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Nanosized Pd/Pt and Pd/Rh catalysts for naphthalene hydrogenation and hydrogenolysis/ring-opening

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Pd/Rh and Pd/Pt catalysts supported on two different mesoporous materials – a Zr-doped MCM-41-type silica [Si/Zr = 5 w/w (SiZr)] and a commercial silica-alumina [Si/Al = 40:60 w/w (SiAl)] – were prepared by incipient wetness impregnation using nanosized suspensions of alloy particles prepared by polyol-mediated synthesis in diethylene glycol (DEG). The catalytic behaviour of these catalysts was investigated in the hydrogenation and hydrogenolysis/ring-opening of naphthalene at 6.0 MPa, by checking the role of both the main reaction conditions (temperature, contact time and H_2/naphthalene molar ratio) and increasing amounts of dibenzothiophene (DBT). The catalysts supported on SiAl showed higher activity than catalysts supported on SiZr, thus suggesting that activity is favoured by higher acidity of the support and/or higher interaction of the nanosized metal particles with the support. While using the SiZr support, weaker metal-support interactions took place by forming catalysts with bigger metal and/or metal oxide particles. Besides, the catalyst with lowest noble-metal content (0.3 wt.%) (SiAl-0.3Pd/Pt-5) had the greatest acidity and metal surface and, consequently, the highest activity. Furthermore, it exhibited a good thiotolerance in presence of increasing amounts of DBT in the feed, thus maintaining a high catalytic activity in the hydrogenation of naphthalene, although with decreased yield in *trans*- and *cis*-decalin (decahydronaphthalene or DeHN) and high-molecular-weight compounds (H.M.W.), with a corresponding increased yield in the partially hydrogenated tetralin (tetrahydronaphthalene or TeHN).

KEY WORDS: naphthalene; dibenzothiophene; hydrogenation; hydrogenolyisis/ring-opening; Pd/Pt; Pd/Rh; supported catalysts; nanosized catalysts; polyol-mediated synthesis; Si/Al; Si/Zr; MCM-41.

1. Introduction

The importance of decreasing the impact of diesel use on air quality has led to future specifications for diesel fuels which will cause the drastic reduction in sulphur content and decreased polyaromatics concentration [1]. In addition, lower product densities and higher cetane numbers are also required [2]. Aromatics have poor ignition properties, and thus, a net increase of the cetane number is obtained by decreasing their concentration in the diesel fuel through hydrogenation processes [3,4].

The hydrogenation of aromatic and polycyclic aromatic compounds (PACs) is typically exhothermic [4,5]: therefore, a lower reaction temperature is thermodynamically favourable. However, in hydrotreating of LCO fractions, where PACs are present, a reaction temperature above 350 °C is usual in conventional processes and, consequently, requires a high H_2 concentration to offset the thermodynamic limitations. Noble-metal supported catalysts are well known for their high activity in the deep hydrogenation of aromatics - even at reaction temperatures below 200 °C [4,6,7] and moderate H_2 pressures – in spite of their low resistance to sulphur poisoning [8,9]. Thus, these catalysts are typically used in the second reactor of a two-stage process, where the feed must suffer previous deep hydrodesulfuration (HDS) in the first reactor [10].

In recent years improvement of catalysts has still been a major challenge in chemistry. The efficiency of heterogeneous catalysts based on metal particles, among other things depends on both the size of the particles and the nature of the support. Traditionally, supported metal catalysts are prepared by incipient wetness impregnation with solutions of the corresponding metal salts, followed by calcination and reduction steps. Thanks to this method, it is possible to prepare small metal particles, although it is quite difficult to obtain a narrow particle size distribution. The use of suspensions containing nanometric metal particles are expected to be suitable candidates to design highly active and selective catalysts, since the good uniformity of the metal particles should contribute to catalytic activity as well as to selectivity [11,12].

In particular, the polyol-mediated synthesis allows an accurate and reproducible control of the mean diameter

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of the particles in a broad size range as well as the mixing of reactants at the molecular level. "Polyols" stands as a general term for polyalcohols with high boiling temperature and sufficient ability to solve inorganic salts. In the preparation of metal particles, polyols were applied because of their mild reducing properties and chelating effects, which avoid particle agglomeration during their preparation. As a consequence, the tailoring of particle characteristics is obtained through the control of the nucleation and growth steps, while their dispersion is achieved either by steric or electrostatic stabilization. Recently, this method has received considerable attention because of its simplicity and advantages over most other methods, for the preparation of metal alloy and highly pure mixed oxides [13–17].

Taking into account the key role of the pore size and distribution of the support that affects both the metal dispersion and the diffusion of the voluminous molecules fed, many research groups have investigated a family denoted as MCM-41-type compounds [18–24]. This family of mesoporous MCM-41 materials has attractive properties, such as uniform pore size distribution, high surface area, and good stability [25,26]. Since mesoporous MCM-41 silica has a small number of acid sites needed for the hydrogenolysis/ring-opening reactions, acidity has to be increased by introducing a heteroatoms (Al, Ti or Zr) inside the siliceous framework [24,27–31]. Mesoporous structures would seem to be ideal for forming a scaffolding in which three dimensional dispersions of metal nanoparticles could be supported. For these reasons, the use of metal nanoparticles deposited on such porous materials has increased recently [32–36].

The aim of the present work is to investigate for the first time the behaviour of nanosized Pd/Pt and Pd/Rh pairs on either Zr-doped MCM-41-type solid or silica-alumina, prepared by incipient wetness impregnation of suspensions of metal nanoparticles in diethylene glycol (DEG), in the hydrogenation of naphthalene. Naphthalene has been chosen as a suitable model for the aromatic compounds present in the LCO diesel fraction. For these novel catalysts, the attention has been focused on both the role of support and the nature of active phase and, finally, on the metal content for the best support.

2. Experimental

2.1. Catalyst preparation

Two materials were used as supports for noble metals: a Zr-doped mesoporous silica with a Si/Zr molar ratio of 5, which was prepared essentially according to the method described elsewhere [24,36], but by stirring the suspension for one day only to speed up the synthesis. The second support was a commercial mesoporous alumina silica prepared by sol-gel method (40:60 w/w), provided by Engelhard. The supports were calcined at 550 °C ($1\ °C\ min^{-1}$ heating rate) for 6 h and were denoted as SiZr and SiAl, respectively. The Pd/Pt and Pd/Rh catalysts, with different atomic ratios, were prepared by incipient wetness impregnation using suspensions of nanometric particles in diethylene glycol (DEG), which were prepared by polyol-mediated synthesis method as reported elsewhere [37]. The average particle sizes were measured by dynamic light scattering using a Malvern Zetasizer Nano S. After impregnation the catalysts were fully dried at 170 °C and then calcined at 550 °C for 5 h, grinded and shaped to a 14–20 mesh particle size. The catalysts were denoted as SiZr(SiAl)-xPd/Pt(Rh)-y, where x refers to the total metal content (wt.%) and y to the Pd/Pt(Rh) molar ratio.

2.2. Catalyst characterization

The metal content in the catalysts was analyzed using a Varian Liberty 150 inductively coupled with a plasma atomic emission spectrometer (ICP). XRD patterns were recorded using a Siemens D5000 diffractometer, equipped with a graphite monochromator and using the CuK_α radiation. ($\lambda = 0.15418$ nm). The specific surface areas were evaluated from N_2 adsorption–desorption isotherms at −196 °C in a QUANTACHROM AUTOSORB-1 apparatus, after degassing at 200 °C and 1.3×10^{-2} Pa for 24 h.

X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non monochromatic MgK_α radiation (300 W, 15 kV, 1253.6 eV), and with a multi-channel detector. Spectra of powder samples were recorded in the constant pass energy mode at 29.35 eV, using a 720μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used to record and analyze the spectra. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves in order to determine the binding energy of the different element core levels more accurately. The reduced samples, before the XPS analysis, were kept in *n*-hexane to avoid contact with air.

The acidic properties were analyzed on the pelletized samples (14–20 mesh) by temperature-programmed desorption of ammonia (NH_3-TPD). Before the adsorption of ammonia at 100 °C, the samples were reduced at 400 °C using a flow of H_2 ($60\ mL\ min^{-1}$). The ammonia desorbed in the 100–550 °C range (heating rate of $10\ °C\ min^{-1}$) was analyzed by an on-line Shimadzu GC-14A gas chromatograph, provided with TCD.

H_2 chemisorption was performed in MICROMERITICS ASAP 2010 equipment, after the *in situ* reduction of samples at 450 °C for 1 h, under a flow of H_2. After reduction, the catalysts were degassed at 10^{-4} Pa for 10 h at the same temperature and cooled at 100 °C, to carry out the chemisorption of H_2. The range of pressure studied was 10–35 kPa and the amounts of H_2 chemisorbed were calculated by extrapolation of the isotherms to zero pressure. Dispersion data have been calculated by assuming a stoichiometry H/Pd, H/Rh and H/Pt = 1. TEM micrographs were performed by means of a Phillips CM-200 high-resolution transmission electron microscope. Previously, the reduced samples were embedded in *n*-hexane solution and suspended on a Cu grid of 3.5 mm in diameter.

2.3. Catalytic tests

Catalytic tests were performed at 6.0 MPa (if not otherwise specified $H_2/N_2 = 1/1$ v/v) and in the 220–340 °C range by using a stainless-steel tubular reactor (i.d. 8 mm, length 54 cm), heated by an electric oven controlled by two J thermocouples. The catalysts (6 cm^3, 14–20 mesh) were placed in the isothermal zone of the reactor. During the test, the catalyst temperature was controlled using a 0.5-mm J thermocouple by sliding a stainless-steel capillary tube inside the catalytic bed. Before the test, the catalyst was activated in a 200 mL/min flow of H_2, using a programmed increase in temperature from room up to 450 °C. The solution of naphthalene in *n*-heptane (10 wt.%) was fed in a gas flow of a H_2/N_2 mixture (if not otherwise specified 1/1 v/v) by using a HPLC Jasco 880-PU pump. Each catalytic test was performed for 5 h, collecting the products in a trap cooled to −10 °C after a preliminary period of 1 h under the same conditions, in order to achieve steady-state activity. The quantitative analysis of the reaction products was carried out using a Carlo Erba GC6000 gas chromatograph, equipped with FID and a widebore PS264 column (5% methylphenylsilicone, length 25 m, i.d. 0.53 mm, film width 1.5 μm). The products were preliminary and tentatively identified by GC-MS using a Hewlett-Packard GCD 1800 system equipped with a HP5 column (5% of methylphenylsilicone, length 25 m, i.d. 0.25 mm, film width 0.25 μm) and the experimental GC-MS patterns were compared with those present in the instrument library. Wide ranges of reaction conditions were investigated (temperature, contact time, H_2/naphthalene ratio). Furthermore, since all the hydrotreated feeds contain small amounts of sulfur compounds responsible for catalyst poisoning, the thio-tolerance of the catalysts was also investigated by feeding increasing amounts of dibenzothiophene (DBT), which is representative of the S-containing compounds usually present in industrial feeds.

3. Results and discussion

3.1. Catalyst characterisation

The average sizes of the Pd/Pt and Pd/Rh particles in the starting DEG suspensions measured by dynamic light scattering ranged between 70 and 170 nm (with polydispersion index values in the 0.250–0.440 range). The ICP analysis confirmed the scheduled total metal content in the catalysts, with atomic ratios similar to the theoretical ones (table 1). The textural parameters of the supports and the calcined and spent catalysts are showed in table 1. The N_2 adsorption isotherms were similar for all the samples and can be classified as type IV in the IUPAC classification, which is characteristic for mesoporous materials. The surface area and total pore volume of pelletized supports were 698 $m^2\ g^{-1}$ and 0.70 $cm^3\ g^{-1}$ for SiZr and 411 $m^2\ g^{-1}$ and 0.76 $cm^3\ g^{-1}$ for SiAl, respectively. As a general trend, the BET surface area and the pore volume hardly decreased by impregnation with the nanosized suspensions and following calcination, but the observed variations were not homogeneous and probably correlated to the formation of small quantity of coke during the solvent decomposition. Nevertheless, the high surface area values of the calcined catalysts indicate that nanoparticles did not block the pores of the supports. In the investigated samples, the pore size distributions were narrow with only a maximum centred in the region of mesoporous materials. The average diameter of the pores in the SiZr

Table 1
Composition and textural properties of the supports, Pd/Pt and Pd/Rh supported catalysts, before and after reaction

Sample	Pd/Pt(Rh) atomic ratio (experimental)	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (Å)
SiZr	–	698	0.70	40
SiAl	–	411	0.76	74
SiZr-1.0Pd/Rh-2[a]	2.1	678	0.75	44
SiZr-1.0Pd/Pt-4[a]	3.9	607	0.65	43
SiAl-1.0Pd/Pt-1[a]	1.9	365	0.66	72
SiAl-0.3Pd/Pt-5[a]	4.9	362	0.64	71
SiZr-1.0Pd/Rh-2[b]	n.d.	602	0.67	45
SiZr-1.0Pd/Pt-4[b]	n.d.	597	0.63	42
SiAl-0.3Pd/Pt-5[b]	n.d.	321	0.68	83

[a] Calcined catalysts.
[b] Catalysts after reaction.

support and derived calcined catalysts ranged between 40 and 44 Å, while for the SiAl support and its catalysts ranged between 71 and 74 Å. The spent catalysts showed further slightly decreased surface area values, probably due to either the adsorption of heavy compounds (tar) or a small sintering process during reduction and/or catalytic tests.

The XRD powder patterns in the $2\theta = 20–80°$ range showed – for all the calcined catalysts, together with the typical patterns of the support – week but well detectable diffraction peaks at 32.8, 55.0 and 60.9°; these peaks are characteristic of PdO and attributable to the partial oxidation of metal nanoparticles during calcination. In the case of the SiAl support, the XRD patterns show reflections also at 44.7 and 67.7° which are characteristic of Al_2O_3. After reaction, the catalysts showed the presence of metallic Pd and/or Pt particles too, since the diffraction peaks corresponding to the (111) planes of Pt and Pd overlapped ($2\theta = 39.8°$ and 40.1°, respectively).

The chemical state of the elements and their relative proportions have been determined by X-ray photoelectron spectroscopy (XPS). The energy regions of Si 2p, Zr $3d_{5/2}$, Pd $3d_{5/2}$ and Pt $4f_{5/2}$ were recorded for catalysts supported on SiZr, either calcined or reduced (table 2). The B.E. values of Si 2p and Zr 3d core electrons were practically constant and similar to those of the support. The direct measurement of both peak position and area of the Pd $3d_{5/2}$ peak was difficult, due to the overlapping of the Pd $3d_{5/2}$ core level with the intense peak of the Zr $3p_{3/2}$ component of the substrate centred at 333.4 eV. The B.E. of the Pd $3d_{5/2}$ level for the calcined samples appeared at 335.7–335.9 eV and was assigned to partially oxidized Pd (Pd $^{n+}$). After reduction this signal was slightly shifted to a lower B. E. (335.1 eV) pointing to the presence of Pd(0) [38]. The position of this peak coincided with that reported for silica-supported Pd [39] and also for bulk metal Pd [40]. For the SiZr-1.0Pd/Pt-4 catalyst, the peak in the core level of Pt $4f_{7/2}$, before and after reduction (figure 1a and b), was made up of two contributions at 71.3 (56.5 %) and 73.0 eV (43.5%) assigned to Pt(0) and Pt(II) respectively [38]. After reduction, the Pt $4f_{7/2}$ signal of Pt(0) increased in intensity with respect to that of Pt(II), slightly shifting to a lower B. E. (70.8 eV). The Rh 3d signal cannot be studied because it appeared poorly defined.

For the catalysts supported on SiAl the binding energies of Si 2p, Al 2p, Pd $3d_{5/2}$, Pt $4d_{5/2}$ were scanned. Although the most intense photoemission lines of Pt were those arising from Pt 4f core levels, this signal was overshadowed by the presence of the very strong Al 2p peak. Consequently, the energy region of the less intense Pt 4d peak was scanned (table 3). The spectra of the unreduced SiAl-0.3Pd/Pt-5 catalyst (figure 2a) contained a single and asymmetric peak centred at ca. 335.8 eV, which can be deconvoluted in two components at 336.2 and 334.9 eV. The first peak can be assigned to the presence of surface PdO, whereas the component at lower binding energy was due to metal Pd [38], confirming that PdO can be easily reduced during calcinations [41]. Once both Pd/Pt catalysts were reduced, the Pd 3d spectra were modified, showing a single peak at 335.1 eV of Pd(0) (figure 2b) [38]. As regards the Pt 4d, this region exhibits a single broad peak centred at ca. 314.6 eV for calcined materials that can be due to the presence of surface platinum oxide. After reduction the Pt 4d core level reveals the formation of surface metal Pt, since this signal is observed at low binding energy (314.1 eV) [38,42].

The metal surface area, metal dispersion and average metal particle size (determined by both H_2 chemisorption and TEM) of reduced and spent catalysts are reported in table 4. It is clear that a better metal dispersion and, hence, a lower particle size was achieved in the samples supported on SiAl. The catalysts supported on SiZr showed dispersion values lower than 7% and metal particles size higher than 10 nm, while those supported on SiAl presented dispersion values higher than 13% and metal particles size lower than 5 nm. Interestingly, this latter support featuring lower surface

Table 2

XPS data for the Pd/Pt and Pd/Rh on SiZr catalysts, before and after reduction at 450 °C for 1 h

	Binding Energy (eV)				
Sample	Si 2p	Zr $3d_{5/2}$	Pd $3d_{5/2}$	Pt $4f_{7/2}$	Rh $3d_{5/2}$
SiZr	103.4	182.8	–	–	–
SiZr-1.0Pd/Rh-2 [a]	103.3	182.8	335.7	–	i.d.
SiZr-1.0Pd/Pt-4 [a]	103.4	182.8	335.9	73.0 (43.5%) 71.3 (56.5%)	–
SiZr-1.0Pd/Rh-2 [b]	103.7	182.9	335.1	-	i.d.
SiZr-1.0Pd/Pt-4 [b]	103.7	182.3	335.1	72.8 (36.1%) 70.8 (69.7%)	-

i.d.: ill defined.

[a] Calcined catalysts.

[b] Catalysts reduced at 450 °C for 1 h.

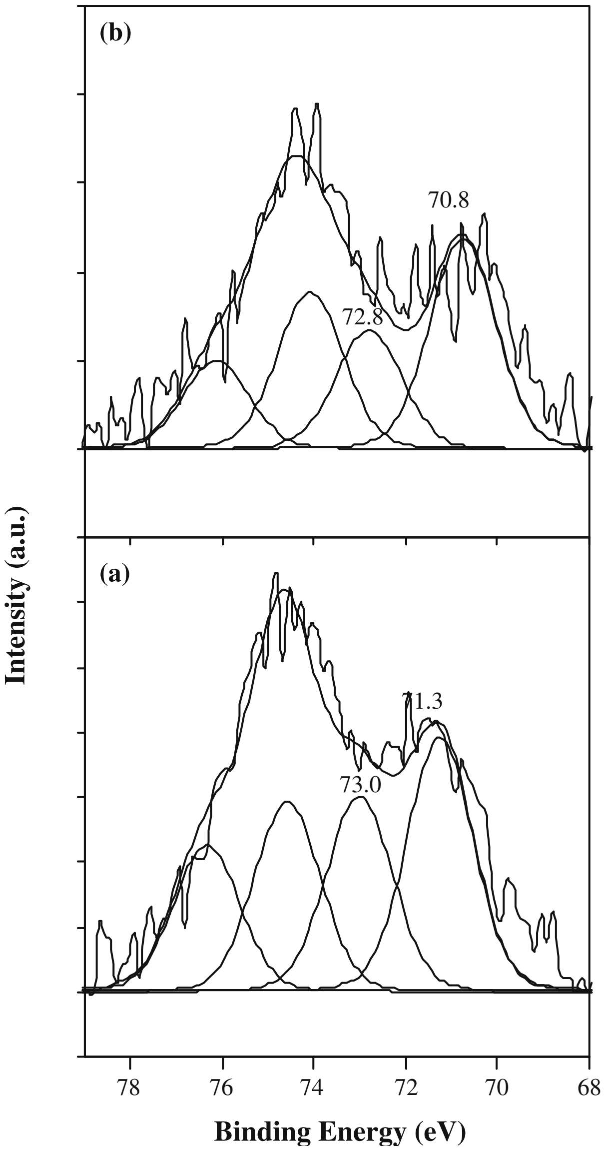

Figure 1. Pt 4f XPS spectra of (a) calcined and (b) reduced (at 450 °C for 1 h) SiZr-1.0Pd/Pt-4 catalyst.

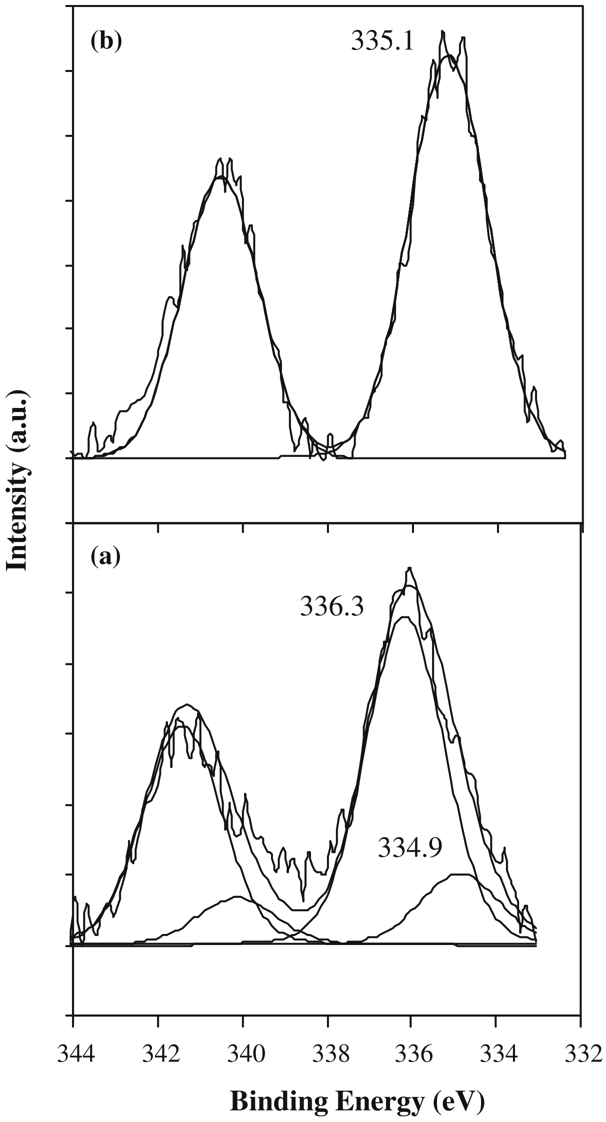

Figure 2. Pd 3d XPS spectra of (a) calcined and (b) reduced (at 450 °C for 1 h) SiAl-0.3Pd/Pt-5 catalyst.

Table 3
XPS data for the Pd/Pt on SiAl catalysts, before and after reduction at 450 °C for 1 h

	Binding Energy (eV)			
Sample	Si 2p	Al 2p	Pd $3d_{5/2}$	Pt $4d_{5/2}$
SiAl	102.7	74.3		
SiAl-1.0Pd/Pt-2 [a]	102.7	74.3	336.2 (82.2%) 334.9 (17.8%)	314.6
SiAl-0.3Pd/Pt-5 [a]	102.8	74.6	336.3 (64.7%) 334.9 (35.3%)	314.8
SiAl-1.0Pd/Pt-2 [b]	103.1	74.8	335.1	i.d.
SiAl-0.3Pd/Pt-5 [b]	103.2	74.7	335.1	314.1

i.d.: ill defined.
[a] Calcined catalysts.
[b] Catalysts reduced at 450 °C for 1 h.

Table 4
Metal dispersion, metal surface area and size of the metal particles for the catalysts after reduction (at 450 °C for 1 h) and after reaction, determined by H_2 chemisorption at 450 °C and TEM analysis

Catalyst	Metal dispersion (%)	Metal surface area		Metal particle size (nm)	
		($m^2\ g_{cat}^{-1}$)	($m^2\ g_{metal}^{-1}$)	H_2chemisorption	TEM
SiZr-1.0Pd/Rh-2 [a]	2.7	0.1	12.0	26.4	9.6
SiZr-1.0Pd/Pt-4 [a]	6.6	0.3	25.4	10.1	6.3
SiAl-1.0Pd/Pt-2 [a]	12.8	0.4	44.7	5.2	1.9
SiAl-0.3Pd/Pt-5 [a]	21.7	0.3	85.1	3.1	1.2
SiZr-1.0Pd/Rh-2 [b]	2.3	0.1	10.4	30.4	13.2
SiZr-1.0Pd/Pt-4 [b]	3.0	0.1	11.6	22.2	8.5
SiAl-0.3Pd/Pt-5 [b]	21.2	0.3	83.3	3.2	1.5

[a] Catalysts reduced at 450 °C for 1 h.
[b] Catalysts after reaction.

area, but higher acidity (see below), led to better dispersion of the metal particles. This result can be justified considering that DEG is very polar, so it has poor ability to form hydrogen bridges with the surface hydroxyl groups of the support. Therefore, thanks to a greater acidity, the SiAl support favoured a better interaction of the nanosized suspensions in DEG with the acid sites of the support leading to the formation of smaller particles [43]. In addition, a lower metal content gave rise to optimum metal dispersion and lowest metal particle size. However, the values of particle sizes lower than those determined by dynamic light scattering for the starting DEG suspensions, suggested the presence of particles aggregates. After the catalytic tests, all the catalysts showed slightly decreased dispersion and metallic surface area, but slightly increased metal particle sizes, thus suggesting a little sintering of the metal particles: This result, however, may be also attributed to the deposition of heavy products (tar) on the catalysts surface, which may partially hinder the metal to H_2 chemisorption [44].

TEM replica have been collected for some catalysts at two different stages: (i) reduced at 450 °C for 1 h; (ii) after catalytic tests. The micrographs of reduced and spent catalysts (figure 3) displayed metal particles within a medium range of sizes. For all catalysts the average diameter values of the metal particles were slightly lower than those estimated by H_2 chemisorption. However, the relative order of the metal particle sizes was maintained. After reaction, the mean diameter of the particles was slightly larger, thus confirming that a little metal sintering took place during the catalytic tests.

The surface acidity of the supports and reduced catalysts was determined by NH_3-TPD in the 100–550 °C range (table 5). NH_3 was employed since it has a sufficiently small cross-sectional area (0.141 nm^2) to enter all the pores. The strength of the acid sites can be related to the corresponding desorption temperatures. The SiZr catalysts had medium acidity (in fact the major percentage of desorbed NH_3 occurred between 200 and 400 °C), while the SiAl catalysts were more acid, desorbing an important amount of NH_3 in the 400–550 °C

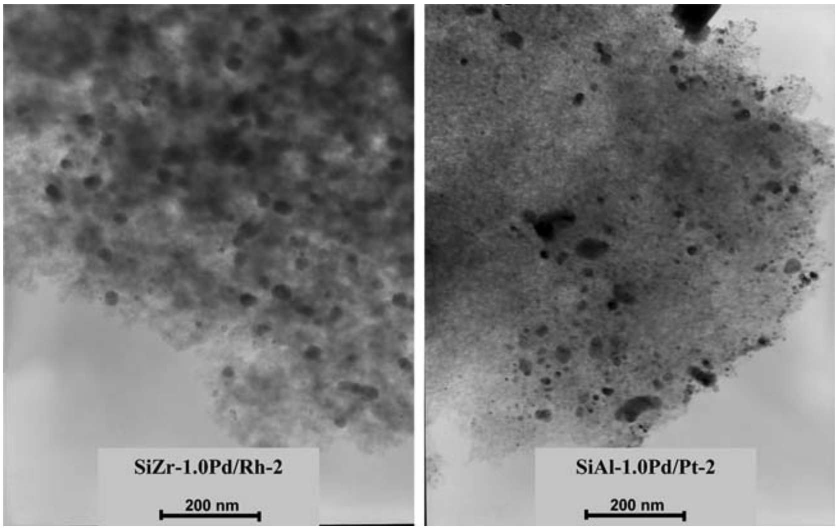

Figure 3. TEM micrographs for the SiZr-1.0Pd/Rh-2 and SiAl-1.0Pd/Pt-2 catalysts reduced at 450 °C for 1 h.

Table 5
Acid properties determined by NH_3-TPD for the different Pd/Pt and Pd/Rh catalysts reduced at 450 °C for 1 h

Sample	Acidity (μmol NH_3 g^{-1})				
	100–200 °C	200–300 °C	300–400 °C	400–550 °C	Total
SiZr	48	186	116	121	471
SiAl-40	77	235	176	254	742
SiZr-1.0Pd/Rh-2	55	147	70	56	327
SiZr-1.0Pd/Pt-4	18	139	84	57	298
SiAl-1.0Pd/Pt-2	51	180	147	202	580
SiAl-0.3Pd/Pt-5	90	252	193	294	829

range. The total acidity of the catalysts with 1.0 wt.% of metal content was lower than that of the corresponding supports. Interestingly, the catalyst SiAl-0.3Pd/Pt-5 showed a total acidity higher than that of the SiAl support. The lower acidity of the catalysts supported on SiZr may be due to the presence of bigger metal particles as well as to lower dispersion values: these large particles located on the surface may block the access of NH_3 molecules to the acid centres located in the internal surface of the pores.

3.2. *Catalytic results*

In the hydrogenation of naphthalene (in both the absence and the presence of DBT) a wide number of products were detected by gas chromatographic analysis. After the identification of the majority of them, they are classified into the following groups: (i) hydrogenation products that include tetralin (TeHN), produced by partial hydrogenation and *trans*- and *cis*-decalin (*t*- or *c*-DeHN), fully saturated products; (ii) high molecular weight products (H.M.W.) formed by hydrogenolysis / ring-opening and/or further alkylation reactions from TeHN or DeHN; (iii) light molecular weight products (L.H.W.) produced by cracking reactions that include non-condensable products, which were calculated from the carbon balance (C balance) of the reaction (figure 4) [45,46].

In the catalytic tests at different reaction temperatures (table 6) all the catalysts investigated did not fully convert naphthalene, although they attained high conversion values ($>80\%$). In general, as the temperature rose, the conversion decreased due to thermodynamic restrictions, since the hydrogenation reaction is exothermic [47,48]. For the catalysts supported on SiZr (SiZr-1.0Pd/Rh-2 and SiZr-1.0Pd/Pt-4), not only the hydrogenation activity decreased with the temperature, but also the production of different hydrogenation products was affected, thus favouring the formation of the partially hydrogenated tetralin to the detriment of the fully hydrogenated decalin (*trans* + *cis*). Both catalysts were active mainly in the hydrogenation reaction since the yield in H.M.W. compounds was low also at 340 °C, where the hydrogenolysis/ring-opening reactions are favoured [49,50]. This behaviour may be mainly attributed to the low acidity of these catalysts, in agreement with the literature [51,52], although the contribution of the large metal particles located on the surface, which may block the access of naphthalene to the acid sites present in the pores of the support, cannot be excluded. It is noteworthy that the catalyst SiZr-1.0Pd/Pt-4 showed poorer performance in the hydrogenation reaction and, mainly, in the formation of H.M.W. products, than a similar catalyst prepared by incipient wetness impregnation of the same support with a solution of metal salts [46,53].

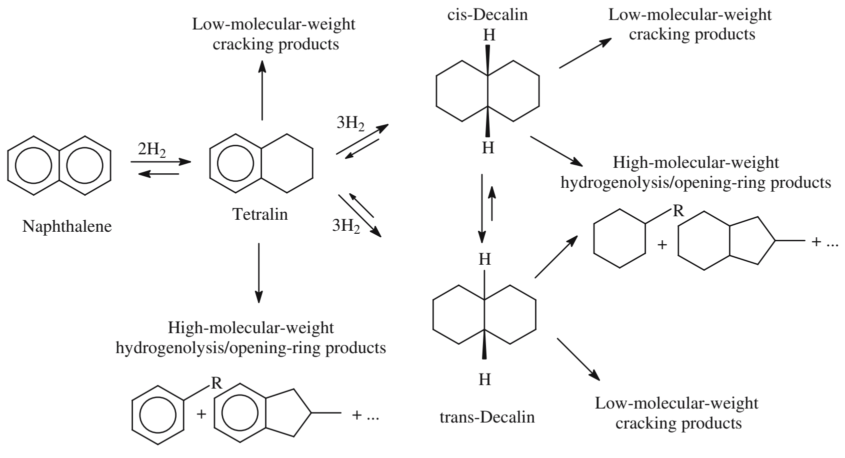

Figure 4. Proposed reaction pathway for the hydrogenation and/or hydrogenolysis/opening ring of naphthalene at high pressure [45, 46].

Table 6
Naphthalene conversion and yields in the different products as a function of the temperature

Catalyst	Temp. (°C)	Conv. (%)	TeHN (yield %)	*t*-DeHN (yield %)	*c*-DeHN (yield %)	H.M.W (yield %)	C balance (Δ%)
SiZr-1.0Pd/Rh-2	260	90.0	12.0	63.2	11.7	0.8	−2.2
	300	85.9	12.7	46.2	10.6	2.3	−14.1
	340	80.3	48.9	10.9	2.8	2.9	−14.8
SiZr-1.0Pd/Pt-4	260	87.4	12.5	59.6	12.3	1.0	−2.0
	300	83.1	85.0	3.6	2.3	1.5	+9.3
	340	81.3	76.2	4.9	2.5	4.4	+6.7
SiAl-1.0Pd/Pt-2	260	89.0	16.2	53.9	8.5	4.7	−5.7
	300	87.1	9.9	34.9	6.3	20.3	−15.7
	340	84.9	8.3	15.5	2.3	31.4	−27.4
SiAl-0.3Pd/Pt-5	260	91.0	14.9	55.5	9.8	5.7	+5.1
	300	89.7	7.1	50.5	6.5	16.2	−9.4
	340	87.6	5.4	19.7	2.2	41.7	−18.6

Experimental conditions: LHSV = 1.0 h^{-1}; contact time = 6.8 s; H_2/naphthalene molar ratio = 21.0; P = 6.0 MPa (H_2/N_2 = 1:1 v/v).

Also the catalysts supported on SiAl (SiAl-1.0Pd/Pt-2 and SiAl-0.3Pd/Pt-5) showed good yields in decalin that decreased by increasing the reaction temperature, although for these catalysts increasing yields in H.M.W. products were obtained, in agreement with the endothermic character of the C–C bond cleavage [47,51]. At 340 °C both catalysts presented very high yield values in H.M.W. products (31.4 and 41.7%), although the highest losses in the C balance were also detected.

These results show that the catalytic activity strongly depends on both the metal dispersion and support acidity. SiAl-based catalysts present metal particles ranging from 3.1 to 5.2 nm and higher acidity values (580–829 μmol NH_3 g^{-1}); the aromatic molecules are adsorbed on the acid sites of the support close to metal particles, where they react with H_2 activated by spillover [52,54]. Interestingly, the catalyst with the lower metal content (SiAl-0.3Pd/Pt-5) displays the better performance in the entire range of temperatures investigated. Its activity at 340 °C is noticeable as evidenced by high conversion and good balance between the yield in hydrogenation products (27.3% decalin + tetralin) and H.M.W. products (41.7%). The catalytic results match well the surface properties of this catalyst, since it has best metal dispersion and highest surface acidity.

To optimize the reaction conditions, the two best catalysts identified (SiAl-1.0Pd/Pt-2 and SiAl-0.3Pd/Pt-5) were selected to study the influence of the experimental conditions on the catalytic performance at 300 °C. Figure 5 shows the evolution of the conversion and yield values when the contact time was increased from 1.8 to 6.8 s by decreasing the gas hourly space velocity (GHSV). For both catalysts, the decreased contact time – while giving rise to a slightly enhanced naphthalene conversion – boosted the formation of the partially hydrogenated tetralin together with a decreased yield in both decalin (trans + cis) and, to a lesser extent, HMW products. These results show that, at low contact times, partially hydrogenated product TeHN did not stay long enough on the active sites for the following hydrogenation and hydrogenolysis/ring-opening reactions.

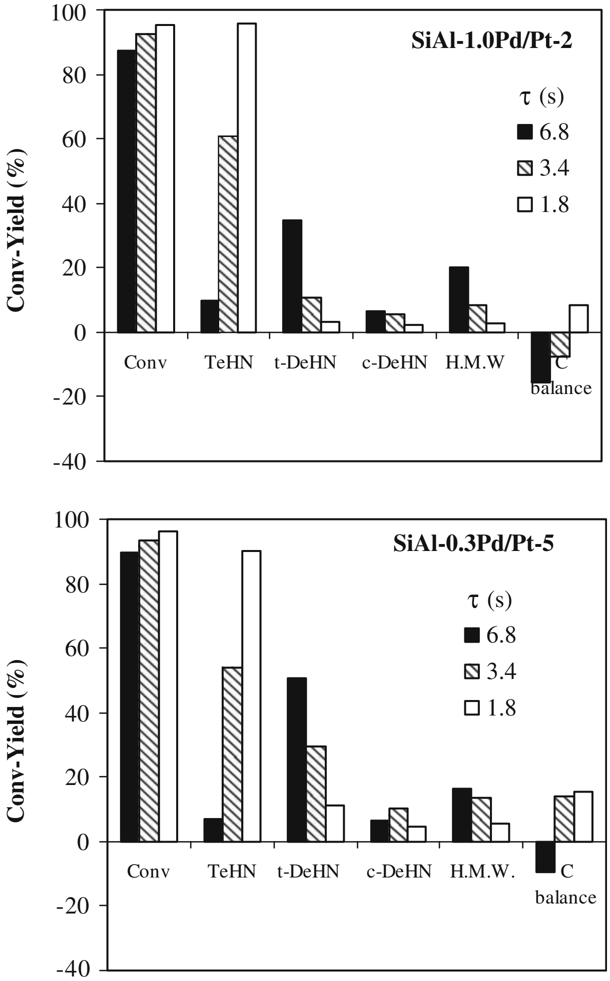

Figure 5. Naphthalene conversion and yields in the different products as a function of contact time (τ) for the SiAl-1.0Pd/Pt-2 and SiAl-0.3Pd/Pt-5 catalysts. Experimental conditions: T = 450 °C; LHSV = 1.0 h^{-1}; H_2/naphthalene molar ratio = 21.0; P = 6.0 MPa (H_2/N_2 = 1:1 v/v).

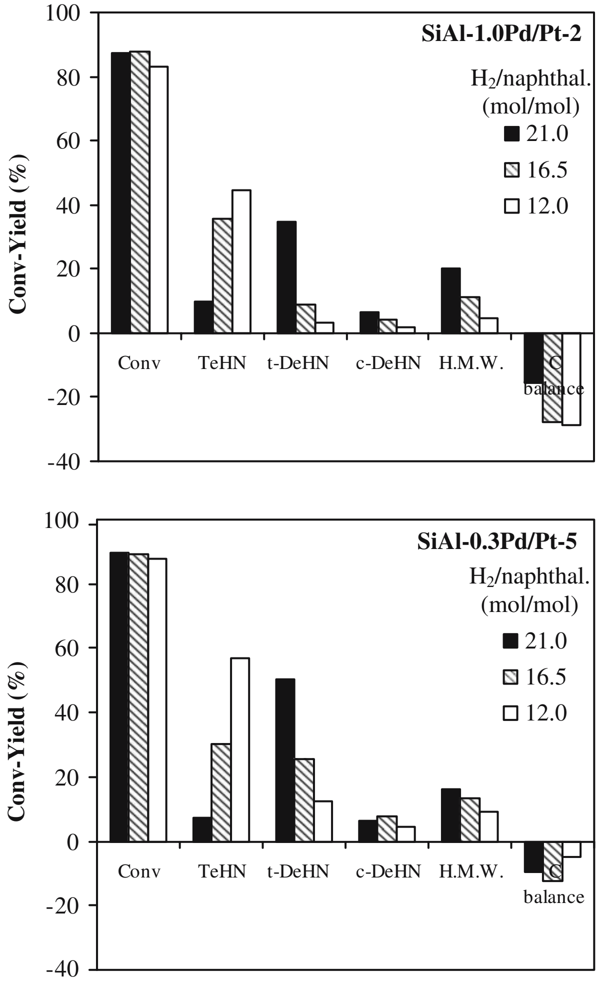

Figure 6. Naphthalene conversion and yields in the different products as a function of H_2/naphthalene molar ratio for the SiAl-1.0Pd/Pt-2 and SiAl-0.3Pd/Pt-5 catalysts. Experimental conditions: T = 450 °C; LHSV = 1.0 h^{-1}; contact time = 6.8 s; P = 6.0 MPa (H_2/N_2 = 1:1 v/v).

The effect of the H_2/naphthalene molar ratio in the feed was studied by decreasing the H_2 flow and adding a corresponding amount of N_2 in order to maintain constant contact time (6.8 s) (figure 6). The decrease in the H_2/naphthalene molar ratio from 21.0 to 12.0 hardly changes the conversion of naphthalene, but worsened significantly the catalytic performances with increasing amounts of tetralin formed. On the contrary, the full hydrogenation and hydrogenolysis/ring-opening activities dramatically decreased, showing that a H_2 excess 3–4 times higher than the stoichiometric molar ratio (i.e. H_2/naphthalene = 5.0) is necessary to overcome thermodynamic limitations [47,48].

The thio-tolerance is an important aspect for industrial applications of hydrogenation catalysts: although feeds are usually hydrotreated before hydrogenation over noble-metal-containing catalysts, low amounts of S-compounds in the feeds are inevitable in industrial practice. So, catalysts were tested with increasing amounts of DBT in the feed (100, 1000 and 3000 wt ppm corresponding to 17, 170 and 510 wt ppm of sulphur, respectively). The higher amount corresponds to DBT present in LCO fractions, while the lower content to DBT present in deeply HDS fractions. The catalyst SiZr-1.0Pd/Rh-2 showed a decreased naphtahlene conversion while increasing the amount of DBT in the feed, with a dramatically decreased yield in decalin and a corresponding increased yield in tetralin (table 7). This catalyst showed a poor thio-tolerance even for low amounts of DBT and the poisoning was not reversible; in fact, when removing DBT from the feed the sample did not recover its initial catalytic activity. The two catalysts on SiAl support (SiAl-1.0Pd/Pt-2 and SiAl-0.3Pd/Pt-5 exhibited better performances, with a slight change in naphthalene conversion while increasing the amount of DBT fed. However, also for these catalysts, DBT worsened both hydrogenation and

Table 7

Naphthalene conversion and yields in the different products as a function of the DBT content in the feed

Catalyst	DBT (wt. ppm)	Conv. (%)	TeHN (yield %)	*t*-DeHN (yield %)	*c*-DeHN (yield %)	H.M.W. (yield %)	C balance (Δ%)
SiZr-1.0Pd/Rh-2	0	85.9	12.7	46.2	10.6	2.3	−14.1
	100	81.5	68.8	1.2	0.5	0.7	−10.3
	1000	78.6	65.7	0.6	0.3	0.6	−11.4
	3000	67.9	53.7	0.2	0.1	0.4	−13.5
	0	74.5	86.2	0.3	0.6	0.7	+ 13.3
SiAl-1.0Pd/Pt-2	0	87.1	9.9	34.9	6.3	20.3	−15.7
	100	80.5	51.2	7.2	4.5	7.2	−10.4
	1000	84.6	43.1	4.2	2.4	4.8	−30.1
	3000	89.9	37.9	1.5	0.9	2.3	−47.3
	0	83.3	50.9	6.2	3.6	8.1	−14.5
SiAl-0.3Pd/Pt-5	0	89.7	7.1	50.5	6.5	16.2	−9.4
	100	88.0	31.9	28.7	9.1	12.7	−5.6
	1000	89.3	41.0	20.4	7.3	11.7	−8.9
	3000	90.7	52.7	11.3	4.6	8.8	−13.3
	0	89.2	31.6	25.8	8.4	13.0	−10.4

Experimental conditions: *T* = 300 °C; LHSV = 1.0 h^{-1}; contact time = 6.8 s; H_2/naphthalene molar ratio = 21.0; P = 6.0 MPa (H_2/N_2 = 1:1 v/v).

hydrogenolysis/ring-opening activities, with a significant increase in the TeHN formation. Again, the initial values could not be restored, although the SiAl-0.3Pd/Pt-5 catalyst showed better recovery in activity after removing DBT from the feed.

The spent catalysts were investigated by H_2-chemisorption, XPS and microchemical analysis. The H_2-chemisorption showed slightly increased particle sizes, thus evidencing a little sintering of metal particles. In general, catalyst deactivation by S-compounds did not occur, because the S-content detected by XPS or microchemical analysis was nil, with the exception of the catalyst SiZr-1.0Pd/Rh-2 for which traces of S were detected (0.021 wt.%). Therefore, the deactivation of these catalysts may be mainly attributed to the deposition of coke. The enhanced thio-tolerance for noble metals on acid supports has been related to modifications in the electronic properties of the metal atoms resulting from the interaction with the acid sites of the support (electron acceptor) [55,56]. So, the catalyst with lower acidity and larger metal particles, SiZr-1.0Pd/Rh-2 had lower thio-tolerance, while the more acid catalyst featuring smaller metal particles exhibited the best thio-tolerance. In this family of catalysts, the formation of electron-deficient metal sites, which lowered the strength of S-metal bonds, may be attributed mainly to the acidity of the support than to an alloy formation.

4. Conclusions

The use of metal-nanoparticle suspensions in such a polar support as DEG for the preparation of supported Pd/Pt and Pd/Rh catalysts by incipient wetness impregnation, requires supports with high acidity: the latter, in fact, favours the interactions of the metal particles with the acid sites of the support, due to the low ability of the solvent to form hydrogen bridges with the surface hydroxyl groups. On the other hand, when the catalysts are prepared by impregnation of DEG suspension of nanometric particles, a low metal content is needed to obtain a catalyst with a high activity and selectivity in the wished for products. In fact, also relatively high metal contents may favour an agglomeration of particles, that not only worsen the hydrogenation activity, but may hinder the access to the acid sites inside the pores, thus decreasing the hydrogenolisis/ring-opening activity.

The best results have been obtained with catalysts supported on acid commercial mesoporous silica–alumina; especially a catalyst having a very low metal content (0.3 wt.%) (SiAl-0.3Pd/Pt-5) showed good performances in the hydrogenation and hydrogenolysis/ring-opening of naphthalene at high H_2 pressure. At 340 °C, this catalyst exhibited a 88.0% naphthalene conversion , together with a high yield in the industrially appealing H.M.W. products (41.7%). This catalyst also showed a relatively good thio-tolerance, because the naphthalene conversion hardly decreasedon increasing the amount of DBT in the feed, although the hydrogenation and hydrogenolysis/ring-opening activities worsened. These catalytic performances may be attributed to suitable metal and acid properties, such as a tailored acidity and a high metal surface area due to the presence of small bimetallic particles.

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References

[1] S. Rossino, Catal. Today 77 (2003) 467.

[2] B.I. Bertelsen, Topics in Catalysis 16–17 (2001) 15.

[3] J.P. van der Berg, J.P. Lucien, G. Germaine and G.L.B. Thielemans, Fuel Process Technol. 35 (1993) 119.

[4] A. Stanislaus and B.H. Cooper, Catal. Rev. Sci. Eng. 36 (1994) 75.

[5] M.J. Girgis and B.C. Gates, Ind. Eng. Chem. Res. 30 (2001) 1991.

[6] K. Salanishi, M. Ohira, I. Mochida, H. Okazaki and M. Soeda, Bull. Chem. Soc. Jpn. 62 (1989) 3994.

[7] Th.J. Nieuwstad, P. Klapwijk and H. van Bekkum, J. Catal. 29 (1973) 404.

[8] C.H. Bartholomew, P.K. Agrawal and J.R. Katzer, Adv. Catal. 31 (1992) 135.

[9] J. Barbier, E. Lamy-Pitara, P. Marecot, J.P. Boitiaux, J. Cosyns and F. Verna, Adv. Catal. 37 (1990) 279.

[10] B.H. Cooper and B.B.L. Donnis, Appl. Catal. A A137 (1996) 203.

[11] M.M. Telkar, C.V. Rode, R.V. Chaudhari, S.S. Joshi and A.M. Nalawade, Appl. Catal. A A273 (2004) 11.

[12] S. Mandal, D. Roy, R.V. Chaudhari and M. Sastry, Chem. Mater. 16 (2004) 3714.

[13] G. Viau, P. Toneguzzo, A. Perrard, O. Acher, F. Fièvet-Vincent and F. Fievet, Scripta Mat. 44 (2001) 2263.

[14] N. Chakroune, G. Viau, C. Ricolleau, F. Fièvet-Vincent and F. Fievet, J. Mater. Chem. 13 (2003) 312.

[15] G. Viau, P. Toneguzzo, F. Guillet, E. Bruneton, O. Acher, F. Fièvet-Vincent and F. Fievet, J. Mater. Sci. 35 (2000) 3767.

[16] E.A. Sales, B. Benhamida, Virginie Caizergues, Jean-Pierre Lagier, F. Fievet and F. Bozon-Verduraz, Appl. Catal. A A172 (1998) 273.

[17] R. Brayner, G. Viau, G.M. da Cruz, F. Fievet-Vincent, F. Fievet and F. Bozon-Verduraz, Catal. Today 57 (2000) 187.

[18] A. Corma, A. Martinez and V. Martinez-Soria, J. Catal. 153 (1995) 25.

[19] A. Corma, A. Martinez and V. Martinez-Soria, J. Catal. 169 (1997) 480.

[20] C. Song and K.M. Reddy, Appl. Catal. A 176 (1999) 1.

[21] A. Wang, Y. Wang, T. Kabe, Y. Chen, A. Ishihara and W. Qiam, J. Catal. 199 (2001) 19.

[22] T. Klimova, E. Rodriguez, M. Martinez and J. Ramirez, Microp. Mesop. Mater. 44–45 (2001) 357.

[23] K.C. Park, D.J. Win and S.K. Ihm, Catal. Today 74 (2002) 281.

[24] D.J. Jones, J. Jiménez-Jiménez, A. Jiménez-López, P. Maireles-Torres, P. Olivera-Pastor, E. Rodriguez-Castellón and J. Roziére, Chem. Commun. (1997) 431.

[25] C.T. Kresge, M.E. Leonowiczz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.

[26] J. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schimitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[27] C.Y. Chen, S.L. Burket, H.X. Li and M.E. David, Microp. Mater. 2 (1993) 21.

[28] A. Corma, V. Fornés, M.T. Navarro and J. Pérez-Pariente, J. Catal. 148 (1994) 569.

[29] R. Schmidt, H. Junggreen and M. Stocker, J. Chem. Soc. Chem. Commun. (1996) 875.

[30] E. Rodriguez-Castellón, A. Jiménez-López, P. Maireles-Torres, D.J. Jones, J. Rozière, M. Trombetta, G. Busca, M. Lenarda and L. Storaro, J. Solid State Chem. 175 (2003) 159.

[31] O.C. Bianchi, M. Campanati, P. Maireles-Torres, A. Jiménez-López and A. Vaccari, Appl. Catal. A 220 (2001) 105.

[32] G. Cocco, R. Campostrini, M.A. Cabras and G. Carturan, J. Mol. Catal. A:Chemical 94 (1994) 229.

[33] S.D. Jackson, G.D. McLellan, G. Webb, L. Conyers, B.T. Keegan, S. Mather, S. Simpson, P.B. Wells, D.A. Whan and R. Whyman, J. Catal. 162 (1996) 10.

[34] M. Englisch, A. Jentys and J.A. Lercher, J. Catal. (1997) 166.

[35] G. Jacobs, F. Ghadiali, A. Pisanu, A. Borgna, W. Alvarez and D.E. Resasco, Appl. Catal. A A188 (1999) 79.

[36] A. Jiménez-López, E. Rodríguez-Castellón, P. Maireles-Torres, L. Díaz and Mérida-Robles, J. Appl. Catal. A A218 (2001) 295.

[37] G. Baldi, A. Barzanti and M. Bitossi, PCT 076,521 A1 (2003) to Colorobbia Italia SpA.

[38] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: *A Reference Book of Standard Spectra for Identification and Interpretation of XPS data*, (ed.) J. Chastain, (Perkin-Elmer Co., MN, USA, 1992).

[39] T.H. Fleisch, R.F. Hicks and A.T. Bell, J. Catal. 87 (1984) 398.

[40] V. I. Nefedov, X-ray Photoelectron Spectroscopy of Chemical Compounds, (Khimia, Moscow, Russia, 1984) p. 26.

[41] F. Basile, G. Fornasari, M. Gazzano and A. Vaccari, App. Clay Sci. 18 (2001) 51.

[42] L. Fiermans, R. De Gryse, G. De Doncker, P.A. Jacobs and J.A. Martens, J. Catal. 193 (2000) 108.

[43] E. van Steen, G.S. Sewell, R.A. Makhothe, C. Micklethwaite, H. Manstein, M. de Lange and C.T. O'Connor, J. Catal. 162 (1996) 220.

[44] M. Mandreoli, A. Vaccari, E. Veggetti, M. Jacquin, D.J. Jones and J. Roziere, Appl. Catal. A A231 (2002) 263.

[45] S. Albertazzi, G. Busca, E. Finocchio, R. Glöckler and A. Vaccari, J. Catal. 223 (2004) 372.

[46] S. Albertazzi, E. Rodríguez-Castellón, M. Livi, A. Jiménez-López and A. Vaccari, J. Catal. 228 (2004) 218.

[47] A. Corma, V. Gonzalez-Alfaro and A.V. Orchilles, J. Catal. 169 (1997) 1.

[48] T. Fujikawa, K. Idei, T. Ebihara, H. Mizuguchi and K. Usui, Appl. Catal. A 192 (2000) 253.

[49] L. Le Bihan and Y. Yoshimura, Fuel 81 (2002) 491.

[50] H. Yasuda and Y. Yoshimura, Catal. Lett. 46 (1997) 43.

[51] D. Kubička, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, H. Karhu, T. Salmi and D.Y. Murzin, J. Catal. 227 (2004) 65.

[52] D. Kubička, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, H. Karhu, T. Salmi and D.Y. Murzin, J. Catal. 227 (2004) 313.

[53] E. Rodriguez-Castellón, J. Mérida-Robles, L. Díaz, P. Maireles-Torres, D.J. Jones, J. Rozière and A. Jímenez-López, Appl. Catal. A 260 (2004) 9.

[54] K. Thomas, C. Binet, T. Chewreau, D. Cornet and J.P. Gilson, J. Catal. 212 (2002) 63.

[55] S.T. Homeyer and W.M.H. Sachtler, J. Catal. 117 (1989) 91.

[56] W.M.H. Sachler and A.Y. Stakheev, Catal. Today 12 (1992) 283.