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Hydrogenation and hydrogenolysis/ring-opening of naphthalene on Pd/Pt supported on zirconium-doped mesoporous silica catalysts

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Abstract

Pd/Pt (0.5, 1.0, and 2.0 wt%) supported on mesoporous Si/Zr MCM-41-type catalysts have been investigated in the hydrogenation of naphthalene under pressure, chosen as the probe reaction for the hydrotreating of light cycle oil fractions, in order to optimize the amount of active phase. On increasing the percentage of Pd/Pt, the productivity in decalins increased, while those in hydrogenolysis/ring-opening and cracking compounds showed an opposite trend. The sample with 1 wt% of Pd/Pt may be considered the best choice, considering both hydrogenation and hydrogenolysis/ring-opening activity. Finally, adding increasing amounts of dibenzothiophene in the feed caused a decrease in the activity, although this deactivation was largely reversible.

Keywords: Naphthalene; Hydrogenation; Hydrogenolysis/ring-opening; Dibenzothiophene; Decahydronaphthalene; Decalin; 1,2,3,4-Tetrahydronaphthalene; Tetralin; Pd/Pt; Mesoporous Si/Zr MCM-41

1. Introduction

The irreversible trend toward increasing regulation of pollutant emission [1,2] increases the global demand for clean fuels, mainly diesels, for which, furthermore, market demand in the EU exceeds the industrial production [3]. Therefore the possibility of hydrotreating light cycle oil (LCO) fractions coming from fluid catalytic cracking (FCC) plants has received considerable attention in recent years [2]. The improvement of LCO fractions may be reached by: (i) reducing the content of aromatics, which also increases the cetane number; (ii) decreasing the sulfur content; (iii) increasing the cetane number by hydrogenolysis/ring-opening reactions [4]. Single-stage and two-stage processes have been proposed [2]. The above technologies, which use acid catalysts, in particular noble metals (Pt and/or Pd) supported on large-pore zeolites, have received more attention [5,6]. Previous studies on the hydrogenation of polyaromatic compounds using acid [7–13] or, more recently, also basic supports [14] evidenced that the hydrogenation and hydrogenolysis activities strongly depended on the Pd:Pt ratio, with maximum activity obtained for a Pd:Pt = 4:1 atomic ratio (a.r.). Furthermore, this latter ratio is the most adequate for a high thio-tolerance, probably on account of the formation of Pd–Pt bimetallic particles [7,9,13,15,16].

Zeolite acidity, however, drastically increases undesirable cracking activity, which accelerates the rate of coke deposition and the yield in lower value gases [17]. Furthermore, due to their pore size, the access to active sites is restricted to molecules with diameters up to 8 Å [18]. Taking into account the key role of the pore size, which affects the diffusion of the largest fed molecules, many efforts have been devoted to investigating a new family of mesoporous molecular sieves

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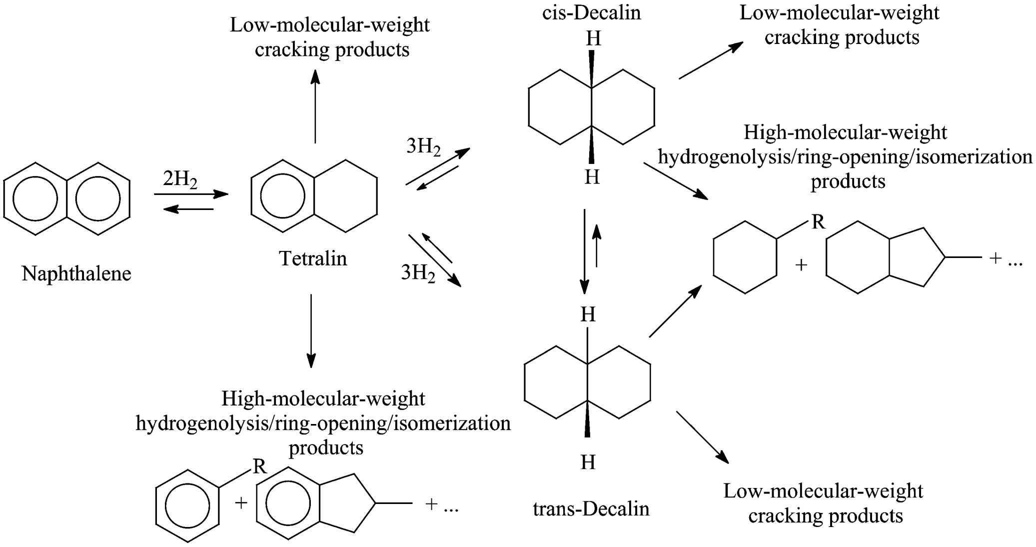

Fig. 1. Proposed reaction pathway for the hydrogenation of naphthalene at high pressure.

named MCM-41 [19,20]. However, mesoporous MCM-41-type silica, with a uniform pore diameter of 3.5 nm, is almost inactive, due to the small number of acid sites strong enough to catalyze the hydrogenolysis/ring-opening reactions. It is well known that the introduction of heteroatoms (such as Al, Ti, or Zr) into the siliceous framework increases the acidity of mesoporous solids. Thus, zirconium-containing MCM-41-type materials (Zr-MCM-41) have shown excellent behavior as an acid catalyst [13,21]. The aim of this paper is to compare the catalytic performances of Pd/Pt on Si/Zr MCM-41-type (Si/Zr = 5.0 as atomic ratio) catalysts, having different total metal contents (0.5, 1.0, and 2.0 wt%, Pd/Pt = 4.0 as atomic ratio), in the vapor-phase hydrogenation of naphthalene at 6.0 MPa (Fig. 1), chosen as probe reaction for the hydrotreating of LCO fractions, in order to optimize the amount of active phase. Naphthalene is easily hydrogenated to 1,2,3,4-tetrahydronaphthalene (tetralin, TeHN), which can be further—and with greater difficulty—hydrogenated to decahydronaphthalene (decalin, DeHN) isomers (*cis* + *trans*). Cracking reactions to low molecular weight compounds (LMW) may also occur and are not desirable, being outside the diesel range. Useful compounds are those derived from hydrogenolysis/ring-opening reactions, called high molecular weight (HMW) compounds (mainly alkylcyclohexanes, alkylbenzenes, methylindanes, and methylindenes, spyrodecane), having a high cetane number.

2. Experimental and methods

Zirconium-doped mesoporous silica with a Si/Zr = 5 atomic ratio was prepared as described elsewhere [21] but with some modifications [22], by adding tetraethoxysilane (TEOS) and Zr tetrapropoxide to an ethanol–propanol solution at room temperature (RT). The solution was stirred at RT for 15 min and then added to an aqueous solution of hexadecyltrimethylammonium bromide (25 wt%), previously stirred at 80 °C for 30 min. The surfactant/(SiO_2 + ZrO_2) molar ratio was 0.5. The pH was adjusted to 10.5 by addition of an aqueous solution of tetraethylammonium hydroxide (25 wt%). The resulting gel was stirred at room temperature for 4 days. The solid was recovered by centrifugation, washed with ethanol, dried at 70 °C, and then calcined at 540 °C for 6 h (1 °C min^{-1} heating rate). Complete removal of surfactant was confirmed by elemental and thermogravimetric analyses. Pd and Pt (0.5, 1.0, and 2.0 wt% of the total catalyst and with Pd/Pt = 4.0 a.r.) were then supported by incipient wetness coimpregnation using an aqueous solution of H_2PtCl_6 and $PdCl_2$. After impregnation, the obtained solids were first heated at 100 °C for 12 h and then calcined at 450 °C for 5 h.

The XRPD analysis was performed using a Philips PW 1050/81 goniometer, equipped with a PW 1710 unit, and Cu-K_α radiation ($\lambda = 0.15418$ nm, 40 mA, 40 mV), in the $2\theta = 10.0$–$80.0°$ range to determine the presence of segregated metal and/or oxide. Surface area data were obtained by N_2 adsorption using a Carlo Erba 1900 Sorptomatic, after outgassing the samples at 200 °C in vacuum.

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 (internal diameter 8 mm, length 54 cm), heated by an electric oven controlled by two J thermocouples. The amount of 6 cm^3 of catalyst (14–20 mesh) was 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 a stainless-steel capillary tube inside the catalytic bed. Before the tests, the catalysts were activated in a 200 ml min^{-1} H_2 flow, using a programmed increase of the temperature from RT to 450 °C. The solution of naphthalene in *n*-heptane (10 wt%, analytical grade) was fed using a HPLC Jasco 880-PU pump, in the H_2/N_2 flow. Each catalytic test was performed for 5 h, with the products collected 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, internal diameter 0.53 mm, film width 1.5 µm). The products were preliminarily tentatively identified by GC-MS using a Hewlett–Packard GCD 1800 system equipped with a HP5 column (5% of methylphenylsilicone, length 25 m, internal diameter 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 sulfur compounds responsible for the catalyst poisoning, the thio-resistance of the catalysts was investigated by adding increasing amounts of dibenzothiophene (DBT), the most representative of this family, to the feed.

3. Results and discussion

3.1. Catalyst characterization

The characterization of the mesoporous SiZr material used as support in the present work has already been widely described elsewhere [21–23]. The support acidity (Table 1) was considerably higher than MCM-41 aluminosilicates, since low coordination Zr^{IV} species in the framework were responsible for strong Lewis acidity. After noble metal impregnation, the acidity, the pore volume, and the surface area of the unreduced 2.0 wt% catalyst (Table 1) were lower than those of the support, due to the partial covering of the pores by the noble metal oxides. The XRPD data at low angle for the unreduced and reduced 2.0 wt% catalyst [18] indicated that the hexagonal structure of the support was maintained. The XRPD patterns at higher angles (Fig. 2) of the Pd/Pt catalysts, before and after reduction/reaction, did not show reflections typical of metal or metal oxides, thus showing a good and stable metal dispersion on these supports. BET measurements highlighted a slight decrease in the surface area values after reaction (Table 1), mainly attributable to adsorbed heavy compounds (tar).

3.2. Catalytic activity of 0.5 wt% Pd/Pt = 4.0 a.r.

On increasing the reaction temperature (Table 2) from 260 to 340 °C, the yield in decalin (*cis* + *trans*) decreased, since hydrogenation is an exothermic reaction, while the yields in HMW and LMW (calculated by the losses in the C balance) compounds increased (endothermic reactions). The conversion of naphthalene and the yield in tetralin remained almost unchanged. A loss in the hydrogenation activity was detected in the further test at low temperature (lower values in the decalin yield) with a corresponding increase of the cracking activity. Decreasing the contact time from 6.8 to 1.7 s (by increasing the gas hourly space velocity, GHSV) at 260 °C boosted the hydrogenation activity to decalin, while the formation of HMW products remained almost stable. The losses in the C balances dropped, since cracking is a

Table 1
Textural characteristics and acidity of the Pd/Pt supported on Si/Zr catalysts

Sample	S_{BET} ($m^2\,g^{-1}$)		V_p	d_p	Acidity
	Before reaction	After reaction	($ml\,g^{-1}$)	(nm)	(µmol $NH_3\,g_{cat}^{-1}$)
Support	850	/	0.72	3.6	1048
0.5% Pd/Pt	661	591	/	/	/
1.0% Pd/Pt	606	532	/	/	/
2.0% Pd/Pt	624	584	0.58	3.4	778

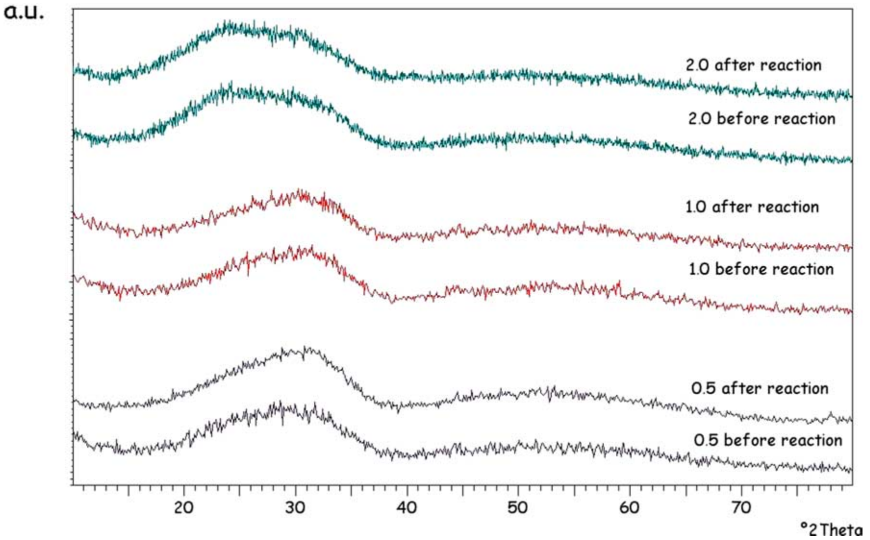

Fig. 2. XRPD patterns of the investigated catalysts, before and after reaction/reduction.

Table 2
Catalytic activity of 0.5 wt%; Pd/Pt = 4 a.r. on mesoporous Si/Zr = 5 a.r. as a function of the reaction conditions

	Conversion of naphthalene (%)	Yield in tetralin (%)	Yield in decalin (*cis* + *trans*) (%)	Yield in HMW products (%)	C balance losses (%)
Temperature[a] (°C)					
260	99.7	6.1	46.9	14.7	34.8
300	98.9	4.5	18.3	17.6	58.4
340	94.3	4.9	3.1	27.1	59.1
260	99.7	8.4	21.0	14.4	56.0
Contact time[b] (s)					
6.8	99.7	6.1	46.9	14.7	34.8
3.4	99.5	3.2	70.8	19.4	6.0
1.7	99.8	1.9	80.5	16.8	0.5
H_2/naphthalene ratio[c] (mol mol^{-1})					
21.0	99.7	6.1	46.9	14.7	34.8
16.0	96.8	15.1	16.5	19.3	54.7
12.5	98.3	5.8	17.4	20.8	54.3
DBT[d] (wt ppm)					
0	99.7	6.1	46.9	14.7	34.8
100 (17 wt ppm S)	97.5	7.1	7.9	14.1	68.2
1000 (170 wt ppm S)	96.6	15.9	1.4	19.7	67.8
3000 (510 wt ppm S)	95.0	15.0	0.1	16.0	64.0
0	99.1	4.5	22.0	17.3	55.2

[a] Contact time = 6.8 s, LHSV = 1 h^{-1}, H_2/naphthalene ratio = 21 mol mol^{-1}.
[b] Temperature = 260 °C, H_2/naphthalene ratio = 21 mol mol^{-1}.
[c] Temperature = 260 °C, contact time = 6.8 s, LHSV = 1 h^{-1}.
[d] Temperature = 260 °C, contact time = 6.8 s, LHSV = 1 h^{-1}, H_2/naphthalene ratio = 21 mol mol^{-1}.

consecutive reaction, thus being inhibited by low contact time values.

On decreasing the H_2/naphthalene ratio, the hydrogenation activity to decalin decreased, while the hydrogenolysis/ring-opening and cracking activities increased. This trend confirms that high pressures of H_2 seem to be necessary to overcome the thermodynamic limitations of the hydrogenation reaction [12]. Adding increasing amounts of DBT to the feed, at 260 °C, caused a dramatic decrease in the yield in decalin with a corresponding increase in the C balance losses and the yield in tetralin, while the yield in HMW compounds remained almost stable. This deactivation slightly affected the naphthalene conversion, thus showing how this parameter is less sensitive than the others. On removing the DBT from the feed, the catalyst almost restored its hydrogenation activity, showing a partially reversible S poisoning.

3.3. Catalytic activity of 1.0 wt% Pd/Pt = 4.0 a.r.

This catalyst showed its best hydrogenation activity at 300 °C, which decreased at 340 °C (Table 3). The yield in HMW compounds was always low except in the test at 340 °C, where the highest loss in the carbon balance was also detected. The decrease in the contact time favored the hydrogenation reaction at 300 °C, and as a consequence the conversion and the formation of HMW and LMW compounds slightly decreased.

On decreasing the H_2/naphthalene ratio, the yield in tetralin increased considerably while the yield in decalin dropped, thus highlighting that the hydrogenation reaction stopped at the first step. At the same time, the formation of LMW compounds increased, while the yield in HMW products remained almost unaffected. The presence of DBT adversely affected both the hydrogenation and the hydrogenolysis/ring-opening activities at 300 °C. Moreover, the naphthalene conversion slightly decreased and the hydrogenation stopped at the tetralin step. This deactivation was very clear on feeding 3000 wt ppm of DBT, when the cracking activity was also dumped. After removing the poisoning agent, the catalyst almost recovered its initial performances, thus showing that also in this case the deactivation was partially reversible.

3.4. Catalytic activity of 2.0 wt% Pd/Pt = 4.0 a.r.

This sample showed a very high hydrogenation activity to decalin (Table 4), which decreased at 340 °C. However, the yields in precious HMW compounds were always low except in the test at the highest temperature, with corresponding low C balance losses. These losses were low even in the test with a contact time of 13.2 s, a condition favorable to consecutive cracking reactions. The yield in decalin remained almost stable and higher than 89% up to a contact time of 4.5 s, and then it decreased due to the fact that the hydrogenation stopped at the tetralin formation.

The hydrogenation activity dropped on decreasing the H_2/naphthalene mole ratio from 21.0 down to the stoichiometric value (5.0), with a relevant increase in the yield in tetralin. The yield in other compounds remained almost stable, although a slight but constant decrease may be observed for both naphthalene conversion and formation of LMW.

Table 3
Catalytic activity of 1.0 wt%; Pd/Pt = 4 a.r. on mesoporous Si/Z $r = 5$ a.r. as a function of the reaction conditions

	Conversion of naphthalene (%)	Yield in tetralin (%)	Yield in decalin (*cis* + *trans*) (%)	Yield in HMW products (%)	C balance losses (%)
Temperature[a] (°C)					
260	96.6	23.3	57.4	1.7	14.2
300	100.0	1.0	75.3	9.6	14.1
340	98.5	5.3	19.4	29.4	44.4
260	98.9	9.1	66.0	1.1	22.7
Contact time[b] (s)					
6.8	100.0	1.0	75.3	9.6	14.1
3.4	99.7	1.5	81.1	4.0	13.1
1.7	99.4	2.4	82.5	3.6	10.9
H_2/naphthalene ratio[c] ($\mathrm{mol\,mol^{-1}}$)					
21.0	100.0	1.0	75.3	9.6	14.1
16.0	96.3	8.0	54.3	5.7	28.3
12.5	96.7	11.5	48.0	6.3	30.9
DBT[d] (wt ppm)					
0	100.0	1.0	75.3	9.6	14.1
100 (17 wt ppm S)	99.1	9.1	54.9	3.8	31.3
1000 (170 wt ppm S)	98.0	11.8	45.8	1.8	38.6
3000 (510 wt ppm S)	93.0	27.7	45.9	1.5	17.9
0	97.2	12.0	66.5	2.3	16.4

[a] Contact time = 6.8 s, LHSV = 1 $\mathrm{h^{-1}}$, H_2/naphthalene ratio = 21 $\mathrm{mol\,mol^{-1}}$.
[b] Temperature = 300 °C, H_2/naphthalene ratio = 21 $\mathrm{mol\,mol^{-1}}$.
[c] Temperature = 300 °C, contact time = 6.8 s, LHSV = 1 $\mathrm{h^{-1}}$.
[d] Temperature = 300 °C, contact time = 6.8 s, LHSV = 1 $\mathrm{h^{-1}}$, H_2/naphthalene ratio = 21 $\mathrm{mol\,mol^{-1}}$.

Table 4
Catalytic activity of 2.0 wt%; Pd/Pt = 4 a.r. on mesoporous Si/Z $r = 5$ a.r. as a function of the reaction conditions

	Conversion of naphthalene (%)	Yield in tetralin (%)	Yield in decalin (*cis* + *trans*) (%)	Yield in HMW products (%)	C balance losses (%)
Temperature[a] (°C)					
260	97.4	5.1	87.8	0.5	4.0
300	99.8	0.5	88.5	4.2	6.6
340	99.4	1.8	56.7	22.1	18.8
260	99.4	1.0	92.2	1.2	5.0
Contact time[b] (s)					
13.2	99.9	0.9	89.2	1.2	8.6
6.8	99.4	1.0	92.2	1.2	5.0
4.5	99.7	5.1	89.3	2.6	2.7
3.4	99.7	20.0	75.3	2.6	1.8
H_2/naphthalene ratio[c] ($\mathrm{mol\,mol^{-1}}$)					
21.0	99.4	1.0	92.2	1.2	5.0
15.0	98.9	2.2	90.3	1.8	4.6
10.0	98.9	4.7	88.1	2.4	3.7
8.0	98.6	27.6	64.9	2.7	3.4
5.0	92.4	66.6	21.2	1.3	1.3
DBT[d] (wt ppm)					
0	99.4	1.0	92.2	1.2	5.0
100 (17 wt ppm S)	98.9	1.9	89.7	2.5	4.8
1000 (170 wt ppm S)	99.5	23.9	70.7	3.5	1.4
3000 (510 wt ppm S)	98.5	53.6	39.8	4.3	0.8
0	98.9	1.6	88.7	2.3	6.3

[a] Contact time = 6.8 s, LHSV = 1 $\mathrm{h^{-1}}$, H_2/naphthalene ratio = 21 $\mathrm{mol\,mol^{-1}}$.
[b] Temperature = 300 °C, H_2/naphthalene ratio = 21 $\mathrm{mol\,mol^{-1}}$.
[c] Temperature = 300 °C, contact time = 6.8 s, LHSV = 1 $\mathrm{h^{-1}}$.
[d] Temperature = 300 °C, contact time = 6.8 s, LHSV = 1 $\mathrm{h^{-1}}$, H_2/naphthalene ratio = 21 $\mathrm{mol\,mol^{-1}}$.

The presence of increasing amounts of DBT dramatically inhibited the hydrogenation activity to decalin, with mainly formation of tetralin. However, removing the DBT from the feed, the initial performances were almost recovered, thus confirming the reversible effects on Pd/Pt containing Si/Zr MCM-41-type catalysts.

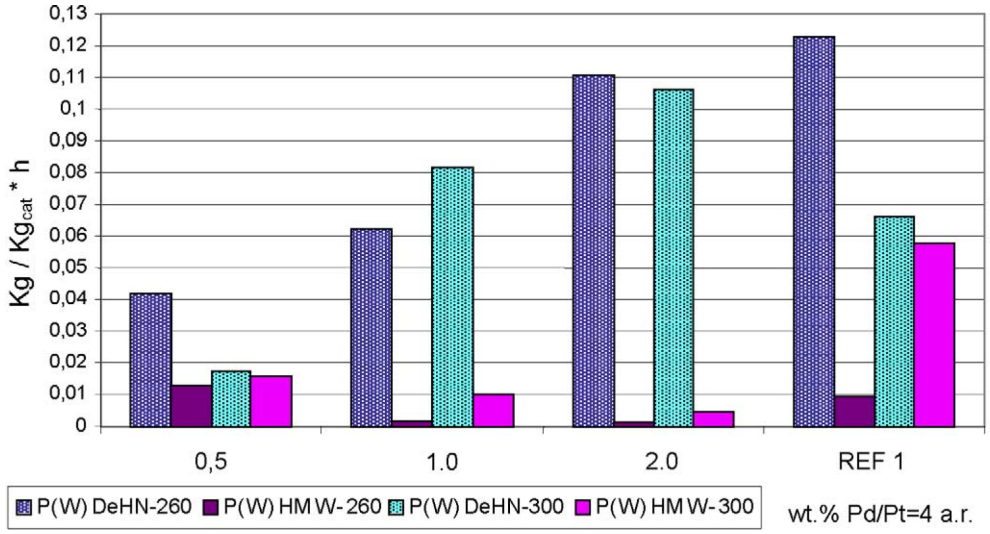

Fig. 3. Productivity in decalin (DeHN, *cis* + *trans*) and hydrogenolysis/ring-opening (HMW) products for kg (W) of catalyst ($T = 260$ and 300 °C; $\tau = 6.8$ s; H_2/naphthalene = 21 mol mol^{-1}; LHSV = 1 h^{-1}).

3.5. Optimization of the Pd/Pt amount

By comparing the activity of these mesoporous catalysts as a function of the amount of active phase (Fig. 3), it may be noted that increasing the percentage of the active phase increased the productivity in decalin per kg of catalyst, while that in HMW compounds (Fig. 3) and the cracking activity (Fig. 4) showed an opposite trend. Therefore the percentage of active phase (as well as the reaction conditions) can be tailored to favor the total dearomatization of the feed and the formation of the high cetane number HMW compounds. Due to the lowest content of the active phase (0.5 wt%), the cracking activity, highlighted by the losses in the C balance, was very high (more than 50%), while the sample with 2.0 wt% of Pd/Pt showed the lowest values. Thus, the sample with 1 wt% of Pd/Pt, at 300 °C, may be considered the best choice in terms of hydrogenation, hydrogenolysis/ring-opening, and cracking activities, being also interesting from the financial point of view, since the significant cost of the noble metals.

3.6. Comparison with a Pd/Pt reference catalyst

The performances of the 1 wt% Pd/Pt on Si/Zr MCM-41 sample was compared with those of a noble metal-containing reference catalyst (REF1) [1.0 wt% Pd/Pt = 4.0 a.r., on an Engelhard silica alumina (SiO_2/Al_2O_3 = 40:60 wt/wt)] [10]. In comparison to the analogous Si/Zr catalyst (1.0 wt%, Pd/Pt = 4.0 a.r.), the reference catalyst REF1 showed a higher productivity in precious HMW compounds (Fig. 3), although together with a higher formation of cracking compounds (Fig. 4), in agreement to its higher acidity due to the presence of alumina. The reference catalyst also evidenced at 260 °C a higher productivity in decalin than the Si/Zr sample (Fig. 3); however, at 300 °C the Si/Zr catalyst had the highest value among both samples. Finally, the thio-tolerance of the reference catalyst was also investigated, showing a very good stability to increasing amounts of DBT in feed. In conclusion, these data confirm that the acidity of the support is a key parameter, which must be carefully tuned, in order to obtain the useful hydrogenolysis/isomerization/ring-opening reactions and avoid the side cracking reactions. The hydrogenation activity is mainly attributed to the noble metals, while the thio-tolerance is due to both the support acidity and the Pd/Pt alloy, since recently an intrinsic thio-resistance was found also for Pd/Pt on basic supports [14].

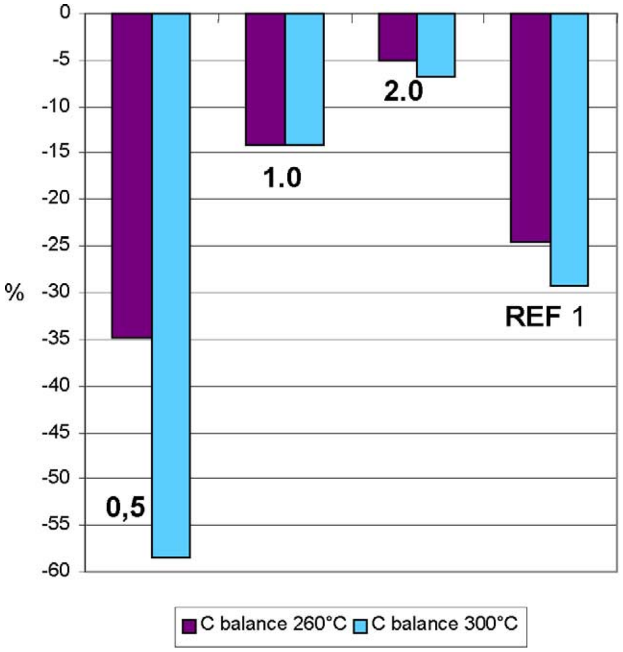

Fig. 4. Carbon balance losses ($T = 260$ and 300 °C; $\tau = 6.8$ s; H_2/naphthalene = 21 mol mol^{-1}; LHSV = 1 h^{-1}).

4. Conclusions

The zirconium-doped mesoporous silica is an appropriate support for Pd/Pt hydrotreating catalysts, since they showed interesting results in the hydrogenation of naphthalene at high pressure. Moreover, the thio-tolerance of these catalysts was sufficiently high to envisage their use in the final stages of a refinery process producing diesel fuel of high cetane number by hydrodearomatization. Investigating different amounts of active phase $\mathrm{Pd/Pt} = 4.0$ a.r. (0.5, 1.0, and 2.0 wt%) it was found that the sample with 1.0 wt% of Pd/Pt may be considered the best choice in terms of both the catalytic performances and the catalyst cost, since the increase of the percentage of the active phase increased the productivity in decalin (*cis* + *trans*), while that in hydrogenolysis/ring-opening and cracking compounds showed an opposite trend.

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