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Conversion of methanol into light olefins over ZSM-5 zeolite: Strategy to enhance propene selectivity



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1. Introduction

The rational design of heterogeneous catalysts to optimize activity and selectivity in a targeted reaction often remains a key challenge in state-of-the-art catalysis research [1-3]. In this context, zeolites occupy a prominent place since they are used in numerous acid-catalyzed reactions [4,5].

Discovered in Mobil laboratories, the transformation of methanol-to-hydrocarbons (MTH) to make high-octane gasoline [6,7], represents a timely and valuable process involving zeolite catalysts. Indeed, the MTH technology has received considerable industrial interest [8–10]. For instance, the Mobil Oil methanol to gasoline (MTG) process [11], the Topsøe integrated gasoline synthesis (TIGAS) process [12], the Lurgi methanol to propene (MTP) process [13] and the Norsk Hydro/UOP's methanol to olefins (MTO) process [14], have either been commercialized or are ready for commercialization [15].

The MTO reaction is considered to be a valuable option for the valorization of stranded gas reserves, and therefore several studies devoted either to the reaction mechanism or to the technology were

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ABSTRACT

Four ZSM-5 zeolite materials with varying crystal size, acid site density and morphology were prepared, characterized by BET, XRD, SEM, FT-IR, H/D exchange and n-hexane cracking experiments and tested as catalysts for the Methanol to Olefins (MTO) reaction at 350 °C, WHSV = 1.8 g/gh under atmospheric pressure.

Optimal propene to ethene ratios (>5) were obtained over a material prepared via the fluoride route. Its superior selectivity was tentatively ascribed to its low density of strong acid sites in combination with a long diffusion pathway and few crystal defects.

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undertaken [16–23]. In addition, the increasing market worldwide demand toward ethylene and propylene is gradually raising and projected growth rates in coming decades are expected to remain high [24,25]. SAPO-34 silico-aluminophosphate, having the CHA structure, is recognized as a valuable catalyst to generate a high selectivity to light olefins due to its moderate acid strength and small pore opening [22]. However, a high rate of deactivation is usually observed for this kind of material due to the rapid coke deposition [26,27]. ZSM-5 zeolite catalysts are therefore often used despite usually lower olefin yield [28–31].

Several strategies targeted to achieve an increasing selectivity toward light olefins over these MFI catalysts have been tempted: modification of the reaction conditions, raising the steric constraints to increase shape selectivity, change in the reactor configuration [32], or proper tailoring of the Brønsted acidity (density and strength) [29,33]. Moreover, in order to limit/inhibit the consecutive formation of higher alkenes, alkanes and aromatics, the development of new catalyst design at the mesoscopic and macro-scale have also been explored [28–30]. Nevertheless, the preparation of such catalysts remains quite complex and costly.

During the past decade, the exploration of ethane-rich shale gas in the US has made ethane crackers economically favorable over naphta crackers, and led to the construction of ethane crackers as well as retrofitting of naphta crackers [34]. Naphta cracker co-products such as propene are therefore in increasingly short supply, and tuning of MTH selectivity toward propene production



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becomes increasingly attractive. Only few studies have yet been devoted to the optimization of propene yields in the MTH reaction over ZSM-5 catalysts. Chang et al. explored the interaction between catalyst Si/Al ratio, temperature and pressure in MTH reaction over ZSM-5 zeolite [35]. Two SiO₂/Al₂O₃ ratios were tested, i.e., 35 and 1670, while intermediate Brønsted acid site densities were obtained by partial H⁺–Na⁺ cationic exchange. At 370 °C and full conversion, the C₂–C₄ olefins selectivity increased from 30% to 46% for SiO₂/Al₂O₃ = 35 and 1670, respectively. Increasing the temperature to 500 °C led to higher olefins selectivities; with a maximum of 38% propene selectivity and a propene to ethene ratio of 4.9 at full methanol conversion for the SiO₂/Al₂O₃ = 1670 catalyst. Lower Si/Al ratios led to higher ethene selectivities and lower propene selectivities, e.g. 10.5 and 22.6%, respectively, for SiO₂/Al₂O₃ = 35 [35].

In line with those results, Prinz and Riekert tested ZSM-5 catalysts with varying Si/Al ratios (34–660) or crystal sizes (0.5–8 μ m) for the MTO reaction at 290–360 °C in a batch reactor, and reported that increasing Si/Al ratios led to increasing light olefins selectivities and propene-to-ethene ratios. A similar effect was reported for decreasing crystal sizes (0.5 versus 2 × 2 × 6 micron-sized crystals); however, it is worth noting that for conversions exceeding 80%, the selectivity differences due to crystal size vanished [36]. Recently, Hua et al. reported that mesopore formation by desilication of ZSM-5 zeolite with Si/Al ratio 72 led to enhanced propene selectivities; up to 42% with a propene to ethene ratio of 10 at full methanol conversion at 470 °C. The authors ascribed the selectivity increase to a shorter diffusion pathway [37].

Zhao et al. studied the effect of adding ZrO_2 and H_3PO_4 to an H-ZSM-5 catalyst with Si/Al ratio of 84, and obtained a propene to ethene ratio of 10 (45% propene selectivity) at 450 °C and full DME conversion. After 30 h on stream, the propene to ethene ratio increased to 16, due to lower ethene selectivity, exhibiting still full conversion and 45% propene selectivity [38]. The authors ascribed the propene yield improvements to the modification of acid strength toward lower values while the number of acid sites was increased. A slight reduction of pore width was also observed.

Later, Liu et al. tested ZSM-5 samples with Si/Al ratios ranging from 12 to 360 at 460 °C, and observed a gradual increase in propene selectivity from 16% to 52%, respectively, at full methanol conversion [39]. Concurrently, the propene to ethene ratio increased from 2.0 to 6.5. Screening tests of the Si/Al = 220 sample after modification with a large variety of promoter elements showed that phosphorus gave the highest propene selectivity, 56%, at full methanol conversion, with a propene to ethene ratio of 7. Aromatics production was almost fully suppressed (<1% selectivity) after P modification. The P/ZSM-5 sample was thoroughly characterized. It was found that the main change induced by P doping was a reduction of the number and strength of acid sites in the catalyst, while the pore size was maintained or slightly increased [39].

In the present study, we investigate the influence of Brønsted acid site density and also the crystal size in the performance in the MTH reaction. The principle aim is to raise and then maintain a high selectivity toward propene, and therefore develop a simple strategy to design a new generation of MTP (methanol-to-propene) catalyst exhibiting the MFI structure.

2. Experimental

2.1. Methodology for the catalysts preparation: molecular and microscopic design

Four different MFI zeolites were synthesized via different routes in order to vary several factors: Brønsted acidity, Si/Al ratio, crystal size and internal porosity. One ZSM-5 zeolite prepared via the classical alkaline route was prepared as a reference material and named ZSM-5R. In addition, the former procedure was slightly modified to introduce mesoporosity by allowing the growth of MFI crystals on a structured glass monolith [40,41]. This material was named ZSM-5MS (mesoporous and structured). To further investigate the incidence of the length of diffusion within the crystal, we have prepared MFI nanocrystals and thus called this sample ZSM-5N (for nano). Finally, very large prismatic ZSM-5 crystals were prepared in fluoride medium, named ZSM-5F (fluoride), for comparison.

The influence of these modifications on the catalytic performance in the MTH reaction was investigated in terms of degree of methanol conversion and selectivity toward propene and ethene.

2.2. Preparation of the different MFI catalysts

2.2.1. Synthesis of ZSM-5 under alkaline conditions, ZSM-5R (reference)

ZSM-5 zeolite was prepared following the procedure previously reported [42]. This method consisted of adding at room temperature sodium aluminate (52.5 wt.% NaAlO₂, Riedel-de Haën), sodium chloride (99.5 wt.% NaCl, Fluka), tetrapropylammonium hydroxide (20 wt.% in water, TPA-OH, Fluka) in demineralized water. After 20 min, tetraethylorthosilicate (TEOS, 98%, Sigma–Aldrich) was introduced under vigorous stirring. The molar ratio was set as follows: TPA-OH:TEOS:NaCl:NaAlO₂:H₂O = 2.16:5.62:3.43:0.13:1000. Aging and homogenization of the mixture were performed during 2 h. Subsequently, the gel was introduced in a 70 mL Teflon-lined autoclave and the hydrothermal treatment was performed at 170 °C during 48 h. After filtration, washing with demineralized water, and drying at 110 °C, a white powder was obtained. These synthesis steps were followed by calcination over night at 500 °C in air to remove the structure directing agent.

2.2.2. Synthesis of large ZSM-5 crystals in fluoride medium, ZSM-5F

The synthesis gel was prepared by adding, at room temperature, 2.07 g of aerosil 200 and 70 mg of glass monolith (used as a cosilica source) [43] in distilled water (30 mL). The gel was left 15 min under vigorous stirring to homogenize the system. Then, 0.65 g of tetrapropylammonium bromide (TPA-Br), 0.028 g of NaAlO₂, an additional 20 mL of distilled water and 1.44 g of ammonium fluoride (NH₄F) were introduced into the mixture. Few drops of hydrofluoric acid were then added to reach a pH value of about 6. Once the gel had formed, aging and homogenization of the mixture were performed during 2 h. The gel was then placed in a 75 mL Teflon-lined autoclave. The temperature was increased within 1 h to 170 °C. The synthesis time was set to 22 h. The catalyst was recovered by filtration, washed with distilled water and dried at 100 °C for 2 h. The NH₄-zeolite form was obtained and calcined at 450 °C for 5 h in air to obtain the zeolite H-form.

2.2.3. Synthesis of ZSM-5 nanocrystals, ZSM-5N

The synthesis mixture was prepared by first mixing deionized water with cationic template solution (TPAOH, 1 M, Sigma–Aldrich) under stirring for 10 min. Sodium hydroxide (NaOH, 98%, Fluka) and sodium aluminate (NaAlO₂, Riedel de Häen) were then added and the solution was again stirred for 15 min. The silica source, TEOS (98%, Fluka), was then introduced dropwise under vigorous stirring. The mole ratio was as follows: NaAlO₂:TPA-OH:TEOS:NaOH:H₂O=1:56:23:14:7714, respectively. Afterwards, 300 mg of sacrificial sugar cane bagasse [44] was added to the gel and the mixture was aged for another 2 h under vigorous stirring. It was then transferred into an autoclave and the synthesis was performed during 48 h at 167 °C under autogeneous pressure. After the hydrothermal synthesis, the solid was filtered off, rinsed

with distilled water and dried in an oven at 100 °C for 15 h. The amine-derived organic template and the lignocellulosic biomass were removed by treating the material under air atmosphere at 450 °C for 5 h.

2.2.4. Synthesis of structured ZSM-5, ZSM-5MS

The zeolite was prepared according to our earlier procedure [42]. The same recipe as described in Section 2.2.1 was followed, thus adding at room temperature sodium aluminate, sodium chloride, tetrapropylammonium hydroxide in distilled water. Afterwards, TEOS as a silica source was introduced under vigorous stirring. Likewise, once the gel has formed, aging and homogenization of the mixture were performed during 2 h. Then, the stirring was stopped and 0.180 g of mesoporous glass monoliths (approximately 30-35 mg per piece) were placed into the synthesis mixture for 30 min. The gel was then poured in a 75 mL Teflon-lined autoclave containing the support packing. The temperature was increased within 1 h to 170 °C. The synthesis duration was 24 h. The packing was recovered upon filtration, washed with distilled water and dried at 100 °C for 2 h. Then, the composite was kept in an ultrasonic bath (45 kHz) for 20 min to remove weakly attached crystals and dried at 100 °C for 2 h. Finally, the monolith was calcined at 450 °C in air over night to remove the template.

2.2.5. Ion-exchange of ZSM-5 samples

All ZSM-5 samples obtained in the Na-form were ion-exchanged and calcined. Ion exchange was repeated three times, using 20 mL 1.0 M NH₄NO₃ solution per gram of catalyst. The solution was kept at 75 °C for 2 h before separation of catalyst and liquid by centrifugation. The catalyst was dried overnight in an oven at 100 °C before calcination in static air during 6 h at 550 °C, subsequently to a heating ramp of 5 °C/min.

2.3. Characterization of the catalysts

BET surface areas (S_{BET}) of the ZSM-5 samples were determined by N₂ adsorption–desorption mesurements performed at –196 °C employing the BET-method (Micromeritics sorptometer Tri Star 3000). Prior to nitrogen adsorption, the samples were outgassed at 350 °C for 4 h in order to remove moisture adsorbed at the surface and inside the porous network.

X-ray diffraction (XRD) was used to assess the fingerprint of asprepared zeolite structure. The different patterns were compared with those from the JCPDS tables. Patterns were recorded on a Bruker D8 Advance diffractometer, with a Ni detector side filtered Cu K α radiation (1.5406 Å) over a 2θ range of 5–60° and a position sensitive detector using a step size of 0.02° and a step time of 2 s.

Scanning Electron Microscopy (SEM) micrographs were recorded on a JEOL FEG 6700F microscope working at 9 kV accelerating voltage. The Si/Al ratios of the materials were determined by energy dispersive X-ray analysis (EDX) coupled with the SEM chamber.

An evaluation of the Brønsted acid site density of the samples was performed following an H/D isotope exchange method developed by Louis et al. [45,46].

Infrared spectroscopy (FTIR) spectra were recorded in controlled atmosphere at 2 cm^{-1} resolution on a Bruker Vertex 80 FTIR spectrophotometer, equipped with a MCT detector and using a homemade IR cell. FTIR spectra were collected in transmission mode on a thin film prepared by deposition of zeolite water suspension on a silicon wafer. The difference in the Brønsted acid strength of these samples was derived from CO adsorption. Prior to the CO adsorption, samples were pretreated for 1 h at 500 °C in vacuum and CO adsorption–desorption was followed at liquid N₂ temperature (i.e. –196 °C). Carbon monoxide (99.97% purity) used was supplied by Aga. In order to compare the IR band intensities, spectra were normalized to the overtone mode at 2005 cm^{-1} .

2.4. n-Hexane cracking procedure

The number of strong Brønsted acid sites of as-prepared zeolites was evaluated in a conventional n-hexane cracking reaction at 500 °C. The catalytic cracking of n-hexane (99.89% pure, water 0.005 wt.%) was performed in a high throughput unit as already detailed elsewhere [47]. A flow of 60 ml/min of 11% (v/v) nhexane in nitrogen was used. A typical run was carried out with 0.1–0.03 g of catalyst (the amounts of catalyst were adjusted in order to provide iso-conversion). Reaction products were analyzed on-line after three different times on stream (3, 17 and 32 min) by gas chromatography using a Shimadzu GC-2010 equipped with a Chrompack KCl/Al₂O₃ column operated under isothermal conditional (303 K) and nitrogen flow (2 ml/min). Catalytic activities were estimated at degrees of conversion between 9 and 11%, as the average of results obtained after 17 and 32 min time-on-stream. These values differed by less than 10% (relative) in activity (each catalyst were analyzed three times). The catalysts showed a moderate to low deactivation with an activity at 3 min on time on stream differing less than 15% (relative), than the one measured after 32 min.

2.5. Catalysts evaluation in the methanol to hydrocarbons (MTH) reaction

The zeolites were pressed into wafers and subsequently crushed and sieved to obtain particles in the range 250-420 µm. Each catalytic test was performed with 60 mg of catalyst in a fixed bed quartz reactor configuration, with 3.0 mm inner diameter. 30 mL He was passed through a saturation evaporator containing methanol (BDH Laboratory Supplies, >99.8% chemical purity) kept at 0°C, before being fed to the reactor, thus giving a WHSV (weight hourly space velocity) of 1.8 g methanol/g zeolite/h. The product stream was analyzed with an Agilent 6890 A gas chromatograph with FID detector and automatic sampling (Supelco SPB-5 capillary column, 60 m, 0.530 mm internal diameter, stationary phase thickness 3 µm). The pressure of the carrier gas was 42 kPa and the temperature was programmed to 5 min at 45 °C before heating (25 °C/min to 260 °C). The catalyst temperature was adjusted to 350 °C before onset of methanol for all tests, and once the reaction had started the oven temperature was not further modified. The test was stopped when the catalyst had deactivated or after 48 h on stream.

Additional catalytic tests for sample ZSM-5F were performed by varying catalyst mass (5–60 mg) while all other parameters were kept constant as described above. WHSV was varied between 1.8 and 21 g methanol/g_{zeolite}/h.

The activity of the catalysts is expressed in terms of methanol conversion, calculated from the difference between inlet and outlet concentrations of methanol (and dimethyl ether, DME, which was considered as a reactant). The Q factor for reaction (1):

$$2CH_3OH \leftrightarrow (CH_3)_2O + H_2O \tag{1}$$

$$Q = P[(CH_3)_2O] \cdot P(H_2O)/P[(CH_3OH)]^2$$

where P(i) represents the partial pressure of compound i, was calculated and found to be constant under all conditions (except at close to full methanol conversion where the measurement uncertainty is high), thus indicating that reaction (1) was at equilibrium and that there was no bypass of reactant gas in any experiment. The Q value curves are shown in Supporting information, Figs. S1 and S2.



Fig. 1. SEM micrographs of as-prepared zeolites ZSM-5R (a); ZSM-5F (b); ZSM-5N (c) and ZSM-5MS (d).

Product selectivity was defined as the mole ratio of each product (on C_1 basis) referred to the moles of converted methanol. The following products were detected during reaction: light olefins (ethene, propene), higher alkenes, alkanes (C_5 – C_8) and aromatics.

3. Results

3.1. Characterization of the zeolites

(a)

(c)

The XRD patterns of each zeolite sample confirmed the MFI structure [42–44]. Fig. 1 shows the SEM images of the four catalysts. ZSM-5R and ZSM-5MS exhibited the classical coffin-shape morphology (Fig. 1a and d) along with crystal sizes of 5 and 2 μ m, respectively. The material prepared via the fluoride-mediated route led to the formation of large prismatic crystals having ~15–20 μ m in size (Fig. 1b). In contrast, ZSM-5N catalyst consisted of rectangular nanocrystals, 0.05–0.10 μ m in size, which assembled into a spherical superstructure of approximately 1–2 μ m (Fig. 1c).

Table 1 presents the BET surface areas (S_{BET}), the total number of Brønsted acid sites, Si/Al ratios, crystal sizes and the rate of nhexane cracking for all catalysts. S_{BET} values are in line with those usually found for ZSM-5 zeolites. However, ZSM-5MS exhibited a higher S_{BET} value of 453 m²/g. This finding is in line with previous HRTEM measurements which showed that it contains 10–20 nanometer-sized mesopores [43]. EDX analysis allowed to estimate the Si/Al ratio of the different zeolites (Table 1).

H/D isotope exchange was performed to evaluate the number of Brønsted acid sites present in the different materials. It appears that the number of Brønsted acid sites diminished among the zeolites in the order: ZSM-5R > ZSM-5N > ZSM-5F > ZSM-5MS. It is noteworthy that the fluoride-mediated route allowed a decrease in the total number of Brønsted acid sites when compared to MFI catalyst prepared under alkaline conditions. Such influence of the preparation method on the density of Brønsted acid sites for ZSM-5 and [F]ZSM-5 zeolites has already been reported in an earlier study [48]. In parallel to this loss in the number of Brønsted acid sites, the Si/Al ratio was enhanced as expected. The ZSM-5MS sample exhibited a low number of acid sites, 0.26 mmol/g; however it is important to remember that this structured composite contained only 34 wt.% of zeolite crystals coated on a glass monolith. The catalytic activity of these zeolites was evaluated in the nhexane cracking reaction and nearly the same rate was achieved over ZSM-5R and ZSM-5F zeolites, 120 and 107 mmol_{n-hexane} converted/g min, respectively, in spite of the much higher Al content in the ZSM-5R material. This result is further discussed below. Zeolite nanocrystals (ZSM-5N) led to an improved reactivity for n-hexane cracking, thus confirming the higher effectiveness of nanocrystals (183 mmol_{n-C6} converted/g min) compared to their micrometer counterparts [49-51]. Interestingly, ZSM-5MS zeolite

Table 1

BET surface areas, Si/Al ratio, crystal sizes, number of Brønsted acid sites and rate of n-hexane cracking.

Catalyst	Si/Al	Crystal size (µm)	$S_{\text{BET}} (m^2/g)$	Number of Brönsted acid sites (mmol/g)	Rate of n-hexane cracking (mmol/g min)
ZSM-5R	25	5	320	1.00	120
ZSM-5F	53	15-20	305	0.31	107
ZSM-5N	19	0.05-0.10	345	0.78	183
ZSM-5MS	43	2	453	0.26	322



Fig. 2. FTIR spectra (ν (O—H) region) of ZSM-5X samples collected at room temperature after vacuum degassing at 500 °C for 1 h. These spectra are normalized to the overtone modes in the 1944–2092 cm⁻¹ region. For clarity spectra have been shifted along the ordinate.

led to a higher rate of n-hexane cracking, i.e.; $322 \text{ mmol}_{n-hexane}$ converted/g min, thus suggesting a facilitated diffusion of the alkane through the mesoporous zeolite.

Fig. 2 shows the IR spectra of ZSM-5N, ZSM-5F, ZSM-5R, and ZSM-5MS zeolites in the range $3800-3000 \text{ cm}^{-1}$ ($\nu(O-H)$ region). The wavenumbers and assignment of the observed IR components are given in Table 2. In general, the IR spectra supported the observations made by other methods: The isolated silanol peak at 3750 cm⁻¹ increased in abundance with a decrease in zeolite crystal size, as shown by the SEM images in Fig. 1 (ZSM-5F > ZSM-5R > ZSM-5MS > ZSM-5 N). All samples contained Si–OH–Al bridge sites, as well as extra-framework Al (EFAL) sites. The mesoporous sample, ZSM-5MS, further contained a significant amount of silanol nests. Spectra measured during interaction with CO at 77 K are shown in Supporting Information, Fig. S3. The peak of the Brønsted acid sites (3610 cm^{-1}) was red shifted to 3305 cm^{-1} for all samples upon interaction with CO, indicating similar acid strength for all samples. When considering the ν (C–O) region (2050–2250 cm⁻¹) the main peak was observed at 2174 cm⁻¹ for all samples, corresponding to interaction with the Si-OH-Al bridge sites. Furthermore, a significant component centered at 2169 cm⁻¹, associated to CO interaction with EFAL sites, was observed, in particular for ZSM-5R sample, followed by ZSM-5F sample. The significantly lower

Table 2

Assignments of infrared spectra.

Wavenumber (cm ⁻¹)	Assignment					
3745 (intense)	Isolated external silanol (SiO—H)					
3663 (small band)	Extra-framework aluminum species (AlO—H)					
3612 (intense)	Bridging hydroxyls (Si—OH—Al)					
3510 (broad)	Silanol nests					
2174	CO interacting with bridging OH					
2169	CO interacting with EFAL					
2157	CO interaction with silanol					
2138	Liquid like CO					



Fig. 3. Methanol conversion-product selectivity plot for ZSM-5F at 350 °C.

n-hexane cracking rate observed for sample ZSM-5R compared to sample ZSM-5N in Table 1 and aforementioned, in spite of the similar Si/Al ratios determined for those samples by EDX analysis and H/D exchange experiments, may be explained by the higher fraction of EFAL sites present in the ZSM-5R zeolite, when assuming that a high acid strength is required for alkane activation.

3.2. Evaluation of catalytic properties in the methanol to hydrocarbons (MTH) reaction

MTH test data for the four samples are shown in Table 3. Conversion versus time on stream curves for the various samples are shown in Supporting information (Fig. S4). All samples gave an initial conversion close to 100%. The initial C_3/C_2 ratio in the effluent increased from 1.6 over the ZSM-5N material, via 1.8 over the reference sample ZSM-5R, to 2.5 over ZSM-5MS and finally to 5.5 over ZSM-5F, thus:

ZSM-5F > ZSM-5MS > ZSM-5R > ZSM-N

An inverse correlation was found between the C_3/C_2 ratio and the hydrogen transfer index (HTI), which was calculated for the C_4 fraction [i.e. $\Sigma C_{4-}/(\Sigma C_{4-} + \Sigma C_{4-})$]. As one would expect, a positive correlation was found between the HTI and the selectivity to aromatic products (Table 3).

From the Conversion versus Time on stream plots shown in Supporting Information (Fig. S4), no direct correlation was found between product selectivity and deactivation rate. The deactivation rate decreased in the order:

$ZSM-5R > ZSM-5MS > ZSM-5N \sim ZSM-F$

With increasing times on stream, an increase in the $C_{3=}/C_{2=}$ ratio and a decrease in HTI were observed for all catalysts. The reference catalyst, ZSM-5R, was the only catalyst which deactivated below 50% conversion. At such low conversions, the C_2 selectivity increased faster than the C_3 selectivity, leading to a gradual decrease in the propene-to-ethene ratio with decreasing conversion.

Since the aim of this study was to optimize a catalyst for high propene yields, more tests were carried out with the most promising material, ZSM-5F, using different contact times. Product yield versus methanol conversion data for ZSM-5F are shown in Fig. 3. The yield versus conversion curves were linear for all products in the 2 to 98% methanol conversion range, and the C_3/C_2 ratio was in the range 5–7 for all contact times. The yield to aromatic products never exceeded 5%.

Sample	Conv. (%)	TOS (min)	Selecti	Selectivities [%]						$C_{3=}/C_{2=}$	$C_4/C_{4=}$	$HTI(C_4)$
			C ₂	C ₃	C4=	C ₄₋	C ₅	C ₆₊ ar	C ₆₊ al			
ZSM-5R	99	5	15	27	14	13	11	9	10	1.8	0.9	0.5
ZSM-5N	100	5	14	23	11	17	10	17	7	1.6	1.5	0.6
ZSM-5MS	99	5	12	30	18	9	11	9	11	2.5	0.5	0.3
ZSM-5F	98	5	7	36	23	4	13	5	12	5.5	0.2	0.2
ZSM-5N	99	2490	10	29	19	8	12	10	11	2.9	0.4	0.3

Table 3Test data for the MTH reaction over ZSM-5 samples at 350 °C.

(1) Hydrogen Transfer Index (HTI) was calculated for the C₄ fraction as $\Sigma C_{4-}/(\Sigma C_{4-} + \Sigma C_{4-})$

4. Discussion

In order to rationalize the observed data, a brief recapitulation of the mechanistic aspects of the Methanol to Hydrocarbons (MTH) reaction is required: Chang and Silvestri published the first study of the MTH reaction using a ZSM-5 catalyst in 1977. They showed how product selectivity was shifted from mainly light olefins toward a mixture of aromatics and alkanes with increasing contact times [6]. Two years later, Chen and Reagan re-plotted the rate versus contact time data and suggested that the reaction was autocatalytic, with olefins acting as the autocatalytic species [52]. During the past three decades, huge efforts have been made to reveal further mechanistic details of the MTH reaction. Today, the general view is that both C₃₊ alkenes and various arenes, polymethylated benzenes in particular, may act as autocatalytic species in ZSM-5 (see ref. [15] and references therein). Methylation of C₃₊ alkenes have been found to produce mainly more C3+ alkenes by cracking reactions, while methylation of polymethylated benzenes have been shown to produce mainly ethene and propene, in ZSM-5 zeolite [31,53].

Taking the mechanistic aspects into account, a high $C_{3=}/C_{2=}$ ratio, and a low selectivity to aromatics, may be ascribed either to low acid site density and/or low diffusion hindrance, thus facilitating transport of alkene products out of the catalyst before they are eventually converted to aromatic products. Such a hypothesis has already been validated by previous studies referred in the Introduction, which indicated that high Si/Al ratios, as well as small crystal sizes, favor light olefins selectivity and elevated propene-to-ethene ratios [35-37]. An alternative hypothesis could be an enhanced selectivity for one or the other catalytic cycle, i.e., alkene-mediated versus arene-mediated, beyond the two parameters already mentioned. Such an explanation would be in line with the studies showing that addition of phosphorous to the ZSM-5 material led to lower acid strengths and concurrently to higher propene-to-ethene ratios and high light olefins selectivities in the materials studied [38,39].

A key challenge when comparing several catalysts for a target reaction is that the materials normally differ by more than one parameter, and that several parameters may influence product selectivity. This is the case even for the four samples studied here. Let us therefore compare product selectivities versus each of the parameters suggested above:

Overall, the selectivity to C_2 - C_4 olefins diminishes in the order:

ZSM-5F(66%) > ZSM-5MS(60%) > ZSM-5R(56%)

> ZSM-5N(48%)

Furthermore, the propene-to-ethene ratio decreases in the order:

ZSM-5F(5.1) > ZSM-5MS(2.5) > ZSM-5R(1.8) > ZSM-5N(1.6)

4.1. Product selectivity versus crystal size

The crystal size of the materials decreases in the order: $ZSM-5F(15-20 \mu m) > ZSM-5R(5 \mu m) > ZSM-5MS(2 \mu m)$ $> ZSM-5N(0.05-0.10 \mu m)$

A larger crystal size represents longer diffusion pathways, but also a lower fraction of external sites. A positive correlation between crystal size and light olefins selectivity was indicated when considering the two ends of the row. However, an inversion was observed for the two materials in the middle, thus suggesting that there is no direct correlation between crystal size and selectivities for the samples studied here.

4.2. Product selectivity versus accessible Brønsted acid sites

The number of accessible Brønsted acid sites in the materials decreases in the order:

ZSM-5R(1.00) > ZSM-5N(0.78) > ZSM-5F(0.31)

> ZSM-5MS(0.26) (H/D titration)

ZSM-5MS(322) > ZSM-5N(183) > ZSM-5R(120)

> ZSM-5F(107)(n-hexane cracking)

The two methods gave quite different results, possibly because H/D exchange may take place at Si—OH—Al bridge sites as well as EFAL sites, while n-hexane cracking may only proceed at the Si—OH—Al bridge sites with higher acid strength.

The FTIR spectra indicated that the acid strength of the Si–OH–Al bridge sites is similar for all materials. However, they further suggested that the fraction of EFAL sites is highest for ZSM-5R, followed by ZSM-5F, while ZSM-5MS and ZSM-5N contain a low fraction of EFAL sites. In either case, it is not obvious that there is a direct correlation between the number of Si–OH–Al bridge sites and selectivity in the materials tested.

4.3. Tentative reaction path occurring for raising propylene formation

The aforementioned catalytic results remain quite difficult to explain in terms of reaction pathway occurring especially in the ZSM-5F giant crystals. Indeed, the nearly five-times higher propylene formation versus ethylene may involve a rather complex mechanism. It is important to remind that Froment and Park have already presented a detailed MTO mechanism involving 726 elementary steps including protonation, deprotonation, hydride transfer, methyl-shift, methylation, oligomerization, cracking [54]. Nevertheless, one may expect that under specific reaction conditions or catalyst formulation, it can be conceived that one path becomes dominant with respect to the others. Wu et al. [55] have demonstrated, while co-feeding methanol and C_2-C_6 alkenes in



Fig. 4. Schematic representation of the methanol reaction over Brønsted acid sites in the ZSM-5R and ZSM-5F crystals.

a multi-stage adiabatic fixed-bed reactor, that methylation and cracking of C_4-C_7 olefins became predominant.

The question arises what would induce this impressive propylene selectivity at complete methanol conversion over ZSM-5F synthesized via the fluoride-mediated route?

Following the Mulhouse's group key researches [56–58], it is now well admitted that larger zeolite crystals with fewer defects are produced via the non-alkaline procedure. In addition, the F[–] anion has been reported to be occluded in [$4^{1}5^{2}6^{2}$] cage, pentacoordinated and interacting with a silicon framework atom, thus forming [SiO_{4/2}F][–] entities [59]. Guth and Kessler have reported a possible modification of the catalytic properties in calcined materials even after complete fluorine removal [56]. Indeed, the co-templating role of fluoride anion contributes to the stabilization of small 4MR cavities [58,59] and may also induce distortion in the geometry of tetrapropylammonium (TPA) cations located at the channel intersections. Besides those materials exhibit very few connectivity defects and thus allow the synthesis of rather hydrophobic zeolites.

The main difference between ZSM-5R and ZSM-5F zeolites relies in different BA sites densities. Whereas the later catalyst exhibits a three- to four-time larger crystal size, it possesses at the same time nearly the third of BA sites. One can therefore roughly estimate a ten-time higher density of BA sites per crystal of ZSM-5R zeolite. The higher deactivation rate observed is directly connected to this high acidity. A higher density of BA sites should also induce more proximity among these sites, thus to ease consecutive reactions up to extensive coke formation. If we consider a high dispersion of BA sites in the ZSM-5F regular prismatic crystals, whilst ZSM-5R presents a high degree of twinning, one can understand the higher selectivity toward light olefins over the former catalysts. In spite of their huge diffusion length, giant ZSM-5F crystals which contain few defects, being rather hydrophobic, exhibits few BA sites and warrant therefore reduced aromatization reactions (and thus lower extend of aromatics hydrocarbon pool), allowing the catalyst to maintain its steady-state behavior during the whole course of the reaction (Fig. S4). Fig. 4 tends to rationalize the main reaction path occurring over this highly MTP-selective zeolite. The reduced acidity of ZSM-5F catalyst with respect to ZSM-5R plays in favor of higher propylene selectivity as already observed by Liu et al. [39] while reducing the acidity of ZSM-5 zeolites via doping with phosphorous.

In line with these tentative interpretations, we have recently performed an analysis of coke deposits (via TPO measurements) after long-term experiments by flowing methanol at 400 °C over the two zeolites prepared in alkaline and fluoride-media, respectively. It appeared that the amount of carbon present on the former ZSM-5R zeolite was about nine times higher than for the ZSM-5F zeolite [60]. One can therefore conclude that the zeolite prepared via the fluoride route is much more resistant to coke formation when compared to the other zeolite catalysts. Thanks to its reduced number of Brønsted acid sites and an important diffusion length, thus to a drastically reduced density of acid sites, ZSM-5F appears to be at the same time an active and stable MTP-catalyst. Whereas the peculiar behavior of this catalyst remains partly unrevealed, the high selectivity to propene may be related to (some extend at least)

aforementioned peculiarities: lower BA sites density, huge diffusion length, absence of crystal twinning, presence of EFAL. Fig. 4 tempts to summarize an eventually favored alkene methylationcracking cycle over large ZSM-5F crystals. Further studies are under progress to evaluate the exact nature of the coke formed over these zeolites. In addition, we aim to deeper investigate via a multinuclear NMR study the structure of ZSM-5 zeolites prepared in fluoride medium.

5. Conclusions

Different ZSM-5 zeolites possessing various crystal sizes and acid site densities were synthesized and thoroughly characterized by BET, XRD, SEM, FT-IR and H/D exchange techniques.

Their catalytic activities were evaluated in the Methanol to Olefins (MTO) reaction with the objective to maximize the propylene selectivity.

A high propylene to ethylene ratios (\sim 5) was achieved over ZSM-5F catalyst prepared via the fluoride route. The superior selectivity of this promising MTP-catalyst was tentatively ascribed to the lower density of strong Brønsted acid sites in combination with a long diffusion pathway and few crystal defects.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.09. 025.

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