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Pt and Pd catalysts supported on Al_2O_3 modified with rare earth oxides in the hydrogenation of tetralin, in the presence of thiophene

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Abstract

Due to stringent environmental regulations, the reduction of aromatic compounds present in diesel fuel, precursors of particulate matter, is becoming one of the most important technologies in petroleum refining industries. However, the high quantity of nitrogen and sulfur compounds limits the use of catalytic processes. In this work Pt and Pd catalysts supported on alumina modified with rare earth oxides (Ce and Pr) were prepared, characterized by XRF, XRD, UV–vis-DRS and XPS, and tested in the hydrogenation of tetralin reaction, in the presence of different concentrations of thiophene. The results showed that the use of a Pr-modified alumina support enhanced the tolerance of the Pt/Al_2O_3 catalyst to thiophene. The addition of a second metal, Pd, despite a loss in activity, increased tolerance to this poison. The combination of both promoters exhibited a synergic effect, as the bimetallic catalyst supported in the Pr-modified alumina showed a very low sensitivity to thiophene, up to 2600 ppm, explained by the electron-deficiency of the metallic Pt.

Keywords: Catalysts; Al_2O_3; Rare earth oxides

1. Introduction

The legislation on limits on the emission of pollutant materials in automotive exhausts is becoming increasingly rigorous all over the world [1]. Initially these laws were imposed for the reduction in polluting gases emitted by Otto's engines. However, recently, environmental interest has turned to diesel engines.

Diesel is composed predominantly of aliphatic hydrocarbons containing from 9 to 28 atoms of carbon in the chain, obtained by distillation in the range of 433–683 K, but it can also contain other compounds that by chance distil in the same range, such as aromatic polycyclic hydrocarbons and their alkyl derivatives [2]. The presence of the polyaromatic compounds, allied to the high amount of sulfur (0.05–0.5%), has been identified as the main cause of pollution generated by diesel engines. These compounds remain intact in the process of combustion inside these motors, producing particulates in the emissions to the atmosphere, while the high concentration of sulfur is responsible for the sulfate aggregation to the particulate.

Particulate matter, or simply particulate, consists basically, of agglomerates of nucleus of carbon, which can occlude inorganic oxides and even metallic particles. Depending on the temperature, water, sulfate and sulfuric acid can condense in these particles. These substances contribute therefore to increase the mass of the particulate matter produced, as well as its noxious effect [2].

Given stringent environmental regulations, the reduction of aromatic compounds present in diesel fuel is becoming one of the most important technologies being developed in petroleum refining industries [3]. However, one of the difficulties found in the hydrogenation of aromatics is the high amount of sulfur (and nitrogen) compounds present in diesel fuel, which cause many problems for commercial catalysts. Thus, the development of catalysts resistant to sulfur and nitrogen compounds for the removal of such aromatic and polyaromatic compounds has become the target of much research in this field.

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In this work, Pt and Pd catalysts supported on alumina modified with rare earth oxides (Ce and Pr) were prepared, characterized and tested in the hydrogenation of tetralin reaction in the presence of different concentrations of thiophene. Tetralin was chosen as it is the intermediary in the hydrogenation of the naphthalene (representative compound of the aromatics in diesel fuel) and thiophene was chosen as representative of sulfur pollutants.

2. Experiment

2.1. Catalyst preparation

The preparation of the catalysts was divided in three stages, which consisted of: (1) modification of the supports with different promoters, (2) impregnation of the metallic active phase and (3) preparation of bimetallic catalysts. The support used in the preparation of all catalysts was alumina supplied by Alcoa, with the following characteristics: surface area 62 m^2/g, γ phase, pore volume 0.6 cm^3/g and zero point charge (ZPC) at 5.9. The supports Al_2O_3-1%Ce, Al_2O_3-1%Pr e Al_2O_3-4%Pr were prepared by impregnation of γ-Al_2O_3 with aqueous solutions of the salts $(NH_4)[Ce(NO_3)6{\cdot}6H_2O$ and $Pr(NO_3)_3{\cdot}5H_2O$, respectively, for 24 h at room temperature. After impregnation, the water was slowly removed by evaporation, under vacuum from the room temperature to 100 °C. The samples were dried in an oven at 100 °C overnight and calcined at 300 °C, with a heating rate 10 °C/min, for 2 h under ultra pure air flow (50 mL/min). The catalysts Pt/Al_2O_3, Pt/Al_2O_3-%Ce, Pt/Al_2O_3-%Pr e Pt/Al_2O_3-%Pr, were prepared by impregnation of the modified supports with a solution of $H_2PtCl_6{\cdot}6H_2O$. The impregnation process, drying and calcination of the precursors was similar to that used in the modification of the support. After calcination, all the samples were reduced under ultra pure H_2 (50 mL/min) at 300 °C, with a heating rate 10 °C/min, for 2 h. For all samples, the amount of Pt was about 1 wt%. Bimetallic catalysts Pt-Pd/Al_2O_3, Pt-Pd/Al_2O_3-%Ce and Pt-Pd/Al_2O_3-%Pr were prepared by impregnation of the monometallic catalysts with a solution of $Pd(NO_3)_2$. The procedure was the same for the preparation of the monometallic catalyst. For all samples, the amount of Pd was about 1 wt%.

2.2. Catalyst characterization

The chemical composition of the supports and catalysts was determined by X-ray fluorescence spectroscopy in a Shimadzu XRF 1800, using a semi-quantitative method. X-ray diffraction analysis of the samples was carried out by a Shimadzu XRD 6000 diffractometer, using Cu Kα radiation. The step-scans were taken over the range of 2θ from 10° to 80°, using a scan rate of 2°/min. UV–vis diffuse reflectance spectra were recorded over the wavelength range λ = 200–800 nm using a VARIAN Cary 5E UV-Vis-NIR DRS spectrometer, with a scan rate of 500 nm/min. X-ray photoelectron spectra were obtained with ESCALAB MK2, with a Mg Kα X-ray source (1253.6 eV), under about 2.10^{-8} mbar, pass energy 50 eV for the high resolution spectra. The binding energies (BE) were referenced to the C 1s (284.8 eV) and determined by computer fitting.

2.3. Catalytic tests

The performance of the catalysts, in terms of their activity and thiotolerance, was evaluated through the tetralin hydrogenation reaction in the presence of thiophene. The catalytic tests were carried out using a very simple system in which the injector of a gas chromatograph was used as a micro-reactor. The catalyst was placed inside the internal glass tube of the injector, between wools of quartz, and the reagents were injected with a micro-syringe to produce a pulsed catalytic experiment This system offers several advantages: (1) it is applicable to any model of chromatograph, with or without sample division, (2) the internal tube used as reactor can be easily removed, (3) control of the temperature of the reaction can be carried out through the modification of the temperature of the injector, (4) it allows the study of a great variety of reactions, modifying the catalyst, the carrier gas and the injected reagents, (5) study of the space time is carried out varying the carrier gas flow and the amount of catalyst, (6) the concentration of the reagents can be varied through the amount of injected reagents and (7) the products of the reaction can be analyzed directly in a few minutes [4].

The catalytic tests using this micro system were carried out as follows: several tetralin solutions were prepared (95% (v/v) of cyclohexane and 5% (v/v) of tetralin; in a total volume of 1000 μL), and one was reserved and called ‘‘sample pattern’’, while different concentrations of the poison thiophene, that varied from 100 to 2600 ppm, were added to the other solutions.

Firstly, the ‘‘sample pattern‘‘ was injected under the following operation conditions: pressure of the column 30 psig, temperature of the injector 220 °C, temperature of the detector 250 °C, carrier gas H_2, column and reactor flow 3 mL/min, division of the sample (split) 70 mL/min, capillary column CP SIL 5CB for sulfur, and their components were identified and quantified. The catalyst was then placed inside the internal tube of the injector, and the catalytic tests began starting with the ’’sample pattern’’, followed by the samples with growing concentrations of the poison. The liquid space velocity in the conditions of the experiments was calculated to be 1.3 h^{-1}.

3. Results and discussion

3.1. X-rays fluorescence

The chemical composition of the supports and catalysts are presented in Table 1, showing a good agreement with the calculated values:

3.2. XRD spectra

The XRD patterns of the support γ-Al_2O_3 and the catalyst 1%Pt/Al_2O_3 (Fig. 1) show the presence of a diffraction peak of small intensity, at about $2\theta = 39.5°$, attributed to the metallic

Table 1
Chemical composition of the supports and catalysts (wt%)

Support/catalyst	Pt (%)	Pd (%)	Ce (%)	Pr (%)
Al_2O_3-1%Ce	–	–	0.87	–
Al_2O_3-1%Pr	–	–	–	1.05
Al_2O_3-4%Pr	–	–	–	4.53
1%Pt/Al_2O_3-1%Ce	1.19	–	0.87	–
1%Pt/Al_2O_3-1%Pr	1.55	–	–	0.96
1%Pt/Al_2O_3-4%Pr	1.38	–	–	4.48
1%Pd-1%Pt/Al_2O_3-1%Pr	1.13	0.90	–	0.94
1%Pt/Al_2O_3	1.24	–	–	–
1%Pd-1%Pt/Al_2O_3	1.23	1.14	–	–

platinum, but an alteration in the region of $2\theta \cong 33^\circ$ was also observed suggesting the presence of a small amount of platinum oxide, PtO, in this catalyst.

The XRD patterns of the samples impregnated with 1% of cerium are presented in Fig. 2. The characteristic peaks of CeO_2 phase were not observed, probably because below 6 wt%, ceria is in an amorphous state or the particles are too small and consequently indetectable by XRD [5–7]. In the sample 1%Pt/Al_2O_3-1%Ce (Fig. 2c) peaks attributed to the metallic platinum were observed, but the presence of the phase platinum oxide, PtO, was not observed. In this catalyst, the presence of metallic cerium ($2\theta \cong 15.5^\circ$), as indicated in Fig. 2c, is clear.

The diffractograms of the samples modified with praseodymium are presented in Fig. 3. The presence of the Pr_2O_3 phase ($2\theta = 30.4^\circ$) was detected, but the presence of the PrO_2 phase cannot be discarded, both in the modified support (Fig. 3b), and in the monometallic catalyst 1%Pt/Al_2O_3-1%Pr (Fig. 3c). In all the samples containing praseodymium, the presence of the Pr metallic is clear, as indicated in Figs. 3b–d. With the addition of the second metal, Pd (Fig. 3d), an intense peak at $2\theta = 40^\circ$, attributed to metallic platinum can be observed, and another at $2\theta = 46.8^\circ$, attributed to metallic palladium. The sharp increase in intensity observed in the diffraction peak of the Pt phase indicates a great loss of the dispersion of this phase. In this catalyst a clear alteration of the structure of the support can be noticed, as some characteristic peaks of the original γ-alumina were altered or disappeared.

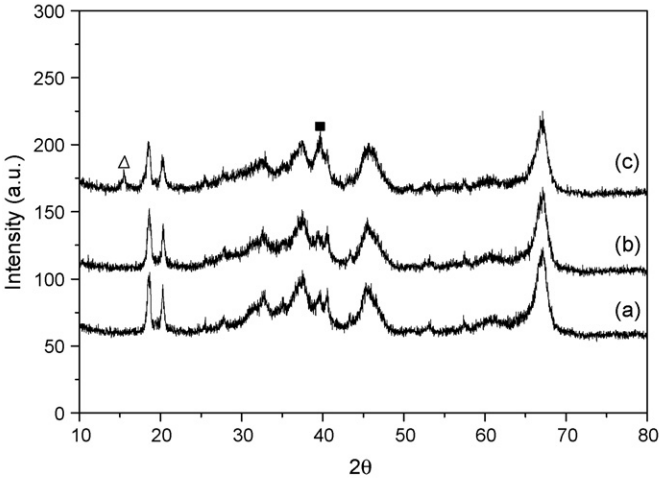

Fig. 2. XRD patterns of the supports γ-Al_2O_3 (a), Al_2O_3-1%Ce (b) and the catalyst 1%Pt/Al_2O_3-1%Ce (c); where (■ Pt) e (△ Ce).

3.3. *Diffuse reflectance spectra*

Figs. 4a–b shows the UV–vis DR spectra of the support γ-Al_2O_3 and the catalyst 1%Pt/Al_2O_3. Two alterations in the spectrum of the catalyst in relation to the one of the supports are observed: the first is the elevation of the medium level of the absorbance in the visible region (the spectrum is presented without artificial displacements), an expected finding given that the sample impregnated with Pt after reduction goes gray, a characteristic color of the (Pt) metallic phase dispersed, while the support is white, presenting low absorbance in the visible region.

The second alteration is related to a slight elevation in the line of the spectrum, in the direction of UV, starting from 500 nm, which suggests the presence of a platinum oxide phase

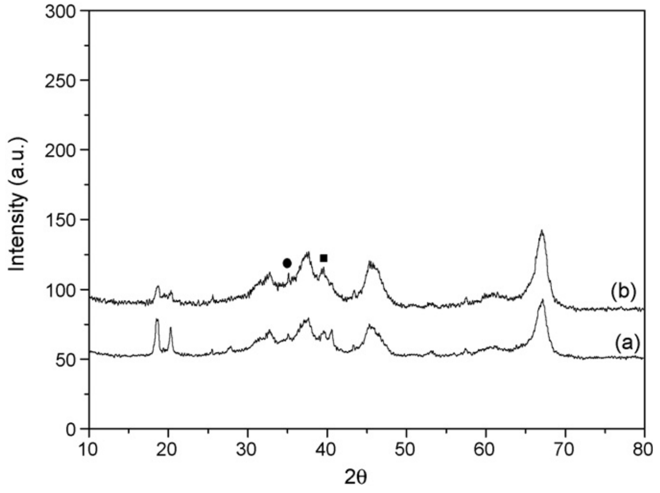

Fig. 1. XRD patterns of γ-Al_2O_3 support (a) and 1%Pt/Al_2O_3 catalyst (b); (■ Pt) and (● PtO).

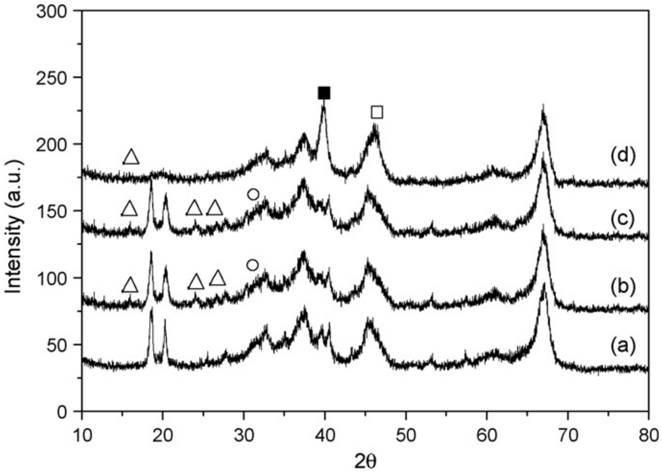

Fig. 3. XRD patterns of the supports γ-Al_2O_3 (a), Al_2O_3-1%Pr (b) and the catalysts 1%Pt/Al_2O_3-1%Pr (c), 1%Pt-1%Pd/Al_2O_3-1%Pr (d); where (■ Pt), (○ Pr_2O_3), (△ Pr) e (□ Pd).

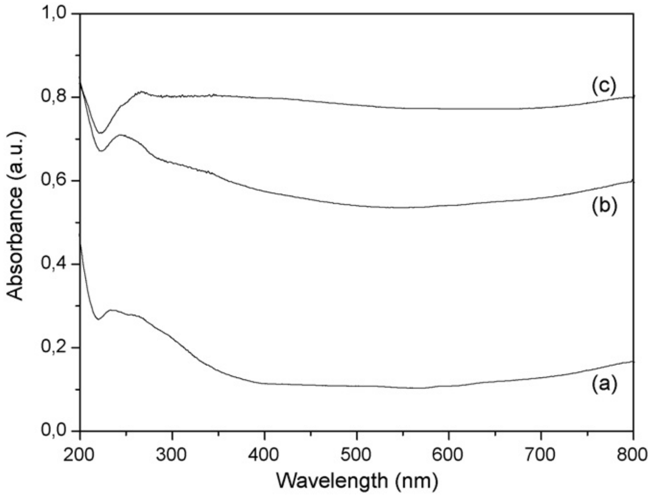

Fig. 4. UV–vis diffuse reflectance spectra of the support γ-Al_2O_3 (a), and the catalysts 1%Pt/Al_2O_3 (b) and 1%Pd-1%Pt/Al_2O_3 (c).

dispersed on the surface. Therefore PtO is a semiconductor of type n, and when the particle size of a semiconductor decreases, the band gap increases, displacing the absorption threshold to lower wavelengths according to the quantum confinement effect [8]. In fact, the presence of this phase was also considered likely from the XRD analysis, suggesting that the reduction of the platinum had not been complete. With the incorporation of the second metal (Pd), the spectrum (Fig. 4c) suggests the complete reduction of both metals, as well as the absence of the precursory species.

The DR spectra of the samples impregnated with cerium are presented in Fig. 5. For comparison, the spectrum of bulk CeO_2 was included (Fig. 5b). The presence of an absorption threshold between the visible and UV can be seen in the sample Al_2O_3-1%Ce (Fig. 5c), and attributed to the cerium oxide phase, CeO_2. This phase was not identified by the XRD analysis, as seen previously, probably because of its amorphous state, or high dispersion [5–7].

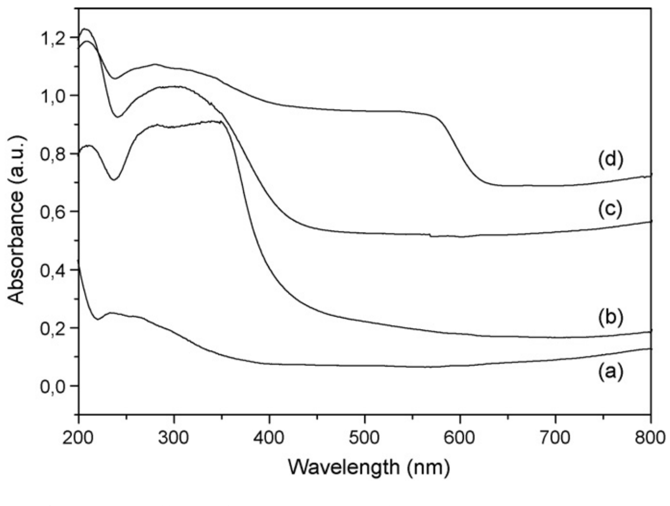

Fig. 5. UV–vis diffuse reflectance spectra of the supports γ-Al_2O_3 (a), CeO_2 (b), Al_2O_3–1%Ce (c) and the catalyst 1%Pt/Al_2O_3-1%Ce (d).

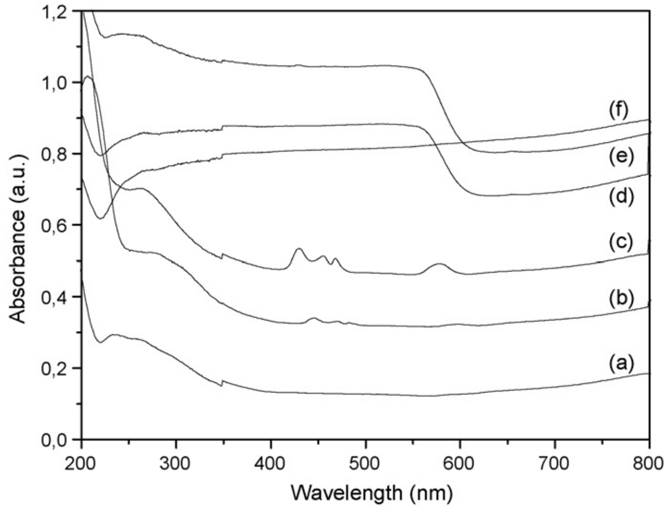

Fig. 6. UV–vis diffuse reflectance spectra of the supports γ-Al_2O_3 (a), Al_2O_3-1%Pr (b), Al_2O_3-4%Pr (c), and the catalysts 1%Pt/Al_2O_3-1%Pr (d), 1%Pt/Al_2O_3-4%Pr (e), and 1%Pd-1%Pt/Al_2O_3-1%Pr (f).

A new absorption threshold was observed in the sample 1%Pt/Al_2O_3-1%Ce spectra (Fig. 5d) at around 620 nm, indicating the presence of a new phase, with characteristics of a narrow band gap semiconductor oxide. Complementary analyses are being carried out to elucidate its chemical nature.

Absorption peaks at 263, 429, 455, 468 and 579 nm were observed in the DRS spectra of the supports modified with 1% and 4% of praseodymium (Fig. 6b–c), all of them characteristics of f-f transitions attributed to the Pr(III) species [9]. The samples 1%Pt/Al_2O_3-1%Pr and 1%Pt/Al_2O_3-4%Pr (Fig. 6d and e) demonstrated completely different DR spectra from the supports: the f-f transitions are no longer observed; an absorption threshold was noted in the visible region, at around 600 nm, which indicates the presence of a new phase, also with characteristics of a narrow band semiconductor oxide. With the addition of palladium (Fig. 6f, catalyst 1%Pd-1%Pt/Al_2O_3-1%Pr), this phase is no longer detected, and the spectrum is typical of dispersed metals in the reduced state, in other words, high and uniform absorption for all wavelengths (this spectrum is shown without displacement).

3.4. XPS analysis

Fig. 7 shows the XPS spectrum of the 1%Pt/Al_2O_3-4%Pr catalyst, in the Pr 3d orbital region, including deconvolution peaks of three suggested species, as shown in Table 2.

These surface species are the same "bulk" species identified by XRD (Fig. 3), but the XPS analysis provided information about the relative amount of each species on the surface, revealing the predominance of PrO_2. Very similar information was obtained for the catalysts 1%Pt/Al_2O_3-1%Pr and 1% Pt-1%Pd/Al_2O_3-1%Pr, altering only the proportion between the species, as shown in Table 2, but maintaining the predominance of PrO_2 on the surface.

Unlike the Pr containing catalysts, the XPS spectra of the 1%Pt/Al_2O_3-1%Ce catalyst did not show any peak related to

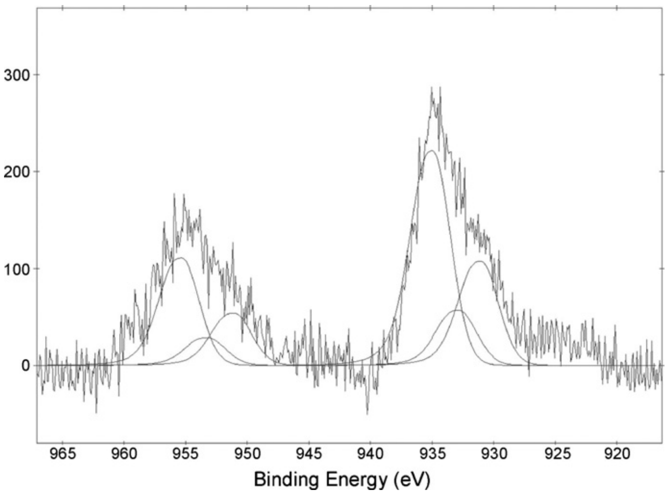

Fig. 7. XPS spectrum of the Pr 3d orbital, in the catalyst 1% Pt/Al_2O_3-4%Pr, including a three peak deconvolution proposal.

cerium species, indicating the absence, or very low concentration of these species on the outer surface of this catalyst.

3.5. Thermodynamic study

Thermodynamic studies of tetralin hydrogenation reaction were carried out to understand the behavior of the reaction system during the catalytic tests in more detail.

According to Zhorov [10], the value of K_p (equilibrium constant) for aromatics hydrogenation can be calculated using the expression below:

$$K_p = 10^{[(-20.0+0.16n)+(12.66-010n)\frac{10^3}{T}+(-5.16+0.06n)\frac{T}{10^3}(0.28-0.02n)\frac{T^2}{10^5}]}$$

where "T" is the absolute temperature and "n" is the number of carbons atoms of the aromatic compound to be hydrogenated.

The equilibrium constant K_x, expressed in terms of equilibrium conversion is deduced as:

$$K_x = \left[\frac{(4-3x)^3x}{9(1-x)^4}\right]$$

It is known that:

Considering $K_\gamma = 1$, iterative calculus was used in order to obtain the equilibrium conversion data for each temperature, and the results are shown in Fig. 8, for the pressures of 1, 3, 20 and 30 atm.

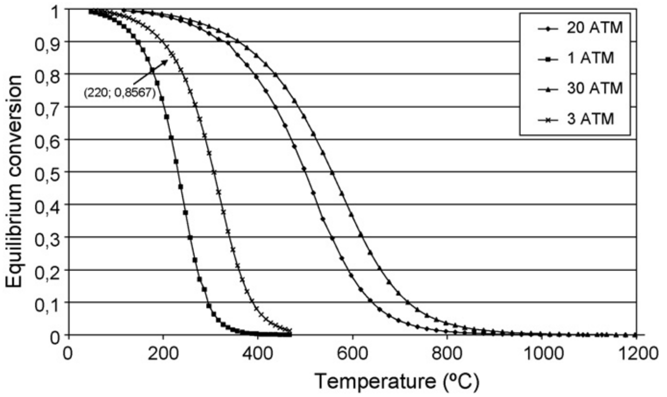

Fig. 8. Tetralin hydrogenation equilibrium conversion versus temperature (°C), to several pressures.

The equilibrium conversion in the conditions of the catalytic tests, 3 atm and 220 °C is 85.7% (as indicated in Fig. 8). The catalytic tests were carried out with conversions lower than this value (maximum 50%) in order to minimize the possibility of kinetic control by the physical processes of mass and heat transfer.

3.6. Catalytic tests

The hydrogenation of tetralin reaction is used as a model in several studies about HDA. This reaction gives as products *cis*- and *trans*-decalin, and the product kinetically favored is the *cis*-decalin, while the *trans*-decalin is favored thermodynamically [11,12].

Fig. 9 synthesizes the main results of the catalytic tests. It shows the loss of conversion (%) as a function of the concentration of the poison thiophene injected in each experiment, using several catalysts.

The monometallic catalyst 1%Pt/Al_2O_3 decreased significantly in the conversion in the presence of thiophene. The addition of cerium to the support did not have a significant effect in the thiotolerance of the catalyst 1%Pt/Al_2O_3-1%Ce, as shown in Fig. 9.

Conversely, the modification of the support with ca. 1% of praseodymium showed an efficient effect in increasing thiotolerance, as shown in Fig. 9. With higher loads (4% Pr), the beneficial effect was smaller.

4. Discussion

The addition of a second metal, in this case palladium, in spite of reducing the activity favored the tolerance of the

Table 2
XPS binding energies of the Pr $3d_{5/2}$ orbital and composition of identified species, for the 1%Pt/Al_2O_3-4%Pr, 1%Pt/Al_2O_3-1%Pr and 1%Pt-1%Pd/Al_2O_3-1%Pr catalysts

Identified species	Pr $3d_{5/2}$ (eV)	Surface concentration (%)		
		Catalyst 1%Pt/Al_2O_3-4%Pr	Catalyst 1%Pt/Al_2O_3-1%Pr	Catalyst 1%Pt-1%Pd/Al_2O_3-1%Pr
Pr (0)	931.0	29.27	15.52	24.21
Pr_2O_3	932.8	9.53	30.24	30.23
PrO_2	935.0	61.19	54.24	45.56

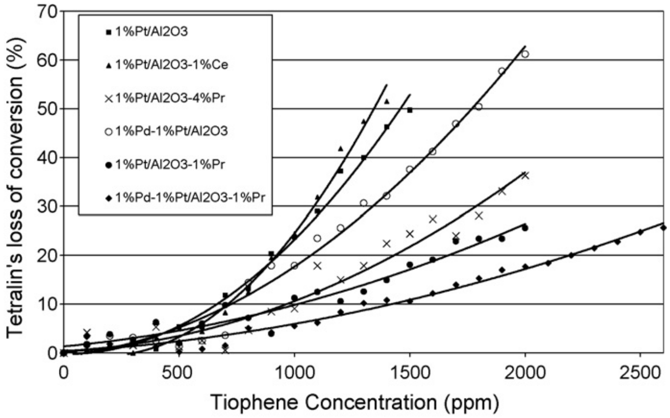

Fig. 9. Effect of the concentration of thiophene on the catalytic conversion, in the hydrogenation of tetralin reaction, with several catalysts.

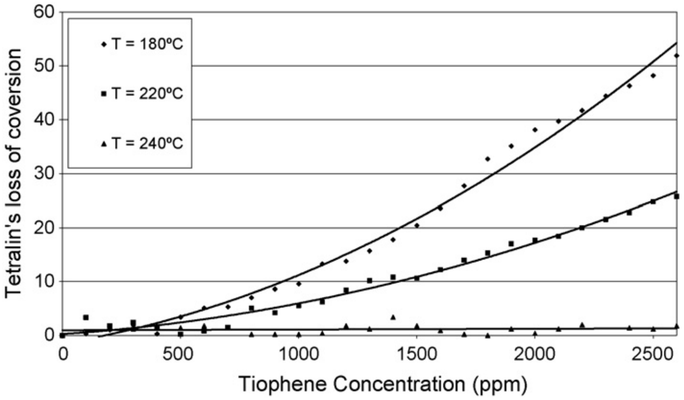

Fig. 10. Effect of the temperature and concentration of thiophene on the catalytic conversion, in the hydrogenation of tetralin reaction, using the catalyst 1% Pt-1%Pd/Al_2O_3-1%Pr.

catalyst to the poison thiophene. Several works in the literature report this [13–17] and explain the electronic effect altering the properties of the metallic sites. The Pt metal has the capacity to accept electrons from the sulfur atom in an empty d orbital forming a weak dative bonding, as sulfur is a weak base of Lewis. Knowing the electron acceptor character of the sulfur (empty 3d orbital), a retro-dative bonding between the sulfur and the metal will occur. The increase in the metallic electron-deficiency weakens the retro-dative bonding reducing the strength of sulfur adsorption.

The formation of electron-deficient metallic particles, $M^{\delta+}$, that theoretically would increase the thiotolerance and the thioresistance, can also be favored by using different acid supports, which can be amorphous materials such as SiO_2, Al_2O_3, SiO_2–Al_2O_3, B_2O_3–Al_2O_3, or modified acid zeolites [17–28]. Furthermore, the geometric characteristics of the catalytic sites can be altered, with reflexes in the adsorption of the compounds, because it is known that sulfur compounds adsorbs preferentially in low coordination sites, such as metallic atoms in angles and vertexes of the crystallites [29].

In this work, an acid support was used, alumina, modified with cerium and praseodymium, which have significant characteristics, such as sulfur compounds stockage capacity and ability to generate electronic effects in the support, altering its acidity, or changing the structure of the metallic phase. For example, modifications in the electronic properties of the platinum in catalysts Pt/Al_2O_3-CeO_2 were observed [6].

The catalyst 1%Pd-1%Pt/Al_2O_3-1%Pr showed a synergic effect, as it combined the beneficial action of the second metal with the modification of the support. The result can be seen in Fig. 9, where this catalyst is seen to have a very low sensitivity to the thiophene, for concentrations up to 2600 ppm.

Fig. 10 presents the results of some catalytic tests carried out with this bimetallic catalyst, varying the temperature, and the beneficial action already observed was upgraded with an increase of 20 °C in the reaction temperature, as this catalyst exhibited almost no sensitivity to the thiophene at 240 °C, keeping all the other conditions used for the catalytic test constant.

When two modifiers of the alumina, Ce and Pr, are compared, there are important differences in the supports and prepared catalysts, as revealed by the characterization techniques. The treatment of the catalysts in oxidant and reductive atmospheres promotes redox reactions, and, in both catalysts as well as the oxides phases, with oxidation states III and IV, metallic phases (Ce and Pr) were detected in the final catalysts. In the catalysts containing praseodymium, all these phases were also detected on the surface, by XPS, which partly explains its greatest effect in relation to the cerium.

These redox reactions facilitate the formation of vacancies, which in turn induce electronic transfers among the metals [5]. As the redox potential of the system Pr^{4+}/Pr^{3+} (3.2 V) is practically the double of that of cerium Ce^{4+}/Ce^{3+} (1.7 V), which in turn is close to the system Pt^{2+}/Pt^0, an electronic transfer from the platinum to the praseodymium should be more likely, generating an electron-deficiency in the platinum which favors its thiotolerance and thioresistance.

5. Conclusions

The catalyst 1%Pt/Al_2O_3-1%Pr was very active in the hydrogenation of tetralin reaction, and tolerant to the poisoning by thiophene, when compared to the reference catalyst 1%Pt/Al_2O_3. This could be related to the presence of several praseodymium-containing phases detected on the surface by XPS which are interacting with the Pt active phase, including a new semiconductor phase, observed by DRS.

The addition of palladium as a second metal increased the tolerance to the sulfur pollutant, despite a reduction in catalyst activity. The two combined aspects caused a synergic effect, as the catalyst 1%Pt-1%Pd/Al_2O_3-1%Pr excelled expectations, and exhibited almost no sensitivity to the poison thiophene up to 2600 ppm at 240 °C, explained by the electron-deficiency of the metallic platinum.

Complementary studies are being carried out including catalytic tests of long duration in a semi-continuous regime to give continuity to the development of this very promising catalytic system.

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