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Conversion and hydroconversion of hydrocarbons on zeolite-based catalysts: an FT-IR study

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Abstract

The interaction of HZSM5 and Mo-ZSM5 with benzene, naphthalene, toluene, *ortho*-xylene, *para*-xylene, *n*-butane, isobutane, *n*-heptane, and methylcyclohexane, in the range 100–773 K has been investigated using FT-IR spectroscopy. Hydrogen bonded species with the internal bridging and the external terminal OHs has been detected. The reactivity at high temperature has also been studied. The access to the internal cavities and to the strongly acidic OHs is at least partly hindered in the case of Mo-ZSM5. The catalytic activity of ZSM5 was moderated by the addition of molybdenum, with lower cracking and higher liquid yields. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: HZSM-5; Mo-ZSM5; FT-IR spectroscopy; Benzene

1. Introduction

The growing need for high octane and low sulphur gasoline, and the future perspective of processing heavier petroleum cuts, has prompted the refining industry to look for alternative catalysts and processes in order to comply with the future restricted environmental regulations. Hydroconversion processes [1–3], that promote the skeletal isomerization leading to high octane branched paraffins and limited aromatization are a useful option. Also, the liquid yield should be high and therefore, the hydrogenolysis and the cracking of *n*-paraffins, leading to gaseous products like methane, ethane and propane should be minimized. Based on the above requirements, the catalyst for the selective hydroconversion should be bi-functional, with zeolitic (acid function) and metallic (hydrogenating function) components. To have information on the mechanisms involved in hydroconversion processes we have investigated by FT-IR spectroscopy, catalysts based on ZSM5 zeolites with and without impregnation with molybdenum. The results have also been compared with those obtained in flow reactor converting benzene/toluene/*n*-heptane model feed.

2. Experimental

Two commercial HZSM5 catalysts hereinafter called A (with Si/Al atomic ratio $= 23$) and B (with Si/Al atomic ratio $= 45$) were used as reference materials. Molybdenum was incorporated to a commercial HZSM5 by impregnation, using an aqueous solution of ammonium heptamolybdate to obtain a solid with

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6 wt.% MoO_3. This catalyst was dried at 393 K for 12 h and calcined at 673 K for 2 h. The IR spectra were recorded on a Nicolet Magna 750 Fourier transform instrument, using pressed disks of pure zeolite powders, activated by outgassing at 773 K into the IR cell.

The catalytic experiments have been carried out with catalysts extruded with alumina as binder material, using a tubular stainless steel reactor. The feed was added continuously by a Milton Roy high pressure pump and mass flow controllers controlled the flows of hydrogen and nitrogen. The reaction was conducted at 588 K and 28 kg/cm^2, using an LHSV of 2.5 h^{-1}, and a hydrogen/hydrocarbon ratio of 3.56×10^{-2} m^3 (STP) per liter of liquid. The liquid reaction products were analyzed by gas chromatography, using a 50 m PONA capillary column. Prior to the catalytic test, the catalysts were pretreated at 28 kg/cm^2 with nitrogen (588 K, 1 h) and then with hydrogen at 673 K during 4 h.

3. Results

3.1. Interaction of aromatics with HZSM5: benzene and naphthalene

In Fig. 1 the IR spectra of A (Fig. 1a) and B (Fig. 1c and e) ZSM5 samples, recorded at 300 K after previous activation at 773 K, are reported in the OH stretching region. In agreement with the data reported previously for similar catalysts [4] the spectra show a sharp maximum near 3745 cm^{-1} and a broader band in the region 3620–3600 cm^{-1}. The sharper higher frequency band has been found to be mainly due to terminal silanols exposed at the external surface of the zeolite while the broader lower frequency one is due to the acidic bridging Si–(OH)–Al thought by us to be exclusively located in the internal cavities [5,6]. In the case of the A and B samples, the intensity ratio of these two bands is inverted, according to the quite different Si/Al ratio and the higher crystal size for A.

The contact of B with benzene (Fig. 1d) results in the disappearance of the very strong band at 3746 cm^{-1} with the growth of four components in the lower frequency at 3607 cm^{-1}, very strong at 3505 cm^{-1}, definitely weaker at 3250 cm^{-1} and strong and broad near 3200 cm^{-1}. The adsorption of benzene at room temperature over sample A (Fig. 1b), causes the complete disappearance of the band at 3746 cm^{-1} with the corresponding formation of two broad bands centered at 3510 and 3253 cm^{-1}. The band at 3612 cm^{-1} seems only partially involved in the interaction with the aromatic compound, being the band in this position still present, although strongly weakened and perhaps broadened.

The band split at 3250 and 3200 cm^{-1} is actually due to the interaction of the bridging OHs absorbing (when unperturbed) at 3607 cm^{-1} with benzene

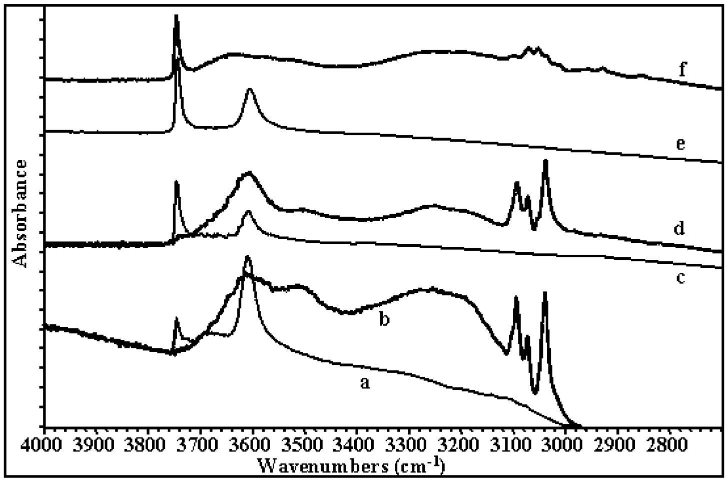

Fig. 1. FT-IR spectra of samples A (a and b) and B (c–f) activated at 773 K (a, c and e) and put into contact with benzene vapor at 5 Torr for 10 min (b and d) and naphthalene (f) at 0.1 Torr for 10 min.

molecules. The splitting suggests that either the bridging OH groups of ZSM5 are composed of two families with different acidity, or possibly for steric reasons, two different interaction modes can occur. The strong band at 3606 cm^{-1} and, likely, also that at 3505 cm^{-1} are instead associated to the terminal silanols absorbing at 3747 cm^{-1} (when free) with benzene. It has been quite ascertained that actually two types of terminal silanol groups differing in their acidity contribute to this band [5,6].

These data are confirmed by the adsorption of naphthalene over the same catalysts (see Fig. 1f for sample B). The first dose of naphthalene vapor go rapidly into the cavities allowing the perturbation of the band of the bridging hydroxyls giving rise to two strong and broad bands nearly at the same frequencies than for benzene, 3250 and 3200 cm^{-1}. The perturbation of the terminal silanols (only partial in the conditions of Fig. 1f due to the low partial pressure of the adsorbate) gives rise to two bands again near 3610 and 3500 cm^{-1}, although near 3600 cm^{-1} a third component is likely to be present.

3.2. Interaction of alkyl-aromatics with HZSM5 toluene, o-xylene and p-xylene

Similar results are obtained in the case of toluene adsorption (Fig. 2b for sample A) and of *p*-xylene adsorption (Fig. 2d for sample A). In both cases the adsorption gives rise to the disappearance of the band at 3746 cm^{-1} concomitant to the appearance of a broad band centered at 3500 cm^{-1} (for toluene) and at 3550–3500 cm^{-1} (for *p*-xylene), due to the interaction with the external silanols. The band at 3612 cm^{-1} is only in part disappeared, and a broad band appears near 3200–3180 cm^{-1}. The extent of the shift undergone by the OH stretching band depends on the electron density around the aromatic nucleus (the stronger the electron density the more the methyl groups).

When contact is carried out with *o*-xylene (Fig. 2f for sample A) the band at 3610 cm^{-1} is essentially unperturbed while the band at 3745 cm^{-1} is shifted to the 3650–3500 cm^{-1} region. This evidences that, at least after a few minutes of contact, most of *o*-xylene did not reach the internal cavities, but it is only adsorbed on the outer surface of the zeolite crystals. This agrees with the shape selectivity effect favoring the formation of *p*-xylene with respect to *o*-xylene upon toluene dismutation on ZSM5 zeolite, due to the hindered diffusion of the more bulky *ortho* isomer [7].

Looking at the gas-phase spectra, we could not detect any new molecule upon benzene interaction with the zeolite up to 673 K. On the contrary, reaction certainly occurred upon contact of the zeolite catalyst with toluene above 473 K. In fact at 673 K the strongest IR active band of benzene gas (ν_{11}, C–H

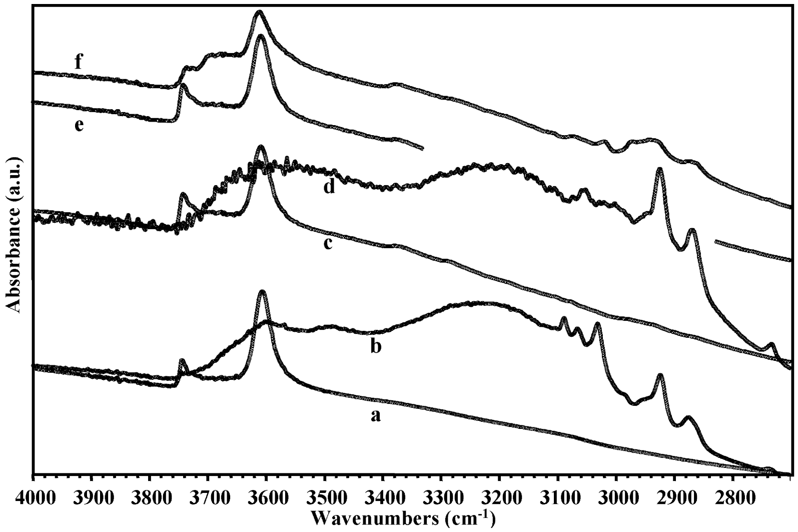

Fig. 2. FT-IR spectra of different disks of sample A activated at 773 K (a, c and e) and put into contact with toluene (b) *p*-xylene (d) and *o*-xylene (f) vapor at 5 Torr for 10 min.

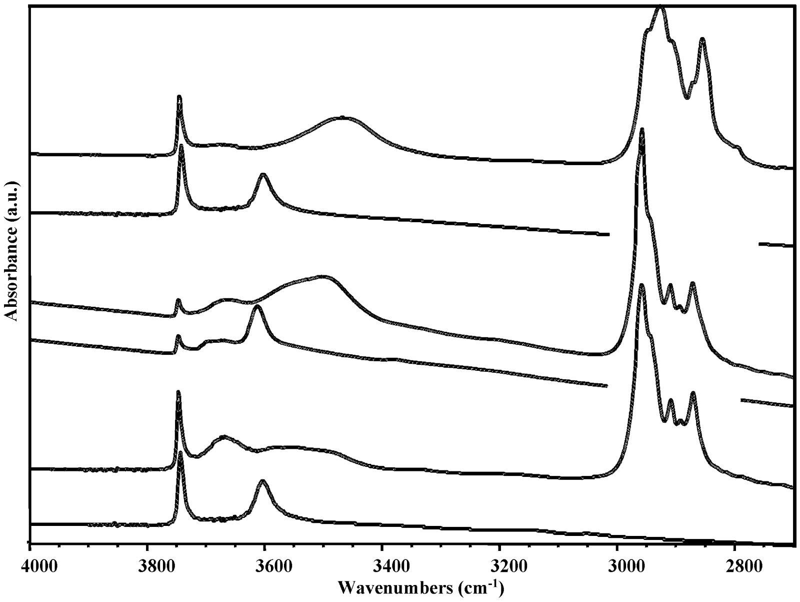

Fig. 3. FT-IR spectra of the gas-phase in contact with sample A after introduction of toluene at 300 K (a) and 600 K (b); (c) subtraction (b)–(a); (d) benzene vapor.

wagging) clearly appears at 672 cm^{-1} together with the three C–H stretchings of benzene in the region 3100–3000 cm^{-1}. This clearly indicates that demethylation of toluene or transmethylation has occurred. Xylenes, if present, would be hardly detectable because most bands are nearly covered with those of adsorbed toluene.

3.3. Interaction of aliphatics with HZSM5: butane, isobutane, n-heptane and methylcyclohexane

The contact of the activated A and B samples with small aliphatic hydrocarbons gas at room temperature (r.t.) (Fig. 3) causes first the complete disappearance of the band near 3610 cm^{-1} in both cases, and the later at least partial disappearance of the silanol band at 3745 cm^{-1}, depending on the total amount of the adsorbate. In the case of *n*-butane adsorption on sample B (Fig. 4a and b) the appearance of broader bands centered at 3650, 3560 and 3485 cm^{-1} is observed together with bands in the region 3000–2700 cm^{-1}, due to the C–H stretchings of butane. The disappearance of the bands both due to the acidic internal OHs of the zeolite and the external silanols with the concomitant appearance of the broader bands at lower frequencies certainly due to “perturbed” hydroxy groups (O–H stretching mode, νOH), is a clear evidence of the “σ-basicity” of the C–C and/or C–H bonds of butane and of their interaction with both the strongly acidic and weakly acidic silanols.

Parallel phenomena were observed when the HZSM5 zeolite was contacted with other alkanes. In the case of the interaction with isobutane (Fig. 3c and d for sample A), the “perturbed” νOH of the acidic zeolite OHs is also apparently split with components at 3560 and 3500 cm^{-1}, while for *n*-heptane we observe a broader band centered at 3460 cm^{-1}. This means that the heptane acid silanols interaction is the strongest one with respect to the other alkanes. The perturbations of the “external” silanols follow a similar trend, with $\Delta\nu$OHs of 80 cm^{-1} for isobutane and 95 cm^{-1} for *n*-heptane.

Methylcyclohexane immediately reaches the bridging internal sites of sample B shifting the OH band down to 3465 cm^{-1} (Fig. 3e and f). The band of the terminal external silanols is fully unperturbed. Actually, the subtraction spectrum shows that this band is fully shifted to higher frequency of 3 cm^{-1}. This behavior suggests that the molecules allowed (due to their low steric hindrance) to enter the cavities are strongly

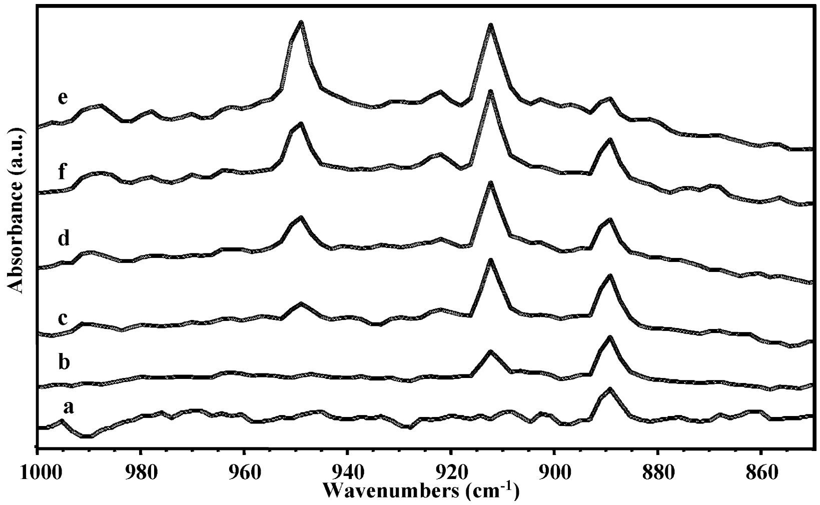

Fig. 4. FT-IR spectra of samples A (c) and B (a and e) activated at 773 K (a, c and e) and put into contact with *n*-butane (b), isobutane (d) and methylcyclohexane (f) vapor at 5 Torr for 10 min.

attracted by the acidic internal OHs. So the interaction with the weaker external OHs can only occur after saturation of the cavity sites.

The interaction of alkanes on HZSM5 zeolite is molecular and reversible, with no significant amount of more strongly adsorbed species up to near 573 K. Beyond this temperature, strongly adsorbed species begin to appear. Interestingly, the spectra of the adsorbed species arising from the high temperature interaction of the alkanes are very similar to each other and with those aroused from butenes. The same or very similar oligomeric species, all saturated and highly branched are formed starting from the hydrocarbons under study. These species have been identified previously as polyisobutene [8].

Upon high temperature contact with alkanes, also gas-phase spectra show that reaction occurred. The spectra in Fig. 4, e.g., are relative to heating zeolite in the presence of *n*-butane gas at 723 K. It is evident that, upon contact, bands grow first at 888 cm^{-1} (CH$_2$ wagging of isobutene) and later at 912 cm^{-1} (propylene), 922 cm^{-1} (1-butene), and at 948 cm^{-1} (ethylene). So, simultaneously to the production of the above cited polymeric species, isobutene is formed from *n*-butane, but also linear butene and cracking products (propylene and ethylene) are observed. The spectra arising from isobutane are virtually identical.

If the surface polymeric species has been left to form starting from *n*-butane and (after evacuation of the gas) decomposed thermally in the *T* range above 673 K, the first gas-phase IR band formed is at 889 cm^{-1}, due to isobutene. This behavior further supports the idea that the polymeric species is due to polyisobutene, as proposed earlier. Later, propylene is formed while finally ethylene and 1-butene are detected.

In the case of *n*-heptane interaction, starting already near 573 K we observed PQR shaped bands at 672 and 1035 cm^{-1}, which are the most intense peaks of gaseous benzene, suggesting that cyclization and aromatization occurred. Additional peaks at 948 cm^{-1} (ethylene) and 912 cm^{-1} (propylene) show that extensive cracking has also occurred.

3.4. Interaction of hydrocarbons with Mo-HZSM5 catalyst

The spectrum of the Mo-HZSM5 sample (Figs. 5 and 6) in spite of the higher noise shows also a strong band at 3613 cm^{-1}, due to the acidic internal HZSM5 OHs. On the contrary the band due to external silanols is not present. This suggests that a fraction of the Mo species are located at the external zeolite surface, where silanols are suppressed and that the

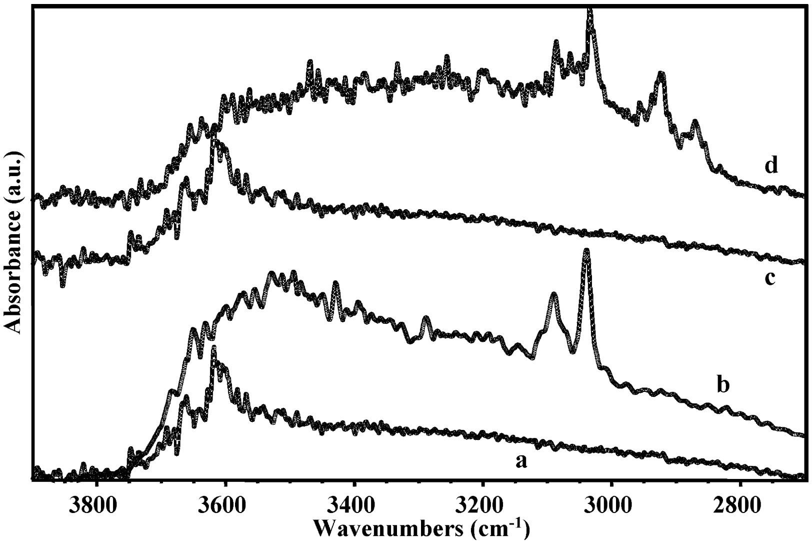

Fig. 5. FT-IR spectra of the Mo-ZSM5 catalyst after activation at 673 K (a and c) and in contact with benzene (b) and toluene (d) vapor at 5 Torr for 10 min.

incorporation of Mo does not entirely destroy or exchange the internal OHs of HZSM5.

The band due to the acidic internal OHs seems to be almost not involved upon benzene adsorption on Mo-HZSM5 (Fig. 5b). Accordingly, the band at $3250\,cm^{-1}$ formed by the interaction of benzene with the internal OH is being weak, if at all. These data indicate that the Mo species hinder the molecular diffusion of benzene into the zeolite cavities. On the other hand, the overtones involving the out-of-plane C–H

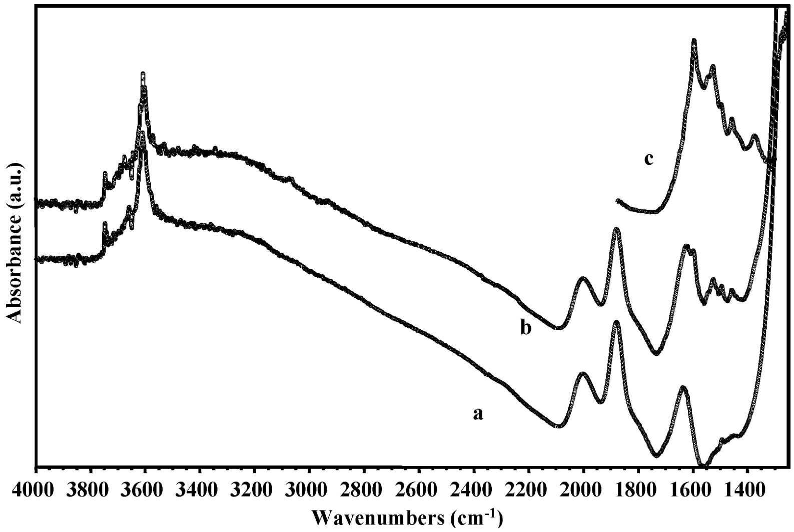

Fig. 6. FT-IR spectra of the Mo-ZSM5 catalyst after activation at 673 K (a) and after contact with toluene vapor at 5 Torr, 600 K for 10 min (b).

deformation modes of benzene in the 2000–1600 cm^{-1} region are shifted to higher frequency with respect to the liquid. Also, the ν_{11} fundamental (an out-of-plane C–H deformation mode too) is strongly shifted upwards with respect to the liquid. These perturbations, typically observed when the π-type electron cloud of benzene interacts strongly with electron withdrawing centers, provides evidence for the interaction of benzene with Mo centers.

Additionally, the interaction of benzene with Mo-HZSM5 was also studied at higher temperatures (up to 588 K). No new gas-phase species were found in these experiments, except for small amounts of CO due to the oxidation of benzene by incompletely reduced Mo centers. Small amounts of carbonaceous species, associated to main bands at 1605 and 1540 cm^{-1}, are also formed.

Also in the case of toluene adsorption, the band at 3617 cm^{-1} is almost not perturbed (so no diffusions into the cavities). Toluene adsorbed species (Fig. 5c and d) show a shift of the out-of-plane deformation bands, implying some kind of strong interaction with Mo centers.

Experiments performed at 588 K allow the observation of gas phase CO, but also new weak bands at 673 and 748 cm^{-1}. The former band is certainly associated to benzene, showing that dealkylation and/or transalkylation occurred also on Mo-HZSM5. The band at 748 cm^{-1} can tentatively be assigned to the presence of *o*-xylene (out-of-plane deformation). The formation of *o*-xylene and benzene can be explained assuming that toluene disproportionation occurred. Also, at 588 K, new bands, not due to toluene adsorbed as such, appear in the spectrum of adsorbed species on Mo-HZSM5 (Fig. 6a and b). These bands are due to coke precursor species. The more evident formation of these species from toluene than from benzene suggests that the methyl group of toluene might be involved.

After contact of *n*-heptane with Mo-HZSM5 at 588 K, in the gas-phase spectrum (not shown), we detect, besides CO, a CO_2 and a band at 1745 cm^{-1} certainly due to the C=O stretching of an aldehyde. We also find, bands at 948 cm^{-1} (ethylene) and at 1035 and 673 cm^{-1}, due to benzene.

3.5. Catalytic experiments

Catalytic experiments with pure aromatics feeds did not give rise to significant conversion in the reactor filled with the catalysts. On the contrary, *n*-heptane was converted over these catalyst giving rise mainly to gaseous light hydrocarbons with small amounts of C5, C6 and C7 isomers and even smaller amounts of alkylaromatics (C8 and C9). Benzene and toluene were produced in traces. The behavior of the reactant mixture, *n*-heptane (80 vol.%)/toluene (10 vol.%)/benzene (10 vol.%), with the catalysts was studied in three cases: (i) over HZSM5–alumina in the presence of hydrogen, (ii) over HZSM5–alumina in the absence of hydrogen and (iii) over Mo/HZSM5–alumina in the presence of hydrogen. The results are summarized in Table 1. The conversion of *n*-heptane is higher on all catalysts with respect to that of benzene and

Table 1
Summary of catalytic results

	$HZSM5/Al_2O_3$	$HZSM5/Al_2O_3$	$Mo\text{-}ZSM5/Al_2O_3$
Gas atmosphere	H_2	N_2	H_2
n-Heptane conversion	44.9	17.0	18.4
Benzene conversion (%)	28.1	23.3	11.4
Toluene conversion (%)	19.2	11.8	0
Liquid yield (%)	83.0	96.2	89.1
Products (wt.%)[a]			
C5	21.6	6.7	11.2
C5–C6 aliphatics	6.0	3.4	0.2
Iso-C7 and cyclo-C7 aliphatics	1.4	1.1	4.2
C7+ aromatics	8.2	5.6	0.2
C7+ aliphatics	0.8	0.7	<0.1
Unidentified	4.5	2.6	0.5

[a] Balance: unreacted feed components.

toluene. However, these are actually apparent conversions since aromatics can also be formed at the expense of *n*-heptane. In fact, the observed absence of toluene conversion on the Mo/HZSM5–alumina catalyst is actually the balance between its formation from *n*-heptane and its transformation to alkyl-toluenes, detected in small amounts. Analysis of the reactants conversion and reaction products clearly indicate that HZSM5–alumina is by far the most active system, giving both higher conversions and lower liquid yields, according to the high cracking activity exhibited by this catalyst. The presence of hydrogen is beneficial for the cleaning of the catalyst partially cocked surface.

4. Conclusions

The data presented in this paper provide evidence for the interaction of aliphatic and aromatic hydrocarbons with the internal and the external hydroxy groups of ZSM5 zeolite. Some details concerning the cracking activity are reported, providing evidence, in particular, of a key role of isobutene as the first gas-phase species formed by cracking of aliphatic chains. FT-IR experiments provide evidence for the formation of light olefins by cracking of alkanes, which are likely the result of the evolution of the H-bonded complexes evidenced at low temperature to carbenium ions. These carbenium ions, intermediates in the formation of light olefins from *n*-heptane, are very likely those involved in the alkylation of aromatics which has been evidenced in the flow reactor experiments.

The lower conversion observed in the experiments carried out in the flow reactor with the Mo-ZSM5 catalysts are interpreted, on the basis of FT-IR data, as due to the blocking of the access to the ZSM5 cavities by molybdenum species. In fact, it is evident that the strongly Bronsted acidic sites are retained in the Mo-ZSM5 although they are apparently not interacting with the hydrocarbons. Thus, Mo species appear to moderate the strong acidity of ZSM5 zeolite, improving the liquid yield of the process.

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