SYNTHESIS OF METHYL TERBUTYL ETHER (MTBE) OVER TRIFLIC ACID LOADED ZSM-5 AND Y ZEOLITES

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Triflic acid loaded Y-type zeolite appears to be as active as the Amberlyst 15 in the (gas phase) synthesis of MTBE. However, the zeolite catalyst produces less by-products and is more thermally stable than the resin based catalyst.

1. Introduction

As lead antiknock additives in gasoline will be banned in most developed countries within the end of this decade, octane boosters for fuels such as light alcohols and MTBE (methyl-ter-butyl ether), have been increasingly used in gasoline blends. MTBE is an excellent candidate for replacing tetraethyl lead in gasoline. If compared to aromatic hydrocarbons which can be used to upgrade gasoline, MTBE does not evolve any toxic products of incomplete combustion in engines. Furthermore MTBE does not provoke any demixing problems when blended to gasoline (which is not the case with methanol, for instance). MTBE, with specifications close to those of gasoline, does not require dramatic modifications in the engine technology.

MTBE is currently synthesized from methanol and isobutene over acidic ion-exchange resins, mostly the Amberlyst 15 [1–3]. Even though the catalyst performance is good, there are several drawbacks to the commercial catalyst (thermal instability, acid leaching from the resin surface, and high methanol/isobutene ratio which requires some recycle efforts in the industrial process). The ZSM-5 zeolite from Mobil Oil avoids such inconveniences [4]. However, this zeolite is not as strong an acid as the Amberlyst type resin [5]. Coating the

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ZSM-5-type (or Y-type) zeolites with triflic acid (TFA), and organic super acid [6–9] has provided acid catalysts which show exceptional catalytic activity and product selectivities in the ethanol dehydration [6–8] and acetone conversion to hydrocarbons [9].

In this work, three catalyst types have been investigated for the gas phase synthesis of MTBE from isobutene and methanol: the commercial Amberlyst 15, the parent Y and ZSM-5 zeolites, and the TFA treated Y and ZSM-5 zeolites.

2. Experimental

PREPARATION OF CATALYSTS

The Amberlyst 15 was purchased from Aldrich. The Y-type zeolite (LZY-82, ammonium-form) was obtained from Union Carbide. The ZSM-5 zeolites were synthesized according to the known method of Argauer and Landolt [10]. The acid form of the Y was obtained by activating the LZY-82 in air at 550 °C for 10 hours. The acid forms of the ZSM-5 zeolites were prepared using the method as described by Le Van Mao et al. [6–9].

The triflic acid loading (3 wt%, as an example) was done according to the following procedure: About 0.3 g of triflic acid (TFA) or trifluoromethane-sulfonic acid, CF_3 SO_3H, 98% from Fluka Chemie AG) were dissolved in 15 ml pure acetone. This solution was then slowly added to 10 g of zeolite (powder, acid-form). The resulting suspension was allowed to settle and dry in the air at room temperature. The obtained solid was washed quickly with 5 ml of acetone and then heated at 120 °C in air for 12 hours.

The final zeolite catalysts were prepared according to the following procedure: the powder acid form of the parent or TFA loaded zeolite was intimately mixed with bentonite (20 wt% by weight) and made into a paste with distilled water, 1 ml of water was used for each gram of zeolite. Finally, the extrudates were dried at 120 °C for 12 hours. Parent zeolites or catalysts are called H-ZSM-5 or H-Y whereas the TFA bearing zeolites or catalysts are called H-ZSM-5/TFA or H-Y/TFA. In the following sections, powder forms are referred to as zeolites and final catalysts, as catalysts.

ZEOLITES CHARACTERIZATION

The zeolites (acid form) were characterized by atomic absorption (chemical composition), X-ray powder diffraction (structure identification and degree of crystallinity [12]; in particular, a 100% crystallinity was assigned to the parent zeolites), nitrogen adsorption/desorption (BET and Langmuir specific surface area and pore size distribution using an automatic Micromeretic ASAP 2,000 apparatus), water and n-hexane adsorption (degree of hydrophobicity or RAI

Table 1
Some physico-chemical and adsorptive properties of the zeolite catalysts

Zeolite	Si/Al	TFA loading (wt%)	Degree of crystallinity (%)	Surface area (Langmuir m^2/g)	Adsorption (vol %)		
					n-hexane	water	RAI
H-ZSM-5	18	0	100	360	14.3	10.6	1.4
H-ZSM-5/TFA (3)	18	3	99	209	9.1	10.9	0.8
H-Y	2.5	0	100	576	22.8	35.8	0.6
H-Y/TFA (3)	2.5	3	99	300	14.9	24.2	0.6

relative affinity index, which is the ratio of adsorbed n-hexane volume to the adsorbed water volume, and which can be measured using the method of Le Van Mao et al. [13]) and Thermogravimetric (TGA) and Differential Thermal (DTA) analyses (using a PL Thermal Sciences, STA-1,500 Model TGA/DTA apparatus). Reflectance FT-Infra Red (Bonem M 102 Model apparatus, for OH groups study) and ^{27}Al and ^{1}H MAS-NMR (Varian XR-300 spectrometer) analyses were also performed and resulting data were published elsewhere [11]. It is worth mentioning that any change in the RAI value is assigned to either a change in sorptive properties of the zeolite surface [13] or some pore narrowing which may affect the larger molecule, i.e. n-hexane [11]. Table 1 reports the main physico-chemical properties of the tested zeolites.

CATALYST TESTING

A vertically mounted, stainless-steel, fixed-bed reactor 2.5 cm in diameter and 30 cm in length was used. The reactor had a preheating and a reaction zone that were monitored by two chromel-alumel thermocouples in a thermocouple well positionned at the center of the reactor. The temperature controller was a potentiometric, time-proportioning controller, with the temperature control achieved by adjusting power input to each zone. Nitrogen was used as the carrier gas. The flow rate was monitored by using a gas transducer connected to a digital mass flowmeter and a gas volume totalizer. Fig. 1 shows the experimental set-up used in the present work and which is similar to that previously used [14].

A dynamic on-line sampling procedure was used for analysis of the gas phase with a Hewlett-Packard 5790 GC equipped with a FID and a reporting integrator, Model HP-3392. Separation of the gaseous phase was achieved on series-packed columns of 5 m of squalane on Chromosorb P and 2.5 m of Carbopack (Supelco Co.), graphite coated with picric acid. Analysis of the liquid phase was done by using a 50 m PONA HP capillary column and a FID using 2,2 dimethylbutane as external standard.

Results from the gas phase synthesis of MTBE were computed as follows. Since the two by-products of the reaction were diisobutene (or 2,2,4-trimethyl-1-

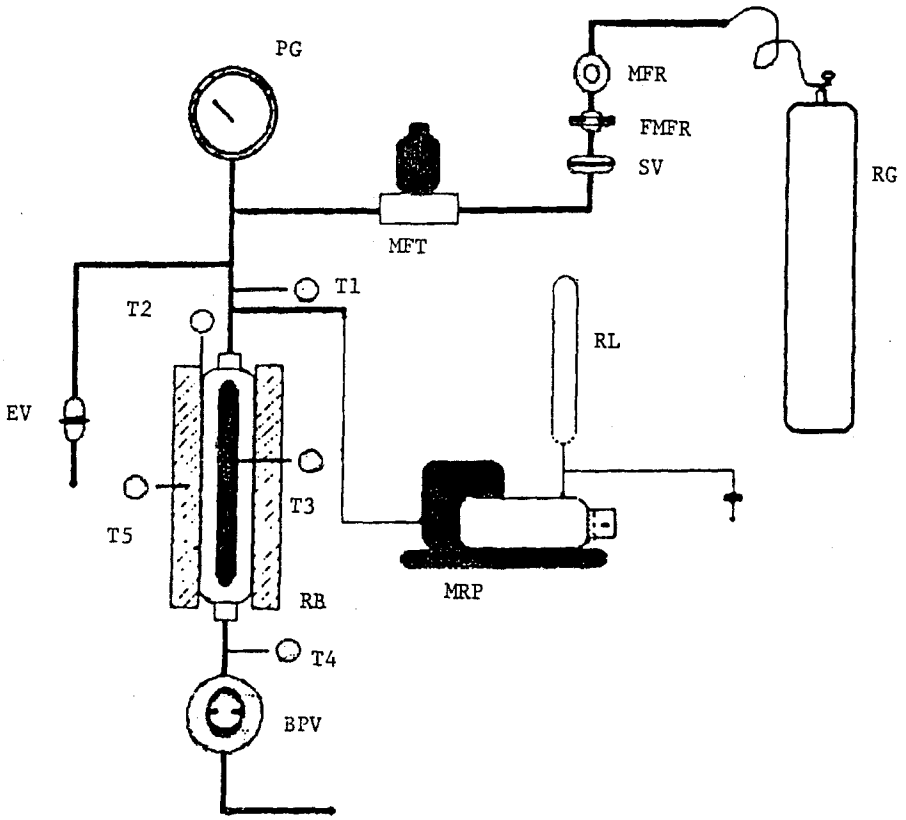

Fig. 1. Experimental set-up for the catalyst testing: RG: Gas reservoir; RL: Liquid reservoir; T*i*: Thermocouples; RB: reactor body; PG: pressure gauge; MFT: Mass flow transducer; MRP: Milton Roy pump; MFR: Mass flow regulator; FMFR: (Fine) mass flow regulator; SV: shut off valve; BPV: Back pressure regulator; EV: Emergency valve.

pentene) and its isomer 2,2,4-trimethyl-2-pentene, and the production of ter-butanol was negligible, the conversion of isobutene was calculated as follows:

$$C(\text{C atom\%}) = \frac{N\,(\text{MTBE}) + N\,(\text{C8})}{N\,(\text{ISO})} \times 100$$

where N (MTBE), N (C8) and N (ISO) are the numbers of carbon atoms of respectively: product MTBE, product C8 (diisobutene and its isomer) and feed isobutene.

The selectivity toward reaction products is calculated as follows:

$$S(\text{C atom\%}) = \frac{N\,(i)}{N\,(\text{MBTE}) + N\,(\text{C8})} \times 100,$$

where N (i) is the number of carbon atoms of product i.

The yield in MTBE was given by:

$$Y(\text{MTBE}) = \frac{N\,(\text{MTBE})}{N\,(\text{ISO})} \times 100\ (\text{C atom\%}).$$

Finally, the molar ratio R (methanol/isobutene) was determined as the ratio of number of moles of methanol/number of moles of isobutylene in the feed. The reaction parameters were as follows: weight of catalyst = 10 to 12 g; flow rate of feed isobutene = 0.08 to 0.06 mole/h; R = 0.8 to 1.2; temperature = 55–100 °C (±1 °C).

3. Results and discussion

Previous works [6–9,11] has shown that triflic acid, which normally boils at 161 °C, is removed quantitatively only at a temperature above 240 °C once incorporate into the ZSM-5 zeolite. This means that TFA chemisorbs to the zeolite surface and is strongly anchored to it. The DTA spectra obtained with a TFA loaded H-ZSM-5 in the presence of air exhibit two exothermic peaks with maximums located at 275 °C (peak 1) and 310 °C (peak 2) [11]. Thus, two species of TFA (A and B) do exist on the zeolite surface and this is in agreement with our hypothesis on the existence of two dissociated forms of TFA species on the zeolite surface [6,11]. The more firmly bound TFA species might be sorbed on loci which are close to the Al sites. Results obtained from FT-IR and ^{1}H Solid State NMR [11] are also in agreement with such a conclusion.

DTA of the TFA loaded H-Y zeolite in an air atmosphere also shows two exothermic peaks with peak maximums located at 280 ° and 370 °C (see fig. 2). This constitutes another piece of experimental evidence that the bound TFA component undergoes oxidation only at temperatures higher than 240 °–250 °C.

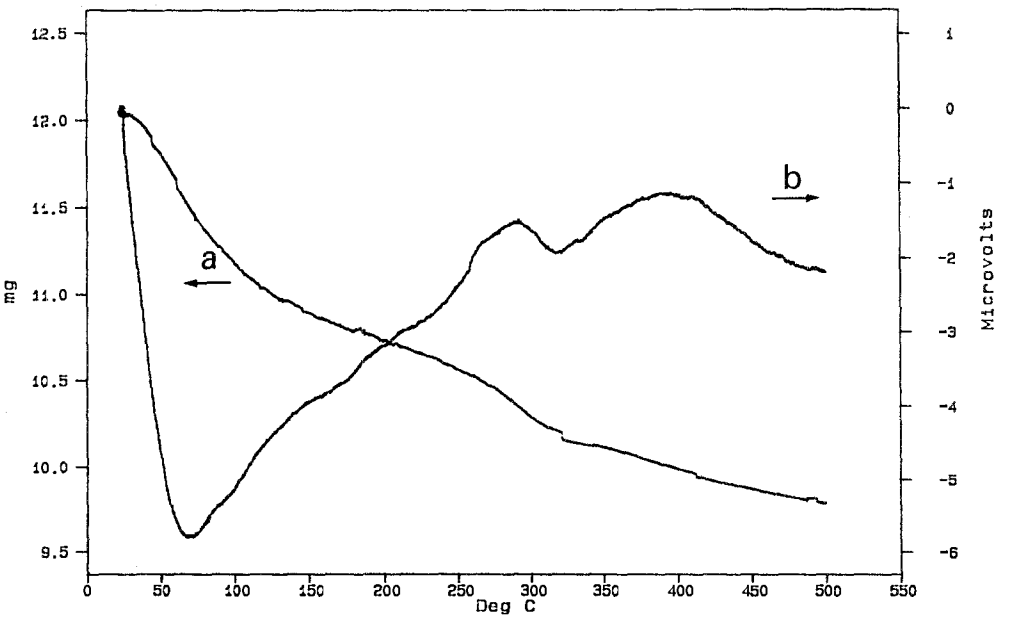

Fig. 2. TGA (a) and DTA (b) of the H-Y/TFA (3) in air atmosphere (heating rate: 5 °C/mn).

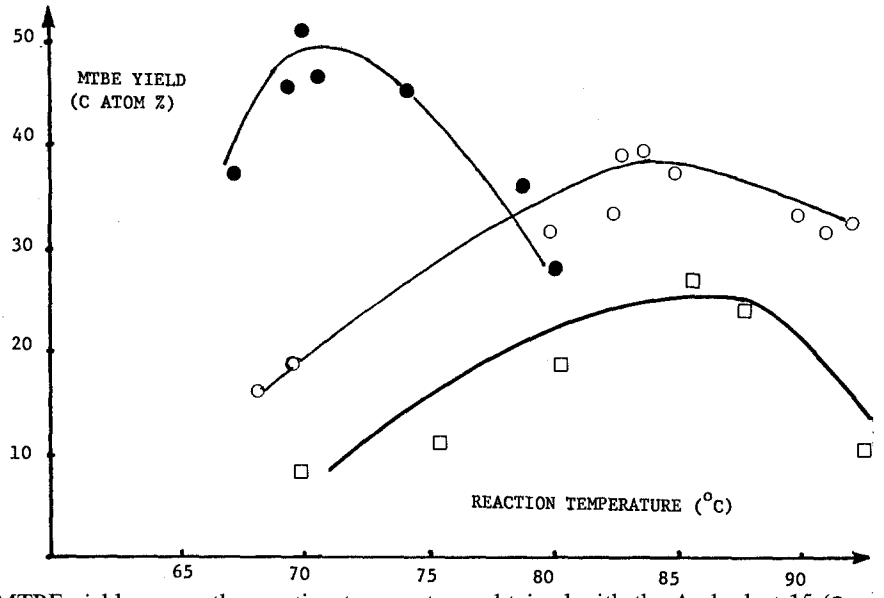

Fig. 3. MTBE yields versus the reaction temperature, obtained with the Amberlyst 15 (●——●), the H-ZSM-5 (○——○) and the H-Y (□——□) catalysts, respectively.

As also shown in our previous papers [6,11], an increasing TFA loading onto the H-ZSM-5 zeolite, although it increased the total acidity of the catalyst led to a progressive narrowing of the zeolite pore size and a decrease in the RAI (see also table 1). However, this was not due to the variation in surface hydrophilicity as it might seem to indicate at first with the RAI variation, but it did derive from the increased sieving effect exerted by the H-ZSM/TFA zeolite pore system on the larger n-hexane molecule. With the larger pore sized Y-type zeolite (0.74 nm versus 0.55 nm of the H-ZSM-5), there was practically no variation of the RAI upon TFA loading, although there were significant decreases in the sorptive capacities with respect to n-hexane and water.

On the other hand, the TFA loading did not provoke any loss of the degree of crystallinity on both ZSM-5 and Y zeolites (table 1) and thus there was not any significant dislodgement of framework Al atoms upon "reaction" of the triflic superacid with the zeolite surface.

Fig. 3 shows the yield of MTBE versus the temperature of the reaction performed in the presence of the Amberlyst 15. There was a maximum of MTBE yield at 68 °C–70 °C. The sharp decrease in MTBE yield above 75 °C was due to larger amounts of by-products formed. Fig. 3 also shows the MTBE yield versus the temperature of the reaction carried out on the parent H-ZSM-5 and Y-type zeolites. The maximum of MTBE yield was observed at 85 °C for both zeolites. The more expanded bell curves (towards values of temperature higher than that of the maximum) of the H-ZSM-5 and Y-type zeolites with respect to the Amberlyst 15, was probably due to the micropore channel system of the ZSM-5

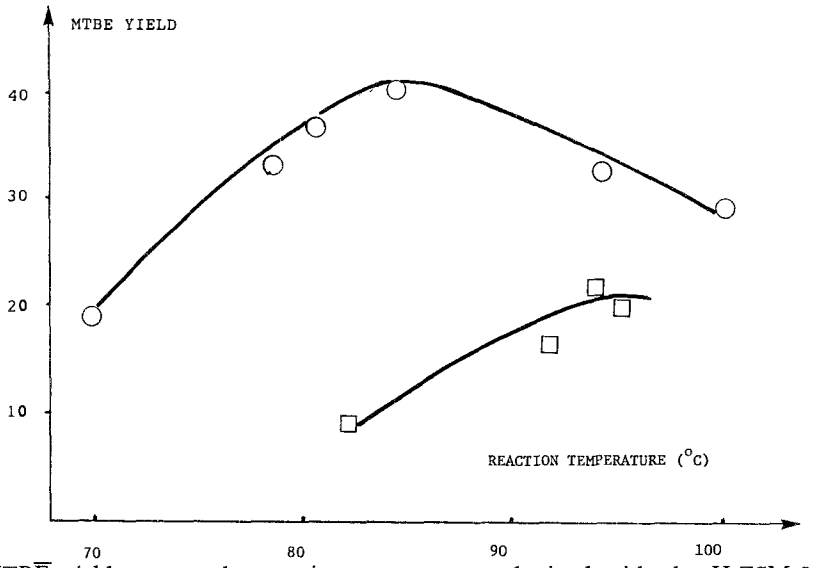

Fig. 4. MTBE yields versus the reaction temperature, obtained with the H-ZSM-5/TFA (3) (○——○) and the H-ZSM-5/TFA (4) (□——□).

and Y-type zeolites (where is effective a diffusion regime defined as configurational [15]). It is worth mentioning at this stage that the maximum MTBE yield obtained with the three catalysts corresponds to the following sequence:

Amberlyst 15 ≫ H-ZSM-5 > H-Y.

This sequence reflects the situation in terms of acid strength of the catalyst. In particular, the Y-type zeolite is much less active than the ZSM-5 zeolite because of its weaker acid strength although its acid density is much higher than that of the ZSM-5 zeolite.

Fig. 4 shows the MTBE yield versus the temperature of the reaction performed on H-ZSM/TFA with two TFA loading of 3 and 4 wt%. It appears that the MTBE yield increased with the TFA loading of 3 wt%. However, it sharply decreased when the TFA content was 4 wt%. This was due to the more important pore size restriction with higher TFA loading which restricted the access of the "bulkier" isobutene in the zeolite pore system. In the B.E.T.E. process, the maximum ethylene production was observed with a TFA loading of 4–5 wt% [6]. This can be easily understood because the reactant, ethanol, has a kinetic molecular diameter much smaller than that of isobutene.

Fig. 5 reports the catalytic performance of the H-Y/TFA with two loadings, 3 and 3 wt% respectively. Particularly, the TFA laoding of 3 wt% provided a catalyst which was as active as the Amberlyst 15 (see figs. 2 and 5). However the temperature for having the maximum performance is slightly higher (85 °C, see also table 2). A higher TFA loading (4 wt%) did not provide any better MTBE yield.

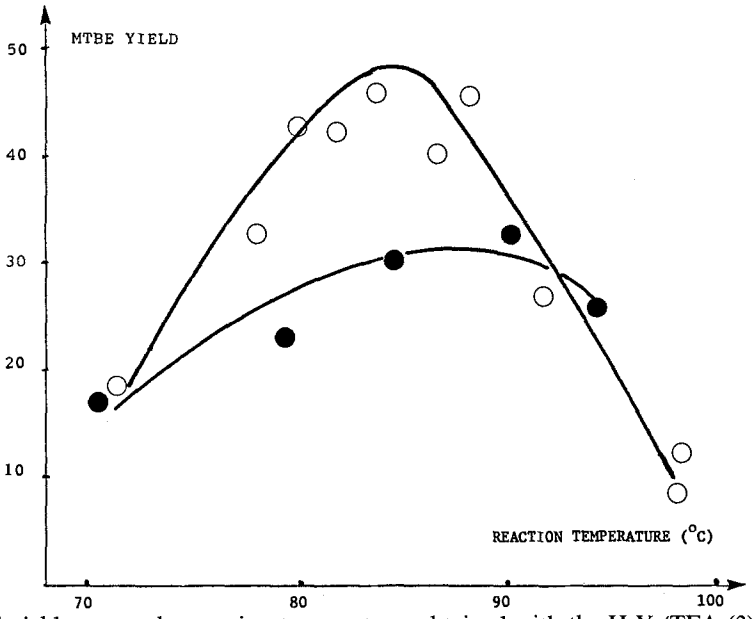

Fig. 5. MBTE yields versus the reaction temperature, obtained with the H-Y/TFA (3) (○——○) and the H-Y/TFA (4) (●——●).

Fig. 6 reports the yield in C8 by-products versus the reaction temperature. The amount of C8 formed by the catalytic reaction of Amberlyst 15 increased steadily with the temperature and reached almost a 11 C-atom% at 80 °C. On the

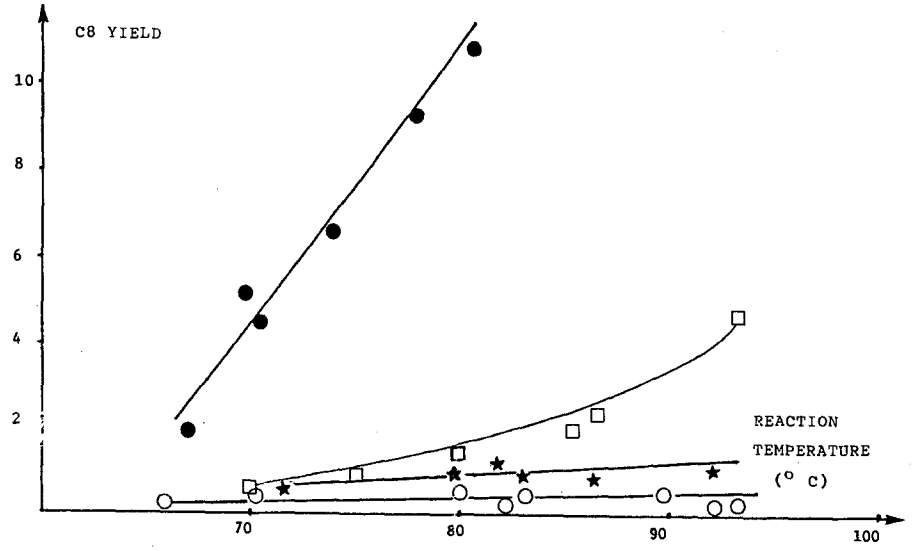

Fig. 6. C8 by-products yields versus the reaction temperature, obtained with the Amberlyst 15 (●——●), the H-Y (□——□), the H-Y/TFA (3) (★——★) and the H-ZSM-5/TFA (3) (○——○), respectively.

Table 2
Maximum MTBE yield obtained with the TFA loaded zeolites

Catalyst	Amberlyst 15	ZSM-5/TFA (3 wt%)	Y/TFA (3 wt%)
Temp. °C	68	85	85
MTBE yield (C-atom%)	47.5	40.8	46.1
C8 yield	9.7	0.2	0.4

contrary, the yield of such by-products given by the ZSM-5 and Y-type zeolites was extremely low: this is due to the shape-selectivity of these zeolite structures in contrast with the Amberlyst 15. In fact, the latter has a pore size which is larger than 3 nm as measured by the technique of nitrogen adsorption/desorption with our Micromeretic apparatus.

4. Conclusion

ZSM-5 zeolite exhibits some advantages with respect to the conventional ion-exchange resin (Amberlyst 15). However, its lower surface acidity cannot be readjusted by loading the triflic acid because of the (negative) influence of the TFA coating on the diffusion of reactant and product molecules. In that prospect, TFA loaded Y-type zeolite appears to be more interesting: it exhibits the same MTBE yield with much lower production of by-products (see table 2) and is more thermally stable than the commercial catalyst. Triflic bearing Y zeolite are therefore a very valid alternative to the conventional catalyst for the MTBE synthesis.

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