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Transformation of thiophene, benzothiophene and dibenzothiophene over Pt/HMFI, Pt/HMOR and Pt/HFAU: Effect of reactant molecular dimensions and zeolite pore diameter over catalyst activity

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Abstract

Pt-based catalysts were prepared by ionic exchange over three zeolites with different pore sizes, HMFI, HMOR and HFAU. With them, the effect of zeolite pore size over the transformation of sulfur containing compounds with different molecular dimensions, such as: thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) was analyzed. For the Pt-containing catalysts, reaction data reveal changes in the overall conversion of T, BT and DBT with zeolite pore size (Pt/HMFI < Pt/HMOR < Pt/HFAU). Hydrogenated sulfur compounds such as tetrahydrothiophene (THT), dihydrobenzothiophene (DHBT) were detected in high yields, being Pt/HMOR the more active catalyst, indicating that hydrogenation took place on some metallic Pt clusters that remained un-poisoned by the sulfur molecule. Moreover, the yields of THT, DHBT and tetrahydrodibenzothiophene (THDBT) remain stable with time on stream, indicating that poisoning by H_2S and/or the sulfur compound was not enough to inhibit completely the hydrogenating function of the metal and that at least a fraction of Pt^0 was protected by the zeolite from sulfur poisoning.

Keywords: Sulfur resistance; Sulfur poisoning organic sulfur compound; Hydrogenation; Hydrodesulfurization; Pt/HMFI; Pt/HMOR; Pt/HFAU; Thiophene; Benzothiophene; Dibenzothiophene

1. Introduction

Due to the more stringent environmental regulations, deep hydrogenation and sulfur content reduction in transport fuels have received considerable attention. Hydrogenation of intermediate distillates reduces aromatic content and improves cetane number. Although mild hydrogenation can be achieved during hydrotreatment process, commercial hydrodesulfurization (HDS) catalysts become efficient only at high temperatures and pressures (∼593 K, ∼5.5 MPa) and under these conditions hydrogenation (HYD) is thermodynamically limited [1].

It has been reported that the HDS of partially hydrogenated organosulfur compounds is faster than direct HDS [2–4] (i.e., for dibenzothiophene (DBT), the relative HDS rate constant for tetrahydrodibenzothiophene is about 33 times higher than that of dibenzothiophene one [5]). Consequently, the design of catalysts capable of efficiently achieving the hydrogenation of thiophenes can lead to the development of HDS process operating at lower temperatures because of the higher reactivity of the sulfur-hydrogenated compounds.

In general, hydrogenation at low temperature is performed with noble metals catalysts like platinum. However, the presence of organo-sulfur compounds leads to poisoning of the noble metal. Several works have been made to improve the hydrogenation performance of metal catalysts in presence of sulfur compounds. Sulfur tolerance was improved by using

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Pt–Pd alloys ([6] and references there in), or taking advantage of the acid properties of the supports, i.e., zeolites [7,8]. Recently, Song [9,10] proposed an interesting concept for the design of sulfur resistant noble metal catalysts (Pt and Pd) supported on zeolites. According to this author [9], during the hydrogenation of aromatics in the presence of sulfur compounds, metal poisoning can be decreased by: (i) the shape selectivity of the zeolite, which will impede contact of large sulfur molecules with the metal located in small cavities. (ii) The zeolite acidity, which will create an electron deficiency in the metal making it less prone to be poisoned by sulfur compounds [7,8] and (iii) spillover of active hydrogen produced over the metal in the small zeolite cavities, which will prevent the formation of PtS_2 induced by the H_2S presence. In a recent work, Pd/MOR was used, for the hydrogenation of naphthalene in the presence of thiophene, benzothiophene and dibenzothiophenes [11]. Naphthalene hydrogenation activity changed according to the dimensions of the used sulfur molecule, thus indicating the importance of shape selectivity in the increase of catalyst sulfur poisoning resistance.

In the present work, we analyze the transformation of sulfur compounds of different molecular size, such as thiophene (5.3 Å [12]), benzothiophene (6 Å [13]) and dibenzothiophene (8 Å [14]) over Pt catalysts supported on zeolites with different pore sizes (HMFI, HMOR, and HFAU). In this study, special attention will be paid to the following key points: (i) the effect of the zeolite pore diameter and sulfur molecule dimensions on the conversion of the sulfur compound, (ii) the relative importance of the HYD, HDS, and hydrocracking (HCK) reactions over the different catalysts, (iii) the stability of the catalysts hydrogenating function. To this end, Pt/HMFI, Pt/HMOR and Pt/HFAU catalysts were prepared, characterized by different techniques (nitrogen physisorption, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and infrared spectroscopy (FTIR).

2. Experimental

2.1. Catalysts preparation and characterization

Commercial zeolites, HMFI ($SiO_2/Al_2O_3 = 30$), HMOR ($SiO_2/Al_2O_3 = 20$) and HFAU ($SiO_2/Al_2O_3 = 30$), obtained from Zeolysts Int. were used as supports for Pt catalysts (1.8 wt.% Pt). Catalysts were prepared following the method reported by de Graaf et al. [15], briefly Pt was added by ion exchange using an aqueous solution of $[Pt(NH_3)_4](NO_3)_2$ (purity of 99%, Strem Chemicals) followed by drying (353 K, 14 h) and calcination (723 K, 2 h). Hereafter, the prepared catalysts were called Pt/HMFI, Pt/HMOR and Pt/HFAU.

Catalysts were characterized by nitrogen physisorption using a Micromeritics ASAP 2000 equipment; before every measure, samples were outgassed at 546 K in vacuum for 2 h.

FT-IR analysis of the catalysts in the hydroxyl region was conducted on a Nicolet Magna 750 spectrometer. To avoid the presence of adsorbed water, samples were pretreated as follows: self-supported wafers of pure powders were introduced into a quartz cell to be outgassed in vacuum (aprox. 10^{-5} mm Hg) at 673 K during 4 h. The pretreated sample was then used for the analysis. The spectra were collected at room temperature using a resolution of 4 cm^{-1} and 100 scans. When necessary catalysts were reduced *in situ*, under H_2 flow at 673 K for 4 h.

XRD patterns for pure and Pt-containing zeolites were collected in the $2^\circ \leq 2\theta \leq 80^\circ$ range on a Siemens D5000 diffractometer using the Cu Kα ($\lambda = 1.5406$ Å). Pt/HMFI, Pt/HMOR and Pt/HFAU catalysts were reduced *ex situ* before XRD analysis.

HRTEM observations were carried out on reduced samples using a Jeol 2010 microscope at 200 kV with 1.9 Å point-to-point resolution.

2.2. Catalytic activity test

Before reaction, oxide Pt catalysts were reduced *in situ* under H_2 flow at 673 K for 4 h. These reduced catalysts were used for the catalytic activity tests. Hydrotreatment of thiophene (T), benzothiophene (BT) and DBT was realized on a ISRI HP100 automated apparatus equipped with a flow microreactor operating in steady-state at 5.5 MPa, 493 K and WHSV = 61.8 h^{-1}. All activity tests were performed using 500 ppm of S in the feed by dissolving the corresponding sulfur compound (T or BT or DBT) in *n*-hexadecane. Reaction products were collected every hour and analyzed by gas chromatography with a HP 6890 chromatograph, equipped with FID detector and a HP Pona capillary column (50 m × 0.2 mm × 0.5 μm). Product identification was made with GC-MS (HP 61800B GCD system), and Varian Chrompack 3800 GC equipped with a RTX-1 (Restek) capillary column (105 m × 0.25 mm × 0.25 μm) and PFPD specific sulfur and FID detectors. The reported values of conversion and yields were calculated as follows: conversion $(X) = [(n_i - n_f)/n_i] \times 100$ and yield $(Y) = [n_p/(n_i - n_f)] \times 100$, where n_i = initial moles of the organo-sulfur reactant (i. e.: T or BT or DBT), n_f = final moles of the organo-sulfur reactant and n_p = moles of product for the analyzed reaction.

Finally using a mass balance, the H_2S formation was estimated.

3. Results and discussion

3.1. Textural properties characterization

The measured BET area for the used zeolites, see Table 1, is in accord with the ones reported by the commercial supplier [16]. Pt addition to the zeolites causes only a slight decrease in

Table 1
Specific surface area and microporous volume for worked samples

Sample	Total surface (m^2/g)	Microporous volume (cm^3/g)
HMFI	392	0.11
Pt/HMFI	377	0.11
HMOR	479	0.19
Pt/HMOR	462	0.18
HFAU	744	0.23
Pt/HFAU	686	0.21

the specific surface area, while pore volume shows no considerable changes, indicating no significant changes in the zeolite supports after Pt incorporation. The adsorption-desorption isotherms (not shown here) for HMFI and Pt/HMFI samples correspond to a combination between types I and IV isotherms, from IUPAC classification [17]. The same behavior was observed for supports and catalysts of HFAU and HMOR. Type I (Langmuir) isotherms for purely microporous solids, and type IV for mesoporous materials in which capillary condensation takes place at higher pressures of adsorbate.

3.2. XRD characterization

Fig. 1 shows the X-ray diffraction patterns for supports and catalysts. For pure zeolites, the diffractograms correspond well with those already published by IZA [18]. Comparison of the samples show that the diffractograms of the catalysts present the same peaks as the corresponding parent zeolites although Pt incorporation to zeolites causes a small decrease in the peaks intensities owing either to the presence of the heavy metal in the zeolite [19], and/or to small loss in zeolite crystallinity. No metallic or oxidic Pt phases were detected due to the low Pt content of the samples.

3.3. FT-IR characterization

The infrared spectra of zeolites and their corresponding, after Pt incorporation, reduced catalysts are shown in Fig. 2. In Fig. 2a and b, the spectra in the hydroxyl region for the couple HMFI and Pt/HMFI show four bands at 3780, 3746, 3660, and 3610 cm^{-1}, which are typical of HMFI zeolite. According to literature, the bands at ~3780 and ~3665 cm^{-1} are associated to the presence of hydroxyl groups on extraframework alumina; the band located at 3746 cm^{-1} is assigned to external silanols [20–22]. Jacobs and von Ballmoos [23] and Zecchina et al. [24] signaled that the band at ca. 3610 cm^{-1} is assigned to vibrations of the Si–OH–Al groups. Comparing the HMFI zeolite and reduced Pt/HMFI samples a slight decrease in the external silanols band is observed suggesting that a part of Pt was deposited on the external surface of this zeolite.

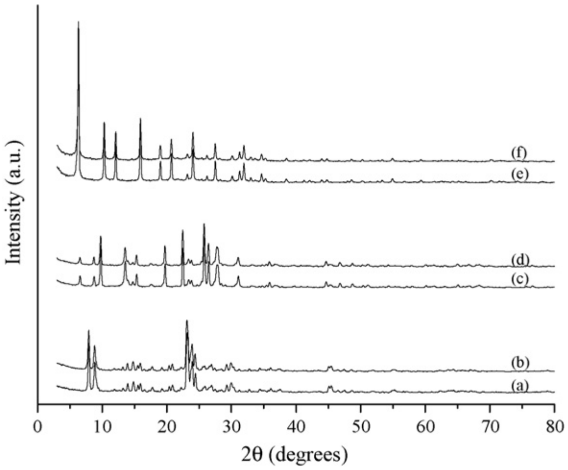

Fig. 1. XRD pattern for zeolites and reduced catalysts. (a) HMFI, (b) Pt/HMFI, (c) HMOR, (d) Pt/HMOR, (e) HFAU, (f) Pt/HFAU.

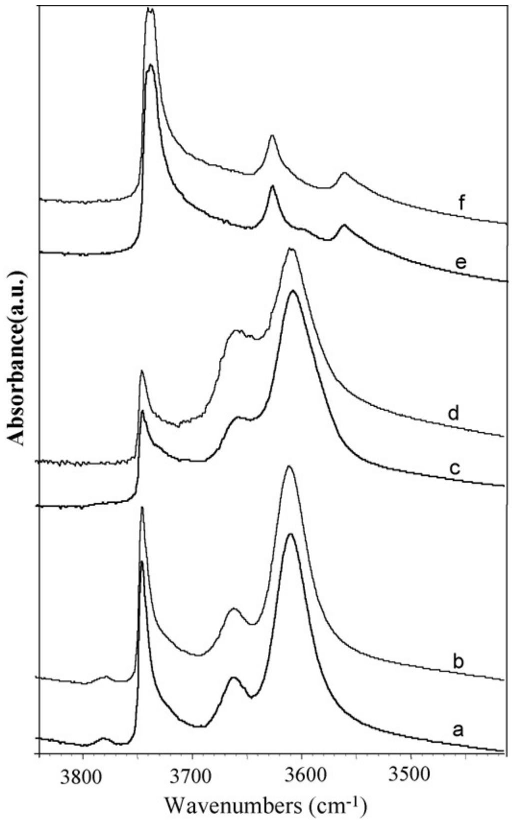

Fig. 2. FT-IR spectra for the zeolites and reduced catalysts: (a) HMFI, (b) Pt/HMFI, (c) HMOR, (d) Pt/HMOR (e) HFAU and (f) Pt/HFAU.

In the case of HMOR and Pt/HMOR (Fig. 2c and d) three bands located at 3746, 3660 and 3610 cm^{-1} are observed. The band at 3746 cm^{-1} has been assigned to silanol groups in the external surface of the zeolite; the band at ca. 3660 cm^{-1} is associated to OH's in extraframework alumina (EFAL); and the band at 3610 cm^{-1} is related to the Si–OH–Al groups [22,25]. In MOR zeolite, the incorporation of Pt causes an increase in the intensity for the band at 3660 cm^{-1}.

Finally, for HFAU and Pt/HFAU, the spectra (Fig. 2e and f) show three well-defined bands with maxima located at 3744, 3630 and 3565 cm^{-1}. It has been suggested [26,27] that the band at 3744 cm^{-1} is assigned to external silanol groups, the band at 3630 cm^{-1} corresponds to OH groups on Si–OH–Al located in the supercages and the band at 3565 cm^{-1} corresponds to OH groups on Si–OH–Al located in the sodalite cages. Comparison of the spectra of reduced Pt/FAU and FAU zeolite show that the ionic exchange and platinum oxide reduction do not cause considerable changes.

3.4. High resolution transmission electron microscopy

The diameter of the Pt particles on the samples was obtained from enlarged HRTEM micrographs. For Pt/HMFI, a heterogeneous size distribution of Pt metal clusters was observed. Pt clusters from 12 Å (micrographs not shown) up to 125 Å were determined. For this case, a few Pt metallic particles were

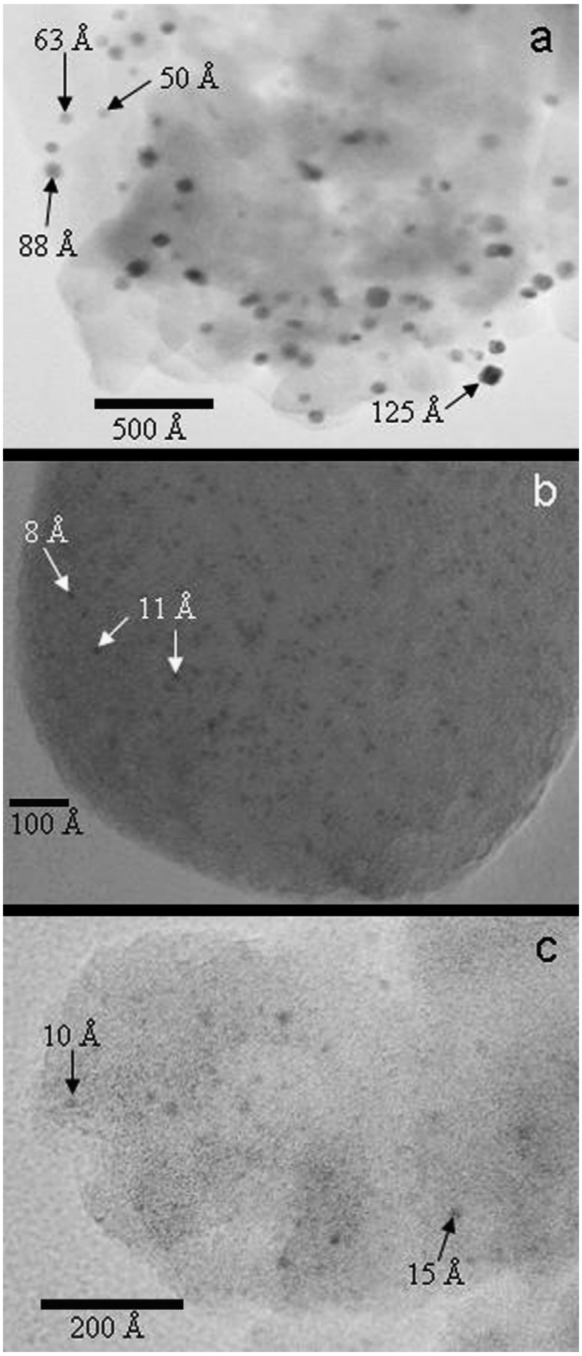

Fig. 3. HRTEM micrographs for reduced Pt catalysts: (a) Pt/HMFI, (b) Pt/HMOR and (c) Pt/HFAU.

observed on the external zeolite surface. An example of these external particles is the one signaled with 125 Å in Fig. 3a. The presence of Pt particles on the external zeolite surface could be caused by diffusional hindrance of the large Pt precursor, i.e. $[Pt(NH_3)_4]^{2+}$, during the preparation of Pt/HMFI catalysts; since $[Pt(NH_3)_4]^{2+}$ presents a size of 4.82 Å [28], which is close to the HMFI pore size (5.3 × 5.6 Å). The presence of external Pt metallic particles has been reported in the past for Pt/HMFI zeolite catalysts [29–31].

For HMOR and HFAU, Fig. 3b and c, the observed Pt cluster size distributions are more homogenous, as reported in the literature [32], and the observed particle sizes ranges are 8–11 Å for HMOR and 10–15 Å for HFAU. Since the channel sizes of HMOR and HFAU are 7 × 6.5 Å (main channel) and 7.4 × 7.4 Å, respectively, no diffusional restrictions for the penetration of the Pt precursor are expected; it is then likely that most of the Pt particles are located inside the porous system.

3.5. *Catalytic activity*

Reaction tests with the three pure zeolite samples, i.e. supports without Pt, showed a decay in the activity in short reaction times; besides almost all of the observed products came from hydrocracking reactions. No hydrogenated products from T and DBT were observed; except for BT where a small yield of dihydrobenzothiophene was detected. In the same way, for Pt/HMFI the conversion of the solvent, *n*-hexadecane, was about 9% while the same conversion for Pt/HFAU and Pt/HMOR was <3%. These result points out that, as a support, HMFI is the most acid of the used zeolites. In agreement with literature reports which indicate that HMFI is more acidic than HFAU [33]. The observed products were C_3–C_{15} hydrocarbons and isomers, the presence of light products interfere with the chromatographic analysis, mainly with the thiophene reaction product.

The Pt/zeolite catalysts displayed conversions of sulfur compounds higher than the pure zeolites and only small activity decay was observed during the evaluation tests. The main products were: for thiophene, tetrahydrothiophene (THT), 1-butene, 2-butene, butane and H_2S; for BT, dihydrobenzothiophene (DHDBT), ethylbenzene (ETB), ethylcyclohexane (ECH) and H_2S; finally for DBT, tetrahydrodibenzothiophene (THDBT), biphenyl (BF), phenylcyclohexyl (FCH), bicyclohexyl (BCH), benzene (B), cyclohexane (CH) and H_2S. According to the observed products, three main reactions (HYD, HDS and HCK) were identified. The results of the overall conversion for each sulfur compound as a function of the pore zeolite size are shown in Fig. 4; all the results correspond to samples after the pseudo-steady state behavior was reached.

For Pt/HMFI, the zeolite with the smallest porous system, thiophene conversion was about 38%; see Fig. 4a, while for zeolites with larger pores, Pt/HMOR and Pt/HFAU, the observed conversions were 83% and 77%, respectively.

The conversion of benzothiophene, which is a larger molecule than thiophene, was 52% on the Pt/HMFI zeolite, see Fig. 4b. This unexpectedly high conversion could be related to the fact that BT is more reactive towards hydrogenation than thiophene; because the double bond in the thiophenic ring has a more olefinic character than those in T [34]. Using Pt/HMOR or Pt/HFAU leads to increased BT conversions.

In agreement with its larger molecular critical size (8 Å) [14], the overall conversion for DBT has the smallest value (Fig. 4c). In this case, the size of DBT is larger enough to present diffusion problems in Pt/HMOR and Pt/HMFI; but not in Pt/HFAU. In this case, the overall conversion is also related to the pore zeolite size with conversions going from 17% for Pt/HMFI to 18% for Pt/HMOR and 56% for Pt/HFAU.

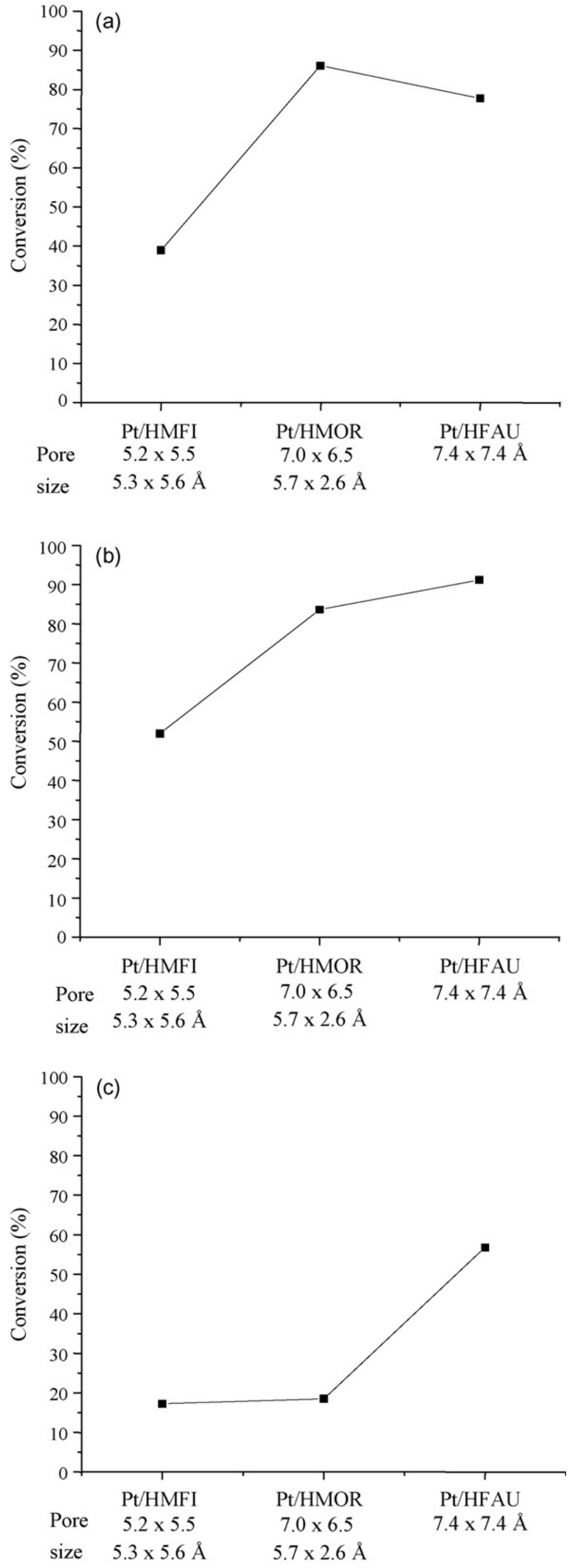

Fig. 4. Overall conversion for (a) thiophene, (b) benzothiophene and (c) dibenzothiophene as a function of type of zeolite and considering the aperture of pore diameter. Reaction conditions of 5.5 MPa, 493 K and WHSV = 61.8 h^{-1}, sulfur content 500 ppm, solvent used *n*-hexadecane.

In general, conversion increases with zeolite pore size in the following order: Pt/HMFI < Pt/HMOR < Pt/HFAU. If the reactant molecular critical diameter was, also, an important parameter in the reactivity then the following order should be obtained: T > BT > DBT. Instead, the reactivity order was BT ≈ T > DBT. This order can be explained taking into consideration that benzothiophene is more reactive towards hydrogenation than thiophene as already was explained [5]. The overall behavior indicates that it is likely that in all cases the major part of the reactions took place inside the zeolite structure and that conversion is related to the zeolite mean pore size and to the accessibility of the reactants to the active sites, in the zeolite porous structure.

The products yields obtained for the different reactions (HDS, HYD, HCK) taking place on the catalysts are shown in Fig. 5. Yield depends on the nature and morphology of the

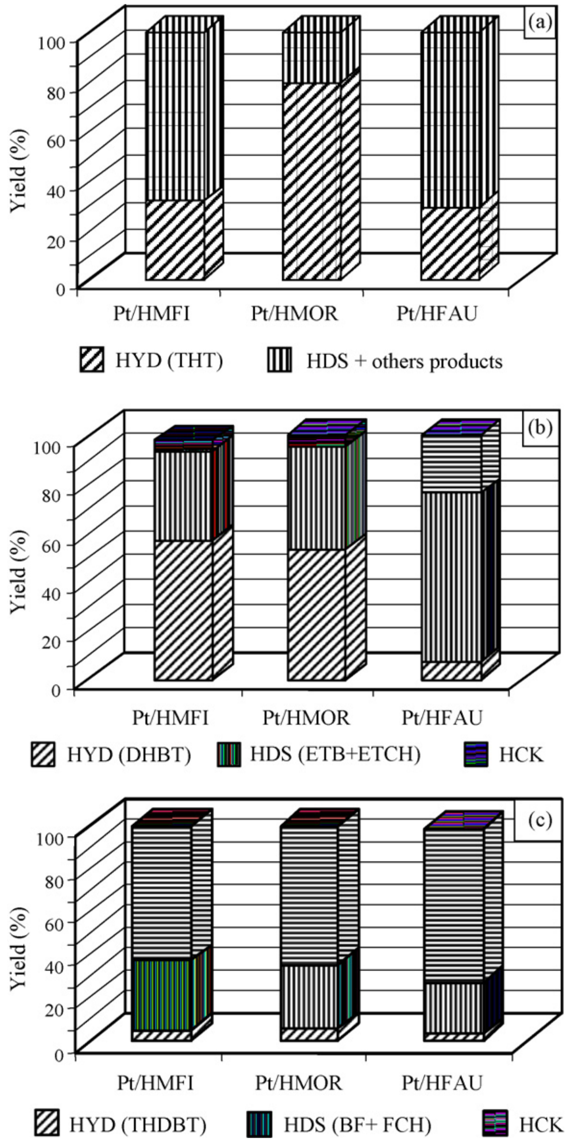

Fig. 5. Yields (%) for HYD, HDS and HCK reactions for each of the organosulfur compounds as function of the used zeolite: (a) thiophene, (b) benzothiophene, (c) dibenzothiophene. Reaction conditions of 5.5 MPa, 493 K and WHSV = 61.8 h^{-1}, sulfur content 500 ppm, solvent used *n*-hexadecane.

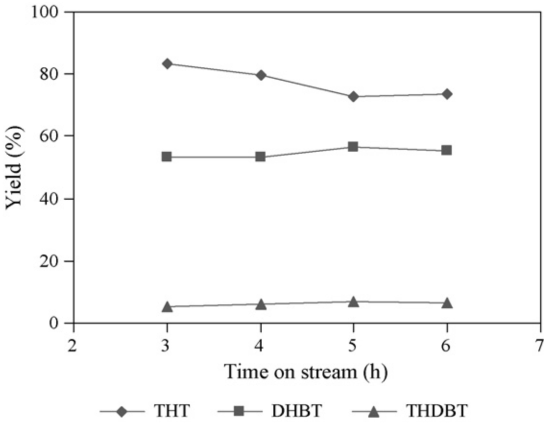

Fig. 6. Hydrogenated sulfur compounds yields (%) versus time on stream for Pt/HMOR catalyst. Reaction conditions of 5.5 MPa, 493 K and WHSV = 61.8 h^{-1}, sulfur content 500 ppm, solvent used *n*-hexadecane.

present phase. Mainly reduced Pt exists at the start of the reaction but later some particles of Pt^0 are transformed to PtS_2, as a result of the hydrogenated organo-sulfur compound and H_2S presence. Hydrogenated sulfur compounds such as THT, dihydrobenzothiophene (DHBT) were detected in high yields despite of its high reactivity. Therefore, it appears that part of the HDS products came from the HYD route. In the DBT case, the HCK reaction was also improved by the higher hydrogenation activity; for example, the lower yields of THDBT could be ascribed to the substantial scission of the C–C bond in the thiophenic ring on the acid sites of the zeolite, as has been reported in the past [35].

The fact that high yields of THT and DHBT remain stable at the time scale of our experiments, as is show in Fig. 6 for the Pt/HMOR case, suggests that at least a fraction of Pt^0 was protected from sulfur compounds poisoning; taking into consideration that the metal phase is responsible for the major part of the hydrogenation reaction. The higher hydrogenation yields obtained with Pt/HMOR (Fig. 5) respect to the other zeolites can be related to the existence, of small lateral channels [36] of 3.4 × 4.8 Å. It is possible that a fraction of Pt^0 clusters is located in these side-pockets and remains un-poisoned by T, BT and DBT, since the critical diameters of these reactive molecules are 5.3, 6.0 and 8.0 Å, respectively, and therefore these reactants do not penetrate to the lateral channels.

Although the H_2S produced in the hydrodesulfurization reactions (~80–420 ppm S) can enter into lateral channels (side pockets) and poisons the metallic Pt, it appears that in this case the concentration of H_2S was not enough to inhibit completely the hydrogenating function of the metal. In another hand, the sulfur resistance to H_2S poisoning could be related to the electron deficiency of the Pt^0 clusters induced by the acidic character of the zeolite and/or to the high concentration of active spillover hydrogen [7,8,37–39].

The presence of HDS products detected for all the catalysts at the temperature used in this study is related to the presence of PtSx. Previously, in a study of Yoshimura et al. [6] ascribed the HYD to the metallic phases and the HDS reaction to the PtSx phases. Based in the HDS yields, Fig. 5, it appears that greater amounts of PtSx are present in Pt/HMFI and Pt/HFAU, which is the zeolite with larger pore size. Also, it must be taken into account that the hydrogenated sulfur compounds are more easily hydrodesulfurized than the non-hydrogenated compound [2–4]. So, it is possible that the HDS products are obtained by two reaction paths: hydrogenation–hydrodesulfurization, and direct hydrodesulfurization. Generally, it is possible to establish the main path by making a study of the reaction selectivity; however, in our case it is difficult because the Pt/zeolite system also yields hydrocracking products that obscure the analysis.

Despite of thiophene and BT diffusion problems, high conversions of T and BT are found in the Pt/HMFI catalyst. This behavior can be explained by the existence of some Pt in the external surface of the catalysts as evidenced by the HRTEM and FTIR results. So, in this case, the observed conversions must be due to the contribution of both external metal clusters and pore mouths [40].

4. Conclusions

From the above results, it can be concluded that conversion of thiophene, benzothiophene and dibenzothiophene over Pt/HMFI, Pt/HMOR, and Pt/HFAU catalysts leads to hydrogenation, hydrodesulfurization and hydrocracking products. The catalyst activity is related to the zeolite pore size and follows the order: Pt/HMFI < Pt/HMOR < Pt/HFAU.

There is not a straight correlation between the different reactant molecular dimensions and their conversions: The conversion order BT ≈ T > DBT, can be explained because BT is more easily hydrogenated than the other sulfur compounds, and because the intrinsic reactivity of BT is higher than thiophene and DBT.

The stability of the yields of THT, DHBT and THDBT with time on stream at the time scale of our experiments suggests the presence of an un-poisoned fraction of Pt^0 clusters. It is possible that these Pt^0 clusters are protected against sulfur poisoning either by the electron deficiency created in the metal by the zeolite acid sites, or by the spillover of active hydrogen generated on the surface of Pt^0 particles located in the small cavities of the zeolite structure, especially in the case of Pt/HMOR.

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