



Hydrogenation of aromatics over supported noble metal catalysts ex organometallic complexes

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Abstract

In the present work, organometallic complexes were used as metal precursors for the synthesis of sulphur-resistant noble metal catalysts. The catalysts were tested in the hydrogenation reaction of diesel model-type molecules. Dibenzothiophene (DBT) was used as the source of sulphur. The organometallic-based catalysts activity was compared with the activity displayed by a commercial Pt/Al₂O₃ hydrogenation catalyst. Comparable activity results were obtained when the reaction was carried in the presence of sulphur containing molecules. However, the organometallic-based catalysts were only active once the ligands had been removed from the metal coordination sphere, thus allowing the reactant molecules to adsorb on the metallic surface centres. Accordingly, the major advantage of this methodology may lie in improved metallic dispersion, which will be reflected in catalysts with greater sulphur resistance, rather than in the electronic or steric effects ascribed to organometallic precursors.

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1. Introduction

The hydrogenation of aromatic molecules of the diesel fraction is a field of major interest both from an academic and industrial point of view [1,2]. The increasingly more stringent restrictions regarding the aromatics contents of transportation fuels [3] is currently pressing refineries to find suitable catalysts to achieve fuels containing low aromatics levels, but with no increase in costs [4]. A decrease in the aromatics

content of diesel fuel will result in an increase in the number of cetane. Several approaches are currently being explored, most of them being those focused on the use of platinum metals as catalysts for the hydrogenation process. It is well established that platinum catalysts present excellent hydrogenation properties at moderate pressures [1]. Furthermore, such catalysts can operate at lower temperatures where thermodynamic limitations are not as severe as those of the metal sulphide type. However, this approach has its own restrictions since noble metals are known to be poisoned by sulphur, even at very low concentrations [5]. Sulphur is present in the diesel of refineries. In order to overcome this poisoning, the initial attempt

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should focus on a previous deep HDS step of the fuel feedstock [6]. However, it is also well known that complete sulphur removal is not possible, at least from the economic point of view [7], and hence other alternatives must be found out. In order to develop noble metal sulphur-resistant catalysts [8–11], both the control of the acidity of the support [12] and the addition of a second noble metal to the catalyst, i.e. bimetallic catalysts, typically Pd–Pt, but also Re, Rh, Ge, W, Zr, and Tm, among others, have been proposed as the major routes to achieve the desired sulphur-resistant hydrogenation catalysts [13–16]. However, it still remains an open question whether the co-existence of Pd with Pt in the same particle might play any role or not in the sulphur resistance of the catalysts [17]. The key point of these approaches is to avoid the sintering and migration of the metal particles by decreasing the sulphur–metal bond strength, although aspects other than this should also be taken into account [13].

Hydrogenation with organometallic-based catalysts is usually carried out under mild conditions in homogeneous phase; that is, at room temperature and atmospheric pressure [18]. Coordination complexes have been used in the hydrogenation and hydrogenolysis of thiophene molecules in order to gain insight into the HDS mechanism in relation to the development of more efficient industrial catalysts [19]. Traditionally, heterogeneous hydrogenation catalysts are prepared by impregnation of a metal salt precursor over the adequate support. An alternative route for the preparation of supported catalysts consists in the immobilization of organometallic or coordination complexes onto different carriers, as a manner to combine the advantages of both homogeneous and heterogeneous catalytic process [20]. Quiroga et al. [22] studied the hydrogenation of cyclohexene to cyclohexane with supported and unsupported Wilkinson's complex and concluded that the Rh catalyst was more active and sulphur resistant than the Pd and Ni counterparts.

In the present work, we explored the use of noble metal-supported catalysts prepared from organometallic precursors as an alternative route to prepare hydrogenating catalysts. By supporting the complexes over different carriers the metallic dispersion can be improved, which can affect positively the catalytic performance [22].

2. Experimental

2.1. Catalyst preparation

A 0.3 wt.% Pt on 3 mm alumina pellets type 73 catalyst (hereafter named as PtA) was provided by Johnson-Matthey and was used as received as a reference catalyst. Reaction conditions, such as particle size and the liquid and gas flows rates, i.e. the mass-transfer limitation test studies, were determined using the PtA catalyst and were maintained for all other catalysts.

All manipulations were carried out under a dry nitrogen oxygen-free atmosphere, using standard Schlenk techniques. The phosphorous, sulphur and metal content of the silica-supported bulk catalysts was measured by ICP-AA at Mycroanalytisches Labor Pascher (Germany).

2.1.1. Metal complexes precursors and supports

$[\text{PdCl}_2(\text{NCPH})_2]$ was prepared according to a published method [23]. $[\text{Rh}(\text{COD})(\text{S})_2]\text{BF}_4$ (S: acetone) was prepared in situ by the addition of AgBF_4 (0.16 g, 0.80 mmol) to an acetone solution of $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]$ (0.20 g, 0.40 mmol). After stirring for 1 h and filtering out, a yellow acetone solution of $[\text{Rh}(\text{COD})(\text{S})_2]\text{BF}_4$ was obtained. $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]$, $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ and AgBF_4 were purchased from Aldrich. Silica PQ MS-3040 ($S_{\text{BET}} = 423 \text{ m}^2/\text{g}$) was purchased from PQ Corporation, US.

Triethoxysilylpropyldiphenylphosphine was prepared by a procedure described in [24] and then reacted with an excess of sulphur in dichloromethane for 48 h at room temperature yielding triethoxysilylpropyldiphenylphosphine sulphide. This is a well established methodology for phosphine sulphidation [25], yields as high as 95% to the desired sulphide phosphine could be reached [26]. The phosphinated silica (hereafter referred to as S1) was prepared from silica previously outgassed at 473 K under vacuum and triethoxysilylpropyldiphenylphosphine sulphide in toluene under reflux for 24 h, filtered out, washed with toluene and methylenechloride, and dried under a vacuum. Silylated silica (hereafter referred as S2) was prepared by the addition of an excess of hexamethyldisilazane to the previously modified phosphine sulphide silica S1, in toluene, under reflux for 24 h. The resulting mixture was filtered out

Table 1
Catalysts nomenclature

Catalyst	Metal	Support	Metal precursor	Area (m ² /g)	Pore volume (ml/g)	Metal loading ^a (wt.%)
PtA	Pt	Al ₂ O ₃	–	–	–	0.3 ^b
Rh1	Rh	S2	[Rh(COD)(S) ₂]BF ₄	286	1.6	0.2
Rh2	Rh	S1	[Rh(Cl)(PPh ₃) ₃]	343	2.3	0.3
Rh3	Rh	S2	[Rh(Cl)(PPh ₃) ₃]	343	2.9	0.7
Pd1	Pd	S1	[PdCl ₂ (NCPh)]	263	1.5	1.1
Ni1	Ni	S1	[Ni(CO) ₂ (PPh ₃) ₂]	250	1.6	0.3

S: acetone; the metallic content of each sample was measured by IC Plasma. The metallic content of the Johnson-Matthey catalyst was provided by the suppliers.

^a Determined by IC Plasma.

^b Provided by Johnson-Matthey.

washed with toluene and dried under vacuum for 24 h.

2.1.2. Immobilised metal catalysts

Supported catalysts were prepared according to the following method. A solution of the corresponding complex [PdCl₂(PhCN)₂], [RhCl(PPh₃)₃] and [Rh(COD)(S)₂]BF₄, in methylenechloride, toluene and acetone, respectively, was added to the modified SiO₂, previously outgassed under vacuum at 323 K for 12 h. The mixture was refluxed for 24 h, after which it was cooled to room temperature and filtered out. After washing with CH₂Cl₂ until a colourless extract was obtained, it was dried under vacuum for 1 day at room temperature and kept under nitrogen. Hereafter, the catalysts used in the present work will be referred to as: PtA, a commercial catalyst Pt/Al₂O₃; Pd1, prepared using [PdCl₂(PhCN)₂] and support S1; Rh1, prepared using [Rh(COD)(S)₂]BF₄ and support S2; Rh2, prepared using [RhCl(PPh₃)₃] and support S1; Rh3, prepared using [RhCl(PPh₃)₃] and support S2. Finally, Ni1 was prepared using [Ni(CO)₂(PPh₃)₂] and S2.

Table 1 shows the nomenclature, organometallic precursors and some physical properties of the catalysts.

2.2. Thermogravimetric analysis

Thermal analyses of the fresh catalysts were performed on a Perkin-Elmer TGA-7 apparatus. Typically, 20 mg of the sample was heated from 298 to 1223 K at a rate of 10 K/min under He or a dry air flow. Similar profiles were obtained for each sample in both atmospheres.

2.3. Specific surface area determination

N₂ adsorption–desorption isotherms of the samples were recorded at the temperature of liquid N₂ with a Micromeritics ASAP 2000 apparatus. Samples were previously outgassed at 333 K for 24 h. Specific areas were calculated by applying the BET method to portions of the isotherms within the 0.05 < P/P₀ < 0.30 relative pressure range.

2.4. Temperature programmed reduction (TPR)

TPR of fresh and calcined samples was performed on a semiautomatic Micromeritics TPD/TPR 2900 apparatus connected to a computer. Typically, ca. 75 mg of the sample was introduced into the reactor and heated under dry air at 383 K for 1 h to remove water and other contaminants. Then, the temperature was cooled to 298 K in air. TPR profiles were obtained in a 10% H₂/Ar flow (50 ml/min) from 253 to 1123 K at a rate of 10 K/min. H₂ consumption was measured with a TCD detector. The effluent gas was passed through a cold trap to remove water from the outlet stream.

2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were acquired with a VG Escalab 200R spectrometer fitted with a Mg K α ($h\nu = 1253.6$ eV, 1 eV = 1.6302×10^{-19} J) 120 W X-ray source and a hemispherical electron analyser. A DEC PDP 11/53 computer was used for collecting and processing the spectra. The powdered samples were pressed into small stainless steel cylinders and then mounted on a sample rod, placed in a pretreatment chamber and outgassed at 298 K and

10^{-5} mbar for 5 h prior to being transferred to the analysis chamber. The residual pressure during data acquisition was maintained below 3×10^{-9} mbar. The 20 eV energy regions of the photoelectrons of interest were scanned a number of times in order to obtain acceptable signal-to-noise ratios. Intensities were estimated by calculating the integral of each peak, after smoothing, subtraction of the S-shaped background, and fitting the experimental curve to a combination of Lorentzian and Gaussian lines of variable proportions. Accurate binding energies (± 0.2 eV) could be determined by referencing to the C 1s peak at 284.9 eV.

2.6. Catalytic activity measurements

The catalytic behaviour of the selected catalysts was studied using a Microactivity Pro Reactor [27]. The reactor consists of a stainless steel tube of 10 cm length and 1.5 cm internal diameter. At the exit of the reactor, liquid products are trapped by a condenser at 293 K. Inside the condenser, a constant liquid volume of ca. 1 ml was maintained while the liquids are collected in continuous mode. Liquid samples were collected every hour over 5 min, after which they were analysed. The gaseous products were conducted through a warmed pipe to the GC.

The catalyst (0.9 g) was diluted with SiC (1:1 volume ratio) and introduced into the reactor. The catalysts were mixed with SiC to avoid hot spots and to ensure plug-flow hydrodynamics [28]. The model liquid was fed with a high performance liquid chromatography (HPLC) liquid pump (Gilson 307 Pump) and consisted of a mixture of toluene, naphthalene and cyclohexene in hexadecane. Dibenzothiophene (DBT) was used as the sulphur source in the feed. Mass-transfer limitation tests were performed with the catalyst Pt/A, using 10 wt.% toluene in the hexadecane feed. The catalyst was tested at 573 K and 3 MPa, maintaining the weight hourly space velocity (WHSV) value constant (4.9 h^{-1}), using liquid feeds between 0.025 and 0.11 ml/min. A 0.09 ml/min feed was found to be the optimal value to overcome external mass-transfer limitations. Study of the internal mass-transfer limitation was performed at 573 K, 3 MPa and WHSV 4.9 h^{-1} and a liquid feed of 0.09 ml/min, with a catalyst particle diameter between $0.2 < \varnothing < 1.1$ mm. The $0.25 < \varnothing < 0.45$ mm diame-

ter was chosen as the optimal particle size range. These conditions were maintained for all catalytic tests.

The catalytic behaviour of Rh1, Rh2, Rh3, Pd1 and Ni1 in the hydrogenation reaction was monitored with the non-reduced and reduced samples.

In the former case, once the catalyst had been introduced into the reactor, both the liquid feed and the gases (a H_2/N_2 mixture) were passed through the reactor. Catalytic activity was tested from 323 to 773 K at 0.1–4 MPa of total pressure.

In the latter case, the catalyst under study was pre-treated at 723 K (10 K/min) under H_2 (40 ml/min) at 1 MPa for 4 h. After the catalyst had been reduced, its behaviour was monitored at 573 and 673 K, at both 3 and 4 MPa of total pressure.

For both sets of reactions, the weight hourly space velocity was set at 4.9 h^{-1} while the hydrogen-to-liquid feed ratio was $1000 \text{ l}_n/\text{l}$.

The reaction was kept under the studied conditions for 8 h; samples were collected and analysed every hour. Following this, the reaction conditions were changed to those selected and so on. To study the sulphur resistance of the catalysts, 1000, 5000 and 10 000 ppm of DBT were added to the liquid feed containing cyclohexene, toluene and naphthalene (10 wt.% of each) in hexadecane.

The behaviour of the catalysts for the sulphur-free feed was studied for 8 h, after which a liquid containing the desired amount of DBT was fed into the reactor and the catalytic behaviour was monitored for 5–8 h. Then, a sulphur-free liquid was fed for 8 h and, again, a sulphur containing liquid (with a different sulphur concentration from the previous feed) was fed in and the catalytic behaviour was monitored for 5–8 h.

Liquid samples were analysed on a Varian 3800 GC equipped with a FID detector and a CP-Sil 5B column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). Cyclohexene, cyclohexane, benzene, toluene, methylcyclohexane, tetraline, decaline, naphthalene, dibenzothiophene, biphenyl and cyclohexylbenzene were the products detected.

3. Results and discussion

3.1. Specific surface area and pore volume

The surface areas of the catalysts are depicted in Table 1 and are around $270 \text{ m}^2/\text{g}$. The catalysts

Rh2 and Rh3 displayed the highest surface areas: ca. 350 m²/g each. Although both catalysts come from the same precursor [RhCl(PPh₃)₃], they have been prepared from S1 and S2 supports, respectively.

Taking into account that both catalysts Rh1 and Rh3 have been prepared by using the support S2, it is noticeable their different area and pore volume values, albeit they come from different Rh precursors. The Rh content of the samples varies from 0.2 to 0.7 wt.% for Rh1 and Rh3, respectively. Furthermore, the solvent used for the anchorage reaction might play a role in the final nature of the samples. Toluene and acetone have been used for the preparation of R3 and R1, respectively.

The hysteresis loops of the N₂ adsorption–desorption isotherms of the catalysts are of type IV of the de Boer classification. The pore size distribution was calculated using the BJH method [29]. Selected data are offered in Table 1.

3.2. Thermogravimetric analysis

The thermal analysis data are shown in Fig. 1. From this figure, two main weight loss regions were ob-

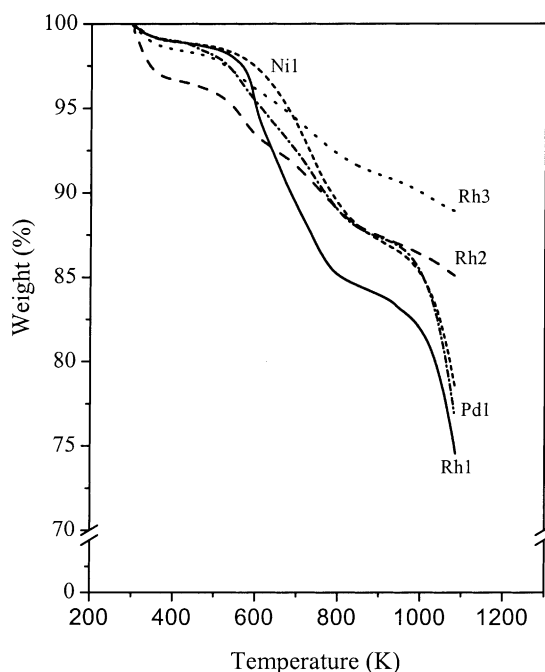


Fig. 1. TGA profiles of selected samples.

served for all the catalysts. The first loss occurred at a temperature range between 273 and 353 K, and was moderate. Another weight loss was observed between 623 and 723 K. This behaviour was similar for all catalysts, although at higher temperatures, starting from 973 K, another important weight loss was observed for Rh1, Ni1 and Pd1 catalysts. The first weight loss was assigned to water and solvent losses. The second and third weight losses were mainly due to the organic molecules surrounding the metal atoms and also to the organic SiO₂ modifiers. Rh1, Pd1 and Ni1 have labile ligands in the coordination sphere of the precursors. Rh2 and Rh3 show similar decomposition profiles indicating thus a similar thermal stability. Both samples were prepared from the same precursor [RhCl(PPh₃)₃], while varying the nature of the support, phosphinated silica and phosphinated-silylated silica, respectively. When the TG analysis was performed under a dry air atmosphere, similar profiles were obtained for all samples.

3.3. TPR analysis

The TPR profiles of the non-calcined catalysts showed several broad peaks, indicative of strong H₂ consumption both due to the metal function and the organic molecules present in the catalysts. When TPR of the calcined samples (at 1223 K) was performed, H₂ consumption was lower than that observed for the non-calcined samples and the peaks were well resolved. In the latter case, H₂ consumption was attributed only to the metallic function of the catalysts. The TPR profiles of the non-calcined and calcined samples are depicted in Fig. 2a and b, respectively. After careful comparison of both series of TPR profiles, it appears that the H₂ consumption assigned to the organic molecules occurred within the 573–823 K temperature range. The TPR profiles of Rh1 and Rh2 are closer in spite of they came from different supports (S1 versus S2) and different Rh precursors ([Rh(COD)S]⁺ versus [RhCl(PPh₃)₃]). The extra H₂ uptake in Rh1 might be attributed to the COD hydrogenation. After catalyst calcination, the three Rh samples behave similarly and the H₂ consumption corresponds to the metallic function. The effect of the organic molecules on H₂ uptake was clearly observed when the profiles of the Rh1, Rh2 and Rh3 samples for the non-calcined and calcined catalysts were

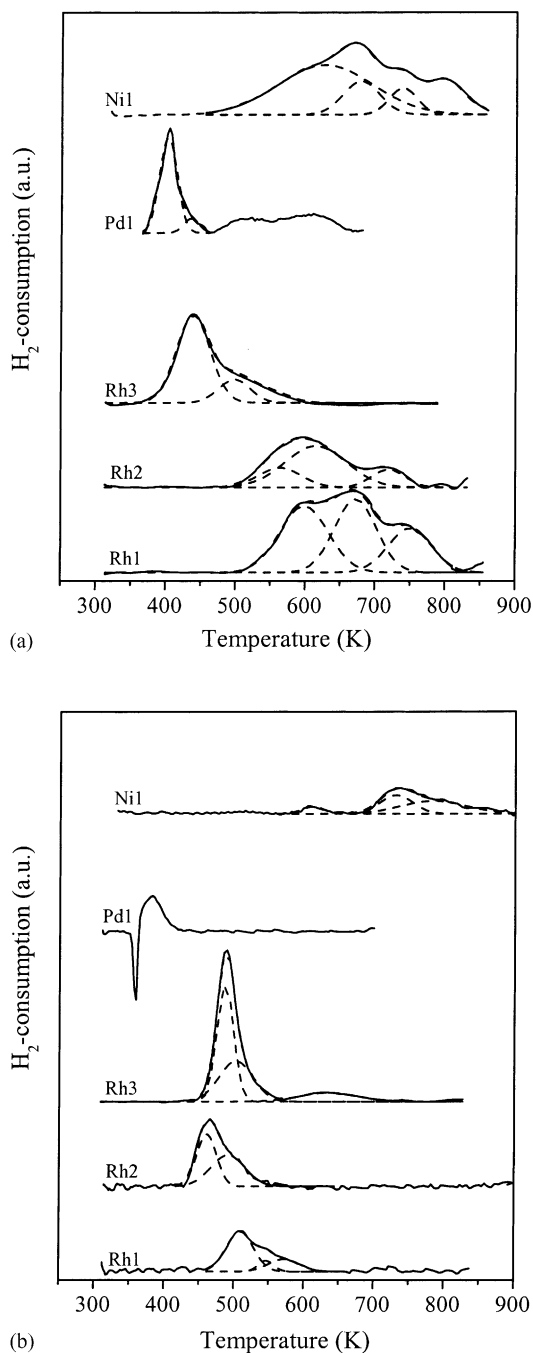


Fig. 2. (a) TPR profiles of the non-calcined catalyst. (b) TPR profiles of the calcined catalysts.

compared. The nature of the ligands coordinated either to the metal function (Rh1 versus Rh2 and Rh3) or to the support (Rh2 versus Rh3) produced different H₂ consumption profiles. However, once calcined, very similar H₂ consumption profiles were observed for the three catalysts.

3.4. XPS analysis

The XPS spectra of the non-calcined samples were recorded without any further treatment. The Rh 3d_{5/2} core-level spectrum of sample Rh1 shows two components centred at 308.1 and 309.4 eV, respectively, ascribed, respectively, to Rh^I and Rh^{III}. Similarly, the spectra of catalysts Rh2 and Rh3 showed two species, each centred at 307.2, 308.6 and 307.7, 309.5 eV, respectively (Fig. 3a shows the 3d Rh region of Rh3). These species were ascribed to Rh⁰ and Rh^I and Rh^I and Rh^{III}, respectively.

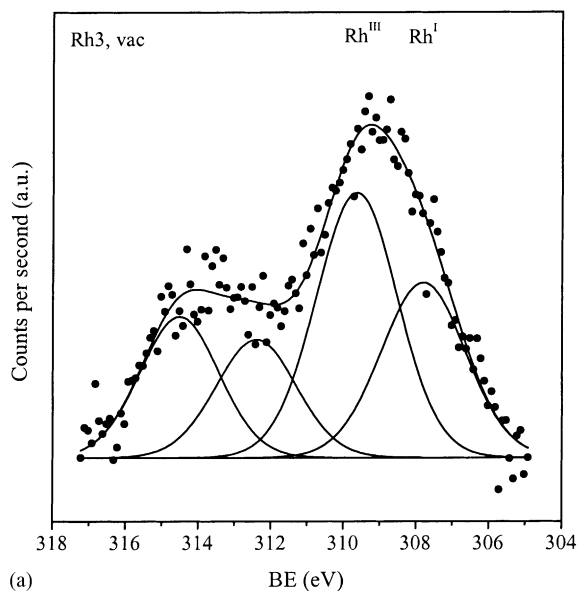
In Rh2 and Rh3, one or more triphenylphosphine ligands of the precursor have been substituted by the phosphine sulphide pendent groups of the functionalised silica. This means that a mixture of ligands with different contributions is present.

For the Pd1 catalyst, the Pd 3d core-level spectrum showed two components centred at 337.0 and 338.7 eV, ascribed to Pd^{II} species (Fig. 3b). The Ni1 catalyst spectrum shows a peak at 856.2 eV, ascribed to a Ni^{II} species. Selected BE are depicted in Table 2.

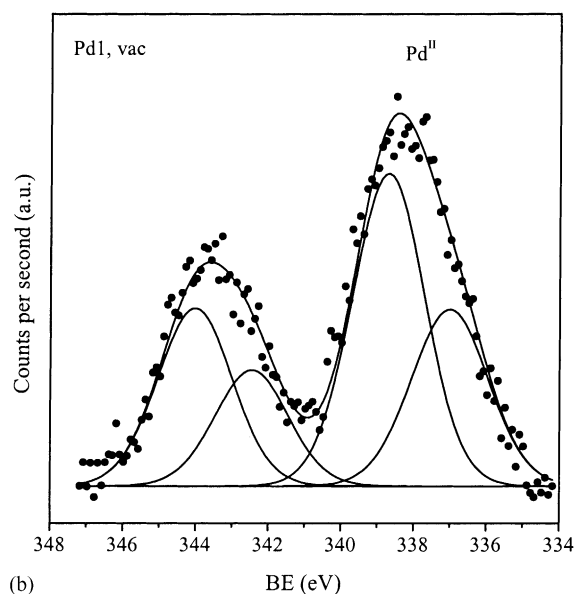
3.5. Catalytic activity

3.5.1. Sulphur-free feed

When the catalytic behaviour of the non-calcined samples was studied, a feed containing toluene and naphthalene in hexadecane was used. Catalysts were not active at reaction temperatures below 573 K. At higher temperatures, hydrogenation products, i.e. methylcyclohexane, decaline (*cis*- and *trans*-) and tetraline were detected. The catalytic activity was enhanced with increasing reaction temperature. During the whole catalytic test, which started at ca. 323 K, the colour of the liquid phase collected was yellow. Only after the catalysts had been subjected to temperatures of ca. 673 K or higher for several hours did the liquid collected become colourless. This feature illustrates that the ligands coordinated to the metallic function of the catalysts were released as long as the reaction



(a)



(b)

Fig. 3. (a) XPS spectra of Rh3 catalyst. (b) XPS spectra of Pd1 catalyst.

temperature was increased, as expected from the TG analyses. The lack of activity of the non-calcined samples, both when the reaction was conducted at low temperatures and in the early stages, when the reaction was conducted at higher temperatures, could be due to the lack of accessibility (steric hindrance) of

the reactants (toluene and naphthalene) to the metallic function. The metal in the non-calcined samples is surrounded by the ligands, as expected from the method used to prepare the solids. We observed that only when the ligands were removed from the solids, i.e. when the liquids collected at the exit of the reactor started to be colourless, the catalysts began to be active in the hydrogenation of naphthalene. These experiments confirm that samples required to be calcined in order to obtain catalytically active species.

In a second set of experiments, the samples Rh1, Rh2, Rh3, Pd1 and Ni1 were calcined at 1123 K under air atmospheres. Also, before the reactivity tests, the samples were reduced in the reactor at 723 K in an H₂/He (1:10 volume ratio) stream with a flow rate of 50 ml/min at atmospheric pressure. All catalysts were tested in the hydrogenation of toluene and naphthalene under different reaction conditions. Table 3 summarises the main results obtained for the different catalysts, including those obtained with the commercial catalyst (PtA). The hydrogenation rate followed the expected order: naphthalene \gg toluene $>$ tetraline. Except for the commercial catalyst, toluene and tetraline were only sparingly hydrogenated under the conditions studied in the present work. The most active catalysts were those prepared using Rh as the metallic precursor, particularly those in which the metallic precursor was the Wilkinson's complex, i.e. catalysts Rh2 and Rh3. For these catalysts, naphthalene conversion was ca. 85%. The main difference between both samples was the nature of the support. The Rh2 catalyst was prepared from a non-silylated SiO₂, whereas the Rh3 catalyst was prepared using a silylated SiO₂. Silylation was performed to ensure that the reacting sites would be exclusively the P=S groups of the modifier [(EtO)₃Si(CH₂)₂P(S)Ph₂] and not the hydroxo surface groups of the SiO₂. Whilst silylation of mesoporous silica does not affect the porosity of the substrate it modifies the density of its active surface groups [30].

The poor hydrogenation activity displayed by the Pd-based catalysts is surprising, since it is well known that Pd-based catalysts are very active in the hydrogenation of aromatic under conditions similar to the ones reported in this paper. However, such studies have been performed using Pd supported on Al₂O₃ or zeolite materials, while in our study Pd was supported on modified SiO₂ and it is known that the support

Table 2
Binding energies (BE) (eV) values of fresh samples and supports

	Rh1	Rh2	Rh3	Pd1	Ni1	S1	S2
Si 2p	103.4	103.4	103.4	103.4	103.4	103.2	103.3
P 2p	131.9 (40) 133.1 (60)	132.5 (79) 134.4 (21)	135.5 (t)	132.0	132.7	132.5 (60) 134.0 (40)	132.3 (58) 133.6 (42)
S 2p	161.7	161.9	162.2 (t)	162.2	161.7	162.6	162.1
Rh 3d _{5/2}	308.1 (53) 309.4 (47)	307.2 (39) 308.7 (61)	307.7 (40) 309.5 (60)	–	–	–	–
Pd 3d _{5/2}	–	–	–	342.3 (22) 343.9 (78)	–	–	–
Ni 3d _{3/2}	–	–	–	–	865.2	–	–

(t): traces.

plays a major role in the performance of the catalysts [12,31,32].

The Ni catalyst was completely deactivated after a 2 h on-stream operation. Quiroga et al. have shown that the both the hydrogenation and sulphur resistance of supported Rh complexes is higher than the one displayed by Pd- and Ni-supported complexes [22].

At this point, it seems pertinent to discuss the characterisation of the catalysts. A proposed an-

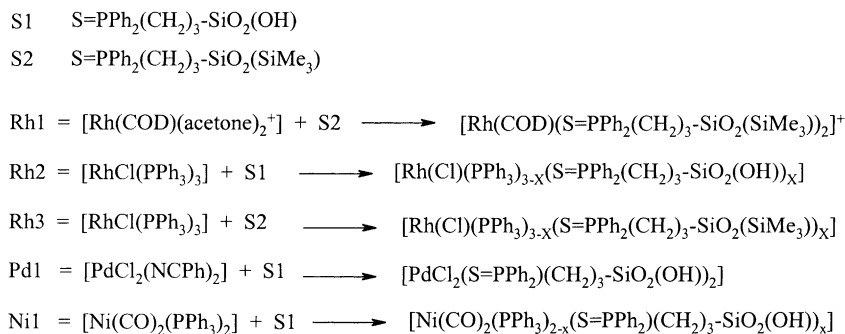
choring pathway for the complexes is depicted in Scheme 1. Yet, reaction others than the one proposed in the scheme could not be ruled out, our aim is to illustrate a plausible anchoring route of the organometallic precursors onto the different supports. However, alternative anchoring routes can also take place simultaneously. Indeed, as we will discuss below, different metallic species are present in the samples.

Table 3
Naphthalene hydrogenation over the different catalysts without added sulphur

Catalyst	P (MPa)	T (K)	WHSV (h ⁻¹)	X _{na^a} (%)	Tetraline (wt.%)	<i>cis</i> -Decaline (wt.%)	<i>trans</i> -Decaline (wt.%)	Time (min)
Rh1	3	573	4.9	41	99.5	0.3	0.1	190
Rh1	4	673	4.9	34	99.4	0.3	0.2	200
Rh1	4	673	2.5	57	98.1	1.3	0.7	200
Rh1	3	473	4.8	13	99.4	0.4	0.3	220
Rh2	3	573	4.8	85	97.0	2.6	0.5	210
Rh2	4	673	4.8	66	96.0	2.3	0.7	200
Rh2	3	673	4.8	54	98.9	0.8	0.3	210
Rh2	3	573	8.1	28	73.5	7.2	19.3	190
Rh3	3	573	4.9	83	98.4	1.2	0.4	210
Rh3	4	673	4.9	52	99.3	0.5	0.2	210
Pd1	3	573	4.9	9	99.9	0.1	–	200
Pd1	4	673	4.9	41	99.7	0.2	0.1	200
Pd1	4	673	13.8	26	100	–	–	200
Pd1	3	673	4.9	17	99.9	0.1	–	200
Pt/A	4	673	4.9	71	69.6	25.0	5.4	210

Some selected kinetic data for catalysts under study. The Ni catalysts were very unstable under every reaction studied. The deactivation of the Ni catalyst occurs within the first 2 h of reaction. The main product arising from the hydrogenation of naphthalene was tetraline, which was barely hydrogenated (conversions below 5%) to *cis*- and *trans*-decalines.

^a Naphthalene conversion.



Scheme 1. Proposed anchoring pathway of the metallic complexes onto the phosphinated silica S1 or S2. Alternative reactions can not be ruled out.

Table 4 compares the atomic ratios of the catalysts and supports under study. These ratios were obtained via XPS and IC Plasma techniques and gave some insight into the actual nature of the catalysts. From them, it appears that the anchoring pathway followed by the metal complex precursors when supported on the modified SiO₂ would be different, or at least partly different, from the one illustrated in the Scheme 1. Only samples Pd1 and Ni1 displayed experimental atomic ratios close to the theoretical values. It seems reasonable to assume that metallic species other than the expected ones, particularly for the rhodium catalysts, would also coexist. For instance, the XPS spectra of supports S1 and S2 displayed two P components centred at BE 132.5 and 134.0 eV for sample S1 and at 132.3 and 133.7 eV for sample S2 ascribed to P (+3) and P (+5) species, respectively. These results are indicative that not all of the phosphine groups have been sulphided. On the other hand, IC Plasma results reveal that the extent of the transformation from the SiO₂-(R)P to SiO₂-(R)P=S has been close to 100% since P/S atomic ratios close

to 1 have been obtained. See Table 4 for further details.

In spite that supported catalysts have been prepared from S1 or S2 supports, whose XPS spectra show two P species, the Rh3 sample shows a single low intensity, P signal (centred at 135.5 eV) in the XPS spectrum. This signal corresponds to a P=S moiety (P (+5)). This will be indicative that all of the phenyl ligands from the RhCl(PPh₃)₃ have been removed out of the sample. Obviously, something different than expected has occurred during the preparation of sample Rh3. Besides, both the XPS and ICP results show that the amount of P and S is much lower than the expected from Scheme 1. The actual nature of sample Rh2 seems akin to the one proposed in Scheme 1 according to both the data obtained from XPS and ICP analysis.

Rh3 and Rh2 samples come from RhCl(PPh₃)₃ precursor. The binding energy of Rh 3d_{5/2} and P 2p atoms in the RhCl(PPh₃)₃ complex are 308.0–309.7 and 132.1 eV, respectively [33]. The authors propose that the BE values of the Rh atom, depend on the actual ox-

Table 4

Proposed and experimental atomic ratio values of the supports and catalysts

	Rh1 Rh/P/S	Rh2 Rh/P/S	Rh3 Rh/P/S	Pd1 Pd/P/S	Ni1 Ni/P/S	S1 P/S	S2 P/S
XPS	1/11/3	1/4/0.5	1/0.1/0.1	1/1.5/0.6	1/3.5/1	0.8	2.7
IC Plasma	1/11/13	1/5/6	1/1/1	1/1/1	1/3.5/4	0.9	0.9
Theoretical ^a	1/2/2	1/3/1	1/3/1	1/1/1	1/3/1	1	1

The atomic ratio values of the samples under study. S1 is the non-silylated SiO₂ and S2 is the silylated SiO₂ support.

^a Proposed atomic ratios values calculated assuming that the anchoring pathway is as depicted in Scheme 1.

idation state and on the nature of the ligands surrounding the metal. Even considering this fact, Rh2 and Rh3 samples consist of a mixture Rh species showing different oxidation states as revealed by the XPS analysis. According to the XPS data (see Table 2) the P in the Rh1 sample consists of a mixture of P (+5) and P (+3) species. This feature is in agreement with the nature of the S1 support. However, the position of the peaks has been shifted towards lower BE values. Furthermore, the relative intensity of the peaks has been modified. Unlike the results showed by Quiroga et al. [22], our results reveal the co-existence of different Rh coexisting species in the samples. Similar results have been reported by Knözinger for the anchoring of RhCl₃ onto a phosphine-modified silica support [34].

Although with the available data it is not possible to propose an accurate description of the nature of the catalysts, some relevant aspects can be clarified. The organic modifiers of the SiO₂ and the ligands of the metallic precursors are present in the catalysts. Such organic molecules can adsorb hydrogen (as shown by the TPR data). Also, for all samples the amount of P and S detected both by plasma and XPS is higher than the amount of metal, except for catalyst Rh3, in which the amount of surface Rh is higher than the amount of P and S detected.

In any case, it seems that the silylated sample Rh3 displays a higher conversion than the non-silylated

counterpart Rh2. This could be due to the higher proportion of Rh atoms to both P and S atoms exposed on the surface of the catalysts Rh3. See Table 4 for further details. Selectivity patterns were similar for both samples.

In a different set of experiments, in order to test whether the lack of activity of these catalyst at low temperature is due to the lack of accessibility of the reactants to the metallic function or to the fact that they are not sufficiently active, the hydrogenation activity of catalysts Rh2 and Rh3 was tested (and compared with that of the commercial catalyst) using a feed containing cyclohexene, which can be easily hydrogenated. The activity results are depicted in Table 5, in which it is shown that the samples became active when the ligands were removed from the catalysts. Again, until the bare metallic function has been obtained, the samples were not active, even if cyclohexene was fed. Clearly, the accessibility of the metallic function seems to play a dominant role in the catalytic behaviour of the samples. The idea of accessibility of the metal phase for the hydrogenation of toluene over supported catalysts has been discussed previously [35]. However, the accessibility concept discussed in that paper is slightly different, since here we do not mean metal dispersion, but instead we give an idea of steric hindrance due to the presence of coordination ligands hindering the adsorption of the reactants on the catalytic surface.

Table 5
Catalytic data obtained for the aromatic hydrogenation in the presence of DBT

Catalyst	DBT	Conversion (%)			Time (h)
		Naphthalene	Toluene	Cyclohexene	
Pt/A	–	71	45	100	8
	5000	46	1	99	6
	–	67	21	100	7
	10000	41	1	99	7
	–	47	1	100	5
Rh3	–	75	5	100	8
	5000	54	1	99	8
	–	79	1	99	7
	10000	51	1	100	8
	–	81	1	100	5
Rh2	–	50	0	94	8
	10000	8	0	75	8
	–	8	0	76	8

The DBT concentration is expressed in ppm.

3.5.2. Sulphur resistance tests

Samples Rh2 and Rh3 were chosen as the catalysts for the sulphur resistance tests. Their activity was compared with the one of the commercial catalysts, PtA, operating under the same reaction conditions, i.e. 4 MPa, 673 K, WHSV 4.8 h⁻¹, 1000 I_n/1 H₂/oil. Sul-

phur was fed as DBT at two different concentrations: 5000 and 10 000 ppm. Some selected data are depicted in Table 5. As expected, the presence of sulphur inhibited the activity of all the catalysts. The activity of Rh3 catalysts for naphthalene, toluene and cyclohexene hydrogenation, using both sulphur containing and

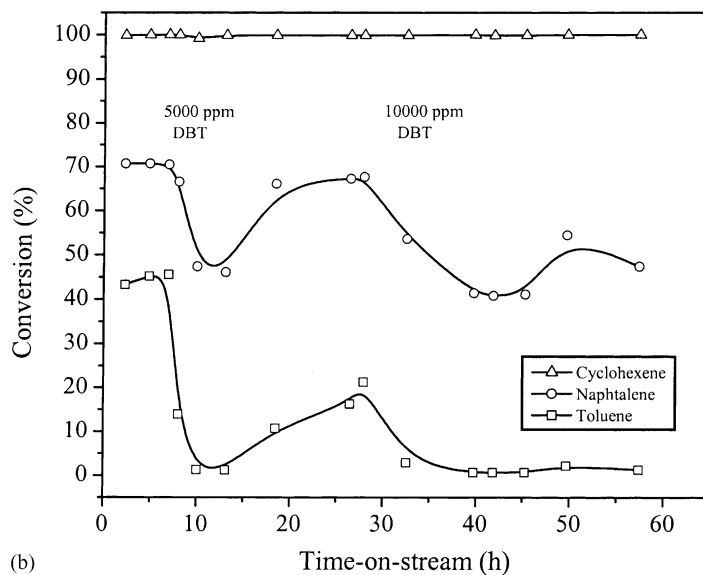
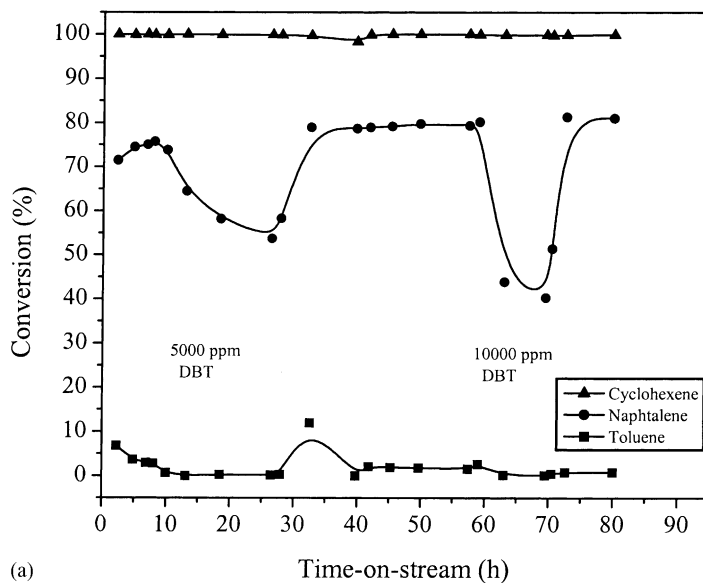


Fig. 4. (a) Effect of the amount of sulfur (as DBT) in the conversion profile displayed by catalysts Rh3. (b) Effect of the amount of sulfur (as DBT) in the conversion profile displayed by the commercial catalyst (Pt/A).

sulphur-free feed, is depicted in Fig. 4a. Fig. 4b shows the activity of the commercial catalyst, PtA, recorded under similar reaction conditions.

High cyclohexene hydrogenation conversions (ca. 98%) were achieved with all the catalysts. When DBT was fed (5000 and 10 000 ppm), cyclohexene conversion was barely not modified and the original activity was recovered when the sulphur was removed from the feed. Naphthalene conversion was lowered when DBT was fed. For the commercial catalyst, conversion decreased from ca. 70 to 45% and ca. 40% for the 5000 and 10 000 ppm DBT feeds, respectively. However, the commercial catalyst failed to recover its previous activity when DBT was removed from the feed, affording naphthalene conversions of ca. 50%. The activity of catalyst Rh2 was decreased when a feed containing 5000 ppm DBT was used, and although partially recovered, it failed to return to its original value once the sulphur had been removed from the feed. The activity of catalyst Rh3 (naphthalene conversion, ca. 70%) was reduced when a feed containing 5000 ppm DBT was used (naphthalene conversion, ca. 55%). However, when the sulphur was removed from the feed naphthalene conversions of ca. 80% were achieved.

When a feed containing 10 000 ppm DBT was used, the catalytic activity of the PtA sample in the naphthalene hydrogenation reaction was lowered to conversion values of ca. 40% and did not return to its original value after sulphur removal.

For the Rh2 catalyst, both cyclohexene and naphthalene conversions were decreased when a 10 000 ppm DBT feed was used. After sulphur removal, the activity of the catalysts was not modified.

In a similar manner, for the Rh3 catalyst, both the cyclohexene and naphthalene conversions were lowered when a 10 000 ppm DBT feed was used. However, activity was totally recovered when sulphur was removed from the feed. This behaviour is superior to that displayed by the commercial catalyst.

We also observed that even in the presence of sulphur (both for the 5000 and 10 000 ppm scenarios) the Rh-based catalysts, unlikely the Pt ones; partly recover their former hydrogenation activity after 4 h on stream. This behaviour has also been described for Pd/TiO₂ catalysts subjected to similar reaction conditions [32].

Under the studied conditions, Rh-supported catalysts proved to be more sulphur resistant than the commercial catalyst. However, the nature of its sulphur

resistance could not be ascribed to the effect of the metal-surrounding ligands in the organometallic precursor, since they had been removed from the catalyst surface during the thermal treatments. One possible reason could be due to the fact that preparation of immobilized metal catalysts by using organometallic (or coordination complex) precursors will render “atomically dispersed” catalytic species [36,37] which is proposed as a way of increasing the sulphur resistance of catalysts.

4. Conclusions

In the present study, although still preliminary, we have shown that organometallic complexes can be used as metallic precursors for the preparation of aromatic saturation catalysts operating at high temperature and pressure, particularly the Rh-based catalysts. However, the activity of the catalysts is hindered by the presence of the organic ligands surrounding the metal. In order to increase their activity, such ligands should be removed from the coordination sphere of the metallic function. Rh/SiO₂ catalysts prepared in this way displayed similar activities in the naphthalene and cyclohexene hydrogenation reaction to that of a commercial catalyst. Noticeably, Rh3 exhibited a higher sulphur resistance than the commercial catalyst. This fact was attributed to an optimal metallic dispersion inherent to the catalyst preparation route which in turn, will prevent the formation of larger Rh aggregates in the presence of sulphur.

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