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Role of the organic feed and the support acidity in hydrotreating reactions on Pd–Pt on MCM-41 catalysts

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The reactivity of different organic compounds (naphthalene, alkylnaphthalenes, decalins, tetralin and their mixtures) and the roles of the support acidity and of the noble metals were studied in Pd/Pt on MCM-41 (with different Si/Al ratios) catalysts. The catalytic tests showed that the hydrogenolysis/ring-opening reactions mainly occurred on saturated compounds, while cracking took places mainly on unsaturated compounds. The presence of alkyl side chains on the polyaromatic ring inhibited the hydrodearomatization activity, proportionally to their length and number. Mixtures of naphthalene and methylnaphthalenes gave rise to a competition between the substrates, with a decrease in both hydrogenation and hydrogenolysis/ring-opening activities. Increasing support acidity favoured hydrogenolysis/ring-opening and cracking reactions, smoothing the hydrogenation activity. Noble metals are shown to be necessary not only in hydrogenation, but also in hydrogenolysis/ring-opening reactions.

KEY WORDS: hydrogenation; hydrogenolysis/ring-opening; cracking; polyaromatics; MCM-41 Si/Al; Pd/Pt.

1. Introduction

The irreversible trend towards increasing regulation of the emission of pollutants [1,2] pushes up the world demand of clean fuels, mainly diesel fuels, for which in the EU furthermore, the market demand surpasses industrial production. Therefore the possibility of hydrotreating light cycle oil (LCO) streams has received considerable attention in recent years [2]. An improvement of LCO fractions can be reached by: (i) reducing the content of aromatics, which also increases the cetane number; (ii) decreasing the content of sulphur; (iii) increasing the cetane number by hydrogenolysis/ring-opening reactions [3]. Single-stage and two-stage processes have been proposed [2]. The single stage hydrotreating process uses S-tolerant CoMo, NiMo and NiW on alumina catalysts, however severe operating conditions such as high temperatures, low space velocities and high hydrogen pressures are necessary to achieve acceptable aromatic reduction. The two-stage hydrotreating process using noble metal catalysts in the second stage can reach deep levels of aromatic hydrogenation under mild operating conditions. However, since the noble metal catalysts are very sensitive to sulphur in the feedstock, which acts as catalyst poison, the first stage of hydrodesulphurization must reduce the level of sulphur to a few ppm. Therefore, in recent years extensive studies have been carried out to develop S-tolerant noble metal catalysts for the two-stage processes [4,5]. In particular, noble metals supported on large-pore zeolites have been receiving attention as aromatic hydrogenation catalysts [6,7]. Zeolite acidity, however, drastically increases undesirable cracking activity, which accelerates the rate of coke deposition and the yield in light hydrocarbons [8]. Furthermore, due to their pore size, the access to these zeolites is restricted to molecules with diameters lower than 8 Å [9]. Taking into account the key role of the pore size, that affects metal dispersion and diffusion of voluminous fed molecules, much effort has been devoted to investigate a family of mesoporous aluminosilicates named MCM-41 [10]. These materials possess a hexagonal arrangement of uniformly sized, unidimensional mesopores. Moreover, the acidity and dimensions of the pores can be tailored by selecting the Si/Al ratio and the size of the template used in the preparation, respectively. These supports exhibit acidic OH groups of strength lower than those in zeolites [11,12]. In previous studies [13,14], the behaviour of different catalysts containing 1–2 wt% of noble metal inside mesoporous (Si/Al = 20 a.r.) frameworks was investigated in the hydrogenation of naphthalene, as preliminary step to the investigation of bimetallic catalysts. The aim of the present work is to investigate the behaviour of bimetallic Pd/Pt on MCM-41 catalysts (with different Si/Al ratios) in the hydrogenation of different substrates, that are models for the organic compounds present in a typical LCO fraction (alkylnaphthalenes, decalins, tetralin or their mixtures).

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2. Experimental

Aluminosilicate mesoporous MCM-41 catalysts, as such or containing 1 wt% of Pd–Pt pair, were prepared with Si/Al = 20 and 10 atomic ratios (table 1). The synthesis reported by Beck *et al.* [15,16] using basic templates was employed [15,16]. The required amount of sodium aluminate was added to a 25 wt% solution of $CH_3(CH_2)_{15}NCl(CH_3)_3$, stirring the mixture for 0.5 h. After 1 h, a 15–20 wt% solution of $(CH_3)_4NOH{*}2SiO_2$ and fumed silica were added. The mixture was stirred for 3–4 h at room temperature (r.t.) and then placed in an autoclave at 150 °C for 48 h. After cooling, the resulting solid was recovered by filtration, washed with water, dried in air at r.t. and calcined at 540 °C for 7 h. The mesoporous samples were impregnated by incipient wetness with a solution of $PdCl_2$ and $PtCl_4$ in amounts corresponding to an atomic ratio of 5.5 : 1, and calcined at 450 °C for 4 h.

XRPD analysis was performed using a Philips PW 1050/81 goniometer, equipped with a PW 1710 unit, and CuK_α radiation ($\lambda = 0.15418$ nm, 40 mA, 40 mV). Two intervals of 2θ were investigated: $2\theta = 1.5$–$8.0°$ to verify the presence of an ordered hexagonal mesoporous structure and $2\theta = 8.0$–$80.0°$ to determine the presence of segregated metal and/or oxide phases. The 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 under vacuum. The surface acidity of the noble metal-containing catalysts was determined by NH_3 adsorption. Samples were outgassed at 350 °C for 3 h and the amounts of ammonia adsorbed at different partial pressures in the equilibrium bulk phase were measured using a Micromeritics ASAP 2010C apparatus. The adsorption temperature was maintained at 80 °C in order to reduce physisorption of ammonia on the solid surface. Successive ammonia doses were then sent on to the sample until a final equilibrium pressure of 5 kPa was reached. The equilibrium pressure was measured after every adsorption step, and the amount adsorbed was calculated. At the end of the first adsorption cycle, the sample was pumped at 80 °C for 30 min, and a second adsorption cycle was then performed at the same temperature. The difference in adsorption between the two cycles is attributed to irreversible adsorption of ammonia. This corresponds to the localized chemisorption of ammonia molecules and allows calculation of the total number of surface acid sites. At first, this quantity changes as the adsorption progresses, but it then levels off. The metal surface area and dispersion were determined for the noble metal-containing catalysts by H_2 chemisorption. The accessible metal surface was measured using a Micromeritics instrument (ASAP 2010C). The samples were first flushed in a flow of He, and then evacuated before chemisorption with H_2 at 300 °C. The metal dispersion value so derived is related to the metal particle size by the relation: $D\% = 1000/d$, where $D\%$, metal dispersion and d, metal particle diameter (Å).

The catalytic tests were performed at 6.0 MPa (mainly 3.0 MPa of H_2 and 3.0 MPa of N_2) using a stainless steel tubular reactor (inner diameter 8 mm, length 54 cm), heated by an electric oven controlled by two J-thermocouples. Six cm^3 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 r.t. to 450 °C. The solutions of organic compounds in n-heptane (10 wt%, Aldrich analytical grade) were 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 h period under the same conditions 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 wide bore PS264 column (5% methylphenylsilicone, length 25 m, inner diameter 0.53 mm, film width 1.5 μm). The products were preliminary tentatively identified by GC-MS using a Hewlett-Packard GCD 1800 system equipped with a HP5 column (5% of methylphenylsilicone, length 25 m, inner diameter 0.25 mm, film width 0.25 μm) comparing the experimental GC-MS pattern with those present in the instrument library. Wide ranges of reaction conditions were investigated (temperature, contact time, nature of the organic feed, 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 investigated adding increasing amounts of dibenzothiophene (DBT) in the feed.

Table 1
Characterization data of all the studied samples

Sample	MCM-41 type Si/Al ratio (a.r.)	1 wt% Pd/Pt = 5.5 a.r.	Porosity (ml g^{-1})	Surface area before reaction (m^2 g^{-1})	Surface area after reaction (m^2 g^{-1})	Surface area after calcination (m^2 g^{-1})
CAT1	20	Yes	n.d.	621	571	630
CAT2	10	Yes	n.d.	611	574	605
CAT3	20	Absent	0.501	840	795	n.d.
CAT4	10	Absent	0.319	655	596	n.d.

3. Results and discussion

3.1. Characterization

The calcined supports (CAT3 and CAT4) showed (figure 1) XRPD powder patterns in the $2\theta = 1.5$–$8.0°$ range typical of ordered MCM-41 hexagonal phases [17]. In the $2\theta = 10$–$80°$ range, the noble metal-containing catalysts (CAT1 and CAT2) showed no segregated metal oxide phase (before reaction) nor any segregated metal phase (after reaction), providing evidence for a good and stable metal dispersion.

Surface area measurements (table 1) show a decrease after reaction for all the investigated samples, probably due to adsorption of heavy compounds (tar). To confirm this hypothesis, samples CAT1 and CAT2 before reaction were calcined at 500 °C for 4 h, to burn out any tar deposited. The new values obtained after calcination are much higher than those of the samples after reaction, confirming that the losses observed were mainly due to tar deposition.

Acidity measurements carried out on CAT1 and CAT2 confirmed that the sample with the lowest Si/Al ratio (CAT2) had the higher number of acid sites (table 2) [18]. CAT1 had a bigger metallic particle size (table 2), with corresponding lower metal dispersion and metallic surface area.

3.2. Role of the fed molecules

The tests carried out on CAT1 feeding different polyaromatics compounds are collected in table 3. On feeding naphthalene an almost complete conversion was obtained, confirming the ease of the first step of hydrogenation [2]. Lowest conversion values were obtained feeding tetralin and decalin. Furthermore, feeding decalins, a small amount of tetralin coming from dehydrogenation reaction was observed. Since high almost no molecular weight (HMW) compounds were formed when feeding decalin, it may be suggested that the hydrogenolysis/ring-opening reactions mainly occur on saturated compounds, while cracking reactions take place mainly on unsaturated compounds (naphthalene and tetralin). Alkyl naphthalenes exhibited high conversion values, demonstrating the easy hydrogenation of the first aromatic ring in polyaromatic compounds. The tests carried out feeding 1- and 2-methyl naphthalene showed a decrease of the yields in decalins and HMW compounds, with a corresponding increase of the yields in alkyltetralins and carbon balance losses. The alkyltetralins identified were mainly 6-methyl tetralin and 5-methyl tetralin, evidencing that the alkyl group reduced the reactivity of the functionalized ring, with hydrogenation occurring in the other ring. Moreover, a methyl in position 2 stabilized the molecule better than that in 1 position, as shown by a higher yield in alkyltetralins and a decrease in HMW and alkyl decalins compounds. Feeding 1,2-dimethyl naphthalene and 1- and 2-ethyl naphthalene showed that the presence of alkyl side chains on the polyaromatic ring inhibited the hydrogenation of the second ring proportionally to their length and number, due to both steric and electron-donating

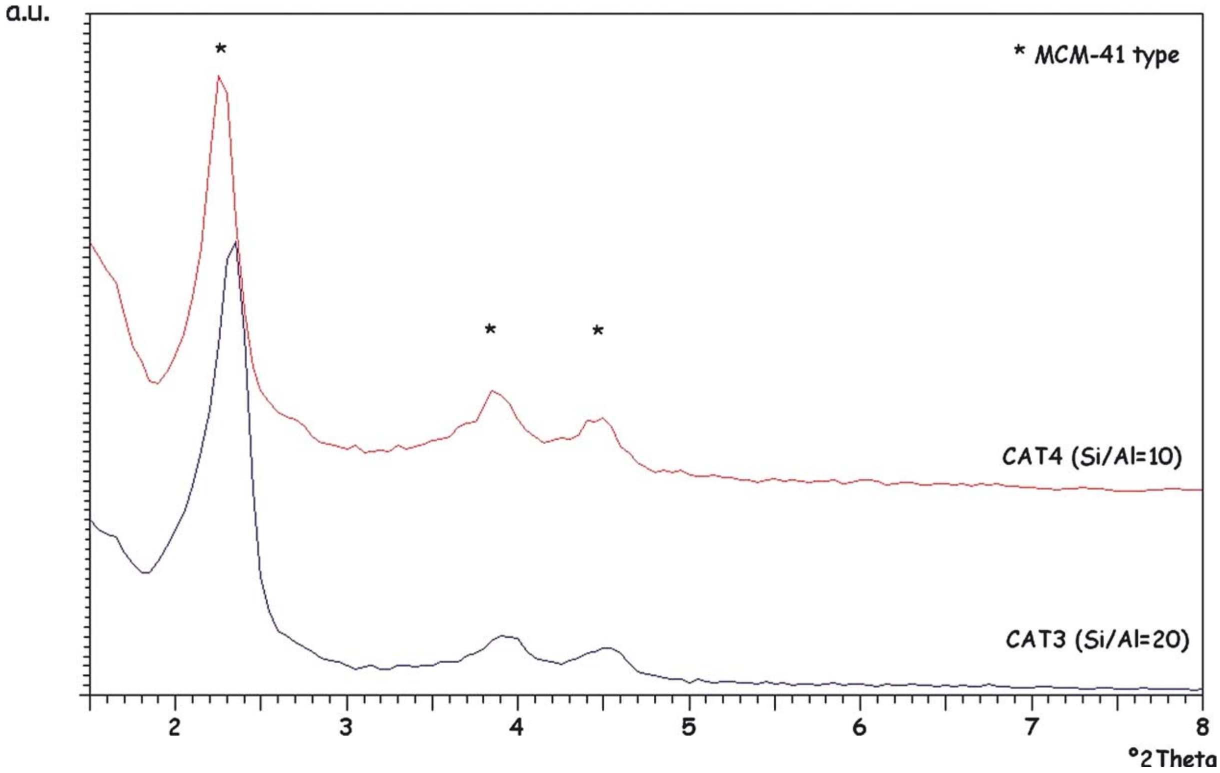

Figure 1. XRD patterns of CAT3 and CAT4 ($2\theta = 1.5$–$2°$).

Table 2
Characterization data of the Pd/Pt on MCM-41 type samples (CAT1 and CAT2)

Sample	MCM-41 type Si/Al ratio (a.r.)	Acidity (μmol NH_3/gcat.)	Metal dispersion (%)	Particle size (Å)	Metallic surface area (m^2/g)
CAT1	20	260	8	126	31
CAT2	10	343	21	48	83

Table 3
Role of the fed molecules for CAT1 (T = 300 °C, $\tau = 3.4$ s, H_2/organic = 21 mol/mol, LHSV = 1.0 h^{-1})

Feed	Conversion (%)	Tetralin yield (%)	Decalins yield (%)	Alkyl tetralins yield (%)	Alkyl decalins yield (%)	HMW products yield (%)	C balance Δ (%)
Naphthalene	99.2	24.5	33.7	0	0	17.7	−23.3
Tetralin	66.2	/	25.1	0	0	7.0	−34.1
Decalin	23.6	0.8	/	0	0	19.9	−2.9
1-Methyl naphthalene	98.9	2.6	1.2	43.6	23.6	23.8	−4.1
2-Methyl naphthalene	99.6	2.2	0.2	72.6	6.3	9.1	−9.2
1,2-Dimethyl naphthalene	96.1	1.2	0	63.9	11.2	16.0	−3.8
1-Ethyl naphthalene	97.8	0	0	68.2	12.7	14.1	−2.8
2-Ethyl naphthalene	98.7	0	0	83.2	2.9	7.5	−5.1
2-Isopropyl naphthalene	98.0	21.7	9.3	38.0	4.6	39.4	−15.0
1 MN + N 50 : 50 w/w	96.2/96.8	51.4	1.9	41.4	0.9	2.6	−3.6
Weighted average	*99.2/98.9*	*13.6*	*17.5*	*21.8*	*11.8*	*20.8*	*−13.7*

effects, these latter increasing the electron density on the aromatic ring, with a corresponding increase of the activation energy. In this case also the ethyl in position 1 is more reactive than in position 2. Finally, feeding 2-isopropyl naphthalene, a clear dealkylation activity was observed, with formation of tetralin, due to both the support acidity and the stability of the formed carbocation. In order to shed light on the possible competition between different substrates, a mixture of 1-methyl naphthalene and naphthalene (1MN/N = 50 : 50 w/w) was fed. The results obtained were lower than those calculated on the basis of weighted average values of the two organic substrates, indicating that competition phenomena between them decreased the hydrogenation and hydrogenolysis activities (higher yields in tetralin and alkyltetralins, lower yields in decalins and alkyl decalins and HMW products than the calculated values). The tests carried out on CAT2 feeding different polyaromatics compounds are collected in table 4. Feeding naphthalene, this catalyst reached almost complete conversion, with high yields in decalins and HMW. On feeding tetralin and decalins, lower conversions were obtained, as already reported for CAT1. Regarding decalins, HMW are mainly formed, confirming that the hydrogenolysis/ring-opening reactions mainly occurred on saturated compounds, while cracking took places mainly on unsaturated compounds. With alkyl naphthalenes, almost complete conversions were obtained, as well as for CAT1. Feeding from 1- to 2-methyl naphthalene, alkyltetralins yield increased, while the yields in alkyl decalins and HMW products decreased, confirming that the methyl in position 1 is more reactive than that in position 2. Also in this case, feeding bulky molecules such as 1,2-dimethyl naphthalene and 1- and 2-ethyl naphthalene, caused a drop in the hydrogenation activity, since the yield in alkyltetralin increased with a corresponding decrease in the yield in alkyldecalins. Such as for CAT1, the ethyl in position 1 is more reactive than that in position 2. Feeding 2-isopropyl naphthalene, a sensible dealkylant activity (yield in decalins) was noticed also for this sample. Feeding different mixtures of 1-methyl naphthalene and naphthalene (MN/N = 25 : 75, 50 : 50 and 75 : 25 w/w), better results (except for carbon balances) than the weighted average were obtained for the 25 : 75 and 75 : 25 w/w mixtures, while the 50 : 50 w/w mixture gave worse results than expected. Therefore, the competition among different substrates was present in both catalysts when feeding the 50 : 50 w/w mixture, while when one component was in a large excess respect to the other, the phenomenon was smoothed.

3.3. *Role of the support acidity*

The catalytic tests performed on CAT1 in the hydrogenation of naphthalene investigating several reaction

Table 4
Role of the fed molecules for CAT2 ($T=300$ °C, $\tau=3.4$ s, H_2/organic=21 mol/mol, LHSV = 1.0 h^{-1})

Feed	Conversion (%)	Tetralin yield (%)	Decalins yield (%)	Alkyl tetralins yield (%)	Alkyl decalins yield (%)	HMW products yield (%)	*C* balance Δ (%)
Naphthalene	99.9	0.2	42.1	0	0	29.8	−27.8
Tetralin	95.3	–	51.8	0	0	16.1	−27.4
Decalin	19.6	0	–	0	0	22.8	+3.2
1-Methyl naphthalene	99.7	2.0	0	31.4	39.0	21.8	−5.7
2-Methyl naphthalene	99.7	1.3	0	42.4	35.1	8.1	−12.8
1,2-Dimethyl naphthalene	99.4	0	0	51.9	2.8	12.3	−32.4
1-Ethyl naphthalene	99.5	0	0	50.3	12.9	18.3	−18.0
2-Ethyl naphthalene	99.5	0	0	61.1	1.7	8.8	−27.9
2-Isopropyl naphthalene	96.2	0.2	34.2	0	0	27.8	−34.0
1MN + N 25 : 75 w/w	99.9/99.9	0.2	25.9	0	6.0	28.8	−45.0
Weighted average	*99.9/99.7*	*0.7*	*31.6*	*7.9*	*9.8*	*27.8*	*−22.3*
1MN + N 50 : 50 w/w	99.5/99.4	15.8	10.1	29.0	30.8	6.7	−11.2
Weighted average	*99.9/99.7*	*1.1*	*21.1*	*15.7*	*19.5*	*25.8*	*−16.8*
1MN + N 75 : 25 w/w	99.9/99.9	0.8	13.3	1.0	36.1	28.5	−28.8
Weighted average	*99.9/99.7*	*1.6*	*10.5*	*23.6*	*29.3*	*23.8*	*−11.2*

Table 5
Catalytic tests of CAT1 in the hydrogenation of naphthalene at 6.0 MPa

Temperature (°C)[a]	*C* (%)	Tetralin (Y%)	Decalin (Y%)	HMW (Y%)	Δ*C* (%)
220	95.6	7.5	82.4	6.2	0.5
260	89.5	30.9	44.2	10.0	− 4.4
300	99.5	2.9	47.6	25.3	−23.7
340	87.7	41.9	13.1	12.9	−19.8
260	98.5	75.5	15.5	3.2	− 4.3
Contact time (s)[b]					
3.4	99.0	15.1	47.6	24.5	−11.8
6.8	99.5	2.9	47.6	25.3	−23.7
13.6	98.2	2.0	34.6	21.8	−39.8
H_2/naphthalene (mol/mol)[c]					
21	99.5	2.9	47.6	25.3	−23.7
15	74.1	56.6	5.5	3.7	− 8.3
10	44.1	24.4	0.0	1.0	−18.7
DBT (wt ppm)[d]					
0	99.5	2.9	47.6	25.3	−23.7
100 (17 wt ppm S)	97.5	72.2	12.4	3.9	−9.0
1000 (170 wt ppm S)	80.8	75.5	4.5	2.2	1.4
3000 (510 wt ppm S)	95.8	76.1	2.4	2.0	−15.3
0	95.8	80.1	10.9	3.4	−1.4

[a] $\tau=6.8$ s, LHSV=1.0 h^{-1}, H_2/naphthalene=21 mol/mol.
[b] $T=300$ °C, H_2/naphthalene=21 mol/mol.
[c] $T=300$ °C, $\tau=6.8$ s, LHSV=1.0 h^{-1}.
[d] $T=300$ °C, $\tau=6.8$ s, LHSV=1.0 h^{-1}, H_2/naphthalene=21 mol/mol.

conditions (temperature, contact time, H_2/organic feed ratio, thio-tolerance) are collected in table 5. Increasing the reaction temperature from 220 up to 340 °C, the hydrogenation activity decreased (increased yield in tetralin with a corresponding decrease of that in decalin) while the hydrogenolysis/ring-opening and cracking activities increased, in agreement with the thermodynamic features of these reactions. Repeating the test at

260 °C after those at higher temperatures showed evidence for catalyst deactivation. Increasing the contact time from 3.4 up to 13.6 s boosted production of gases, because cracking is a consecutive reaction, while the formation of tetralin was inhibited. Decreasing the H_2/naphthalene molar ratio from a H_2 excess equal to 5 down to 2 times the stoichiometric value dropped the naphthalene conversion and the yields in decalins and HMW compounds, while the formation of tetralin went through a maximum for H_2/naphthalene = 15 mol/mol, attributable to the low conversion in the test at H_2/naphthalene = 10 mol/mol, in which almost tetralin and light gases were formed. Finally, feeding DBT caused a worsening of both hydrogenation and hydrogenolysis/ring-opening activities and the initial values could not be restored even removing DBT from the feed. The same tests carried out on CAT2 are collected in table 6. Also for this sample, on increasing the reaction temperature the hydrogenation activity decreased while the hydrogenolysis/ring-opening and cracking activities increased. Increasing the contact time boosted the gases production, as observed for the previous CAT1, while the formation of decalins and HMW compound was inhibited. The yield in tetralin slightly increased. Then, DBT was added to the feed, highlighting a poor thio-tolerance of this catalyst even for low amounts of S (100 ppm wt of DBT). The poisoning was not reversible, since removing DBT from the feed did not allow the sample to restore its initial catalytic performances. A comparison of the productivities in decalins and HMW compounds (figure 2) put in evidence that the sample with the lowest acidity (CAT1) had the best hydrogenation activity at both investigated temperatures (260 and 300 °C), while the sample with the highest acidity (CAT2) had the best productivities in hydrogenolysis/ring-opening compounds. About gas formation (tables 5 and 6) CAT2 had the highest losses in carbon balance, due to its highest acidity that favoured cracking reactions. These results showed that the acidity of the support is a key factor in both the useful hydrogenolysis/ring-opening and the side cracking reactions and it must be carefully tuned, in order to obtain the wanted products.

3.4. *Role of the Pd/Pt as active phase*

In order to put in evidence the role of the active phase, the samples CAT1 and CAT2 were compared with the corresponding single supports CAT3 and CAT4. Hydrogenation of tetralin at 6.0 MPa was carried out to better discriminate about these catalysts, since the hydrogenation of the second aromatic ring is more difficult than the hydrogenation of the first one [2]. The tests, which are collected in figure 3, showed that the noble metal-containing samples had much better hydrogenation and hydrogenolysis/ring-opening activities than the corresponding single supports. Moreover, considering these latter samples, the tests evidenced a relevant dehydrogenation activity (yield in naphthalene), which was absent for CAT1 and CAT2. The samples with the highest acidity (CAT2 and CAT4) had the highest values in the tetralin conversion and in the yields in decalins, HMW and LMW compounds in the conditions tested. Concluding, this last study confirmed the key role of the bimetallic Pd/Pt couple, in terms of enhanced hydrogenation but also in hydrogenolysis/ring-opening activities, combined with another key role, that of the acidity of the support.

4. Conclusion

The aim of this contribution was to shed light on the reactivity of the different organic compounds

Table 6
Catalytic tests of CAT2 in the hydrogenation of naphthalene at 6.0 MPa

Temperature (°C) [a]	C (%)	Tetralin (Y%)	Decalin (Y%)	HMW (Y%)	ΔC (%)
220	97.0	33.4	38.6	2.8	−22.2
260	98.9	4.9	49.9	12.4	−31.7
300	99.4	1.1	33.5	31.2	−33.6
340	99.7	1.7	17.2	35.1	−45.7
260	99.6	3.4	39.3	22.2	−34.7
Contact time (s) [b]					
3.4	99.9	0.2	37.9	26.5	−35.3
6.8	99.4	1.1	33.5	21.2	−43.6
13.6	97.5	2.2	25.2	16.8	−53.3
DBT (wt ppm) [d]					
0	99.4	1.1	33.5	21.2	−43.6
100 (17 wt ppm S)	98.3	77.4	12.1	1.8	−7.0
1000 (170 wt ppm S)	98.8	88.7	7.5	1.8	−0.8
0	98.9	72.0	18.9	2.5	−5.5

[a] τ = 6.8 s, LHSV = 1.0 h^{-1}, H_2/naphthalene = 21 mol/mol.

[b] T = 300 °C, H_2/naphthalene = 21 mol/mol.

[c] T = 300 °C, τ = 6.8 s, LHSV = 1.0 h^{-1}, H_2/naphthalene = 21 mol/mol.

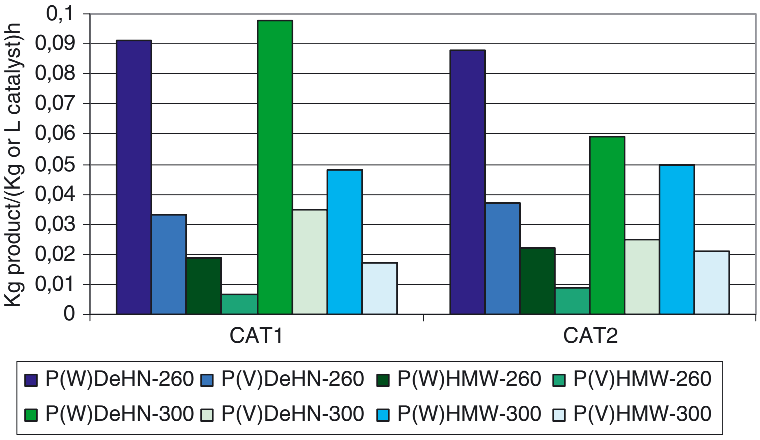

Figure 2. Productivity in decalins (DeHN) and hydrogenolysis/ring-opening (HMW) products for kg (W) or L (V) of CAT1 and CAT2 ($\tau = 6.8$ s, H_2/naphthalene = 21 mol/mol, LHSV = 1 h^{-1}).

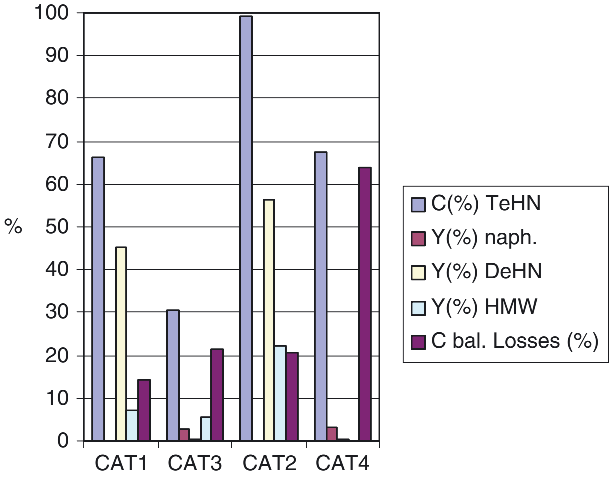

Figure 3. Comparison of the catalytic perfomances among the noble metal-containing catalysts (CAT1 and CAT2) and their corresponding single supports (CAT3 and CAT4) in the hydrogenation of tetralin at 6.0 MPa: T, 300 °C; $\tau = 6.8$ s; H_2/tetralin, 21 mol/mol LHSV, 1 h^{-1}.

present in a typical LCO fraction and on the role of the support acidity and on the role of the active phase (Pt/Pt). The catalytic tests showed that the hydrogenolysis/ring-opening reaction mainly occurred on saturated compounds (decalins), while cracking took places mainly on unsaturated compounds (naphthalene and tetralin). Alkylnaphthalenes exhibited high conversion values, confirming the easy hydrogenation of the first aromatic ring in polyaromatic compounds. The presence alkyl side chains on the polyaromatic ring inhibited the hydrogenation of the second ring, proportionally to their length and number, due to both steric and electron-donating effects. Different Si/Al ratios in the MCM-41 supports allowed evidencing the role of the catalyst acidity: increasing acidity favoured hydrogenolysis/ring-opening and cracking reactions, smoothing the effects of the alkyl side chains. Mixtures of naphthalene and methylnaphthalenes gave rise to a competition between the substrates, with a decrease in both hydrogenation and hydrogenolysis/ring-opening activities. Finally, comparing the activity of Pd/Pt supported catalysts and their corresponding supports, it was evidenced that noble metals are necessary not only in hydrogenation, but also in hydrogenolysis/ring-opening reactions. These latter, however, require the presence of acid sites with medium strength, to favour isomerization of saturated compounds, while strong acid sites favoured mainly useless cracking reactions.

Acknowledgments

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