles, there is a shift of the oxychlorinated species reduction peak of  $-2.6$  and  $22.9$  K, for WPt/Al and PtW/Al, respectively, indicating that the presence of W modifies the reducibility of Pt. These shifts point to the presence of different active sites on the catalysts surface and suggest an interaction or electronic effect between Pt, W, and  $\text{Al}_2\text{O}_3$ . Besides, the slight shift to lower temperatures of the main reduction peak of WPt/Al suggests that the reduction of oxychlorinated species is more easily accomplished on WPt/Al: when platinum is impregnated over the monometallic W/Al catalyst. On the other hand the marked shift of the main peak of reduction of the PtW/Al catalyst to higher temperatures suggests that the Pt particles are harder to reduce (in comparison to the monometallic catalyst) when tungsten is impregnated after Pt. This could be due to an effect of decoration of Pt particles by W species

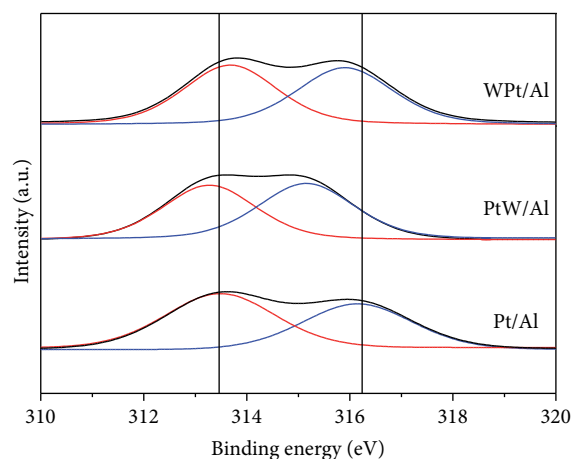


FIGURE 2: XPS spectra of the Pt  $4d_{5/2}$  region.

as reported by Sica and Gigola [22] for Pd- $\text{WO}_x/\text{Al}_2\text{O}_3$  catalysts with low metal content. The possible decoration of  $\text{Pt}^{\delta+}\text{O}_x\text{Cl}_y$  particles by  $\text{WO}_x$  species is an example of metal-support interaction related to the mobility of support surface species. Surface species would migrate onto Pt particles during heat treatments, mobility being only important at high temperatures.

It can also be seen that the high temperature peak ( $>950$  K) of the TPR traces of the bimetallic catalysts is similar to that of the W/Al catalyst and would therefore be related to the reduction of amorphous  $\text{WO}_x$  species bound to alumina through strong bonds. The second reduction peak of PtW/Al is fairly similar to that of the W/Al catalyst, though it is shifted to higher temperatures in the case of WPt/Al. This indicates that tungsten species on WPt/Al are more refractory to reduction, a property likely related to their double calcination and reduction treatment.

According to the TPR results, the reduction temperature adopted for platinum mono- and bimetallic catalysts (673 K) during the synthesis of the catalysts should ensure, at least partly, the presence of  $\text{Pt}^0$  metal atoms on the surface.

The XPS spectra of the catalysts had a peak next to 198.5 eV that would correspond to Cl  $2p_{3/2}$ , attributed to chloride species that were not eliminated during the thermal treatment stages [37]. Figures 2 and 3 contain the XPS spectra of the Pt  $4d_{5/2}$  and W  $4f_{7/2}$  regions for all catalysts. The maximum binding energy (BE) of Pt  $4d_{5/2}$  and W  $4f_{7/2}$  and Cl/Al, W/Al, and Pt/Al atomic ratios are also listed in Table 1.

As it can be seen in Figure 2 all catalysts had low intensity values of the Pt  $4d_{5/2}$  peak in the  $313.5 \pm 0.2$  eV range. From the literature reports this peak can be attributed to  $\text{Pt}^0$  [37, 38]. In Figure 2 a second peak at 315.2–316.7 eV can be found that can be attributed to the presence of complex electrodeficient  $\text{Pt}^{\delta+}$  species ( $0 < \delta < 2$ ) stabilized by the presence of remaining chloride as oxychloride compounds  $\text{Pt}^{\delta+}\text{O}_x\text{Cl}_y$  [33] formed during the calcination or the following reduction process [38]. When a comparison is made between the Pt high BE peak of the bimetallic catalyst against that of the Pt/Al one, it can be seen that there is a shift towards lower BE values



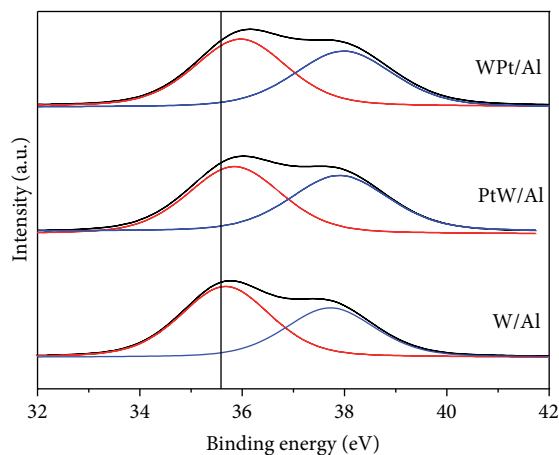


FIGURE 3: XPS spectra of the W  $4f_{7/2}$  region.

of 1.5 for PtW/Al and 0.8 eV WPt/Al. This might indicate the presence of  $Pt^{\delta+}$  species with a higher availability of electrons than those present on the monometallic catalyst.

The spectra of W  $4f_{7/2}$  for W/Al, WPt, and PtW catalysts are plotted in Figure 3. They have a peak at  $35.8 \pm 0.2$  eV and a  $4f_{5/2}$  doublet peak at  $38.0 \pm 0.2$  eV, suggesting the presence of electron-deficient species  $W^{\rho+}$  (with  $\rho < 6$ ) [20, 37, 39]. The BE of W  $4f_{7/2}$  reported in Table 1 indicates that tungsten is present on the alumina surface of WPt/Al and PtW/Al catalysts with slightly higher values of BE than on the tungsten monometallic catalyst. This pattern and the presence of  $Pt^{\delta+}$  electron deficient species suggest the formation of different types of intermediate surface species:  $Pt^{\delta+}O_xCl_y-WO_x-Al_2O_3$  or  $WO_x-Pt^{\delta+}O_xCl_y-Al_2O_3$ . This could be active sites participating in the reaction on the bimetallic catalyst. The formation of intermediate Pd- $WO_x-Al_2O_3$  on Pd-W bimetallic catalysts has been earlier reported by L'Argentière and Fígoli [21] and Lederhos et al. [20].

An inspection of the Cl/Al atomic ratios of Table 1 reveals that WPt/Al has 1.7 and 2.5 times more surface chlorine than Pt/Al and PtW/Al, respectively. Table 1 also shows that the Pt/Al atomic surface ratio is 1.2 and 2.3 times higher than the same ratio on the WPt/Al and PtW/Al catalysts. This indicates that there are more available superficial platinum species on the monometallic platinum catalyst. The value of the W/Al atomic ratio of WPt/Al is quite lower than that of the PtW/Al or W/Al catalysts, because of a possible decoration effect of  $WO_x$  species by  $Pt^{\delta+}O_xCl_y$  oxychloride species.

**3.2. Catalytic Tests.** According to the internal standard method, the selectivity during the tests was ca. 98% for all catalysts. No hydrogenolysis of the poison was detected.

Figure 4 shows the results of total conversion of styrene as a function of time for the mono- and bimetallic catalysts. It can be seen that Pt/Al is the most active material. The order of activity found was Pt/Al > WPt/Al > PtW/Al. It can be noted that WPt/Al has a lower activity than Pt/Al at small values

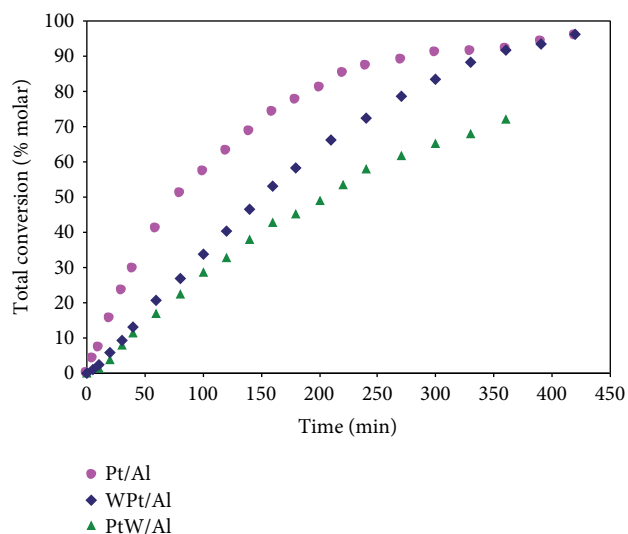


FIGURE 4: Styrene total conversion as a function of time in the absence of poison.

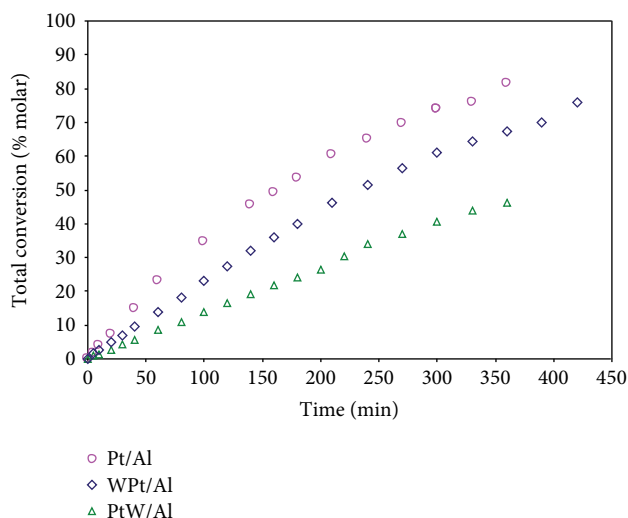


FIGURE 5: Styrene total conversion as a function of time. Sulfur-doped feed.

of time-on-stream but the activity becomes similar at TOS values higher than 320 min.

Figure 5 shows the catalytic test results obtained with the thiophene-doped feed. It can be seen that in comparison to the tests with the sulfur-free feed there is a decrease of the total conversion of styrene for all samples. The catalyst ordering according to activity level is however the same.

For both the sulfur-free and sulfur-contaminated feedstocks, the most active catalyst was the Pt/Al one. In this sense it is well known that electron-rich Pt metallic centers can cleave the bonds in  $H_2$  by means of the interaction of a filled d metal orbital with the empty sigma antibonding molecular orbital of hydrogen [40]. The Pt/Al atomic ratio found by XPS was Pt/Al > WPt/Al > PtW/Al; thus the activity order found during the tests with sulfur-doped and sulfur-free feeds

TABLE 2: Values of the initial rate of hydrogenation of styrene and fraction of poisoned sites ( $\alpha$ ).

Catalysts	$r_{sf}^{\circ}$ (mol L <sup>-1</sup> min <sup>-1</sup> )	$r_{sp}^{\circ}$ (mol L <sup>-1</sup> min <sup>-1</sup> )	$\alpha$
Pt/Al	0.24 ± 0.01	0.14 ± 0.01	0.49
WPt/Al	0.13 ± 0.01	0.09 ± 0.01	0.32
PtW/Al	0.11 ± 0.01	0.05 ± 0.01	0.50

could be related to the amount of accessible surface Pt sites. Pt/Al would have the highest amount of Pt<sup>0</sup> on the surface, Pt<sup>0</sup> in turn having the highest electronic population in the 4d orbital that favors the cleavage of hydrogen. Also, as observed by XPS, Pt/Al has the most electrodeficient Pt<sup>δ+</sup> species (BE = 316.7 eV) thus favoring the adsorption of electron-rich styrene. In summary the differences in activity between the reported catalysts could be attributed to electronic effects. It must be also remarked that two types of sites are necessary to increase the catalytic activity for hydrogenation of styrene.

During the tests with the thiophene spiked feed the activities of all catalysts were decreased. According to the most accepted model for sulfur poisoning of group VIII metals, poisoning occurs by a donation of electrons from the metals to the sulfur atom. Particularly thiophene interacts with the surface of metals in a planar way through the  $\pi$  electrons of the aromatic nucleus (weak  $\eta_5$  bond) [33, 41, 42]. Therefore during the poisoning tests some of the electrons of the 5d Pt orbital would be shared with the S atom and for this reason the metal would have a lower amount of available electrons for cleaving the hydrogen bond. The catalytic activity is thus reduced. In this sense the differences in sulfur resistance between the catalysts can be partly attributed to electronic effects.

The least active catalyst during both kinds of tests (with and without thiophene) was the PtW/Al one. The low activity could be associated to the decoration effect detected during the catalyst characterization. The low dispersion, the shift to high temperatures of the Pt<sup>δ+</sup>O<sub>x</sub>Cl<sub>y</sub> reduction peak, and the high surface W/Al atomic ratio would support this supposition. Therefore another possible source of deactivation would be the geometrical blocking of active sites by WO<sub>x</sub> deposited over the surface of the Pt particles on the PtW/Al catalyst.

Initial styrene reaction rates were determined for all catalysts during the tests with both sulfur-free ( $r_{sf}^{\circ}$ ) and sulfur-doped ( $r_{sp}^{\circ}$ ) feeds. A zero order with respect to styrene was supposed, in accordance with the conversion patterns measured. From the initial reaction values and considering a simple linear deactivation model (zero order for deactivation) [43], the fraction of poisoned sites ( $\alpha$ ) can be calculated as  $\alpha = 1 - r_{sp}^{\circ}/r_{sf}^{\circ}$ . Table 2 shows the values of initial hydrogenation rate as obtained by least squares fitting with the Scientist program. The mean deviation of the initial reaction rates ( $r_{sf}^{\circ}$  and  $r_{sp}^{\circ}$ ) was about 2–4% indicating that the obtained fit was good.

Table 2 shows that WPt/Al had a lower fraction of poisoned sites than Pt/Al. The  $\alpha$  values of PtW/Al and Pt/Al were however similar. The higher sulfur resistance of

the bimetallic WPt/Al catalyst could be related to the high surface Cl/Al ratio, indicating that Pt oxychlorinated species prevent the adsorption of thiophene by means of a steric effect (big size of species) and/or an electronic effect (high electronegativity of chlorine). PtW/Al and Pt/Al turned out to be the least sulfur resistant catalysts, probably because of their low chloride content (as detected by XPS). Chloride is supposed to inhibit the adsorption of thiophene. A high concentration of Pt<sup>0</sup> electron-rich sites with low BE values could also contribute to the poisoning. These would act as electron donor sites, providing available electrons to the bond with the S atom of thiophene. Both effects would promote a strong adsorption of thiophene and thus an enhanced blocking of the catalyst active sites.

## 4. Conclusion

The effect of the sequence of metal impregnation in bimetallic Pt-W catalysts was evaluated. The properties assessed were the catalytic activity and the sulfur resistance, during the selective hydrogenation of styrene.

The XPS results indicated the presence of different Pt<sup>0</sup> and Pt<sup>δ+</sup>O<sub>x</sub>Cl<sub>y</sub> species. The mono- and bimetallic catalysts thus showed different Pt/Al and Cl/Al surface atomic ratios.

During the tests of styrene hydrogenation with pure and sulfur contaminated feeds, the order of activity found was: Pt/Al > WPt/Al > PtW/Al. The differences in activity between the reported catalysts were mainly attributed to electronic effects. This was related to the fact that two types of sites might participate synergically during the hydrogenation of styrene: (a) electron-rich platinum active sites cleaving the H<sub>2</sub> molecule and (b) electrodeficient Pt<sup>δ+</sup> species, acting as Lewis acid sites for adsorption of styrene.

It was found that the order of impregnation of W and Pt in W-Pt/Al catalysts is important for determining the sulfur resistance of the final material.

The higher sulfur resistance of WPt/Al would come from the higher amount of surface chlorine (that produces both electronic and geometrical blocking effects). PtW/Al and Pt/Al had lower chlorine contents and higher concentrations of Pt<sup>0</sup>. They thus had an enhanced capacity for the strong adsorption of thiophene and deactivated more rapidly.

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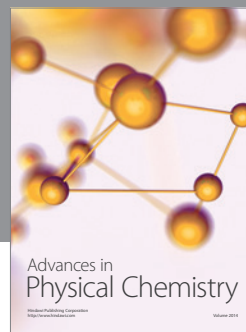
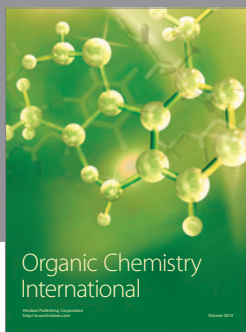
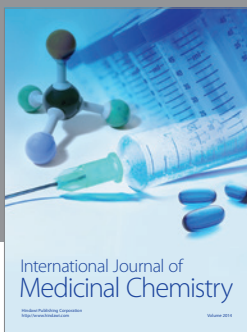
## References

- [1] A. B. Gaspar, M. A. P. da Silva, O. Q. F. Araújo, J. L. de Medeiros, and J. M. Britto, "Kinetic study on the first stage of PYGAS upgrading," in *In Proceedings of the AIChE Spring National Meeting*, p. 630, New Orleans, La, USA, 2003.
- [2] T. A. Nijhuis, F. M. Dautzenberg, and J. A. Moulijn, "Modeling of monolithic and trickle-bed reactors for the hydrogenation

- of styrene," *Chemical Engineering Science*, vol. 58, no. 7, pp. 1113–1124, 2003.
- [3] A. Molnár, A. Sárkány, M. Varga, and J. Molec. Catal. A., "Hydrogenation of carbon-carbon multiple bonds: chemo-, regio- and stereo-selectivity," *Journal of Molecular Catalysis A*, vol. 173, pp. 185–221, 2001.
- [4] D. E. Grove, "Catalysts—myths and reallities," *Platinum Metals Review*, vol. 47, no. 1, p. 44, 2003.
- [5] J. K. Dunleavy, "Sulfur as a catalyst poison," *Platinum Metals Review*, vol. 50, no. 2, p. 110, 2006.
- [6] J. A. Anderson, L. Daza, S. Damyanova, J. L. G. Fierro, and M. T. Rodrigo, "Hydrogenation of styrene over nickel/sepiolite catalysts," *Applied Catalysis A*, vol. 113, no. 1, pp. 75–88, 1994.
- [7] Q. Debuisschert, I. Conso A, and A. Fritz, "Commercial applications of pyrolysis gasoline upgrading," in *Proceedings of the 2nd Russian Petrochemical Technology Conference*, Moscow, Russia, 2003.
- [8] J. A. Rodriguez, "The chemical properties of bimetallic surfaces: importance of ensemble and electronic effects in the adsorption of sulfur and  $\text{SO}_2$ ," *Progress in Surface Science*, vol. 81, no. 4, pp. 141–189, 2006.
- [9] A. Arcoya, X. Seoane, and L. Gómez-Sainero, "Activity of Pd/ $\text{Al}_2\text{O}_3$  and Ru/ $\text{Al}_2\text{O}_3$  catalysts in the hydrogenation of o-xylene: effect of thiophene," *Applied Surface Science*, vol. 211, pp. 341–351.
- [10] J. Badano, C. Lederhos, M. Quiroga, P. L'Argentièrre, and F. Coloma-Pascual, "Low metal loading catalysts used for the selective hydrogenation of styrene," *Quimica Nova*, vol. 33, no. 1, pp. 45–51, 2010.
- [11] J. R. Regalbuto, C. W. Allen, and E. E. Wolf, "An integrated study of Pt/ $\text{WO}_3/\text{SiO}_2$  catalysts for the NO-CO reaction," *Journal of Catalysis*, vol. 108, no. 2, pp. 304–332, 1987.
- [12] J. L. Contreras, G. A. Fuentes, L. A. García, J. Salmones, and B. Zeifert, "WOx effect on the catalytic properties of Pt particles on  $\text{Al}_2\text{O}_3$ ," *Journal of Alloys and Compounds*, vol. 483, no. 1-2, pp. 450–452, 2009.
- [13] M. Humbert, C. Menning, and J. Chen, "Replacing bulk Pt in Pt-Ni-Pt bimetallic structures with tungsten monocarbide (WC): hydrogen adsorption and cyclohexene hydrogenation on Pt-Ni-WC," *Journal of Catalysis*, vol. 271, no. 1, pp. 132–139, 2010.
- [14] L. S. Carvalho, C. L. Pieck, M. C. Rangel, N. S. Fígoli, C. R. Vera, and J. M. Parera, "Trimetallic naphtha reforming catalysts: II. Properties of the acid function and influence of the order of addition of the metallic precursors on Pt-Re-Sn/ $\gamma\text{-Al}_2\text{O}_3\text{-Cl}$ ," *Applied Catalysis A*, vol. 269, pp. 105–116, 2004.
- [15] C. L. Pieck, P. Marecot, J. M. Parera, and J. Barbier, "Influence of chlorine content on PtRe interaction and coke deposition," *Applied Catalysis A*, vol. 126, no. 1, pp. 153–163, 1995.
- [16] S. M. Augustine and W. M. H. Sachtler, "On the mechanism for the platinum-catalyzed reduction of rhenium in PtRe  $\gamma\text{-Al}_2\text{O}_3$ ," *Journal of Catalysis*, vol. 116, no. 1, pp. 184–194, 1989.
- [17] K. C. Taylor, "Nitric oxide catalysis in automotive exhaust systems," *Catalysis Reviews: Science and Engineering*, vol. 35, no. 4, pp. 457–481, 1993.
- [18] C. Betti, J. Badano, M. J. Maccarrone, V. Mazzieri, C. Vera, and M. Quiroga, "Effect of the sequence of impregnation on the activity and sulfur resistance of Pt-Ni/ $\gamma\text{-Al}_2\text{O}_3$  bimetallic catalysts for the selective hydrogenation of styrene," *Applied Catalysis A*, vol. 435, pp. 181–186, 2012.
- [19] Y. Song, G. Seo, and S. Ihm, "Hydrodealkylation reaction of ethylbenzene over a supported nickel-tungsten catalyst," *Applied Catalysis A*, vol. 83, pp. 75–86, 1992.
- [20] C. R. Lederhos, M. J. MacCarrone, J. M. Badano et al., "Hept-1-yne partial hydrogenation reaction over supported Pd and W catalysts," *Applied Catalysis A*, vol. 396, no. 1-2, pp. 170–176, 2011.
- [21] P. C. L'Argentièrre and N. S. Fígoli, "Pd-W and Pd-Co bimetallic catalysts' sulfur resistance for selective hydrogenation," *Industrial & Engineering Chemistry Research*, no. 7, pp. 2543–2546, 1997.
- [22] A. M. Sica and C. E. Gigola, "Interaction of CO, NO and NO/CO over Pd/ $\gamma\text{-Al}_2\text{O}_3$  and Pd- $\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$  catalysts," *Applied Catalysis*, vol. 239, pp. 121–139, 2003.
- [23] S. Huang, C. Zhang, and H. He, "Complete oxidation of o-xylene over Pd/ $\text{Al}_2\text{O}_3$  catalyst at low temperature," *Catalysis Today*, vol. 139, pp. 15–23, 2008.
- [24] C. Martín, G. Solana, P. Malet, and V. Rives, "Nb $_2\text{O}_5$ -supported  $\text{WO}_3$ : a comparative study with  $\text{WO}_3/\text{Al}_2\text{O}_3$ ," *Catalysis Today*, vol. 78, pp. 365–376, 2003.
- [25] T. Onoe, S. Iwamoto, and M. Inoue, "Synthesis and activity of the Pt catalyst supported on CN1," *Catalysis Communications*, vol. 8, no. 4, pp. 701–706, 2007.
- [26] Y. G. Shul, T. Sugiura, T. Tatsumi, and H. Tominaga, "Durability of zeolite supported RuPt bimetallic catalysts for isoalkane synthesis from synthesis gas," *Applied Catalysis*, vol. 24, no. 1-2, pp. 131–143, 1986.
- [27] S. Y. Huang, S. M. Chang, and C. T. Yeh, "Characterization of surface composition of platinum and ruthenium nanoalloys dispersed on active carbon," *Journal of Physical Chemistry*, vol. 110, pp. 234–239, 2006.
- [28] S. S. Chan, I. E. Wachs, L. L. Murrell, L. Wang, and W. K. Hall, "In situ laser Raman spectroscopy of supported metal oxides," *Journal of Physical Chemistry*, vol. 88, no. 24, pp. 5831–5835, 1984.
- [29] H. Lieske, G. Lietz, H. Spindler, and J. Völter, "Reactions of platinum in oxygen- and hydrogen-treated Pt- $\gamma\text{-Al}_2\text{O}_3$  catalysts: I. Temperature-programmed reduction, adsorption, and redispersion of platinum," *Journal of Catalysis*, vol. 81, no. 1, pp. 8–16, 1983.
- [30] J. Völter, "Studies in surface science and catalysis," in *Catalytic Hydrogenation*, L. Červený, Ed., vol. 27, chapter 10, Elsevier Science, 1986.
- [31] P. Reyes, G. Pecchi, M. Morales, and J. L. G. Fierro, "The nature of the support and the metal precursor on the resistance to sulphur poisoning of Pt supported catalysts," *Applied Catalysis A*, vol. 163, no. 1-2, pp. 145–152, 1997.
- [32] R. M. Navarro, B. Pawelwc, J. M. Trejo, R. Mariscal, and J. L. G. Fierro, "Hydrogenation of aromatics on sulfur-resistant PtPd bimetallic catalysts," *Journal of Catalysis*, vol. 189, pp. 184–194, 2000.
- [33] J. M. Badano, M. Quiroga, C. Betti, C. Vera, S. Canavese, and F. Coloma-Pascual, "Resistance to sulfur and oxygenated compounds of supported Pd, Pt, Rh, Ru catalysts," *Catalysis Letters*, vol. 137, no. 1-2, pp. 35–44, 2010.
- [34] J. L. Contreras, G. A. Fuentes, B. Zeifert, and J. Salmones, "Stabilization of supported platinum nanoparticles on  $\gamma$ -alumina catalysts by addition of tungsten," *Journal of Alloys and Compounds*, vol. 483, no. 1-2, pp. 371–373, 2009.
- [35] J. Cruz, M. Avalos-Borja, R. López Cordero, M. A. Bañares, and J. L. G. Fierro, "Influence of pH of the impregnation solution on the phosphorus promotion in W/ $\text{Al}_2\text{O}_3$  hydrotreating catalysts," *Applied Catalysis A*, vol. 224, pp. 97–110, 2002.

- [36] V. Logie, G. Maire, D. Michel, and J. L. Vignes, "Skeletal isomerization of hexenes on tungsten oxide supported on porous  $\alpha$ -alumina," *Journal of Catalysis*, vol. 188, no. 1, pp. 90–101, 1999.
- [37] NIST X-Ray Photoelectron Spectroscopy Database, *NIST Standard Reference Database 20, Version 3.5 (Web Version)*, National Institute of Standards and Technology, Gaithersburg, Md, USA, 2007.
- [38] J. C. Serrano-Ruiz, G. W. Huber, M. A. Sánchez-Castillo, J. A. Dumesic, F. Rodríguez-Reinoso, and A. Sepúlveda-Escribano, "Effect of Sn addition to Pt/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts: an XPS, <sup>119</sup>Sn Mössbauer and microcalorimetry study," *Journal of Catalysis*, vol. 241, no. 2, pp. 378–388, 2006.
- [39] V. M. Benitez, C. A. Querini, N. S. Figoli, and R. A. Comelli, "Skeletal isomerization of 1-butene on WO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>," *Applied Catalysis A*, vol. 178, no. 2, pp. 205–218, 1999.
- [40] D. F. Shriver, P. W. Atkins, and C. H. Langford, *Inorganic Chemistry*, W.H. Freeman, New York, NY, USA, 3rd edition, 1994.
- [41] M. P. Kiskinova, "Poisoning and promotion in catalysis based on surface science concepts and experiments," in *Studies in Surface Science and Catalysis*, B. Delmon and J. T. Yates, Eds., vol. 70, chapter 5, Elsevier Science, Amsterdam, The Netherlands, 1982.
- [42] P. C. L'Argentièrre, M. G. Cañón, and N. S. Figoli, "XPS studies of the effect of Mn on Pd/Al<sub>2</sub>O<sub>3</sub>," *Applied Surface Science*, vol. 89, no. 1, pp. 63–68, 1995.
- [43] G. F. Fromment and K. B. Bischoff, *Chemical Reactor Analysis and Design*, John Wiley & Sons, 1990.





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