

Hydrogenation of tetralin over mixed PtMo supported on zirconium doped mesoporous silica: Use of polynuclear organometallic precursors

M.C. Carrión^a, B.R. Manzano^{a,*}, F.A. Jalón^a, P. Maireles-Torres^b,
E. Rodríguez-Castellón^b, A. Jiménez-López^b

^a Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Universidad de Castilla-La Mancha, Campus Universitario de Ciudad Real, 13071 Ciudad Real, Spain

^b Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al Instituto de Catálisis y Petroquímica del CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain

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Abstract

New mixed PtMo catalysts supported on Zr-doped mesoporous silica have been prepared by using a polynuclear organometallic complex as precursor of the active phase, and tested in the catalytic hydrogenation of tetralin at high hydrogen pressure. The PtMo catalysts have been characterized by XRD, TEM, XPS, N₂ sorption at 77 K, H₂-TPR and NH₃-TPD. In order to evaluate the influence of the precursor, a PtMo catalyst has been also prepared from inorganic monometallic salts.

The PtMo catalysts were very active in the hydrogenation of tetralin, showing conversion values close to 100%, and high selectivity toward the hydrogenation products (*trans*- and *cis*-decalins). The *trans*- to *cis*-decalin ratio varies depending on the type of precursor used. The formation of hydrogenolysis, isomerization and cracking products depends on the acidity of the catalysts, although the selectivity towards these products is always lower than 8.5%. On the other hand, all the studied catalysts showed a poor thiotolerance against the presence of dibenzothiophene in the feed.

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1. Introduction

The current high demand for middle distillates for diesel applications and the stringent environmental legislations directed to the reduction of aromatics and sulphur content in diesel fuels are the origin of many studies aimed to the preparation of new catalysts systems. Among these, the most commonly used are monometallic and bimetallic systems [1–5], and mixed sulphides (CoMo, NiW, NiMo) [6–17] supported on alumina and zeolites. For the new diesel fuel specifications the minimum cetane number will be set to a value of about 53 units. Aromatics, especially polycyclics, usually have very low cetane numbers, while *n*-paraffins have relatively high ones. Thus, a key factor for improving the cetane number is to decrease the aromatic content,

especially polyaromatics, in distillates, but avoiding excessive cracking to obtain high yields of upgraded diesel fuels.

Catalytic hydrogenation is an important process for reducing the aromatic content in liquid fuels [8], because, after a desulphuration and denitrogenation treatment, they usually still contain a relatively high percentage of aromatics, which not only decrease the cetane number but also generate undesired emissions of particles in exhaust gases. The exothermic character of the aromatic hydrogenation reaction produces thermodynamic equilibrium limitations at high temperatures, being this problem only partially overcome by operating at high hydrogen pressures.

An important aspect to be considered in catalysts for hydrotreating is the pore size distribution and the surface area value of the support, especially when processing heavy feedstocks. 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.

In this sense, the use of MCM-41 solids as catalytic supports has given rise to a significant improvement for many reactions

* Corresponding author. Tel.: +34 926295300x3473; fax: +34 926295318.

E-mail addresses: Blanca.Manzano@uclm.es (B.R. Manzano), mairales@uma.es (P. Maireles-Torres).

in comparison to conventional supports. It is well known that MCM-41 type solids display a hexagonal arrangement of cylindrical channels with diameters that vary between 16 and >100 Å, so overcoming the small pore sizes of zeolites. These new supports also exhibit a very high surface area, mild acidity and high stability [18,19]. Recently, many catalytic reactions have been successfully studied by using mesoporous silica or doped silica with different heteroatoms as supports of diverse active phases [20–27]. Mesoporous MCM-41 silica is almost inactive, due to the small number of acid sites. The introduction of heteroatoms such as Al, Ti or Zr increases the acidity of these mesoporous solids. Zr–MCM-41 has shown an excellent behaviour in acid catalysis [27–29].

Due to the size of the aromatic molecules of the diesel oil, the pore size and topology of the catalyst have a strong influence on diffusion and, consequently, on activity and selectivity in ring opening reactions [30]. Recently, MCM-41-type materials have been investigated in these catalytic processes. For example, nickel impregnated Zr–MCM-41 catalysts have been successfully tested in the hydrogenation and ring opening of tetralin (tetrahydronaphthalene or THN) at high hydrogen pressures and 623 K [26], but they are poorly resistant to sulphur poisoning.

High activities and acceptable sulphur tolerances in the hydrogenation/ring opening reaction of different hydrocarbons can be attained by using noble metal catalysts, mainly bimetallic PdPt supported on β -zeolite [31–33], silica-alumina [1,2,33], USY [8,30,34–36], γ -alumina [37], Y-zeolite [38], and a mixed γ -zirconium phosphate-silica [39]. These bimetallic PdPt catalysts have been designed to be used in the second reactor of a two-stage process. Among monometallic noble systems, ruthenium catalysts (with different supports) exhibit a high thiotolerance [40,41], which seems to be related to the low density of states at the Fermi level [42], since the density of states measures the number of quantum states available for bonding reactants.

Since monoaromatics are predominantly present in the hydrotreated LCO (light cycle oil), tetralin has been selected as a model molecule in many catalytic studies [8,30,36–38,43]. DBT (dibenzothiophene) was selected as a sulphur-poisoning agent because it is one of the main sulphur-containing compounds in diesel and its desulphuration chemistry is known [44].

The hydrogenation of tetralin mainly produces *cis*- and *trans*-decalins. The *cis/trans* selectivity has been recently considered as a useful probe for the study of electronic effects on metals and sulphided metal catalysts [38,45,46].

Recently, we have described the synthesis of palladium-platinum supported on zirconium doped mesoporous silica catalysts using the bimetallic derivative $[\text{PdPtCl}_2(\mu\text{-dppm})_2]$ as metal precursor [47]. Their characteristics and behaviour were compared with those of other catalysts containing similar metal loadings but obtained from a mixture of classical inorganic salts. A remarkable higher degree of metal dispersion was attained when using the dinuclear precursor for the catalyst preparation. These catalysts were used in the gas-phase hydrogenation of acetonitrile [47] and also in the tetralin hydrogenation where a good thiotolerance against dibenzothiophene was found [48].

In the present work, we decided to expand our comparative studies of the behaviour of new catalysts obtained from

bimetallic complexes against those prepared from mixture of salts. We tried to find out if also with other different combination of metals (PtMo) and using an organometallic precursor that contained the metals in a specific ratio, smaller metallic particle size could be achieved than that obtained from classical salts.

The metals were supported on Zr-doped mesoporous silica. The choice of this support of moderate acidity lies in its stability against mechanical, hydrothermal and regeneration treatments, and also the excellent results obtained in this reaction when using nickel as the active phase [26]. The catalysts thus obtained were tested in the hydrogenation and ring opening of tetralin at 548–623 K and hydrogen pressure of 6.0 MPa. The thiotolerance (with the addition of DBT to the organic flow) of some catalysts was also evaluated.

2. Experimental

2.1. Preparation and characterization of the organometallic precursor

The cyclopentadienyl precursor used in the preparation of the catalysts, $[\text{Pt}_2\text{Mo}_2\text{Cp}_2(\text{CO})_6(\text{PPh}_3)_2]$, has been synthesized under inert atmosphere, using vacuum lines and Schlenk techniques. The solvents used have been dried by conventional methods and purified by distillation, and have been collected under inert atmosphere. The $[\text{Pt}_2\text{Mo}_2\text{Cp}_2(\text{CO})_6(\text{PPh}_3)_2]$ compound [49] ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) was prepared from PPh_3 and *trans*- $\text{Pt}[\text{Mo}(\text{CO})_3\text{Cp}]_2(\text{PhCN})_2$ [50] that can be obtained from $\text{PtCl}_2(\text{PhCN})_2$ and $\text{Na}[\text{Mo}(\text{CO})_3\text{Cp}] \cdot 2\text{DME}$ (DME = dimethoxyethane) [51]. Slight modifications have been introduced in the synthesis and purification in order to improve the yield and purity. The spectroscopic results are in concordance with the reported data in the literature.

The purity of the organometallic complex was verified by IR (KBr, Perkin-Elmer PE 883 IR spectrometer), and ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR using the following FT-spectrometers: Varian Unity FT-300 (for all the nucleus), Gemini FT-400 (^1H NMR) and Innova FT-500 (^1H and ^{13}C NMR).

For the sake of comparison a Pt/Mo catalysts was also prepared using a mixture of the classical salts $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$. The salts $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ were purchased from Pressure Chemical Co. and Aldrich, respectively.

2.2. Preparation of catalysts

Zirconium doped mesoporous silica support with a Si/Zr molar ratio of 5, SiZr-5, was obtained as described elsewhere [28]. Catalysts were prepared by using the incipient wetness method over the powdered support. The polynuclear precursor was dissolved in CH_2Cl_2 , while metallic salts precursors were used as aqueous solutions. The amount of the $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ salts used for impregnation was calculated in order to get a 1:1 molar ratio of metals and a 2 wt.% of total metal content. After drying in air at 333 K for 12 h, and calcination at 773 K for 4 h (2 K min $^{-1}$ heating rate), the

Table 1
Different catalysts used for the hydrogenation of tetralin

Catalyst	Precursor	Total metal (wt.%)
2PtMoSiZr	[Pt ₂ Mo ₂ Cp ₂ (CO) ₆ (PPh ₃) ₂]	2
1PtMoSiZr	[Pt ₂ Mo ₂ Cp ₂ (CO) ₆ (PPh ₃) ₂]	1
2PtMoSiZr-S	H ₂ [PtCl ₆]·6H ₂ O, (NH ₄) ₆ [Mo ₇ O ₂₄]·4H ₂ O	2

samples were reduced at 673 K in a H₂ flow of 50 mL min⁻¹ for 60 min.

The catalysts prepared are listed in Table 1. In the name of each catalyst, the first number indicates the final total metal wt.% in the calcined material. The catalyst obtained from the metallic salts was marked with S at the end of the name.

2.3. Characterization of catalysts

Powder X-ray diffraction patterns were obtained by using a Siemens D-501 diffractometer (Cu K α -Source) provided with a graphite monochromator. X-ray photoelectron spectroscopy (XPS) analyses were performed using a Physical Electronics 5700 instrument, provided with a multichannel hemispherical electron analyzer Electronics 80-365B. The Mg K α X-ray excitation source ($h\nu = 1253.6$ eV) was at a power of 3000 W and the pressure in the analysis chamber was maintained below 1×10^{-9} Torr during data acquisition. The binding energies (BE) were obtained with ± 0.1 eV accuracy and charge compensation was carried out with the adventitious C 1s peak at 284.8 eV. Atomic concentrations were determined from elemental peak areas corrected for sensitivity differences. The sensitivity factors used are included in the PHI ACCESS data analysis software package.

Textural parameters have been calculated from N₂ adsorption–desorption at 77 K obtained by using a conventional glass volumetric apparatus (outgassing at 473 K and 10⁻⁴ mbar overnight). Temperature-programmed desorption of ammonia (NH₃-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 NH₃-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 (H₂-TPR) experiments were carried out between room temperature and 823 K, by using a flow of Ar/H₂ (10 vol.% of H₂, 40 mL min⁻¹) and a heating rate of 10 K min⁻¹. Water produced in the reduction reaction was eliminated by passing the gas flow through a cold finger (188 K). The H₂ consumption was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a TCD.

2.4. Catalytic tests

The hydrogenation of tetralin was performed in a high-pressure fixed-bed continuous-flow stainless steel catalytic reac-

tor (9.1 mm i.d., 14.3 mm o.d. 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 on a solution of tetralin in *n*-heptane (10 vol.%) and was supplied by means of a Gilson 307SC piston pump (model 10SC). A fixed volume of catalyst (3 cm³ 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 H₂ (flow rate 60 cm³ 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, H₂/tetralin molar ratio of 10.1, and 3.6 s of contact time. 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, and 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). The thiotolerance tests were performed similarly but adding 425 ppm of DBT (corresponding to 70 ppm of sulphur) to the organic feed.

3. Results and discussion

3.1. Catalysts characterization

The characterization of the mesoporous SiZr-5 material used as support in the present paper has been described and discussed elsewhere [27,29]. The incorporation of zirconium into a mesoporous silica framework produces a decrease in the long-range order, as evidenced by the presence in the X-ray diffraction patterns of a sole and broad reflection at low diffraction angle, but the reflection lines corresponding to bulk ZrO₂ (tetragonal or monoclinic) were never observed.

With respect to the different catalysts, the X-ray diffraction patterns exhibit, at low angles, the typical d_{100} reflection of the hexagonal arrangement of channels, pointing to that the mesoporous structure is preserved after the impregnation and calcination processes.

In general, calcined precursors show diffraction signals due to the presence of metallic platinum, which means that at least a fraction of the platinum oxides is reduced during the calcination. The intensity of these diffraction signals are lower for the catalyst prepared from the salt precursors (Fig. 1).

In order to know both the surface composition and the chemical state of the active phase, X-ray photoelectron spectroscopy was used in the case of the catalysts with 2 wt.% of total metal content (Table 2). Thus, the binding energies of Zr 3d_{5/2} (182.6–182.9 eV) are higher than that tabulated for bulk ZrO₂ (182.2 eV), confirming the presence of Zr species into the silica framework, with formation of Zr–O–Si linkages. Moreover, the symmetry of this XPS signal indicates the absence of zirconium oxide particles, as previously deduced by XRD. The signals due to Zr 3d and Si 2p from the support did not change with the

Table 2
Binding energy values and superficial atomic ratios obtained for the PtMo catalysts, with a 2 wt.% of total metal content

	Binding energy (eV)				Superficial atomic ratio	
	Si 2p	Zr 3d _{5/2}	Pt 4f _{7/2}	Mo 3d _{5/2}	Pt/(Si + Zr)	Pt/Mo
2PtMoSiZr precursor	103.0	182.6	72.1	232.2	0.004	0.69
2PtMoSiZr calcined	103.3	182.7	70.9 Pt(0) (82%), 72.1 Pt(II) (18%)	230.4 Mo(IV) (43%), 232.3 Mo(VI) (57%)	0.001	0.36
2PtMoSiZr-S precursor	103.3	182.7	72.3	230.6 Mo(IV) (37%), 232.5 Mo(VI) (63%)	0.003	1.11
2PtMoSiZr-S calcined	103.3	182.9	71.0 Pt(0) (85%), 72.3 Pt(II) (15%)	230.6 Mo(IV) (30%), 232.6 Mo(VI) (70%)	0.003	0.75

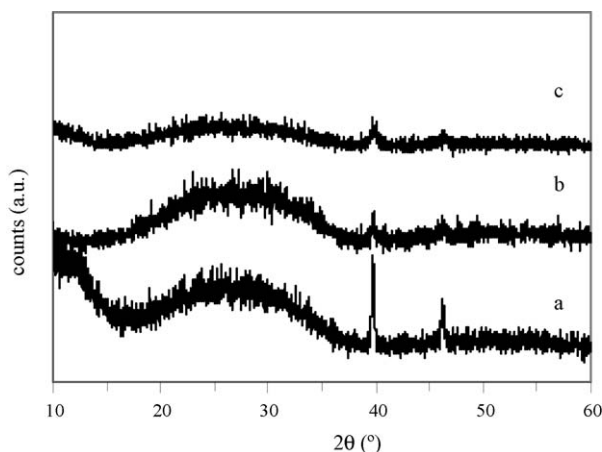


Fig. 1. DRX patterns of the PtMo catalysts in the region of high diffraction angles: (a) 2PtMoSiZr, (b) 1PtMoSiZr and (c) 2PtMoSiZr-S.

different treatments, indicating the stability of the support, as we have seen before by the X-ray diffraction technique. The data displayed in Table 2 reveal that, in both cases, a high percentage of the Pt(II) present in the precursor is reduced to Pt(0) during calcination. The high calcination temperature necessary

for the total removing of the organic ligands of the polynuclear precursors could be responsible of this reduction process. The unusual low values observed for the Pt 4f_{7/2} (72.1–72.3 eV) of Pt(II) species present on the surface of these PtMo catalysts might be attributed to the strong interaction between Pt²⁺ and the partially reduced molybdenum oxide, which could increase the electronic density on the platinum ions.

The observed decrease of the Pt/(Si + Zr) and Pt/Mo molar ratios seems to point to a displacement of the metallic particles into the mesopores, because the XPS signal only comes from the outer surface. However, this effect is more marked in the case of the PtMo catalyst prepared from the organometallic precursor.

On the other hand, the micrographs obtained by transmission electron microscopy allow us to get information about the metal particles sizes and their distribution. Thus, the micrographs displayed in Fig. 2 show that the size of the metal particles is very different from one catalyst to another. For 2PtMoSiZr, all particles are smaller than 6 nm, being the medium size of 2.7 nm, while for 2PtMoSiZr-S the medium size is 19.5 nm, because of the existence of larger metal particles, even of 55 nm. These data indicate that a much better metallic dispersion is obtained for the catalyst prepared from the polynuclear precursor instead of the mixture of salts. These data are in accordance with our

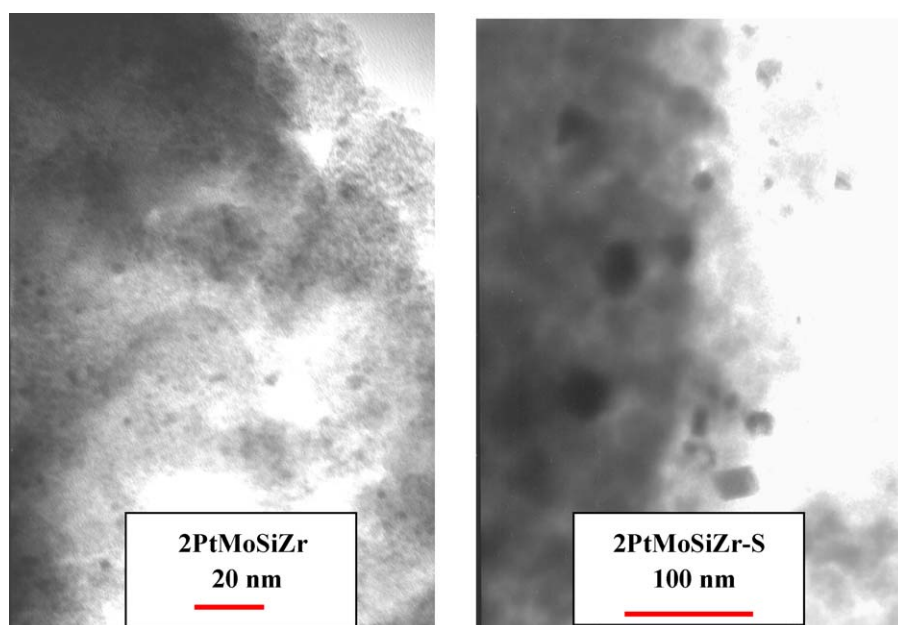


Fig. 2. TEM micrographs of the PtMo catalysts with 2 wt.% of total metal content.

Table 3
Textural parameters of the support and PtMo catalysts

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$) P/Po=0.95	S_{ac}^a ($\text{m}^2 \text{g}^{-1}$)	d_p^a (\AA)
SiZr-5	545	0.56	700	34
2PtMoSiZr	539	0.48	824	43
1PtMoSiZr	561	0.57	808	32
2PtMoSiZr-S	498	0.44	596	32

^a By using the Cranston and Inkley method.

previous findings for the Pd/Pt catalysts prepared from a dinuclear precursor [47,48].

The evaluation of the textural characteristic of the support and the catalysts was carried out by N_2 adsorption–desorption at 77 K. In all cases, isotherms are of Type IV according to the IUPAC classification and reversible, with the typical inflexion at low relative pressure. Isotherms and pore-size distributions of the catalysts are similar to the corresponding support. This indicates that the mesoporous structure is maintained, as stated before. The decrease in the specific surface area, after the impregnation with the metallic compound, is not very high, pointing to that the metal particles are not blocking very efficiently the pores of the support. The decrease is low especially for the catalysts obtained from the organometallic precursor, due to their better dispersion (Table 3). Taking into account that most of metal particles observed in the TEM micrographs possess sizes exceeding the values of the average pore diameters (3.2–4.3 nm), and the almost constancy of the S_{BET} values of SiZr-5 support and the different PtMo catalysts, it can be inferred that these large metal particles must be deposited on the external surface, but without impeding the access to the porous network.

The acidity of the different supports and catalysts used in this study was evaluated by NH_3 -TPD. The NH_3 -desorption curves have a similar shape for all the samples, where a very broad desorption band centred at 453 K could be indicative of a heterogeneous distribution of the acid sites with different strength. As it is possible to see in Fig. 3, the introduction of the active metallic phase produces in all cases a high decrease of the acidity with respect to the support. This acidity reduction can be

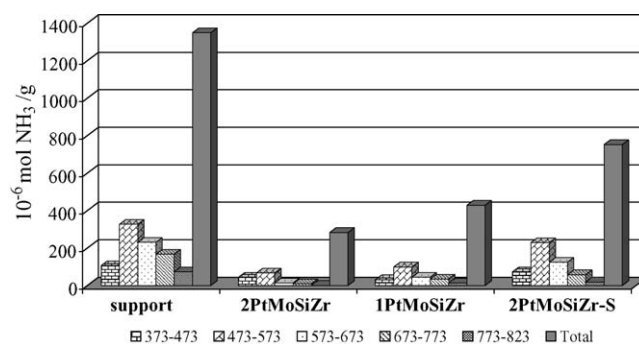


Fig. 3. Acidity of the SiZr-5 support and the reduced PtMo catalysts, obtained by NH_3 -TPD.

explained taking into account the partial covering of the acid sites of the support by the metal particles. The catalyst prepared with salts precursors show a higher acidity, a fact that may be due to their bigger metallic particles already observed from TEM, which block less efficiently the acid sites of the support.

Hydrogen temperature-programmed reduction gives information about reducibility of the different species within the catalysts. In this way, the strength of the metal–metal and metal–support interactions can be deduced. The support, SiZr-5, does not consume any H_2 , and consequently the observed hydrogen consumption peaks correspond to the reduction of the metal oxides.

In general, the reduction of molybdenum oxide is accomplished in two steps [52–54]. The H_2 consumption at low temperature ($T_{\text{red}} < 1073 \text{ K}$) is ascribed to the reduction of Mo(VI) to Mo(IV), depending the peak temperature on the nature of the Mo(VI) species (octahedral, tetrahedral, polymolybdates, etc.). At temperatures higher than 1073 K, Mo(IV) is reduced to lower oxidation states.

For 2PtMoSiZr (Fig. 4), a well-defined peak is observed at low temperature, 368 K, that is assigned to the reduction of platinum (II) species, although it is necessary to take into account that after the XPS results it was found that most of platinum (82%) was reduced during the calcination process. For this reason, in the curve of the 1PtMoSiZr, this peak is barely observed.

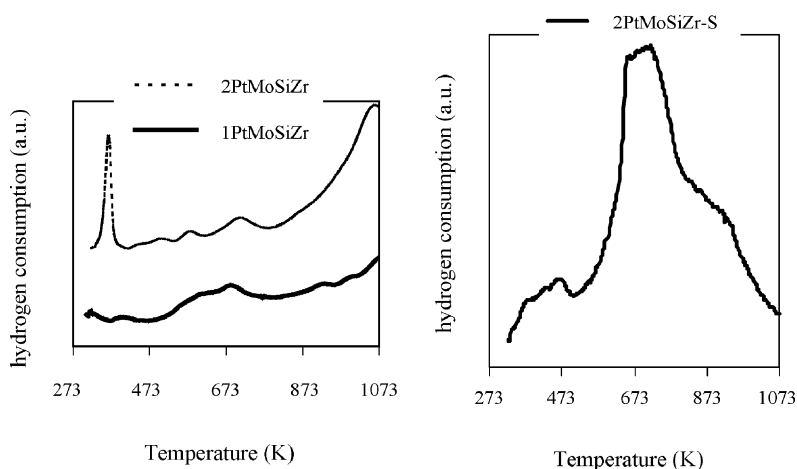


Fig. 4. H_2 -TPR curves for the PtMo catalysts.

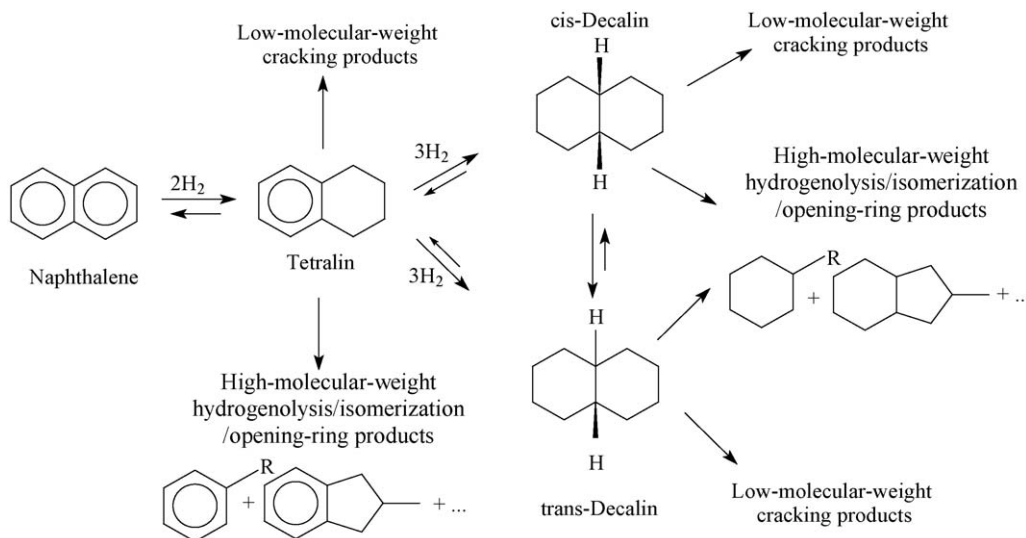
At higher temperatures, there are broad H₂ consumption peaks that correspond to the reduction of a fraction of Mo(VI) to Mo(IV). However, at 1073 K, it is not possible to reduce all the Mo(VI) to Mo(0), because the thermogram finishes at the temperature to which this reduction takes place.

However, the H₂-TPR profile for the platinum–molybdenum bimetallic catalyst obtained from salts is very different. A broad peak between 373 and 503 K is observed which could be assigned to the reduction of Pt(II) species. In this case, the reduction temperature is higher than in the catalysts obtained from organometallic polynuclear complexes. However, reduction of the Mo(VI) to Mo(IV) seems to be easier, as it can be deduced from the intense reduction peak at 698 K (Fig. 4).

3.2. Catalytic hydrogenation of tetralin

The analysis of the liquid products obtained in the hydrogenation of tetralin allows detection of more than 70 compounds. They can be 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*-decalins, (iii) hydrogenolysis, isomerization and cracking 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-butyldiene and (iv) naphthalene (Scheme 1). Among the HC products, all C₁₀ compounds formed by isomerization of tetralin and decalins are included [55–57]. Products heavier than decalins were never found.

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



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

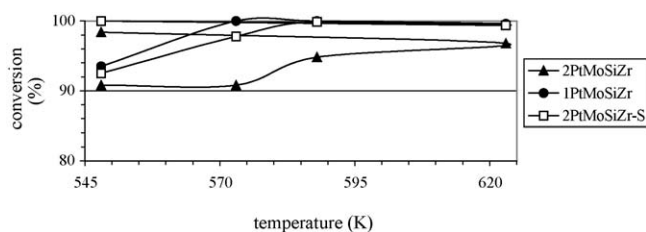


Fig. 5. THN conversion as a function of the reaction temperature in the hydrogenation of tetralin over the PtMo catalysts. H₂/THN = 10.1, P(H₂) = 6.0 MPa, contact time = 3.6 s.

In order to evaluate the effect of the metallic content, the evolution of the THN conversion as a function of the temperature for the 2PtMoSiZr and 1PtMoSiZr catalysts was studied (Fig. 5). This study was carried out by progressively increasing the temperature from 548 to 623 K and then going back to 548 K, being collected the liquid samples after standing 1 h at the different temperatures. The 2PtMoSiZr catalyst shows a THN conversion higher than 90% through all the range of temperatures studied, and the activity slightly increases with temperature. Moreover, when the temperature of 548 K is recovered after a thermal cycle, the conversion is even higher than the initial one. This means that this catalyst suffers some modification during the catalytic run, which makes it more active. Possibly the reduction degree in the active phase is increased under the reaction conditions, and this increases the catalytic activity. This behaviour is remarkable and contrasts with that found for catalysts obtained for Pd/Pt systems, previously described [48]. Similarly to that obtained for the 2PtMoSiZr catalyst, conversion values higher than 90% are attained for 1PtMoSiZr in the full range of studied temperatures. An activation of the catalyst is also observed and when the temperature comes back to 548 K after the thermal cycle, the conversion is higher than the initial one at the same temperature.

For the 1PtMoSiZr catalyst, the conversion is even higher than that obtained for 2PtMoSiZr. The fact that the particle size in both catalysts is of the same order (see above, TEM results) allows us to conclude that the metallic dispersion degree has not

a direct influence on the conversion results. On the other hand, it is necessary to consider that, as deduced from the TPD-NH₃ measurements, 1PtMoSiZr catalyst has a higher acidity than 2PtMoSiZr. Although the hydrogenation of aromatics is generally recognized to be a metal-catalyzed reaction, many authors have reported that, in addition to metal centres, the acid sites of the support might also play an important role in the hydrogenation step [35,58–61]. This phenomenon seems to be attributed to the hydrogenation of aromatics molecules adsorbed on acid sites in the vicinity of metallic particles from which hydrogen is spilt over. The role played by the acid sites could explain the observed difference in the catalytic behaviour of both catalysts.

Concerning the evaluation of the influence of the type of precursor used in the preparation of the catalysts, as it was one of the goals of this work, the results obtained with 2PtMoSiZr can be compared with those of 2PtMoSiZr-S (Fig. 5). The catalyst prepared from the mixture of salts presents a slightly higher activity at all studied temperatures. In the same way than for the results obtained for 1PtMoSiZr, this different behaviour can be explained by considering the higher acidity of the catalyst prepared from the mixture of salts, as it has been deduced from the TPD-NH₃ measurements.

Although the hydrogenation reaction is exothermic [2,3], after increasing the temperature from 548 to 623 K, the THN conversion does not decrease, pointing to the absence of thermodynamic restrictions under these experimental conditions. A similar behaviour has been observed on noble metal supported on the same mesoporous solid, where the conversion only diminishes at temperatures higher than 623 K [26].

As far as the selectivity towards different products of the reaction is concerned, the *trans*-decalin is, in all cases, the main product (Table 4). The *trans*- to *cis*-decalins ratio increases with temperature, being the values corresponding to the 2PtMoSiZr-S higher than 5.7 in the full range of studied temperatures. It is remarkable that also in our previous studies with the Pd/Pt combination, a higher *trans* to *cis* ratio was obtained when classical salts were used as precursors [48]. The higher acidity of this catalyst could be responsible of this behaviour, since the primary hydrogenation product is the *cis*-decalin, which can be isomerised when adsorbed on the acid sites.

For the catalyst with 2 wt.% of metal content obtained from the organometallic precursor, the HC products are practically not formed, while they are produced with a yield of 8.3% with

Table 4
Selectivity of the bimetallic PtMo catalysts in the hydrogenation of tetralin

Catalyst	T (K)	Selectivity (%)				<i>trans/cis</i> -Decalins
		<i>trans</i> -Decalin	<i>cis</i> -Decalin	HC	VC	
1PtMo	548	55.5	31.5	0	12.1	1.76
	623	72.8	14.9	8.3	4.0	4.89
2PtMo	548	57.8	30.3	1.2	9.6	1.91
	623	73.6	19.9	0	6.4	3.70
2PtMo-S	548	76.6	13.4	0	8.5	5.71
	623	78.2	10.4	3.6	7.7	7.52

H₂/THN = 10.1, P(H₂) = 6.0 MPa, contact time = 3.6 s. The reference to the support at the end of the name, SiZr, has been omitted.

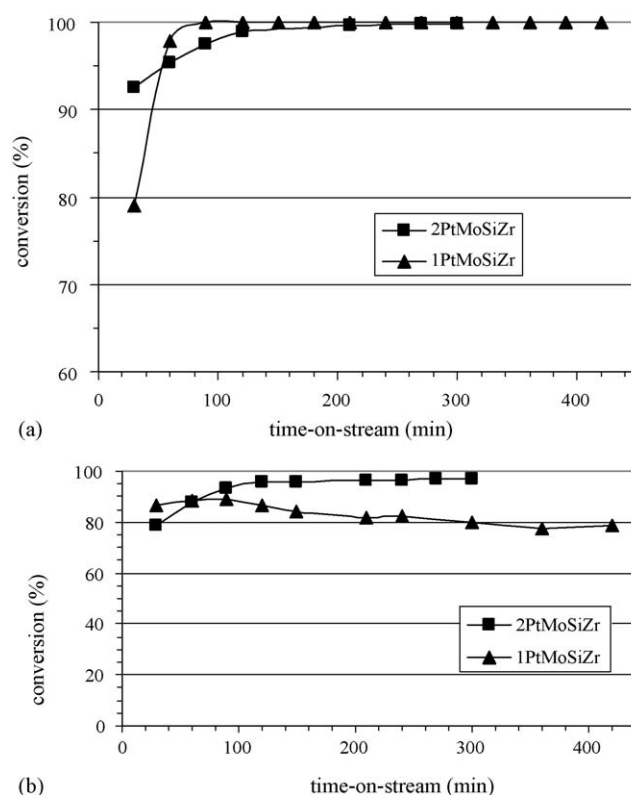


Fig. 6. Evolution of the conversion with the reaction time in the hydrogenation of tetralin for the PtMo catalysts at: (a) $T = 548$ K and (b) $T = 623$ K. H₂/THN = 10.1, P(H₂) = 6.0 MPa, contact time = 3.6 s.

1PtMoSiZr at 623 K, probably due to the higher acidity of this catalyst, which favours the secondary reactions. The same is observed for 2PtMoSiZr-S, which has a moderate low yield (3.6%) of HC products at 623 K. Naphthalene formation is negligible for all the studied catalysts.

The stability of the catalysts was also evaluated by studying the evolution of the conversion and selectivity with the time-on-stream during 5–7 h, at two temperatures: 548 and 623 K for the PtMo catalysts obtained from the polynuclear complex.

It can be observed in Fig. 6a that, at 548 K, catalysts need an induction period before reaching a conversion around 100%. This fact may indicate that the active phase was not totally reduced during the pretreatment. After 180 min, the catalyst with 2 wt.% of metal content exhibits a conversion of THN of 100%, maintaining their activity after 7 h. The metallic content has a moderate influence, because the catalyst with 1 wt.% reached the stability after 90 min, being from this point the behaviour similar to the other catalyst. The main difference found between these catalysts concerns the selectivity. As it has been described before, the PtMo catalysts show almost total selectivity to decalins. For 2PtMoSiZr, the *trans*- to *cis*-decalin ratio is 1.5, while for 1PtMoSiZr is around 1 during all the experiment.

At 623 K, the conversion for 2PtMoSiZr is similar to that obtained at 548 K, reaching almost 100% after 120 min of time-on-stream (Fig. 6b). However, for 1PtMoSiZr, deactivation is observed reaching the stability at a conversion value around 80% after 7 h of time-on-stream. A plausible explanation for

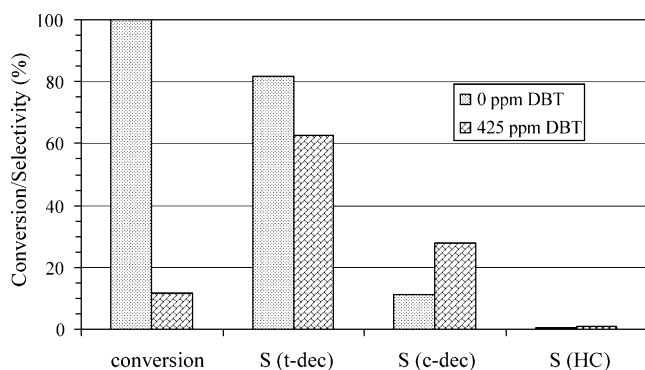


Fig. 7. Conversion and selectivity (*S*) results in the hydrogenation of tetralin in the presence of 425 ppm of DBT, over the 2PtMoSiZr–S catalyst. Reaction time: 7 h, $T = 588$ K, $H_2/THN = 10.1$, $P(H_2) = 6.0$ MPa, contact time = 3.6 s.

this observation is the formation of a deposit of coke on the active centres. This was confirmed by elemental CHN analysis of the spent catalyst, which showed for the 1PtMoSiZr sample 1.16 wt.% C, while this percentage was only 0.11 wt.% before catalysis. This deposition of coke is favoured by the acidity of the support, because the acid sites can catalyze reactions of alkylation, cyclation or dehydrogenation.

3.3. Thiotolerance studies

The thiotolerance of this series of catalysts in the hydrogenation of tetralin was evaluated by adding 425 ppm of DBT to the organic feed. The reaction conditions used initially for these tests, according to previous results, were: H_2/THN molar ratio = 10.1, contact time = 3.6 s, $T = 588$ K, $P(H_2) = 6.0$ MPa. The time-on-stream for each catalytic run was 7 h. This intermediate temperature was chosen because it permits a high conversion, moderate cracking products, and in principle deactivation by coke is expected to be lower than that found at 623 K.

The study of the 2PtMoSiZr–S catalyst reveals that conversion was drastically reduced when using a feed with 425 ppm of DBT, decreasing from 100% to a value around 12% in the steady state (Fig. 7). This result was unexpected, because it has been predicted that the presence of transition elements such as molybdenum or tungsten, in the composition of bimetallic catalysts, would improve their thiotolerance. This result contrasts with the data obtained with PdPt catalysts, which showed good thiotolerance under the same experimental conditions [48]. A change in the selectivity was also observed, decreasing the amount of *trans*-decalin, and increasing that of *cis*-decalin. The formation of small amounts of ring opening products was also detected.

The spent catalyst (after the DBT treatment) has been analyzed by elemental CHNS analysis. The sulphur percentage present is moderate (0.12 wt.% S), and coke deposition has been observed (0.56 wt.% C). This poor thiotolerance could be attributed to the low percentage of molybdenum present on these catalytic systems, which is insufficient to prevent the poisoning of the active phase, platinum particles. Thus, Paál et al. [62] reported the use of Al_2O_3 supported PtMo catalysts for hydrogenation and hydrodesulphurization processes with percentages of Pt and MoO_3 of 3 and 12 wt.%.

As a conclusion, we can state that it has been possible to prepare a family of bimetallic PtMo catalysts using an organometallic polynuclear complex or classical salts as precursors. Similarly to that found for PdPt systems, it has been verified (mainly by TEM) that for the PtMo catalysts a much better metallic dispersion can be achieved using the polynuclear derivative as precursor than when the mixture of classical salts is employed. These catalysts mainly yield decalins with high selectivity, and besides the *trans* to *cis*-decalin ratio can be modulated by a proper choice of the type of precursor.

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