

Influence of the metallic precursor in the hydrogenation of tetralin over Pd–Pt supported zirconium doped mesoporous silica

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Palladium–platinum supported on zirconium doped mesoporous silica catalysts have been prepared by incipient wetness impregnation with two different precursors: (i) a dinuclear precursor $[\text{PdPtCl}_2(\mu\text{-dppm})_2]$ where $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$; and (ii) PdCl_2 and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The catalysts obtained with the bimetallic precursor show a much smaller metallic particle size than those prepared using monometallic precursors. The influence of the precursor in the hydrogenation of tetralin at high hydrogen pressure was studied. Both types of catalysts exhibit a good hydrogenation activity with a poor hydrogenolysis/ring opening activity. The type of precursor has a marked influence in the observed *trans*- to *cis*-decalin ratio being higher for catalysts prepared with monometallic precursors. Both types of catalysts show a good thiotolerance against dibenzothiophene, but the observed poisoning is more reversible in the case of catalysts prepared using monometallic precursors. A positive effect of the hydrogen pressure over the catalyst thiotolerance was observed, and using a $P(\text{H}_2)$ of 6 MPa, the catalyst with a 2 wt% PdPt prepared from monometallic salts was found to be very resistant to sulfur poisoning, with a tetralin conversion higher than 95% in the presence of 1375 ppm of DBT in the feed, at 588 K.

Introduction

The current high demand for middle distillates for diesel applications and the stringent environmental legislations, directed at a reduction in aromatics and sulfur content of diesel, are the reasons for the many studies aimed at the preparation of new catalyst systems and the hydrotreating of Light Cycle Oil (LCO) streams.

Catalytic hydrogenation is an important process for reducing the aromatic content in liquid fuels or solvents,¹ because, after a deep desulfuration and denitrogenation treatment, they usually still contain a relatively high percentage of aromatics, which not only generate undesired emissions of particles in exhaust gases but also decrease the cetane number. For the new diesel fuel specifications, the maximum aromatic content level is limited to 1 v/v% by 2015.

An important aspect to be considered in the hydrotreating catalyst is the pore size distribution, the specific surface area and the acidity of the support, especially when processing heavy feedstocks. In this sense, the support is important in order to obtain not only a high dispersion of the active phase but also to allow the access of voluminous molecules through the pores to the active centres.

For this reason, the use of mesoporous acid solids as catalytic supports has given rise to a significant improvement for many reactions in comparison to conventional supports. As it is well-known, MCM-41 type solids display a hexagonal arrangement of cylindrical channels with diameters that vary between 16 and more than 100 Å, thus overcoming the small pore sizes of zeolites. These new supports also exhibit a very high surface area, mild acidity and high stability.^{2–3} Recently, many catalytic reactions have been successfully studied by using mesoporous silica or doped silica with different heteroatoms as supports of diverse active phases.^{4–11} Mesoporous MCM-41 silica is almost inactive as acid catalyst, due to the small number of acid sites. The introduction of heteroatoms such as Al, Ti or Zr increases the acidity of mesoporous solids. Particularly, Zr-MCM-41 has shown an excellent behaviour in such reactions.^{11–13}

On the other hand, the size of the aromatic molecules of diesel oil makes the pore size and topology of the catalyst have a strong influence on diffusion and, consequently, on activity and selectivity in ring opening reactions.¹⁴ Recently, MCM-41-type materials have been investigated in these catalytic processes.

Very recently, nickel impregnated Zr-MCM-41 catalysts have been successfully tested in the hydrogenation and ring opening of tetralin (THN) at high hydrogen pressures and 623 K,¹⁰ but they are poorly resistant to sulfur poisoning.

High activities and acceptable sulfur tolerances in the hydrogenation/ring opening reaction can be attained by using noble metal catalysts, mainly bimetallic PdPt supported on β -zeolite,^{15–17} silica-alumina,^{17–19} USY,^{1,14,20–22} γ -alumina,²³ Y-zeolite,²⁴ and a mixed γ -zirconium phosphate-silica.²⁵ These

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bimetallic PdPt catalysts have been claimed as the best in terms of activity and sulfur tolerance, and they have been chosen to be used in the second reactor of a two-stage process, where the feed still contains a concentration of about 50 ppm of sulfur.

Since monoaromatics are predominantly present in the hydrotreated LCO, tetralin has been selected as a model molecule in many catalytic studies.^{1,14,22–24,26} DBT (dibenzothiophene) was selected as a sulfur-poisoning agent because it is one of the main sulfur-containing compounds in diesel and its desulfuration chemistry is known.²⁷

The difficult hydrogenation of tetralin mainly produces *cis*- and *trans*-decalins, the *cis/trans* selectivity recently being considered as a useful probe for the study of electronic effects on metals and sulfided metal catalysts,^{24,28,29} and products derived from the hydrogenolysis/hydrocracking reactions, such as alkylbenzenes and alkylcyclohexanes, with a high cetane number.

In a previous paper, we have demonstrated that the use of a dinuclear PdPt complex as precursor gives rise to bimetallic catalysts supported on Zr-doped mesoporous silica with a high degree of metal dispersion, which are very selective in the gas-phase hydrogenation of acetonitrile.³⁰ Following with this study about the influence of the metal precursor on the catalytic performance, in the present work, we report their use in the hydrogenation and ring opening of tetralin at 548–623 K at a pressure of 6.0 MPa (H₂ pressure of 4.5 or 6.0 MPa). The choice of this support of moderate acidity lies in its stability against mechanical, hydrothermal and regeneration treatments. Moreover, this material, used as support of nickel, has already shown excellent results in the hydrogenation and ring opening of THN at high H₂ pressures.¹⁰

One of the main goals of the work was to evaluate the influence of introducing both metals (Pd/Pt) in the form of a dinuclear complex against the use of a mixture of salts on the catalytic performance. In that way, with the unique complex, the ratio 1 : 1 of metals would be already present in each molecule of the precursor and the homogeneity of the metallic dispersion could be improved. Other factors such as the metallic content, temperature, and effect of the hydrogen pressure will also be evaluated. The other aim of our work was to evaluate the thiotolerance (with the addition of DBT to the organic flow) of the catalysts prepared in the search for a catalytic system highly resistant to the sulfur poisoning.

Results and discussion

Catalysts characterization

The catalysts studied are listed in Table 1. In the name of each catalyst, the number indicates the final metal wt% in the

calcined material. After this number, the metals present are indicated and also the support (SiZr for SiZr-5 support). Catalysts obtained from the dinuclear complex are marked with B at the end of the name.

The characterization of the mesoporous support and the bimetallic catalysts studied in the present paper has been previously reported.^{13,30} These studies have shown that, after the incorporation and calcination of the active phase, the hexagonal arrangement of the mesoporous support is preserved, since the typical d_{100} low angle reflection is still observed in their powder X-ray diffraction patterns. In addition, the unreduced catalysts, except sample 2PdPtSiZr, and the reduced ones do not show diffraction signals ascribable to the presence of either metal oxide or metallic phase, indicating that a high dispersion is attained, mainly when the dinuclear precursor is employed. This fact is corroborated by transmission electron microscopy (TEM) which reveals that the catalysts prepared from the dinuclear complex exhibit average metal particles sizes lower than 3 nm, whereas the catalysts obtained from monometallic salts give rise to average values higher than 25 nm.³⁰ All the textural and metallic properties of the catalysts are compiled in Table 1.

Concerning the textural characteristics deduced from the N₂ adsorption–desorption at 77 K (Table 1), the evolution of the specific surface area and pore volume values indicates that, after the incorporation of the active phase, no drastic modifications of the corresponding values of the mesoporous support occur, especially when the dinuclear complex is used as precursor.

As it is reflected in Table 1, a decrease of the acidity after the incorporation of the metallic phase is observed in all cases, this effect being more marked when the dinuclear complex is used.³⁰

On the other hand, H₂ temperature programmed reduction (H₂-TPR) studies have demonstrated that the bimetallic catalysts obtained from the dinuclear precursor are less reducible than the analogous catalysts prepared from salts, because at higher temperatures, between 523–623 and 673–773 K, broad hydrogen consumption signals are detected, revealing a stronger interaction of the metallic particles with the support, and hence a higher dispersion.³⁰

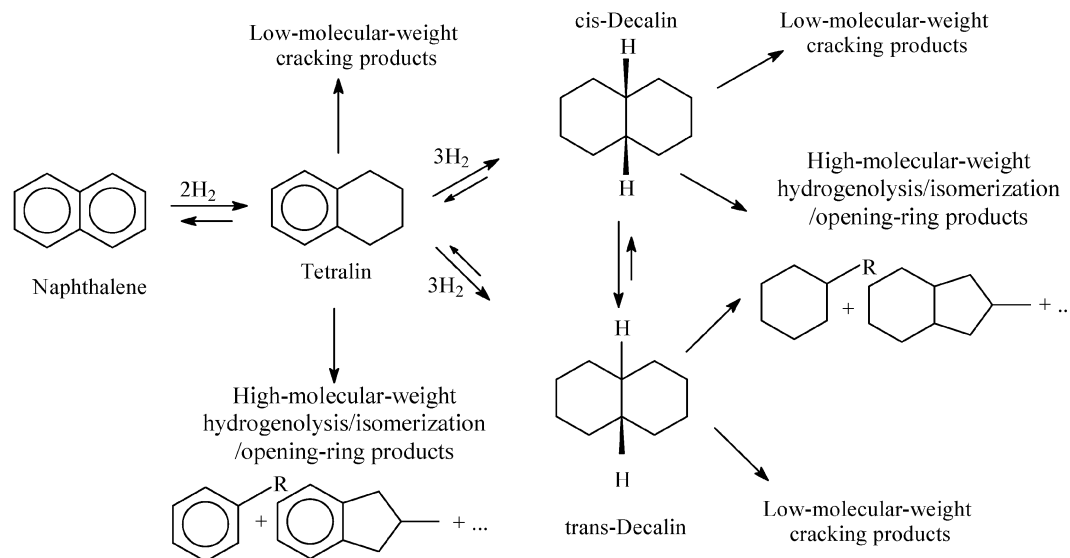
Catalytic hydrogenation of tetralin

The analysis of the liquid products obtained in the hydrogenation of tetralin allows detection of more than 70 compounds. They were classified into the following groups: (i) volatile compounds (VC) that includes non-condensable C₁–C₆ products which were calculated from the carbon balance of the reaction, (ii) hydrogenation products, that include *trans*- and *cis*-decalin, (iii) hydrogenolysis, isomerization and cracking

Table 1 Textural characteristics of the support and the bimetallic catalysts^a

—	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$S_{\text{ac}}/\text{m}^2 \text{ g}^{-1}$	$\Sigma V_{\text{p}}/\text{cm}^3 \text{ g}^{-1}$	$d_{\text{p}}(\text{av})/\text{nm}$	Acidity/ $\mu\text{mol NH}_3 \text{ g}^{-1}$	Metal particles d_{av}/nm (TEM)
SiZr5	545	700	0.592	3.4	1349	—
1PdPtSiZr	493	579	0.442	3.0	—	14.8
2PdPtSiZr	495	649	0.552	3.4	721	26.3
1PdPtSiZr-B	545	781	0.723	3.7	491	2.1
2PdPtSiZr-B	534	679	0.695	4.1	478	2.9

^a From ref. 30. ^b By using the Cranston and Inkley method.³¹ ^c Total acidity of reduced catalysts, as deduced by NH₃-TPD.



Scheme 1 Main products detected in the hydrogenation and ring-opening of tetralin.

products (HC) that include primary products such as toluene, ethylbenzene, *o*-xylene, 1-ethyl-2-methylbenzene, 1-propenyl-2-methylbenzene, *n*-propylbenzene and *iso*-propylbenzene, and secondary products which derived from ring-opening reactions such as polyalkylolefins, decadiene and cyclo-hexene-1-butylidene and (iv) naphthalene (Scheme 1). Among the HC products, all C₁₀ compounds formed by isomerization of tetralin and decalins are included.^{32–34} Products heavier than decalins were never found. To evaluate the thiotorerance of the catalysts, the hydrogenation of tetralin was carried out in the same way, with 6.0 MPa of total pressure (4.5 or 6.0 MPa of hydrogen pressure), and different amounts of dibenzothio-phenone (DBT) (425 and 1375 ppm) added to the organic feed.

The THN conversion values for the bimetallic catalysts obtained from the dinuclear complex are higher than 85% for the 2PdPtSiZr-B catalyst over the full range of temperatures studied. However, the decrease in conversion as the temperature rises from 588 to 623 K is attributed to thermodynamic restrictions since the hydrogenation reaction is exothermic (Fig. 1). These good results with the 2PdPtSiZr-B catalyst are in accordance to other studies, where an excellent hydrogenation activity for bimetallic PdPt systems was described.^{17,35}

Although the hydrogenation of aromatics is generally recognized to be a metal-catalysed reaction, many authors report that, in addition to the hydrogenation on metal centres, the acid sites of the support might also participate in the hydrogenation step,^{21,36–39} where aromatics molecules adsorbed on these acid sites can be hydrogenated by hydrogen spillover from the metal surface. Therefore, the small differences in the catalytic activity could be attributed not only to the higher average metal particle sizes but also to the slightly lower acidity of the 2PdPtSiZr-B compared with the 1PdPtSiZr-B catalyst, as measured by TPD-NH₃, since aromatic molecules could be adsorbed on acidic sites of the support close to the metallic particles.⁴⁰ Thus, the 1PdPtSiZr-B catalyst shows tetralin conversion, between 548 and 588 K, slightly higher than that obtained over 2PdPtSiZr-B. At 623 K, deactivation of the catalyst 1PdPtSiZr-B is important, giving a

conversion close to 80%. We will come back to this fact in the study of the evolution of the catalytic behaviour as a function of time-on-stream (see below).

In order to evaluate the influence of the precursor used in the preparation of the catalysts, as it was one of the goals of this work, results obtained with 2PdPtSiZr-B and 2PdPtSiZr were compared (Fig. 1). For these catalysts there are not important differences, but the catalyst prepared from the mixture of salts has at all temperatures a slightly lower activity. This fact can be due to the worse metallic dispersion for 2PdPtSiZr, as it has been demonstrated by TEM and DRX.

In all cases, the main reaction product is *trans*-decalin, whereas the *trans*- to *cis*-decalin ratio depends on the type of catalyst. For the 2PdPtSiZr-B catalyst, this ratio increases with temperature, while for 1PdPtSiZr-B is almost constant. In the case of 2PdPtSiZr the *trans*- to *cis*-decalin ratio is the highest, close to 10/1 over the range of temperature studied, according to the high acidity of this catalyst.³⁷ For the catalyst with 2 wt% metal content obtained from the dinuclear precursor, HC products are not detected, while they are produced with a yield of 5% on 1PdPtSiZr-B at 623 K, probably due to the higher

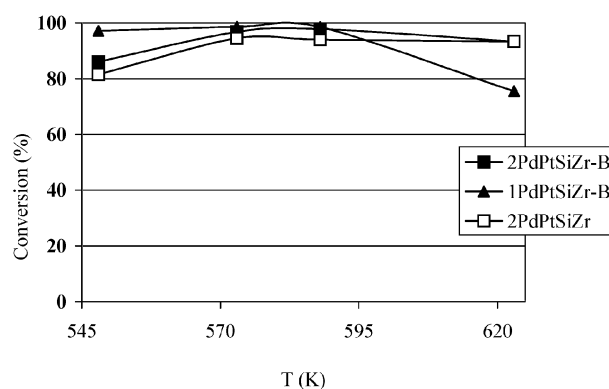


Fig. 1 Evolution of the conversion as a function of the reaction temperature in the hydrogenation of tetralin over bimetallic catalysts. H₂/THN = 10.1, P(H₂) = 6.0 MPa, contact time = 3.6 s.

acidity of 1PdPtSiZr-B, which favours these secondary reactions. The same can be argued for the more acidic catalyst, 2PdPtSiZr, which has a moderate yield (6%) of HC products. However, the amount of naphthalene is negligible in all cases. That is, these catalysts exhibit a very good hydrogenation activity toward decalins, with a poor activity to hydrogenolysis/ring opening compounds.

In order to study the stability of these PdPt catalysts, the analysis of the evolution of the conversion and selectivity with the time-on-stream was carried out at temperatures of 548 and 623 K. Taking into account that the conversion was similar in the full range of temperatures used in the preliminary studies, the temperature of 548 K was chosen in order to minimize the energetic spending. On the other hand, the temperature of 623 K was chosen in order to maximize the ring opening products, which is favoured at high temperatures.

At 548 K, all catalysts need a transient period before reaching the steady state with a conversion around 100% (Fig. 2). Among the catalysts with 2 wt% of metal content, that prepared from the dinuclear complex gets faster the steadier state. After 3 h of time-on-stream, the catalysts with 2 wt% of metal content still exhibit full tetralin conversion. The metallic content has a moderate influence, since the catalyst with 1 wt% required about 5 h to reach this situation, but at this moment the catalytic behaviour is similar to the other catalysts. However, the metal precursor used does not seem to have an important influence on the conversion, because both catalysts with 2 wt% of metal content have similar results in the steady state.

Nevertheless, at 548 K, the selectivity pattern strongly depends on the precursor used to prepare the bimetallic catalyst. As it has been described before, the PdPt catalysts show almost total selectivity to decalins, *trans*-decalin being the main product. For 2PdPtSiZr-B, the *trans*- to *cis*-decalin ratio is 1, while for 1PdPtSiZr-B is around 2 during the whole of the experiment. The best selectivity to this product, at this temperature, is observed for 2PdPtSiZr, with a value around 10 for the *trans*- to *cis*-decalin ratio. This result is different to the data reported for a PdPd supported on zirconium doped mesoporous silica, prepared from a mixture of salts but with a Pd/Pt molar ratio of 5.5, where the *trans*- to *cis*-decalin ratio was 7, working at 588 K.⁴¹

The influence of the metal content on the stability of the catalysts prepared from the dinuclear complex has been

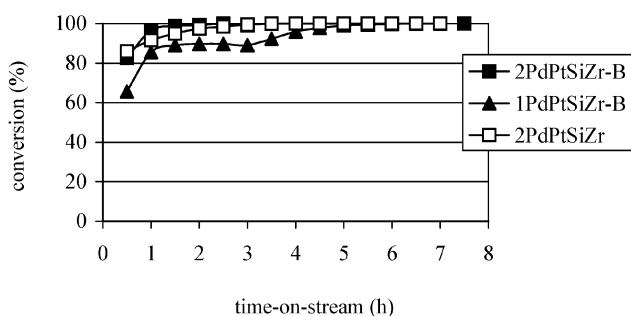


Fig. 2 Evolution of the conversion with the time-on-stream in the hydrogenation of tetralin for the PdPt catalysts. $T = 548$ K. $H_2/THN = 10.1$, $P(H_2) = 6.0$ MPa, contact time = 3.6 s.

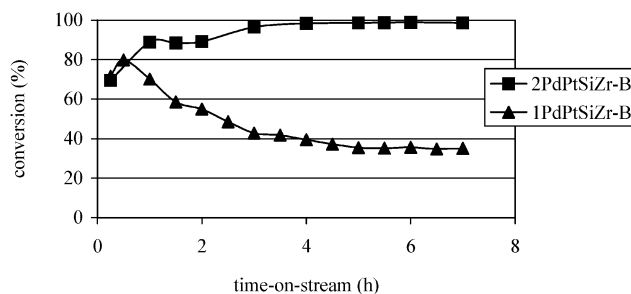


Fig. 3 THN conversion at 623 K as a function of time-on-stream over the PdPt catalysts. $H_2/THN = 10.1$, $P(H_2) = 6.0$ MPa, contact time = 3.6 s.

studied at 623 K (Fig. 3). The conversion for 2PdPtSiZr-B is similar to that obtained at 548 K, being almost 100% after reaching the steady state. However, for 1PdPtSiZr-B, a strong deactivation is observed, leading to a conversion value close to 35%, in the steady state after 7 h of time-on-stream. A plausible explanation for this observation would be the formation of a deposit of coke on the active centres, as confirmed by elemental CHN analysis of the spent catalyst, which showed for the 1PdPtSiZr-B sample a 4.13 wt% of C. A temperature raising produces for both catalysts an increment in the *trans*- to *cis*-decalin ratio. Naphthalene is not observed, and selectivity to HC products is low for 2PdPtSiZr-B (5%) and moderate for 1PdPtSiZr-B (11%), perhaps due to its higher acidity. Thus, the formation of HC products is very low, probably due to the covering of acid sites by the highly dispersed metal particles.

The influence of the hydrogen pressure was also studied. When this pressure was reduced from 6.0 MPa to 4.5 MPa at $T = 588$ K, the conversion on 1PdPtSiZr-B was reduced from 98.5% to 53% (Fig. 4). At 4.5 MPa, a variation in the selectivity is also observed, increasing the amount of *cis*-decalin and ring opening products, and decreasing that of *trans*-decalin. This result was expected because reducing the hydrogen pressure, the competitiveness of the hydrogen molecules for the metal centres is lower, and the formation of HC products from tetralin, by successive steps on active sites, is favoured. Thus, the hydrogen pressure seems to have a

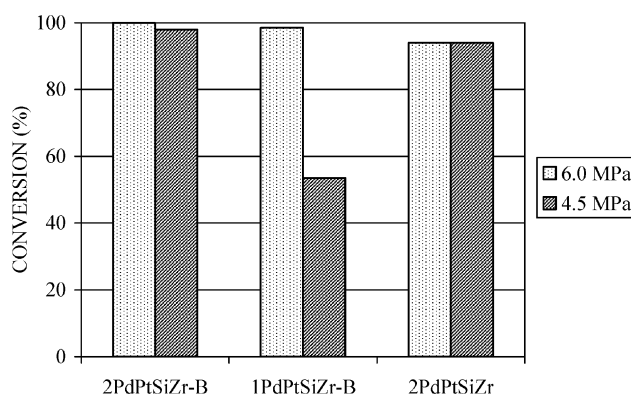


Fig. 4 Influence of the hydrogen pressure in the THN conversion over the PdPt catalysts. $T = 588$ K, $H_2/THN = 10.1$, contact time = 3.6 s.

strong influence on the catalytic results in the THN hydrogenation with this metallic content (1 wt%). When the 2PdPtSiZr-B and 2PdPtSiZr catalysts were tested at the lowest pressure and the results compared with those obtained at 6.0 MPa, at the same temperature, only a small decrease in the conversion and a similar change in selectivity were observed.

Thiotolerance studies

The thiotolerance of this set of catalysts in the hydrogenation of tetralin was evaluated by adding different amounts of DBT (425 and 1375 ppm, corresponding to 70 and 230 ppm of sulfur, respectively) to the organic feed. The reaction conditions initially used for these tests were: H_2 /THN molar ratio = 10.1, contact time = 3.6 s, $T = 588$ K, $P(H_2) = 4.5$ MPa and total pressure of 6.0 MPa reached with N_2 . The time-on-stream for each test was 7 h.

The results for the catalysts with 2 wt% of metal content are displayed in Fig. 5. It can be observed that the deactivation, in the presence of 425 ppm of DBT, is important for both catalysts. Thus, after 7 h of TOS, the 2PdPtSiZr-B shows a THN conversion of 50%, about half the value obtained without sulfur. However, this deactivation is mainly reversible. With 1375 ppm of DBT, there is a drastic decrease in the activity. Concomitantly, a change in the selectivity pattern was also observed, decreasing the amount of *trans*-decalin and increasing that of *cis*-decalin.

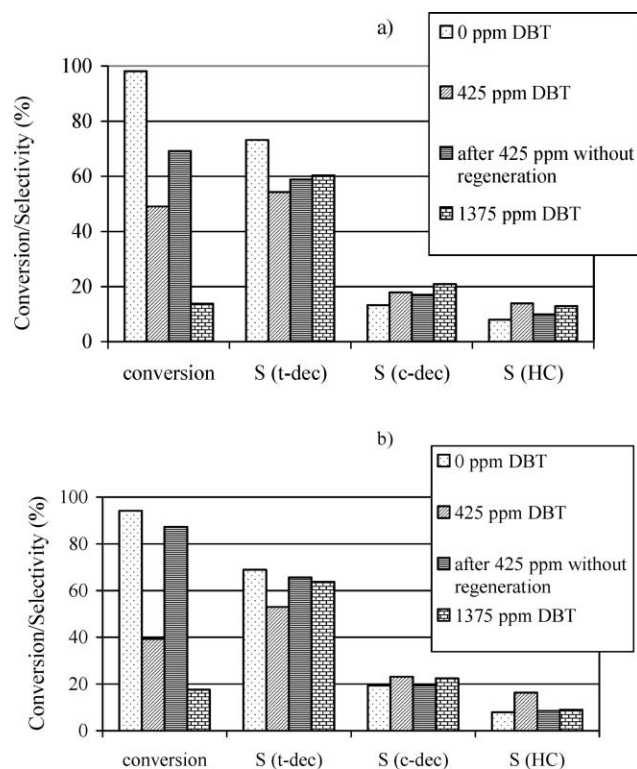


Fig. 5 Conversion and selectivity in the hydrogenation of tetralin for (a) 2PdPtSiZr-B catalyst and (b) 2PdPtSiZr catalyst, with different amounts of DBT. Reaction time: 7 h. $T = 588$ K, H_2 /THN = 10.1, $P(H_2) = 4.5$ MPa, contact time = 3.6 s.

If the behaviour against the presence of sulfur of 2PdPtSiZr and 2PdPtSiZr-B is compared, the conclusion will be that the type of metal precursor used is not a very important parameter. However, 2PdPtSiZr-B is slightly more resistant than 2PdPtSiZr, leading to a 50% of conversion after 7 h of TOS with 425 ppm of DBT (40% for 2PdPtSiZr). This small difference can be due to the better metallic dispersion obtained from the dinuclear complex. After using a feed free from sulfur, the 2PdPtSiZr-B catalyst recovers partially their initial activity and, in the case of the 2PdPtSiZr, the initial value is nearly attained (Fig. 5). With 1375 ppm of DBT the 2PdPtSiZr-B catalyst is also almost inactive.

Taking into account the positive effect of the H_2 pressure over the hydrogenation process, previously observed, we decided to explore this factor in relation to the thiotolerance by studying the catalytic behaviour of the 2PdPtSiZr catalyst at a hydrogen pressure of 6.0 MPa (Fig. 6). This catalyst, under these experimental conditions, is very resistant to the presence of sulfur in the organic feed. Thus, by adding 425 ppm of DBT, there was no appreciable decrease in the conversion with a value around 100% (40% at a $P(H_2) = 4.5$ MPa, Fig. 5.b). In the presence of 1375 ppm of DBT in the organic feed, the conversion is around 95% after 7 h of time-on-stream (below 20% for the lower pressure). The evolution of the selectivity at 425 and 1375 ppm of DBT is similar to that observed in previous tests. With a feed free of sulfur, the conversion and selectivity is totally recovered without the need for catalyst regeneration. Therefore, it is possible to conclude that this catalyst can be considered as thiotolerant in the conditions used and that the hydrogen pressure is a very important factor, at least for our systems, concerning the resistance to sulfur poisoning.

The results of thiotolerance obtained with this catalyst are in contrast with those previously reported for an analogous PdPt catalyst,⁴¹ but with a Pd/Pt molar ratio of 5.5, whose conversion decreases until 32% with 1375 ppm of DBT, at 623 K and 6 MPa of hydrogen pressure. Apparently, the

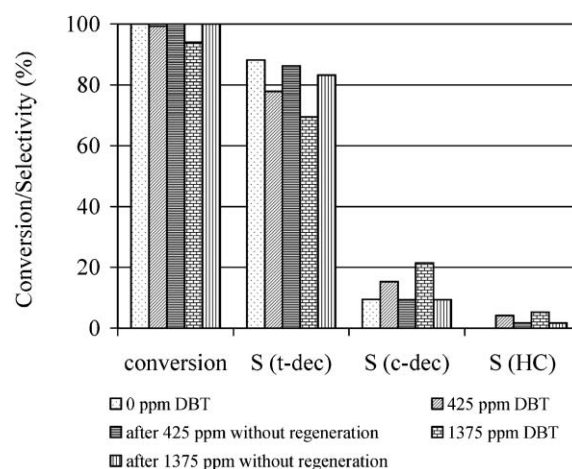


Fig. 6 Conversion and selectivity in the hydrogenation of tetralin for the 2PdPtSiZr catalyst with different amounts of DBT. Reaction time: 7 h. $T = 588$ K, H_2 /THN = 10.1, $P(H_2) = 6.0$ MPa, contact time = 3.6 s.

ratio of metals is also an important factor governing the thiotolerance of these catalysts.

In the literature, two types of poisoning with thiophene or DBT are described. The first one is produced at high temperatures (above 473 K), where chemisorption of thiophene occurs through a strong bond with hydrogenolysis of the adsorbed molecule,⁴² leading to the final formation of a metallic sulfide on the catalyst surface. This type of poisoning is irreversible. The second mechanism takes place at temperatures lower than 473 K, where adsorption with a weak planar interaction of the thiophene molecule over the metallic atoms. This is a quick but reversible poisoning, that may be eliminated with a feed free of DBT.

In our systems, all the poisoning has been found to be reversible without the need for catalyst regeneration. Consequently, and although the temperature used in our experiments is 588 K and the first mechanism could be expected, the second mechanism must be operative and the hydrogenolysis of DBT does not take place, at least in an important percentage. A plausible explanation for that could be the lower tendency of the noble metals used to form metallic sulfides in comparison to other metals like nickel, for which the poisoning is usually irreversible.

After the thiotolerance study, the spent catalysts have been analyzed by elemental CHNS analysis, but after treating them with a tetralin feed free of DBT. The sulfur analysis gives percentages, in all cases, lower than 0.11 wt%, and coke deposition has clearly been observed. This fact confirms that interaction of DBT over catalysts is labile and hence the poisoning is reversible.

On the other hand, the Transmission Electron Microscopy technique reveals that the average sizes of the metallic particles, after the catalytic studies, are not modified in comparison with those of the fresh catalysts, and consequently there is not sintering of the active phase during the catalytic process.

Therefore, we can conclude that this family of PdPt catalysts are very active in the catalytic hydrogenation of tetralin, yielding decalin with high selectivity. Moreover, a clear effect of the hydrogen pressure has been found. The catalysts prepared from the dinuclear complex as precursor exhibit a much better metallic dispersion than those prepared from the mixture of salts. However, there are not clear differences in the catalytic behaviour between both types of catalysts, a fact that might be due to the high activity already obtained with the catalysts exhibiting lower dispersion.

With respect to the resistance to sulfur poisoning, we have found a catalyst that in certain conditions exhibits a high degree of thiotolerance, with the hydrogen pressure and Pd/Pt ratio being extremely important factors.

Experimental

Zirconium doped mesoporous silica support with a Si/Zr molar ratio of 5, SiZr-5, was obtained by following the procedure reported elsewhere.¹³ Catalysts were prepared by using incipient wetness impregnation over the powdered support. The dinuclear complex precursor, $[\text{PdPtCl}_2(\mu\text{-dppm})_2]$,⁴³ where $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, was incorporated as CH_2Cl_2 solution, while the monometallic precursors (PdCl_2 and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$)

were introduced in aqueous solutions. After drying in air at 333 K for 12 h, and calcination at 773 K for 4 h (2 K min^{-1} heating rate), samples were reduced at 673 K in a H_2 flow of 50 mL min^{-1} for 60 min.

Powder X-ray diffraction patterns were obtained by using a Siemens D-501 diffractometer ($\text{Cu K}\alpha$ source) provided with a graphite monochromator. Textural parameters have been calculated from N_2 adsorption–desorption at 77 K carried out in a conventional glass volumetric apparatus (outgassing at 473 K and 10^{-4} mbar overnight). Temperature-programmed desorption of ammonia (NH_3 -TPD) was used to determine the total acidity of the supports and catalysts. Before the adsorption of ammonia at 373 K, the samples were treated at 823 K in a helium flow (50 mL min^{-1}) for 60 min. The NH_3 -TPD was performed between 373 and 823 K, with a heating rate of 10 K min^{-1} . The evolved ammonia was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a thermal conductivity detector.

Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were performed between room temperature and 823 K, by using a flow of Ar/H_2 (10 vol% of H_2 , 40 mL min^{-1}) and a heating rate of 10 K min^{-1} . Water produced in the reduction was removed by passing the gas flow through a cold finger (188 K). The H_2 consumption was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a TCD.

The purity of the dinuclear complex $[\text{PdPtCl}_2(\mu\text{-dppm})_2]$ was verified by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ -NMR using the following NMR spectrometers: Gemini FT-200 (for ^1H -NMR), Varian Unity FT-300 (for all the nucleus), Gemini FT-400 (^1H -NMR) and Innova FT-500 (^1H - and ^{13}C -NMR).

The hydrogenation of tetralin was performed in a high-pressure fixed-bed continuous-flow stainless steel catalytic reactor (9.1 mm id, 14.3 mm od and 230 mm length) operated in the down-flow mode. The reaction temperature was measured with an interior placed thermocouple in direct contact with the top part of the catalyst bed. The organic feed consisted of a solution of tetralin in *n*-heptane (10 vol%) and was supplied by mean of a Gilson 307SC piston pump (model 10SC). A fixed volume of catalyst (3 cm^3 with particle size of 0.85–1.00 mm) without dilution was used in all the studies. Prior to the activity test, the catalysts were reduced *in situ* at atmospheric pressure with H_2 (flow rate 60 $\text{cm}^3 \text{min}^{-1}$), heating from room temperature to 673 K with a heating rate of 10 K min^{-1} , and maintaining at 673 K until 1 h of total time.

Catalytic hydrogenation activities were measured at different temperatures under 6.0 MPa of hydrogen pressure, H_2 /tetralin molar ratio of 10.1, and a contact time of 3.6 s. A liquid hourly space velocity (LHSV) of 6.0 h^{-1} was used in all cases. The reaction was kept at steady state for 5–7 h in the studies of evolution of conversion and selectivity with time, or 1 h at each temperature in the evolution of conversion and selectivity with temperature. Liquid samples were collected and kept in sealed vials for posterior analysis by gas chromatography (Shimadzu GC-14A, equipped with a flame ionization detector and a capillary column TBR-1). First, the influence of reaction parameters, such as reaction temperature on the conversion and selectivity was studied. In previous

experiments, the variation of the amount of catalysts and the total flow rate, maintaining the space velocity constant, led to the conversion values being unmodified. As well, the catalytic behaviour was found to be independent of the particle diameter.

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