Hydrogenation of naphthalene on noble-metal-containing mesoporous MCM-41 aluminosilicates

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Abstract

Aromatic saturation of oil fractions is a key process in the refining industry due to increasing demand for cleanest distillates with superior performances. In this study, the behavior of different catalysts containing 1 wt.% of noble-metal inside a mesoporous MCM-41 (Si:Al = 20) framework was investigated in the hydrogenation of naphthalene, as preliminary step to investigate bimetallic catalysts. While at atmospheric pressure only Rh and Pd showed a low hydrogenation activity, in the tests performed at 6.0 MPa the catalytic activity grew, exhibiting the following order: $Pt > Rh \gg Pd \ggg Ru \approx Ir$. However, all the catalysts required a large H_2 excess, to avoid a decrease in hydrogenation and ring-opening activity, and gave rise to the best performance for a contact time of 6.8 s, favouring at lower values the partial hydrogenation to tetralin and at higher values cracking reactions. Finally, all the catalysts showed low thio-tolerance, with significant deactivation already feeding 100 ppm wt. of dibenzothiophene (DBT), with a partial reversibility only for the Pt-containing catalyst (CAT 3).
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1. Introduction

Dearomatization of oil fractions has become a key process in the modern refining industry due to increasing environmental concerns, which has increased the demand for cleanest distillates [1]. Furthermore, the reduction of the aromatic content has a positive effect on the cetane number [2], thus further decreasing the extent of particulate emission in diesel exhaust gases [3]. The aromatic content of diesel feeds can vary widely: (i) straight-run stocks typically contain 20–40 vol.% aromatics and cracked stocks 40–70 vol.%. Thus, requirements for aromatic saturation range from moderate to severe depending on refinery location and feedstock availability [4,5]. Existing middle-distillate hydrotreaters designed to reduce sulphur level can reduce aromatic content only marginally [6,7], thus considerable attention has, in recent years, paid to catalysts and processes for aromatic saturation. The catalyst systems investigated were:

(1) Conventional hydrotreating catalysts in single-stage operation (high H_2 pressure).
(2) NiMo/NiW in two-stage operation (moderate H_2 pressure).

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(3) Pt/alumina in two-stage operation.
(4) S-tolerant noble-metal (Pd and/or Pt) catalysts in two-stage operation.

Taking into account the key role of the pore size and distribution in the support, that affects the metal dispersion and the diffusion of the voluminous feed molecules, many efforts have been devoted to investigate a new family of mesoporous molecular sieves named MCM-41. In these supports, the acidity and dimensions of the uniform system of channels can be tailored by selecting the Si:Al ratio and the dimension of the template, respectively. Anyway, they exhibit acidic OH groups of lower strength than those in zeolites [8]. Aim of this study was to investigate preliminary the behaviour of single noble-metal ions inserted in a mesoporous MCM-41 aluminosilicate framework, to obtain after reduction high dispersion and stability of the metal particles. Furthermore, this may supply useful information on the behaviour of bimetallic catalysts, claimed as active and stable in dearomatization and ring-opening reactions [9–12].

2. Experimental

Noble-metal-containing aluminosilicate mesoporous MCM-41 catalysts were prepared with a Si:Al = 20 ratio and containing 1 wt.% (referred to the catalyst weight) of Rh^{3+}, Ru^{3+}, Pd^{2+}, Pt^{2+} or Ir^{3+} ions. To prepare the different samples, the synthesis reported by Beck et al. [13,14] using basic templates was employed. The required amount of sodium aluminate was added to a 25 wt.% solution of cetyltrimethylammonium chloride [$CH_3(CH_2)_{15}NCl(CH_3)_3$], stirring the mixture for 0.5 h and then adding the solution of the salt of the noble-metal ion [$RhCl_3 \cdot xH_2O$, $RuCl_3 \cdot xH_2O$; Pt(II) acetylacetonate; Pd(II) acetylacetonate or $IrCl_3$]. After 1 h, the 15–20 wt.% solution of tetramethylammonium silicate [$(CH_3)_4NOH \cdot 2SiO_2$] and the fumed silica were added. The mixture was stirred for 3–4 h at room temperature and then placed in an autoclave and heated at 150 °C for 48 h. After cooling at room temperature, the resulting solid was recovered by filtration, washed with water, dried in air at room temperature and calcined at 540 °C for 7 h.

The XRD analysis was performed using a Philips PW 1050/81 goniometer, equipped with a PW 1710 unit, and Cu Kα radiation (λ = 0.15418 nm). Two intervals of 2θ were investigated: at 2θ = 1.5–8.0° to verify the presence of an ordered hexagonal mesoporous structure and at 2θ = 8.0–80.0° to determine the presence of metal and/or oxide segregated. Surface area, pore volume and distribution were obtained by N_2 adsorption using a Carlo Erba 1900 Sorptomatic, after outgassing the samples at 200 °C in vacuum. H_2 chemisorption was performed using a Micrometrics ASAP 2010C instrument: the samples were preliminary cleaned under a He flow, evacuated and reduced with H_2 at 500 °C.

The catalytic hydrogenation of naphthalene at atmospheric pressure was performed at 200 and 300 °C, using ca. 500 mg of catalyst (80–100 mesh), previously reduced in H_2 flow, and a glass tubular reactor directly connected to a Hewlett-Packard 5890 gas-chromatograph for the on-line analysis of the reaction products. The catalytic tests at high pressure were performed at 6.0 MPa and in the 220–340 °C range using a stainless steel tubular reactor (i.d. 8 mm, length 54 cm), heated by an electric oven controlled by two J-thermocouples. 6 cm³ of catalyst (14–20 mesh) were employed, located in the isothermal zone of the reactor. During the tests, the catalyst temperature was controlled using a 0.5 mm J-thermocouple sliding in a stainless steel capillary tube inside the catalytic bed. Before the tests, the catalyst was activated in a 200 ml/min H_2 flow, using a programmed increase of the temperature from room temperature to 450 °C. The solution of naphthalene in *n*-heptane (10 wt.%) was fed using a HPLC Jasco 880-PU pump, in a gas flow of H_2/N_2 mixture. Each catalytic test was performed for 5 h, collecting the products in a trap cooled at −10 °C after a preliminary 1.5 h period under the same conditions to achieve steady state activity. The analysis of the reaction products was carried out using a Carlo Erba GC6000 gas-chromatograph, equipped with FID and a PS264 column (5% methylphenylsilicone, length 25 m, i.d. 0.53 mm, film width 1.5 μm) comparing the GC patterns with those obtained for pure reference compounds. The products were preliminary 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) comparing the experimental GC–MS patterns with those present in the instrument library. Wide ranges of reaction conditions were investigated

(temperature, contact time, H_2:organic feed ratio); furthermore, since all the hydrotreated feeds contain small amounts of sulphur compounds responsible for the catalyst poisoning, the thio-resistance of the catalysts was also investigated feeding increasing amounts of dibenzothiophene (DBT), representative for the S-containing molecules usually present in the industrial feeds.

3. Results and discussion

3.1. Characterization of the samples

All the calcined samples showed in the $2\theta = 1.5$–$8.0°$ range XRD powder patterns typical of ordered MCM-41 hexagonal phases (Fig. 1A). Moreover, with exception of the Rh-containing sample (CAT 1), all other samples showed also in the $2\theta = 8.0$–$80.0°$ range the presence of segregated phases (metal or oxide) (Fig. 2A). Thus, among the different metal ions investigated only the Rh^{3+} ions were completely inserted in the silicoaluminate MCM-41 structure, replacing partially the Al^{3+} ions. The absence of segregated phases did not lead to a higher surface area, but only to a slightly higher pore volume (Table 1); however, in agreement with the absence of segregated phases, the Rh-containing sample showed the highest metal dispersion value. With the exception of the Pd-containing catalyst (CAT 4), after the hydrogenation tests at 6.0 MPa, all the catalysts showed the presence of segregated metal phases (Fig. 2B), with a general decrease of the cristallinity of the MCM-41 mesoporous structure (Fig. 1B). However, they maintained high surface areas, although the total pore volume decreased significantly and the metal

dispersion was always equal to zero. Since the XRD powder patterns did not evidence any significant sintering of the metal particles, this latter result may mainly be attributed to the deposition of heavy products (tar) on the catalyst surface, that may occlude the metal to H_2 chemisorption [15].

3.2. Catalytic activity at atmospheric pressure

CAT 1 (Rh-containing) and CAT 4 (Pd-containing) exhibited dramatic decrease of the naphthalene conversion values by increasing the reaction temperature, due to the thermodynamic constraints of the reaction (Fig. 3). With the Rh-containing sample the partially hydrogenated tetralin (1,2,3,4-tetrahydronaphthalene) was the main product already at 200 °C, together with a small amount (ca. 5%) of the fully hydrogenated decalins (*cis* and *trans*) (decahydronaphthalene or DeHN). At 300 °C the fully hydrogenated products were not more detected, while, together with tetralin, traces of high-molecular-weight (HMW) ring-opening products and low-molecular-weight (LMW) cracking products were formed. The Pd-containing catalyst formed at 200 °C only tetralin, while at 300 °C were present traces of decalins (ca. 1%), but not the HMW or LMW products. On the other hand, the catalytic activity of the other three samples (i.e. CAT 2, CAT 3 and CAT 5 containing, respectively, Ru, Pt and Ir) set to zero after the first few minutes of time-on-stream at both the temperatures investigated.

3.3. Catalytic activity at high pressure

The Ru- and Ir-containing (CAT 2 and CAT 5) samples showed a very rapid deactivation, loosing

Table 1

Characterization of the noble-metal-containing MCM-41 catalysts investigated (Si:Al = 20 and 1 wt.% of noble-metal) before and after the catalytic tests

Sample	Noble-metal	Surface area (m²/g)		Pore volume (cm³/g)		Metal dispersion (%)		Segregated phases detected by XRD	
		A[a]	B[b]	A	B	A	B	A	B
CAT 1	Rh	734	739	1.41	0.96	12	0	–	Rh
CAT 2	Ru	767	802	1.00	0.67	<1	0	RuO_2	Ru
CAT 3	Pt	833	676	1.28	0.77	2	0	Pt	Pt
CAT 4	Pd	826	761	0.92	0.63	2	0	PdO	–
CAT 5	Ir	763	775	0.91	0.65	<1	0	IrO_2	Ir

[a] A: Before the catalytic tests at 6.0 MPa.
[b] B: After the catalytic tests at 6.0 MPa.
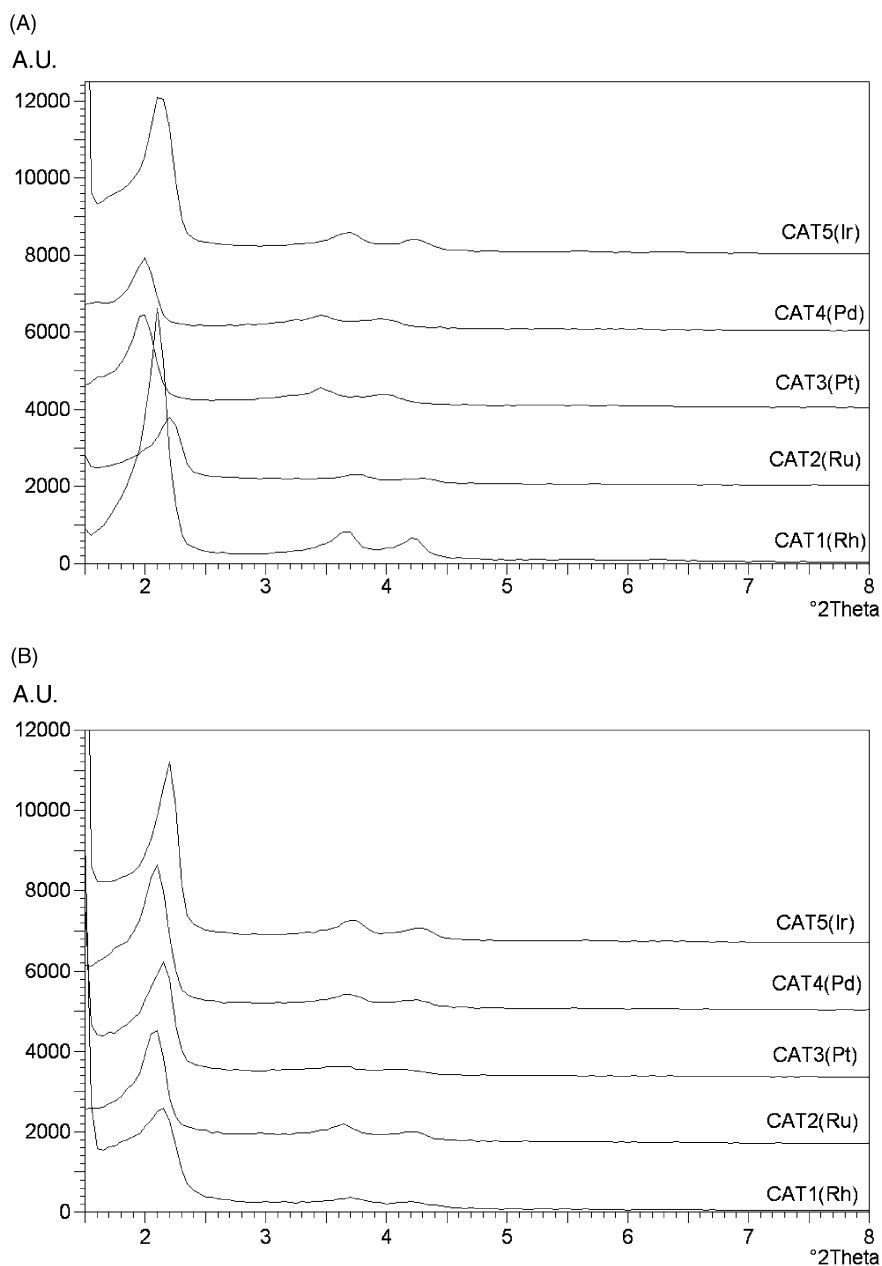
Fig. 1. XRD analysis of the samples CAT 1–CAT 5 before (A) and after (B) the catalytic tests ($2\theta = 1.5$–$8.0°$).

completely the activity in the first 10 h of time-on-stream, with condensation of a high amount of residual naphthalene in the heated lines and a consequent dramatic increase of the pressure drop. For this reason, these two catalysts were not further investigated. The XRD analysis of these two samples showed the presence of large metallic particles (>20 nm), allowing to hypothesise that the loss of catalytic activity may be attributed to the surface saturation.

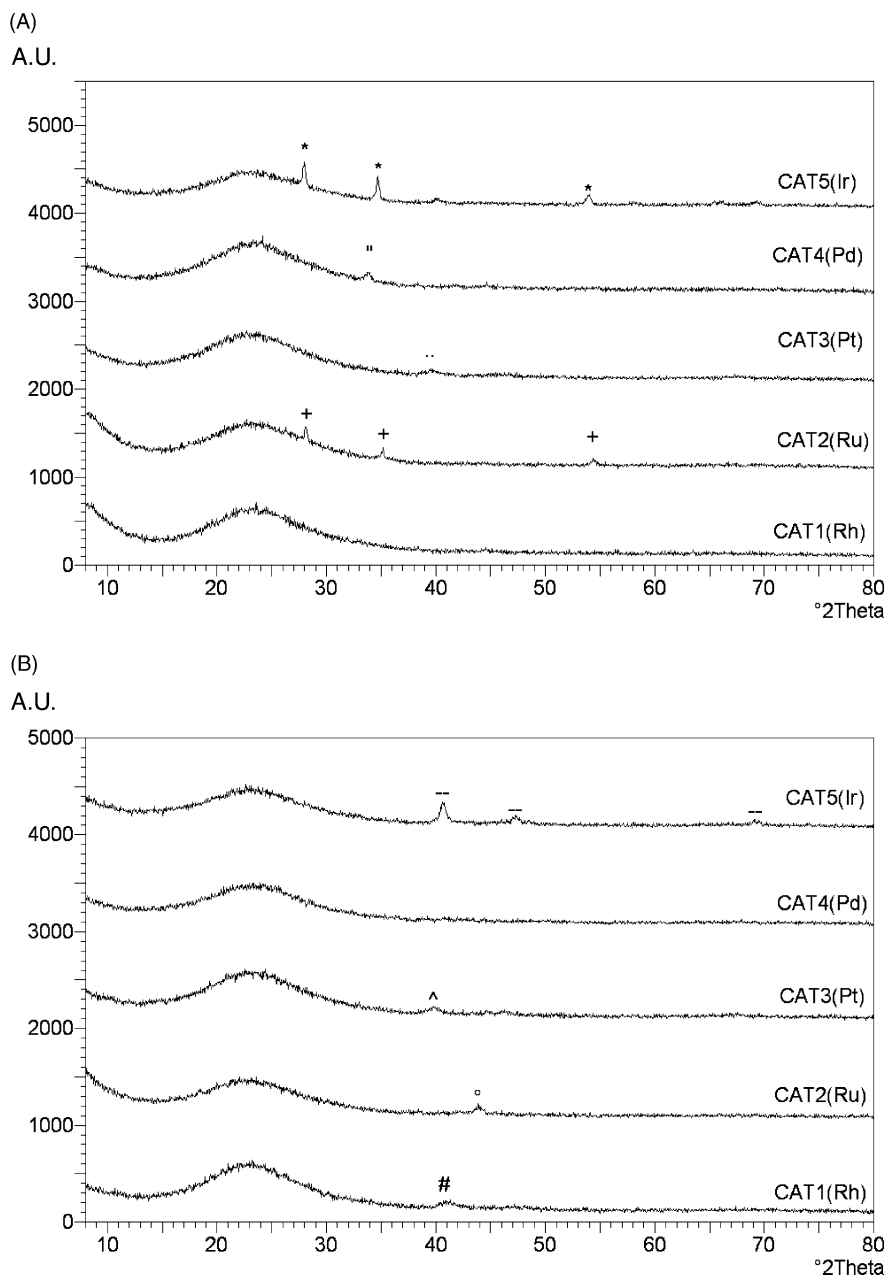Fig. 2. XRD analysis of the samples CAT 1–CAT 5 before (A) [(★) RuO_2, ($''$) Pt, (+) PdO, ($\cdots$) IrO_2] and after (B) [(–) Rh, (^) Ru, (°) Pt, (#) Ir] the catalytic tests ($2\theta = 8.0$–$80.0°$).

3.3.1. Role of the reaction temperature

In the tests performed at different temperatures, the Rh-containing catalyst (CAT 1) (Fig. 4) did not give rise to the complete conversion of naphthalene at all the temperatures investigated. Already at $260°C$ formation mainly of tetralin and *cis*-decalin, demonstrated a significant decrease in the hydrogenation activity. By further increasing the temperature, the
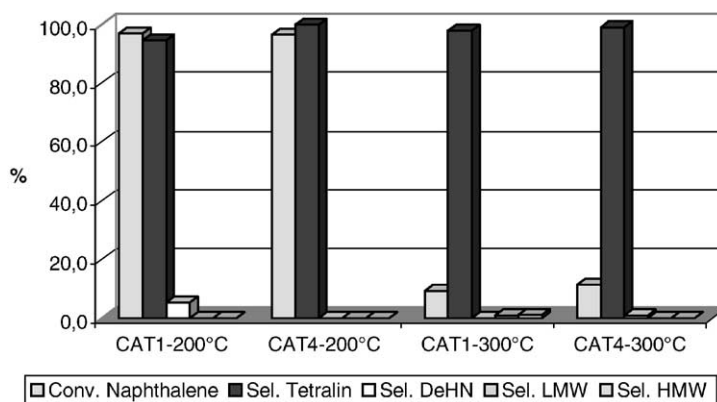
Fig. 3. Catalytic activity of the Rh- (CAT 1) and Pd-containing (CAT 4) catalysts at atmospheric pressure [Tetralin = 1, 2, 3, 4-tetrahydro-naphthalene; DeHN = decahydronaphthalene or decalin (*cis* and *trans*); LMW = C_1–C_4 hydrocarbons; HMW = high-molecular-weight ring-opening products (cyclohexane, toluene and *o*-xylene)].

amount of tetralin remained almost constant, while those of decalins significantly decreased, showing that partial hydrogenation was most favoured than full hydrogenation. On the other hand, the increase of temperature favoured the formation of the ring-opening (HMW) and, mainly, cracking (LMW) products, these latter evidenced by increasing losses in the carbon balance. The HMW products were tentatively identified by GC–MS and showed a high catalyst activity in isomerization and further alkylation reactions.

Also the Pt-containing catalyst (CAT 3) (Fig. 5) did not reach the complete conversion of naphthalene in the temperature range investigated, although with slightly higher conversion values. Furthermore, its activity was less affected by the reaction temperature. It must be noted the very low activity of this catalyst in the cracking reactions involved in the formation of

LMW compounds, as evidenced by the good carbon balance values, regardless of the temperature, unlike to that previously observed with the Rh-containing sample. Furthermore, the yield in ring-opening HMW compounds increased linearly with the reaction temperature, reaching at 340 °C a value (19%) significantly higher than those observed for CAT 1. However, this catalyst was not stable at high temperature, since repeating the test at 260 °C it was observed a significant decrease in the hydrogenation activity, with an increase in the amount of tetralin formed. This deactivation may be attributed to an increased sintering of the metallic Pt particles, according to the XRD results, although it may be also hypothesised that the poor interdispersion of metallic and acid sites may oppose to the desorption of the organic molecules from the surface.
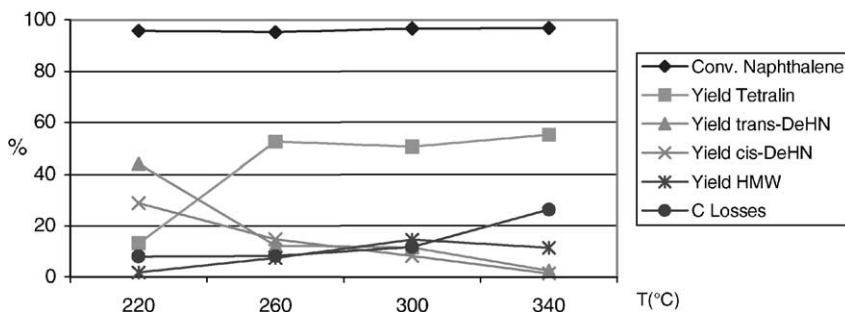

Fig. 4. Catalytic activity of the Rh-containing sample (CAT 1) as a function of the reaction temperature (P = 6.0 MPa, contact time = 6.8 s, H_2/naphthalene = 21 mol/mol, 10 wt.% of naphthalene in *n*-heptane) [Tetralin = 1, 2, 3, 4-tetrahydronaphthalene; DeHN = decahydronaphthalene or decalin (*cis* and *trans*); HMW = high-molecular-weight ring-opening products].
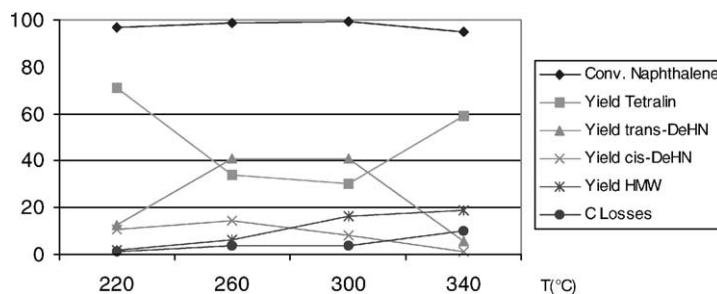
Fig. 5. Catalytic activity of the Pt-containing sample (CAT 3) as a function of the reaction temperature ($P = 6.0$ MPa, contact time $= 6.8$ s, H_2/naphthalene $= 21$ mol/mol, 10 wt.% of naphthalene in *n*-heptane) [Tetralin $= 1, 2, 3, 4$-tetrahydronaphthalene; DeHN $=$ decahydronaphthalene or decalin (*cis* and *trans*); HMW $=$ high-molecular-weight ring-opening products].

Finally, the Pd-containing sample (CAT 4) (Fig. 6) showed a lower activity at all the temperatures investigated, with only a partial conversion of naphthalene and formation mainly of tetralin. Only at 340 °C, the formation of HMW ring-opening compounds became significantly (ca. 13%), although together with a similar amount of LMW cracking products. Finally, repeating the test at 260 °C the deactivation was dramatic, with a decrease of more than 40% of the conversion and formation almost exclusively of tetralin and LMW products.

3.3.2. Role of the H2 naphtalene ratio

The decrease of the H_2 organic ratio was obtained decreasing the H_2 flow and adding a corresponding amount of N_2 to maintain the contact time constant. All the catalysts required a H_2 excess of three to four times the stoichiometric ratio (i.e. H_2 naphthalene $= 5$:1 mol/mol) to avoid a dramatic decrease of the activity, although the deactivation was a function of the

noble-metal present. With Rh (CAT 1), the decrease of the H_2 excess to two times of the stoichiometric value did not worsen significantly the conversion of naphthalene, but gave rise at 260 °C to the formation almost exclusively of tetralin. At 300 °C cracking and condensation reactions were favoured as shown by the carbon balance. On the contrary, with both Pt and Pd, the same reduction of the H_2 excess decreased the conversion of naphthalene to 60–65%, regardless of the temperature. However, while Pd (CAT 4) catalysed almost exclusively cracking and condensation reactions, Pt (CAT 3) gave rise almost only to tetralin, confirming its low hydrogenation activity associated with a very low tendency to form LMW cracking and heavy products.

3.3.3. Role of the contact time

To avoid interference by other parameters, the tests were performed changing both GHSV and LHSV values (Table 2). The decrease of the contact time from 6.8 to 3.4 s gave rise for all the catalysts to
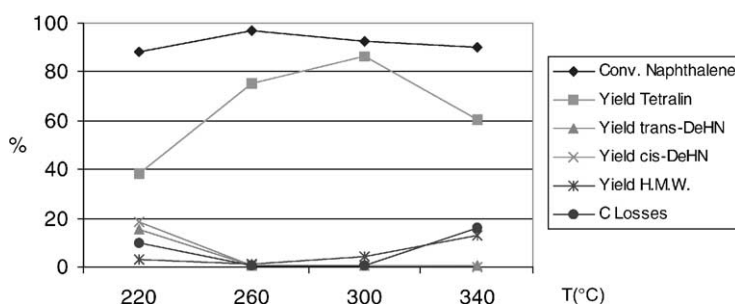

Fig. 6. Catalytic activity of the Pd-containing sample (CAT 4) as a function of the reaction temperature ($P = 6.0$ MPa, contact time $= 6.8$ s, H_2/naphthalene $= 21$ mol/mol, 10 wt.% of naphthalene in *n*-heptane) [Tetralin $= 1, 2, 3, 4$-tetrahydronaphthalene; DeHN $=$ decahydronaphthalene or decalin (*cis* and *trans*); HMW $=$ high-molecular-weight ring-opening products].

Table 2

Catalytic activity of the samples CAT 1, CAT 3 and CAT 4 as a function of the contact time ($P = 6.0$ MPa, H_2/naphthalene $= 15$ mol/mol, 10 wt.% of naphthalene in *n*-heptane)

Sample	Contact time (s)	Conversion (%)	Tetralin (yield %)	*trans*-DeHN (yield %)	*cis*-DeHN (yield %)	HMW (yield %)	C balance (Δ%)
CAT 1							
260 °C	3.4	96.8	85.1	0.8	1.3	0.1	−9.5
	6.8	95.2	52.6	12.3	14.8	7.4	−8.1
300 °C	3.4	98.6	71.3	1.8	1.5	3.4	−20.6
	6.8	96.6	50.6	11.6	8.1	14.6	−11.7
	13.6	96.0	17.2	8.2	3.1	6.0	−61.5
CAT 3							
260 °C	3.4	71.8	66.9	1.2	0.5	0.9	−2.3
	6.8	99.0	34.1	40.7	14.4	6.1	−3.7
	13.6	88.4	73.6	7.8	3.9	1.9	−1.2
CAT 4							
300 °C	3.4	93.6	60.7	1.6	1.1	6.2	−24.0
	6.8	92.6	86.2	0.8	0.6	4.4	−0.6
	13.6	97.4	23.3	2.0	0.9	6.7	−64.7

Tetralin = 1, 2, 3, 4-tetrahydronaphthalene; DeHN = decahydronaphthalene or decalin; HMW = high-molecular-weight ring-opening products.

a significant increase in the formation of the partially hydrogenated tetralin and LMW products, as showed by the increasing losses in the carbon balance. Under these conditions, the fully hydrogenated and the HMW ring-opening products almost disappeared, supporting the hypothesis that these latter derive mainly from the decalins by isomerization to methylperhydroindene and following hydrogenolysis reaction [16]. On the other hand, at the higher contact time investigated (13.6 s) tetralin and cracking products were almost exclusively detected, suggesting that cracking products formed mainly from the unsaturated hydrocarbons, very probably by acid catalysis. It is noteworthy, the very low tendency towards the cracking reactions of the Pt-containing sample. This catalyst, moving from optimum value of contact time, showed a decrease in the naphthalene conversion, with formation mainly of tetralin.

Table 3

Catalytic activity of the samples CAT 1, CAT 3 and CAT 4 in presence of different amounts of dibenzothiophene (DBT) [$P = 6.0$ MPa, contact time $= 6.8$ s, H_2/naphthalene $= 15$ mol/mol, 10 wt.% of naphthalene in *n*-heptane, reaction temperature $= 300$ °C (CAT 1 and 4) or 260 °C (CAT 3)]

Sample	DBT amount (ppm wt.)	Conversion (%)	Tetralin (yield %)	*trans*-DeHN (yield %)	*cis*-DeHN (yield %)	HMW (yield %)	C balance (Δ %)
CAT 1	0	95.2	52.6	12.3	14.8	7.4	−8.1
	10	93.1	50.3	12.7	16.8	8.5	−4.8
	100	98.7	87.7	0.8	1.4	1.1	−7.7
	10	81.4	72.7	0.8	1.2	1.1	−5.6
CAT 3	0	99.0	34.1	40.7	14.4	6.1	−3.7
	100	91.4	85.9	1.9	1.1	1.0	−1.5
	10	94.7	86.3	3.2	1.7	1.2	−2.3
	1000	68.8	64.1	0.5	0.3	1.3	−2.6
CAT 4	0	92.6	86.2	0.8	0.6	4.4	−0.6
	100	55.0	39.8	0.1	0.1	3.8	−11.3
	10	65.3	48.2	0.1	0.1	1.5	−15.4

Tetralin = 1, 2, 3, 4-tetrahydronaphthalene; DeHN = decahydronaphthalene or decalin; HMW = high-molecular-weight ring-opening products.

3.3.4. Role of the presence of dibenzothiophene (DBT) in the feed

All the single-metal-containing catalysts showed a poor thio-tolerance, evidencing significant decreases of activity already for a low amount of DBT fed. The Rh-containing catalyst (CAT 1) showed with a low S-amount (10 ppm wt. of DBT corresponding to 1.7 ppm wt. of S) (Table 3) results very similar to those of the test carried out with the S-free feed, while with the higher amount of DBT, the hydrogenation activity decreased significantly, with formation almost exclusively of tetralin (mainly) and cracking products. This deactivation was irreversible since repeating the test with 10 ppm wt. of DBT a decrease of ca. 12% in the naphthalene conversion was detected, with formation again mainly of tetralin. Also the Pt-containing catalyst (CAT 3) showed a similar trend, although the deactivation observed feeding 100 ppm wt. of DBT was reversible with a partial recovery of activity reducing the DBT amount to 10 ppm wt. These

results were further confirmed feeding 1000 ppm wt. of DBT, with a dramatic decrease in the conversion and formation almost exclusively of tetralin. Finally, the Pd-containing catalyst (CAT 4) showed the worst thio-tolerance, since already feeding 100 ppm wt. of DBT a dramatic decrease of the naphthalene conversion was detected, with a corresponding increase of LMW cracking products. This deactivation was almost fully irreversible, as evidenced by the further test with a reduced amount of DBT.

4. Conclusions

Mesoporous MCM-41-type (Si:Al = 20) catalysts, containing 1 wt.% of noble-metal ions have been prepared using the basic templating agents, according to the method of Beck et al. [13,14]. However, after calcination metal or oxide side phases were generally also present, while after the catalytic tests under H_2
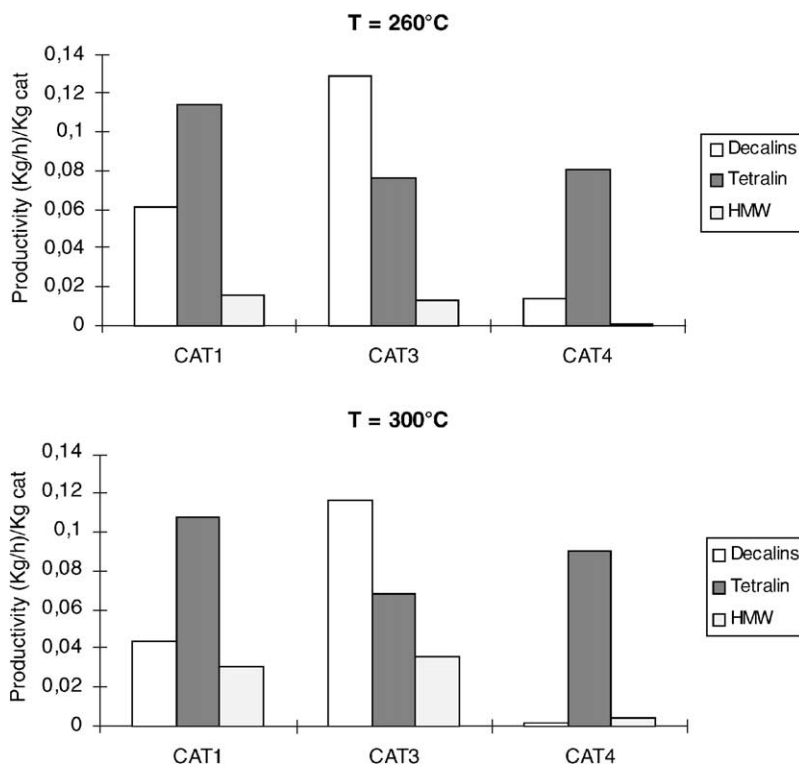

Fig. 7. Comparison of the productivity for catalyst unit weight at (A) 260 °C and (B) 300 °C ($P = 6.0$ MPa, contact time $= 6.8$ s, H_2/naphthalene $= 21$ mol/mol, 10 wt.% of naphthalene in n-heptane) [Tetralin $= 1, 2, 3, 4$-tetrahydronaphthalene; Decalins $=$ decahydronaphthalene (*cis* and *trans*); HMW $=$ high-molecular-weight ring-opening products].

pressure metal side phases were detected. Only the Rh- and Pd-containing catalysts were active in the tests performed at atmospheric pressure, unlike the recent report of Hölderich and co-workers [17], which reported similar activities for Pd- and Ir-containing mesoporous catalysts in the hydrogenation of cyclic olefins. These differences may be attributed to the different reaction conditions adopted or, mainly, the nature of the organic feed, since as reported by the above authors relevant differences of reactivity were detected between the cyclic olefins and attributed to the different values of strain energy (SE) in these compounds.

Performing the tests under pressure (6.0 MPa), the catalytic activity grew significantly, evidencing the following scale of activity for the noble-metals investigated: Pt (CAT 3) > Rh (CAT 1) $\gg$ Pd (CAT 4) $\ggg$ Ru (CAT 2) $\approx$ Ir (CAT 5), with the latter two catalysts that deactivated in the 1 h of time-on-stream. All the catalysts required a large H_2 excess (three to four times the stoichiometric value) and a contact time sufficient to allow full hydrogenation and ring-opening reactions, reducing the extent of side reactions. Moreover, all catalysts exhibited low thio-tolerance, since they deactivated significantly already feeding 100 ppm wt. of DBT, with an effect partially reversible only for the Pt-containing catalyst.

Since all the catalysts contained the same amount (as wt.%) of noble-metal, the comparison of the productivity for kilogram of catalyst allow to evidence the specific features of each metal (Fig. 7). Regardless of the temperature, Pt showed the best catalytic activity, with good yield values in fully hydrogenated and (HMW) ring-opening products, while Rh exhibited a similar ring-opening activity together with a significantly lower hydrogenation activity, forming mainly the partially hydrogenated tetralin. Finally, Pd had a very poor activity, giving rise almost exclusively to tetralin. However, it is noteworthy that in all cases, the catalytic activity as well as the thio-tolerance detected were significantly lower than those reported in the literature for bimetallic catalysts [9–12], evidencing the specific role of new phases formed or synergetic effects in these latter catalysts.

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