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# IM-5: A Highly Thermal and Hydrothermal Shape-Selective Cracking Zeolite

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**Zeolite IM-5 shows a higher thermal and hydrothermal stability than that of ZSM-5, the rate of dealumination being slower, as shown by $^{29}$Si and $^{27}$Al magic-angle spinning nuclear magnetic resonance. This is responsible for the larger acidity of IM-5 after calcination and steaming. When cracking paraffin, cycloparaffin, and olefin model compounds, this zeolite gives a higher activity than ZSM-5 with similar shape selectivity. When used as a fluid catalytic cracking additive, the improved hydrothermal stability of IM-5 is responsible for its higher activity and for increasing the olefin-to-paraffin ratios in the products, having a special impact on the production of propylene.** © 2002 Elsevier Science (USA)

*Key Words:* **hydrothermal stability of zeolites; zeolite IM-5; zeolite ZSM-5; FCC; FCC catalysts; cracking catalysts; fluid catalytic cracking; microactivity test.**

## INTRODUCTION

The fluid catalytic cracking unit (FCCU), which was originally designed as a conversion and gasoline producing unit, has now a new important objective: to increase the yield of propylene and butenes. This can be achieved by introducing some operational changes in the unit, as for instance by increasing the reaction temperature and decreasing the riser contact time. The temperature change produces more C2–C4 olefins due to an increase in the overcracking and a decrease in the extension of hydrogen transfer. Hydrogen transfer reactions result in saturation of olefins with the hydrogen transferred from cycloalkanes during their conversion to aromatics. Shorter contact times also result in lowering the extension of hydrogen transfer reactions, producing therefore higher yields of propylene and butenes. However, the highest impact on short olefin production, and more specifically on the production of propylene in FCC units, has been achieved via catalyst modifications. The use of Y zeolites with low unit cell size and, most important, the use of ZSM-5 as an additive have strongly increased the production of propylene in FCC.

More recently, a new version of catalytic cracking which involves very long contact times with the use of large quantities of ZSM-5 zeolite (DCC) has been developed to increase even further the production of propylene during cracking. The high activity of ZSM-5 together with the dimensions of the pores allows the cracking of linear olefins and paraffins with very low hydrogen transfer and coking yields, and consequently with high selectivity toward the production of C3 and C4 olefins. Since the success of ZSM-5 in FCC much synthesis work has been devoted to produce other 10-member-ring (10 MR) pore zeolites. However, the structures obtained have a unidimensional pore topology (ZSM-22, Theta-1, ZSM-35, ferrierite) with the corresponding catalytic limitations due to diffusion and pore plugging. Recently, the MCM-22 zeolite has been discovered, which presents 10-MR pores, together with an independent pore system formed by 12-MR cavities connected between them and to the exterior by 10-MR windows (1). This zeolite, while technically suitable as an FCC additive, gives a lower activity than ZSM-5 and its benefit has been observed only at large addition rates (2).

Looking into new structures with potential as FCC additives, we looked into a zeolite named IM-5 (3), whose structure is today unknown but which has a pore volume of 0.13 cm$^3$ g$^{-1}$ which, in principle, makes this material attractive for further studies. By adsorption of hydrocarbons with different molecular sieves, and by the use of several test reactions, it was concluded (4) that this zeolite may be formed by a bidimensional system of 10-MR channels. If this is so, there is no doubt that IM-5 could be a good candidate as FCC additive.

In this work it is shown that IM-5 presents an excellent thermal and hydrothermal stability, which is even better than that of ZSM-5. This stability and the pore topology makes this zeolite a very active catalyst for cracking paraffins, olefins, and cycloalkanes, and in any case more active than ZSM-5-activated zeolite. It is shown that this behavior is reflected in the activity and selectivity of IM-5 and ZSM-5 when used as FCC catalyst additives for gasoil cracking. This paper presents the main catalytic cracking features of IM-5, and its behavior as an FCC additive for gasoil

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cracking. The results are compared with those obtained with ZSM-5.

## EXPERIMENTAL

### *Materials*

A sample of IM-5 with a Si/Al ratio of 15 was obtained by starting with a gel of the following composition: $60SiO_2 : 1.5Al_2O_3 : 17Na_2O : 6NaBr : 10R : 2400H_2O$, where $R$ is 1,5-bis(methylpyrrolidinium) pentane in its dibromide form, which was used as a structure-directing agent. The crystallization was carried out at 448 K in PTFE-lined stainless steel autoclaves and the preparation was as follows: The required amount of silica (Aerosil 200, Degussa) was added to a solution of the organic structure-directing agent in water under stirring. Then a solution of sodium aluminate (Carlo Erba, 56% $Al_2O_3$), sodium hydroxide (Prolabo, 98%), and sodium bromide (Scharlau, 99%) in water was added and the mixture was kept under stirring for 30 min. After 10 days of heating, the autoclaves were quenched and the content was filtered and extensively washed with distilled water, dried overnight at 373 K, and calcined at 853 K for 3 h. The calcined sample was twice calcined with intermediate $NH_4Cl$ exchange.

ZSM-5 of Si/Al ratio of 20 was synthesized as follows: Silica (Ludox AS 40 from Dupont) was added to a NaOH solution kept under stirring at room temperature. Then, a basic solution of $AlO_2Na$ (Carlo Erba, 56% $Al_2O_3$) and finally a tetrapropylammonium bromide solution (TPABr, Aldrich) were also added. The resulting gel (300 g) of composition, $40SiO_2 : Al_2O_3 : 3.2Na_2O : 1.2TPABr : 1800H_2O$, was poured into a 500-ml stainless steel autoclave (Autoclave Engineers) under stirring (380 rpm) at 423 K for 20 h. The sample was washed, dried overnight at 353 K, and calcined at 853 K for 3 h. The calcined sample was twice calcined with intermediate $NH_4Cl$ exchange.

Zeolite USY is a commercial sample obtained from Zeolyst International with the code CBV720, corresponding to unit cell of 2.432 nm. The characteristics of these zeolites are given in Table 1.

**TABLE 1**

**Characteristics of Samples Used in this Work**[a]

| Sample | IM-5 | ZSM-5 | USY-2.432 | IM-5 steamed | ZSM-5 steamed |
|---|---|---|---|---|---|
| BET surface area ($m^2\ g^{-1}$) | 352 | 379 | 641 | 285 | 322 |
| Crystal size ($\mu m$) | 0.15 | 0.25 | 0.5 | 0.15 | 0.25 |
| Si/Al (synthesis gel) | 20 | 20 | | | |
| Si/Al (bulk)[b] | 15 | 25 | 19[c] | 15 | 25 |
| Si/Al (NMR) framework | 22 | 33 | — | 235 | >1000 |
| Brønsted acidity ($\mu$mol of Py $g^{-1}$) | | | | | |
| $T = 523$ K | 100 | 63 | 77 | | |
| $T = 623$ K | 76 | 39 | 45 | | |
| $T = 673$ K | 39 | 26 | 28 | | |
| Lewis acidity ($\mu$mol of Py $g^{-1}$) | | | | | |
| $T = 523$ K | 5 | 5 | 9 | | |
| $T = 623$ K | 4 | 4 | 8 | | |
| $T = 673$ K | 3 | 4 | 7 | | |

[a] Acidity and acid strength distribution were determined by IR pyridine measurements at different desorption temperatures.

[b] After calcination + ammonium exchange + calcination.

[c] Framework Si/Al ratio from XRD.

The zeolites for the cracking of methylcyclohexane were prepared as follows: The MFI zeolite with a molar Si/Al ratio of 10 was obtained in a basic medium without a structure-directing agent using sodium aluminate and silica gel as aluminium and silicium precursors. The molar composition of the starting gel was $Si/Al = 11$, $NaOH/(Si + Al) = 0.14$, $H_2O/(Si + Al) = 19$. MFI seeds (1 wt% relative to silica) were added. Crystallization of the gel under hydrothermal conditions at 180°C was completed after 30 h. The sample was washed, dried overnight at 383 K, and calcined at 823 K for 3 h. The calcined sample was three times exchanged with 10 N $NH_4NO_3$ under reflux conditions. The NES zeolite with a molar Si/Al ratio of 18 was synthesized according to (5). The BEA zeolite with a molar Si/Al ratio of 23 was obtained by dealumination of a commercial zeolite from Zeolyst with the code CP811BL-25 (Si/Al 12). The commercial zeolite was submitted to an acid treatment with 0.5 M $HNO_3$ under reflux conditions, then rinsed and dried overnight at 383 K. The OFF sample with a molar Si/Al ratio of 21 was prepared using sodium aluminate and colloidal silica as aluminum and silicium precursors and TMAOH as structure-directing agent. The molar composition of the starting gel was $Si/Al = 6$, $KOH/(Si + Al) = 0.68$, $H_2O/(Si + Al) = 21$, $TMAOH/(Si + Al) = 0.17$. Crystallization of the gel under hydrothermal conditions at 140°C was completed after 24 h. The sample was washed, dried overnight at 383 K, and calcined at 823 K for 10 h under air. The calcined sample was two times exchanged with 10 N $NH_4NO_3$ under reflux conditions, calcined under 50% water steam at 1023 K for 4 h, then submitted to an acid treatment with 1.5 M $HNO_3$ under reflux conditions, and finally rinsed and dried overnight at 383 K. The MOR zeolite with a molar Si/Al ratio of 18 was a commercial zeolite from Tosoh with the code HSZ-675HOA. The FAU zeolite with a molar Si/Al ratio of 5 was a commercial zeolite from Tosoh with the code HSZ-350HUA. The characteristics of these zeolites are given in Table 2.

IR experiments of calcined IM-5 and ZSM-5 samples were performed using vacuum cells. Wafers of 10 mg $cm^{-2}$ were degassed overnight under vacuum ($10^{-3}$ Pa) at 673 K. The spectra were recorded and then pyridine ($6 \times 10^{-2}$ Pa) was admitted, and after equilibration, the samples were outgassed for 1 h at increasing temperatures (523/623/673 K).

**TABLE 2**

**Characteristics of the Samples Used in the Cracking of Methylcyclohexane**

| Sample | MFI | NES | BEA | OFF | MOR | FAU |
|---|---|---|---|---|---|---|
| BET surface area ($m^2\ g^{-1}$) | 350 | 500 | 720 | 620 | 480 | 710 |
| $V_p(P/P_0 = 0.15)$ | 0.16 | 0.21 | 0.30 | 0.26 | 0.21 | 0.30 |
| Crystal size ($\mu$m) | 0.1–0.3 | 0.5–1 | 0.1–0.3 | 1–5 | 0.1–0.2<br>0.7–1.5 | 0.2–0.5 |
| Si/Al (bulk) | 10 | 18 | 23 | 21 | 18 | 5 |

After each desorption step, the spectrum was recorded at room temperature and the background subtracted. Quantitative determination of the amount of Brønsted and Lewis acid sites was derived from the intensities of the IR bands at ca. 1450 and 1550 $cm^{-1}$, respectively, by using the extinction coefficients given by Emeis (6).

Solid state $^{29}$Si NMR spectra were recorded under magic-angle spinning (MAS) at room temperature in a Varian Unity VXR-400WB spectrometer with a spinning rate of 5 kHz at 79.459 MHz and with a 55° pulse length of 40-$\mu$s repetition time. Cross polarization measurements were done at 5 kHz, a 90° pulse of 9 $\mu$s, 3.0 ms of contact time, and 3 s of recycle delay. Chemical shifts were reported relative to tetramethylsilane. Solid state $^{27}$Al NMR spectra were recorded at 104.2 MHz with a spinning rate of 7 kHz and at a 9° pulse length of 0.5 $\mu$s with a 0.5-s repetition time, and chemical shifts were reported relative to $Al(H_2O)_6$. Surface area was measured at 77 K using an automatic ASAP 2000 apparatus (Micromeritics).

### *Reaction Procedure*

Zeolites IM-5 and ZSM-5 were tested directly for the cracking of *n*-decane, 1-hexene, and 4-methyl-1-pentene, which can be representative of the gasoline fraction, and for the cracking of a vacuum gasoil (Table 3) as zeolite additives of a USY zeolite. The reaction experiments were performed in a MAT unit (7), which has been designed to accomplish the ASTM D-3907 standard. It works in an automatic regime with computerized control of reactor, sample collecting, and analysis of gases and coke. Gases were analyzed by gas chromatography (GC) in a HP5890 with a two-column system in series and Ar as carrier gas. Hydrogen, nitrogen, and methane were separated in a 15-m molecular sieve 5A column with a 0.53-mm inside diameter (ID) connected to a thermal conductivity detector. $C_2$ to $C_5$ hydrocarbons were separated in a 50-m, 0.53-mm-ID alumina plot column and analyzed with a flame ionization detector. Liquids from cracking of pure compounds were analyzed in a Varian 3400 with a 100-m, 0.25-mm-ID Petrocol DH column, and in the case of gasoil as feed by simulated distillation (SIMDIS) in a Varian 3800 equipped with a 10-m, 0.53-mm-ID MXT-2887 metal column supplied by Restek Corp., and the software STARD SD from Varian following the ASTM D-2887. Coke was measured by IR monitoring of the $CO_2$ formed during the catalyst regeneration. Complete combustion of CO is achieved by passing the combustion gases through a $CuO/Cu_2O_3$ catalytic bed at 623 K.

Experiments with pure compounds as feed were done at 773 K, 60 s time on stream, and catalyst-to-oil ratios ranging from 0.3 to 0.7 (wt zeolite/wt oil) for *n*-decane cracking. In all the experiments the amount of zeolite was constant and equal to 0.5 g. Zeolites were pelletized, crushed, and sieved and the 0.59–0.84 mm fraction was taken and diluted in 2.5 g of inert silica. When cracking olefins, the catalyst-to-oil ratio was varied from 0.14 to 0.42 and the amount of zeolite was 0.3 g diluted in 1 g of inert silica. In the case of gasoil cracking, the additive zeolite and the USY zeolite were placed in separated beds, as described previously (2). The bed at the top contained the USY zeolite (1.2 g of USY plus 0.3 g of silica) and the bed at the bottom contained the zeolitic additive diluted in 1.1 g of silica. The percentage of additive used in this work refers to weight of zeolite additive per 100 g of USY zeolite. The catalyst/oil ratio was calculated by dividing the amount of USY zeolite by the amount of gasoil fed.

The cracking of methylcyclohexane was performed in a continuous fixed-bed glass tubular reactor at 773 K and atmospheric pressure. The $N_2$/MeCHA was 12 mol/mol and the ratio (MeCHA wt/catalyst wt/h) varied between 0.8 and 360 $h^{-1}$. The reaction products were analyzed by GC using a 150-m-long fused-silica capillary column. The IM-5 zeolite was compared with MFI (Si/Al 10), NES (Si/Al 18), BEA (Si/Al 23), OFF (Si/Al 21), MOR (Si/Al 18), and FAU (Si/Al 5). Prior to the test, the zeolites were activated at 773 K under $N_2$ for 1 h. The data were collected for methylcyclohexane conversions of ∼40 wt%, after 5 min on stream.

**TABLE 3**

**Vacuum Gasoil Properties**

| Density (60°C) ($g\ cm^{-3}$) | 0.916 |
|---|---|
| Aniline point (°C) | 76 |
| Sulfur (wt%) | 2.7 |
| Nitrogen (wt%) | 0.15 |
| Carbon Conradson (%) | 0.09 |
| Na (ppm) | <0.05 |
| Cu (ppm) | 30 |
| Fe (ppm) | 0.5 |
| Ni (ppb) | 30 |
| $V$ (ppb) | <25 |
| ASTM D-1160 (°C) | |
| 10% | 400 |
| 30% | 411 |
| 50% | 425 |
| 70% | 449 |
| 90% | 489 |

## RESULTS AND DISCUSSION

### *Model Reactions*

*n*-Decane was used here as model reactant to study the catalytic cracking behavior of IM-5 and ZSM-5. Indeed, *n*-decane belongs to the gasoline fraction and can diffuse in 10-MR pore zeolites. Moreover, a detailed analysis of the reaction products can give information not only on cracking activity, but also on the olefin-to-paraffin (hydrogen transfer) and protolytic-to-$\beta$-scission cracking (C1+C2/isobutane) ratios that can be expected with a particular zeolite structure.

The results in Fig. 1 show a higher *n*-decane cracking conversion with IM-5 than with ZSM-5. This higher activity of IM-5 is a consequence of its higher density of Brønsted acid sites, as shown by pyridine adsorption (Table 1), which must be related to the lower framework Si/Al ratio. IM-5 produces more liquids and fewer gases than does ZSM-5, and this, together with the lower C1+C2/isobutane and C3/C4 ratios observed with IM-5 (Fig. 2), indicates, respectively, a lower ratio of protolytic (unimolecular) versus $\beta$-scission (bimolecular) cracking, and a lower ratio of cracking to disproportionation reaction in IM-5. The higher contribution of bimolecular reactions in IM-5 can be a consequence of the higher acid site density, as well as of the existence of larger void spaces within the structure (4). Both factors should favor the bimolecular hydride transfer reactions in IM-5 with the corresponding negative effect on the olefin-to-paraffin ratio in the gas products. Indeed, the propylene/propane, butenes/butanes, and isobutene/isobutane ratios are lower for IM-5 than for ZSM-5 (Fig. 2).

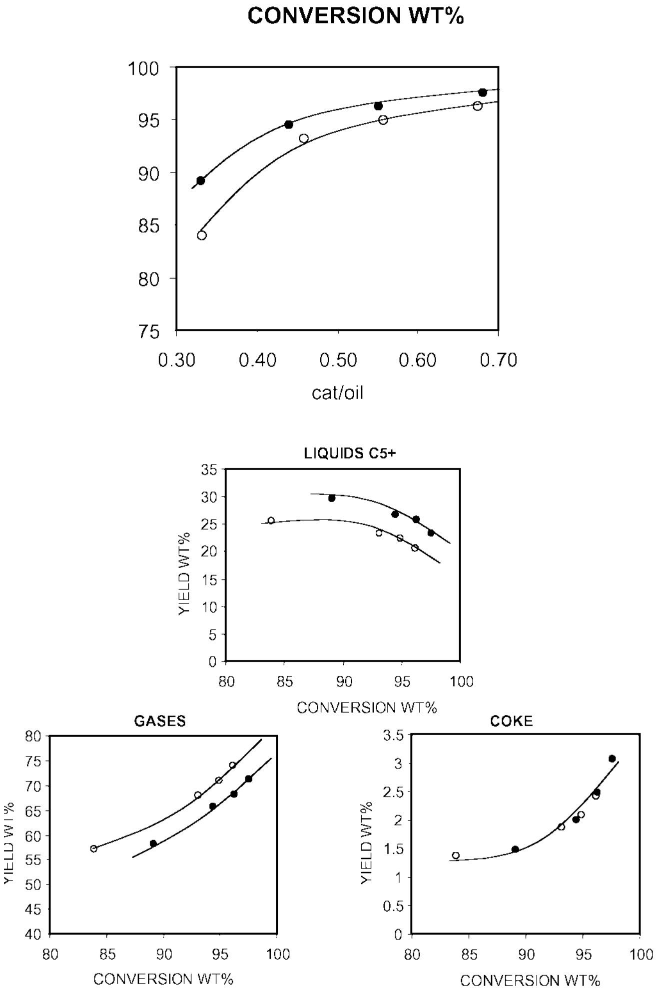

**FIG. 1.** Total conversion and selectivities in the cracking of *n*-decane at 773 K and 60 s time on stream over (●) IM-5 and (○) ZSM-5.

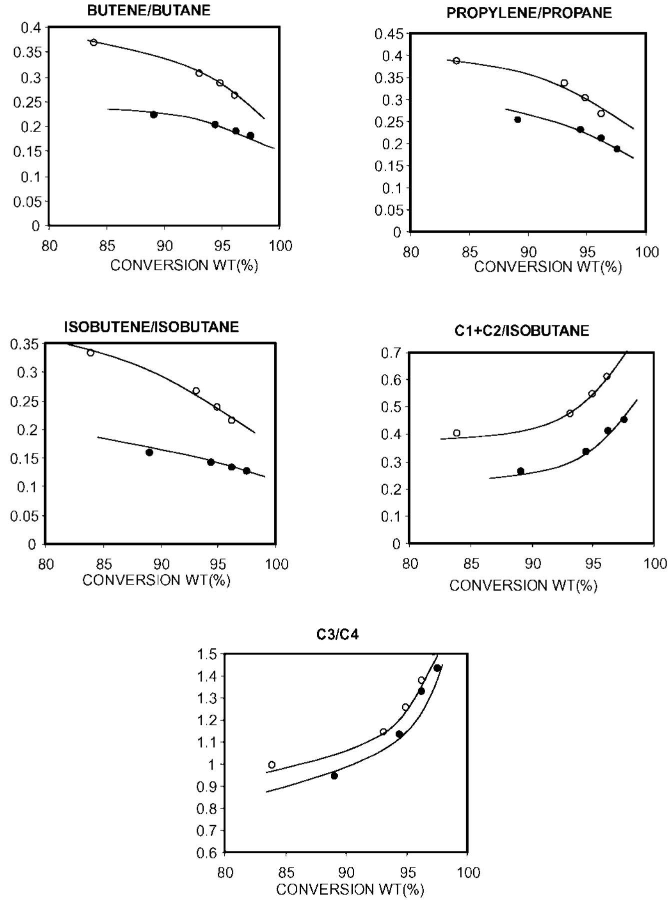

**FIG. 2.** Ratios of interest in the cracking of *n*-decane at 773 K and 60 s time on stream over (●) IM-5 and (○) ZSM-5.

More specifically, the hydrogen transfer (HT) activity of both zeolites has been studied using reacting methylcyclohexane. It has been reported (8, 9) that during cracking of methylcyclohexane with zeolites, hydrogen can be transferred from the cycloalkane feed to the olefins produced by cracking, giving toluene and short paraffins and olefins as products. The HT reactions involving the formation of bulky bimolecular reaction intermediates are mainly controlled by steric constraints and by the space available inside the microporosity of the zeolites. They can therefore

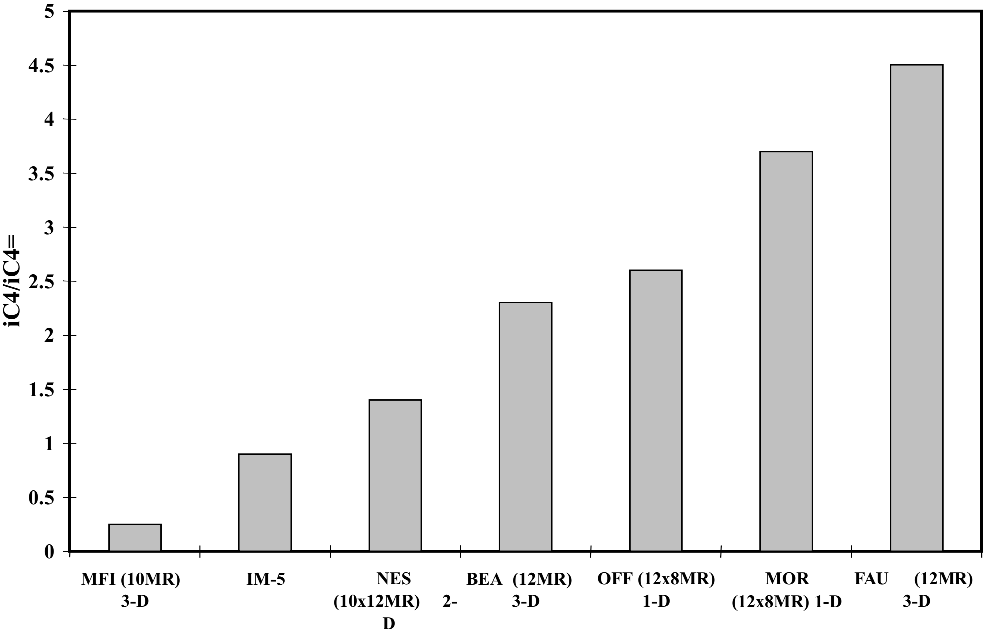

**FIG. 3.** $\mathrm{iC}_4/\mathrm{iC}_4^{=}$ ratio as a function of zeolite structure, obtained in methylcyclohexane cracking at 773 K, $N_2/\mathrm{MeCHA} = 12$, and ratios (MeCHA $\mathrm{catalyst}^{-1}\ \mathrm{h}^{-1}$) varied between 0.8 and 360 $\mathrm{h}^{-1}$.

provide useful information on the porous structure of the zeolite. The $\mathrm{iC}_4/\mathrm{iC}_4^{=}$ ratio was chosen as the parameter to quantify the HT reactions. A high $\mathrm{iC}_4/\mathrm{iC}_4^{=}$ ratio means that the HT reactions are important (10). The results obtained (Fig. 3) confirm that IM-5 is more active for hydrogen transfer than is ZSM-5. Moreover, when the influence of zeolite pore dimensions is considered (Fig. 3), the highest values of $\mathrm{iC}_4/\mathrm{iC}_4^{=}$ are reached for FAU and MOR zeolites and the smallest ones for MFI samples, whereas intermediate values are obtained for NES, OFF, and BEA samples. The range for HT reactions follows well the range of pore diameter or available microporous volume. The $\mathrm{iC}_4/\mathrm{iC}_4^{=}$ ratio obtained for the IM-5 zeolite ranks the IM-5 between the MFI and the NES zeolite, which involves connecting pores with 10 and 12 MR. These results are in good agreement with our previous work (4), which concluded that the IM-5 structure

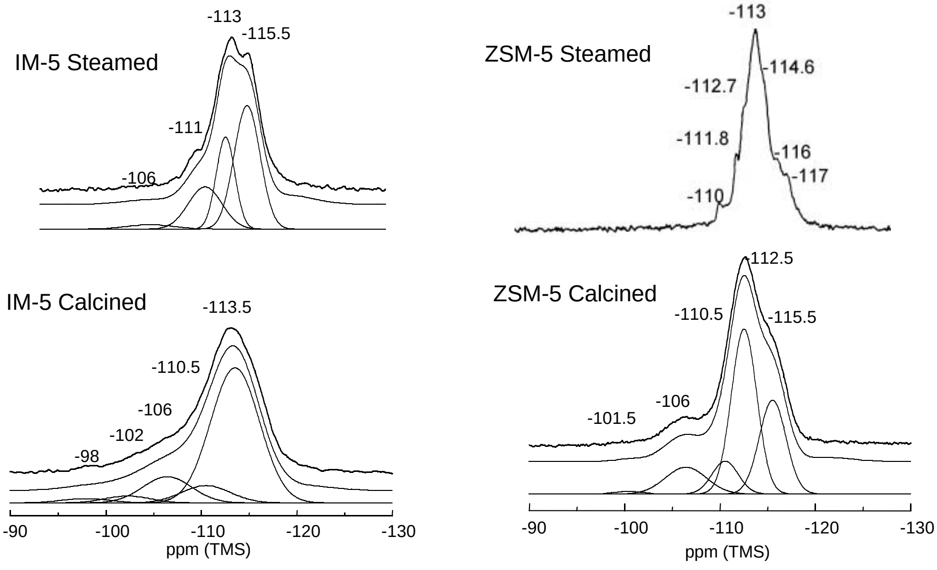

**FIG. 4.** $^{29}$Si NMR–MAS spectra of IM-5 and ZSM-5 calcined and steamed at 1023 K for 5 h.

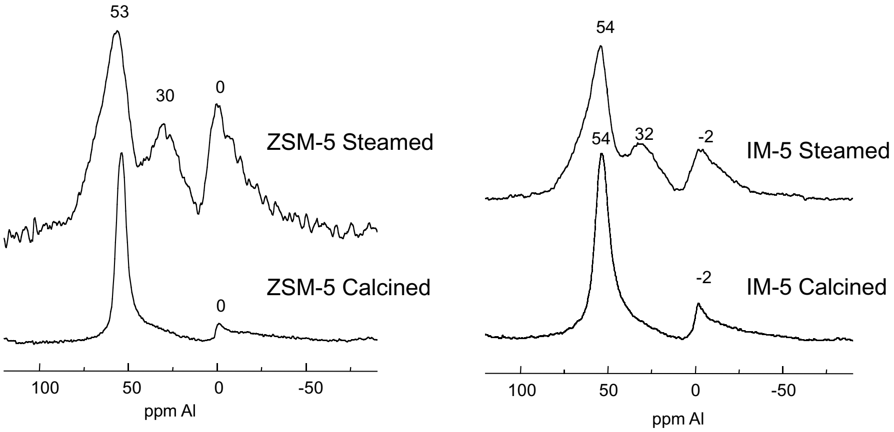

**FIG. 5.** $^{27}$Al NMR–MAS spectra of IM-5 and ZSM-5 calcined and steamed at 1023 K for 5 h.

could involve 10-MR crossing channels with a pore diameter larger than those of ZSM-5 or even may also contain 12-MR pores.

### *Zeolite Stability*

In the case of catalytic cracking, zeolite steam stability, and more specifically the rate of zeolite dealumination at high temperature in the presence of steam, is a factor of paramount importance. In order to better study the hydrothermal stability of this zeolite, ZSM-5 and the IM-5 samples were treated at 750°C in a 100% steam atmosphere during 5 h. It has to be remarked that this is a hard treatment for a zeolite, specially if one takes into account the fact that during this treatment the zeolite was not dispersed in a matrix, which can help to dissipate heat from the surface of the crystallites.

The results presented in Table 1 show that the surface area of both zeolites decrease slightly upon steaming, indicating that a little loss of crystallinity has occurred during the treatment. The $^{29}$Si and $^{27}$Al NMR–MAS spectra of the samples after calcination and after steaming are given in Figs. 4 and 5, respectively. The $^{27}$Al NMR–MAS spectra show that during calcination some dealumination of the zeolites has already occurred, as is shown by a band at ~0 ppm, which corresponds to the presence of octahedrally coordinated Al. From the relative peak intensity of the signals at ~54 (tetrahedral) and 0 pmm (octahedral), it becomes clear that an important dealumination has occurred during steaming.

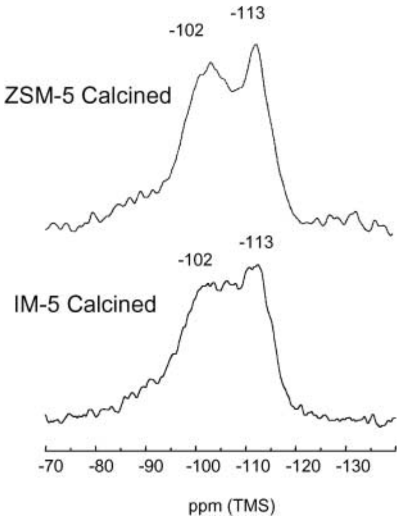

**FIG. 6.** $^{1}$H–$^{29}$Si NMR–MAS cross polarization spectra of IM-5 and ZSM-5 calcined.

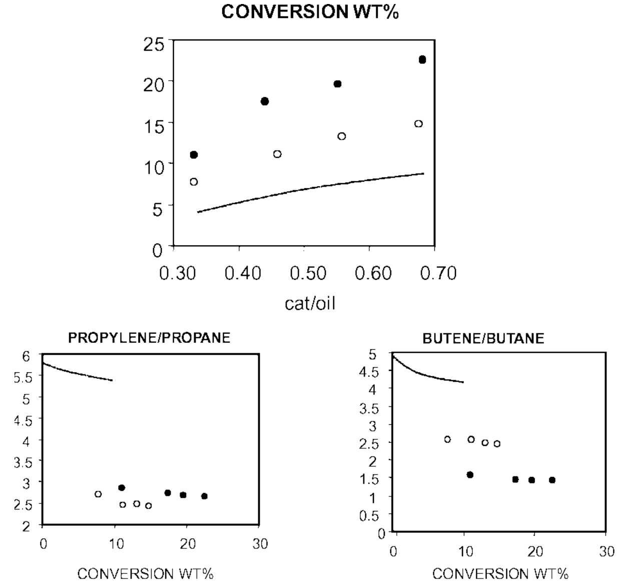

**FIG. 7.** Total conversion, selectivities, and ratios of interest in the cracking of *n*-decane at 773 K and 60 s time on stream over (●) IM-5 and (○) ZSM-5, steamed at 1023 K for 5 h. Line corresponds to thermal cracking.

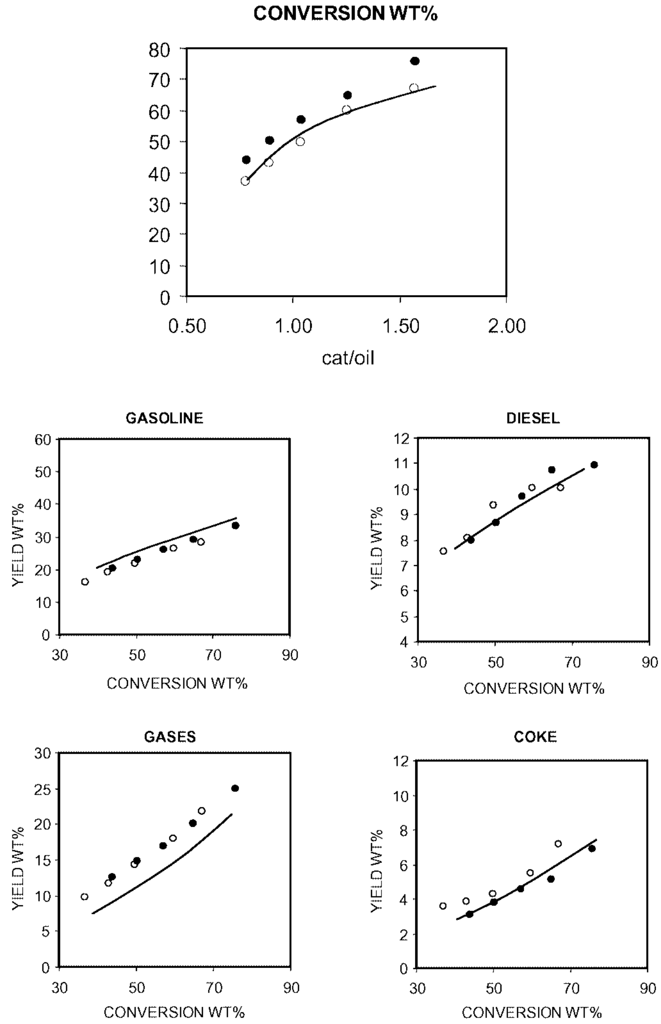

**FIG. 8.** Total conversion and selectivities in the cracking of gasoil at 793 K and 30 s time on stream over (line) USY-2.432 nm as base catalyst and (●) IM-5 and (○) ZSM-5, steamed at 1023 K for 5 h at 13.3 wt% of additive level.

The $^{29}$Si NMR–MAS spectra of the calcined samples show in both zeolites peaks at −110.5, −113.5, and −115.5 ppm, which correspond to Si coordinated with four silicons, a band at −106 ppm corresponding to Si(3 Si, 1 Al), and one additional signal at −98 ppm in the case of IM-5 which is assigned to Si(2 Si, 2 Al). A small broad band at ∼−102 ppm can be observed, which indicates the presence of Si coordinated with 3 Si and 1OH, as shown by cross polarization measurements (Fig. 6) which enhance Si–OH signals. This band could be due to the presence of internal defects in the original zeolite and/or to silanol nest defects generated upon dealumination. From the intensity of the $^{29}$Si NMR–MAS peaks, a framework Si/Al ratio could be calculated, which turns to be 22 and 33 for calcined IM-5 and ZSM-5, respectively. These results indicate that the framework Si/Al ratio is higher than that obtained by chemical analysis and agrees with the $^{27}$Al NMR–MAS results that indicate that some extraframework Al was generated by dealumination during the calcination of the zeolites to remove the organic occluded in the pores.

In the case of the steamed samples, the $^{29}$Si NMR–MAS (Fig. 4) signal at −98 ppm corresponding to Si coordinated to 2 Si and 2 Al has disappeared while the signal at −106 ppm corresponding to Si(3 Si, 1 Al) has strongly decreased in IM-5 and has practically disappeared in ZSM-5. Moreover, the spectra of ZSM-5 steamed show a sharp resolution of signals belonging to the different crystallographic positions of silicon in silicalite, in agreement with what has been reported for highly siliceous ZSM-5 (11). It is clear that with the steamed samples the determination of the framework of Si/Al will be subject to a higher level of uncertainty than with the calcined samples. Nevertheless, the values calculated on the two steamed samples are so different (see Table 1) that it should be possible to conclude that the stability of IM-5 toward dealumination is higher than that of ZSM-5 of a similar starting framework Si/Al ratio.

This conclusion agrees well with the *n*-decane cracking results obtained with the steamed zeolite samples (Fig. 7). Indeed, the steaming produces an important decrease in the *n*-decane conversion with both zeolites, this decrease being larger in the case of ZSM-5.

Taking into account the above results, one could expect that owing to the higher hydrothermal stability of IM-5 to dealumination, this zeolite should be more active than ZSM-5 when used as an additive for gasoil cracking, and consequently a larger effect on product distribution should be expected when using IM-5 than when ZSM-5 is used as additive. The results from Figs. 8–10 clearly show that when recracking gasoline, after steaming of IM-5 and ZSM-5, the

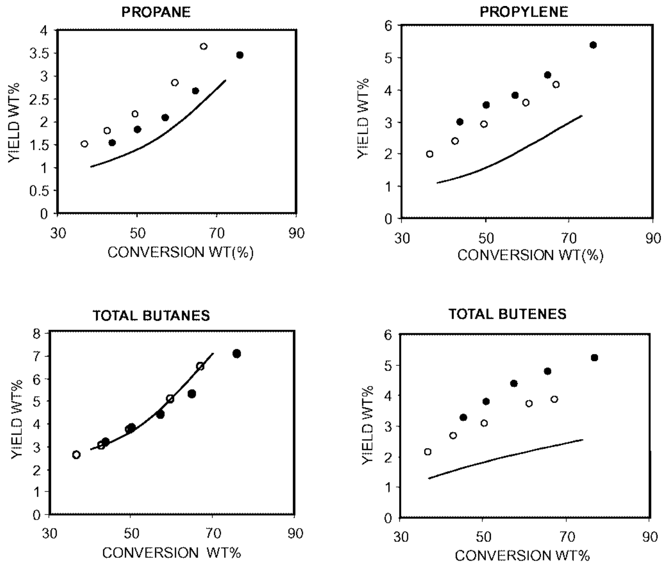

**FIG. 9.** $C_3$–$C_4$ selectivities in the cracking of gasoil at 793 K and 30 s time on stream over (line) USY-2.432 nm as base catalyst and (●) IM-5 and (○) ZSM-5, steamed at 1023 K for 5 h at 13.3 wt% of additive level.

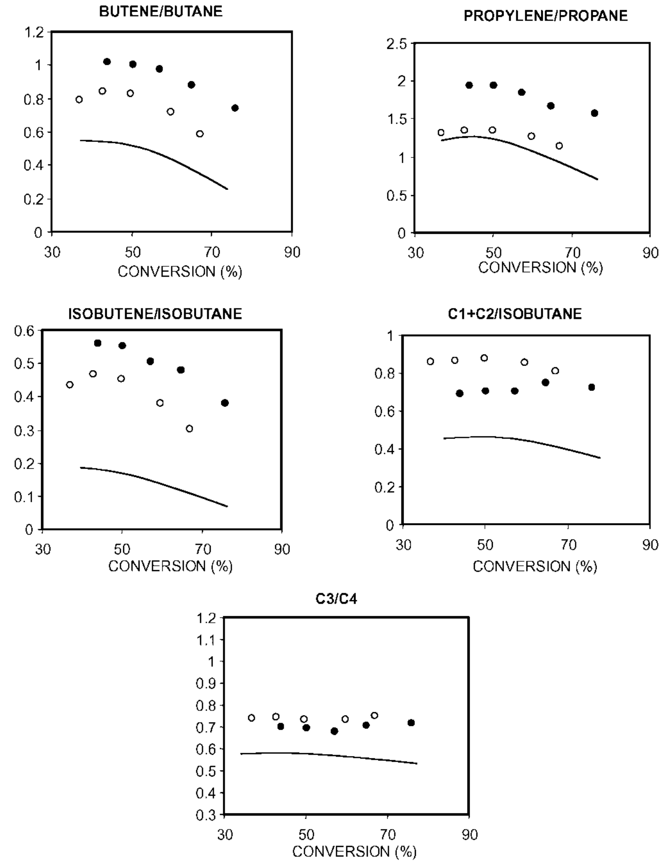

**FIG. 10.** Ratios of interest in the cracking of gasoil at 793 K and 30 s time on stream over (line) USY-2.432 nm as base catalyst and (●) IM-5 and (○) ZSM-5, steamed at 1023 K for 5 h at 13.3 wt% of additive level.

former leads to higher $C_3$ and $C_4$ olefins yields and higher propylene/propane and butenes/butanes ratios than does ZSM-5.

### TABLE 4

**First-Order Kinetic Rate Constants in the Cracking of 1-Hexene, 4-Methyl-1-Pentene, and *n*-Decane at 500°C and 60 s of Time on Stream**

| Feed | IM-5 steamed ($g_{oil}\ g_{cat}^{-1}\ s^{-1}$) ($10^{-3}$) | ZSM-5 steamed ($g_{oil}\ g_{cat}^{-1}\ s^{-1}$) ($10^{-3}$) |
|---|---|---|
| 1-Hexene | 142 | 68 |
| 4-Methyl-1-pentene | 102 | 69 |
| *n*-Decane | 6.7 | 4.2 |

In order to have a better understanding of these results and to see in particular with which type of gasoline molecules IM-5 is active, we studied the catalytic cracking behavior of representative gasoline molecules. We therefore carried out the cracking of 1-hexene and 4-methyl-1-pentene with the steamed IM-5 and ZSM-5. The results, presented in Fig. 11, show that both zeolites readily crack olefins, with the activity of IM-5 being higher. It is important to remark that owing to the larger pore diameter of IM-5, this zeolite is proportionally more active than ZSM-5 for cracking branched olefins. This fact can be responsible for the higher absolute yields of propylene and butenes, and specially isobutene, obtained during gasoil cracking with steamed IM-5. From the conversion results presented in Figs. 7 and 11, we calculated the first-order kinetic rate constants for cracking 1-hexene, 4-methyl-1-pentene, and *n*-decane with steamed IM-5 and ZSM-5 zeolites. The results presented in Table 4 indicate, in agreement with the results of Buchanan using ZSM-5 (12, 13), that with both zeolites the cracking rate of olefins is much higher than the cracking rate of paraffins. Moreover, the rate of olefin cracking is almost twice as large with IM-5 than with ZSM-5.

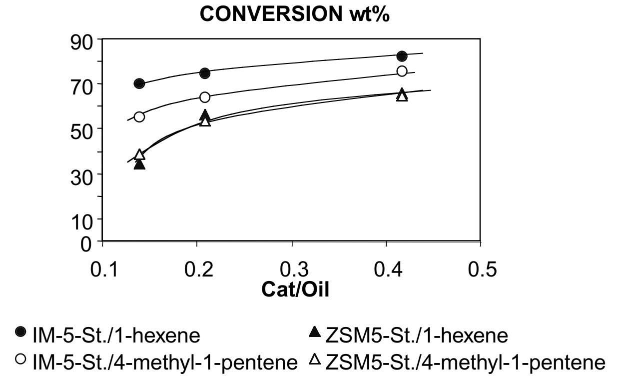

**FIG. 11.** Total conversion in the cracking of 1-hexene and 4-methyl-1-pentene at 793 K and 60 s time on stream over IM-5 steamed and ZSM-5 steamed.

## CONCLUSIONS

IM-5 is a recently synthesized zeolite which shows a very interesting stability and cracking behavior. It is a very active cracking catalyst that gives higher conversions than does ZSM-5. The higher activity of this zeolite is due to its higher thermal and hydrothermal stability which results in a lower dealumination rate.

This material should have larger pores and/or open spaces within the structure than does ZSM-5, giving consequently a higher $\beta$-scission to protolytic cracking ratio than with ZSM-5. These larger internal voids are responsible for favoring proportionally more bimolecular than monomolecular reactions with IM-5 than with ZSM-5, and consequently, they give more hydrogen transfer reactions, resulting in a lower olefin-to-paraffin ratios with the former when the zeolites are calcined but not steamed. However, when the samples were steamed and used as additives for gasoil cracking, larger olefin-to-paraffin ratios were observed in the products in the case of IM-5 owing to the higher hydrothermal stability of IM-5 and consequently to the higher activity of this zeolite, which cracks much faster than ZSM-5 the olefins present in the gasoline fraction.

Taking into account the results obtained when cracking *n*-decane and vacuum gasoil it can also be concluded that test reactions for zeolite additives based on pure compounds should be taken with care when large differences in the activity of the additives exist.

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