

THE ROLE OF ACIDITY OF CeH-EMT-TYPE ZEOLITE FOR CATALYZING TOLUENE ALKYLATION WITH METHANOL TO XYLENES

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The samples of EMT-type zeolite with different level of Ce³⁺ exchange were obtained by ion exchange with 0.25 and 0.75 M cerium nitrate solutions in three cycles. The reason for ion exchange of the zeolite with cerium cations is to decrease the number of strong acid sites (responsible for secondary reactions) and to increase the number of acid sites with medium and weak strength, favourable to xylenes production. Various techniques including X-ray diffraction, chemical analysis, nitrogen physisorption and MAS NMR spectroscopy were used to monitor the physico-chemical properties of these solids. The results revealed a high purity and crystallinity of the materials. The effect of ion exchange degree on the catalytic activity was studied over CeH-EMT zeolite and the results are compared with H-EMT-type zeolite.

INTRODUCTION

Alkylation of toluene with methanol to produce xylenes, is one of the most important processes used on industrial scale. Xylenes are very much demanded compounds in the organic chemical industry due to their importance in the production of polyester fibers via terephthalic acid.^{1,2} Various acidic zeolites^{3–8} have been used as catalysts in toluene alkylation with methanol and it was concluded that the catalytic activity is related to their acidities. The acidity is the most important property of zeolites with respect to their use as catalysts. Zeolites can be converted into the acidic form by ion exchange with either ammonium or multivalent cations, followed by thermal treatment. In the case of ion exchange with multivalent cations, these will polarize and hydrolyse water present in their hydration sphere following the Plank-Hirschler mechanism.⁹

Alkylation of toluene with methanol using EMT-type zeolite exchanged with multivalent cations have not yet been reported. In this paper we investigate the potential of CeH-EMT-type zeolite

as a catalyst for the alkylation of toluene with methanol at 673 K. The alkylation activity and selectivity to xylenes are compared with parent H-EMT-type zeolite.

EMT-type zeolite is the hexagonal analogue of cubic Y faujasite and contains two different types of large cages.^{10,11} The first type of cages (13 × 14 Å), called hypercages, has two circular apertures (7.1 Å) and three elliptical apertures (7.4 × 6.5 Å). The hypercages are connected directly by the circular apertures forming a straight channel. The second type of cages, called hypocages, has three elliptical apertures (7.4 × 6.5 Å). Hypercages are interconnected via hypocages which form side channels perpendicular to the main straight channels.

RESULTS AND DISCUSSION

Synthesis and characterization

The samples with different level of Ce³⁺ exchange were obtained by ion exchange with 0.25 and 0.75 M cerium nitrate solutions in three cycles. The ion exchange degree was determined by

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chemical analysis, calculated as $3 \times (\text{number of Ce}^{3+} \text{ cations}) / (\text{number of aluminium atoms})$. The results are presented in Fig. 1. It can be seen that the amount of exchanged Ce^{3+} cations increases after each cycle and with the concentration of exchange solution.

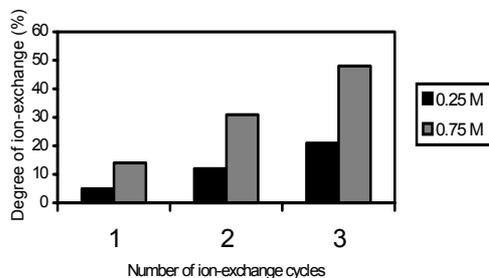


Fig. 1 – The degree of ion-exchange EMT-zeolite after each cycle.

The samples exchanged and used in the catalytic tests are denoted CeH-EMT-21 and CeH-EMT-48. The number after structure indicates the final exchange degree.

The XRD pattern of as-synthesized (Fig. 2) and calcined (Fig. 3) of EMT-type zeolite was very similar to that reported previously.¹² The high intensity of the peaks indicates that the parent sample of EMT-type zeolite has a high degree of crystallinity and does not contain detectable impure phases. The ion exchange process with ammonium and cerium, followed by thermal treatment, leads to a slightly decrease in crystallinity (Fig. 4 and Table 1).

The Si/Al ratio of the H-EMT, CeH-EMT-21 and CeH-EMT-48 determined by chemical analysis was 3.6 and by ^{29}Si MAS NMR was 3.9 and 4.2, respectively. The discrepancy between the ^{29}Si NMR (in the framework) and the chemical analysis (in the bulk) indicates the existence of the aluminium atoms in the extraframework positions, in all the three samples.

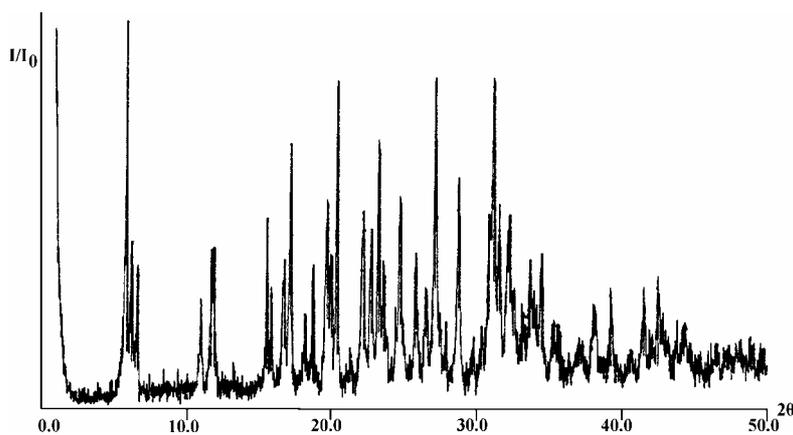


Fig. 2 – X-ray powder diffraction pattern of the as-synthesized sample of EMT-type zeolite.

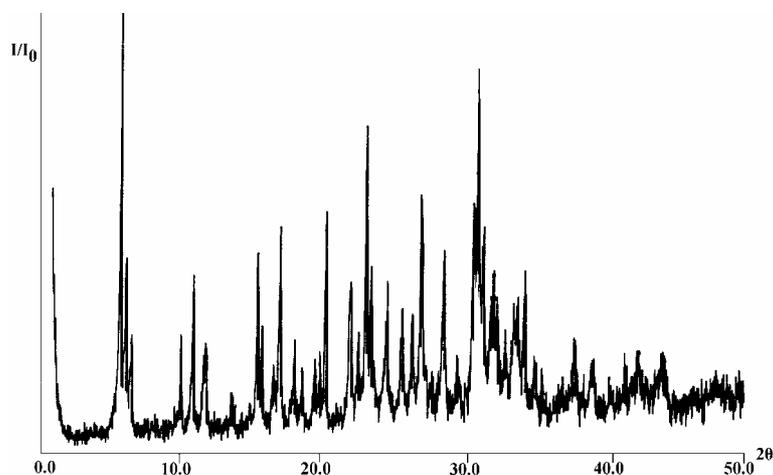


Fig. 3 – X-ray powder diffraction pattern of the calcined sample of EMT-type zeolite.

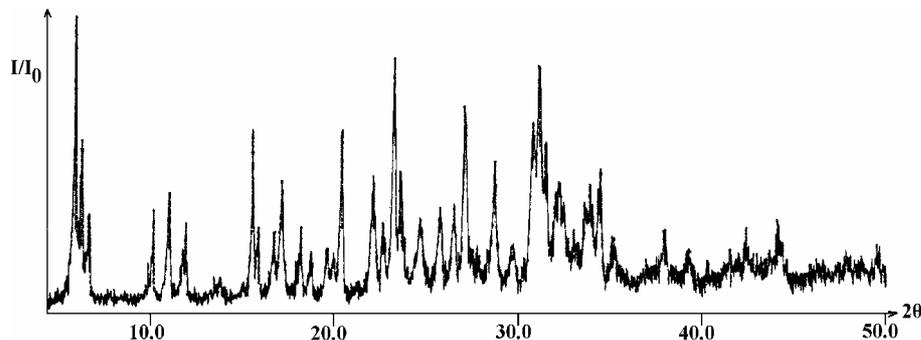


Fig. 4 – X-ray powder diffraction pattern of the CeH-EMT-48-type zeolite.

Table 1

The physicochemical characteristics of the parent and ion-exchanged EMT-type zeolite

| Sample | Crystallinity (%) | Si/Al | | BET, m ² g ⁻¹ |
|------------|-------------------|-------------------|----------------------|-------------------------------------|
| | | Chemical analysis | ²⁹ Si NMR | |
| H-EMT | 95 | 3.6 | 3.9 | 860 |
| CeH-EMT-21 | 95 | 3.6 | 3.9 | 870 |
| CeH-EMT-48 | 90 | 3.6 | 4.2 | 890 |

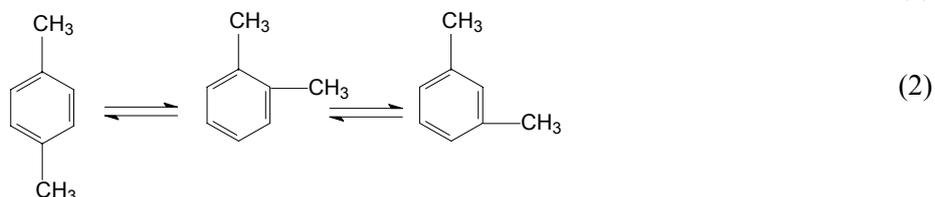
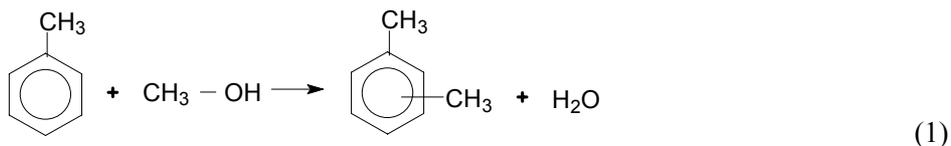
The sorption characteristics of H-EMT and CeH-EMT zeolites were determined by adsorption of nitrogen at the temperature of liquid nitrogen (Fig. 5). Specific surface area results are presented in Table 1. All the samples show high specific surface but the exchange degree did not cause any significant changes of the surface. The increase of surface area might be due to the decrease in the crystallite size and improvement in the microporous nature on exchange of hydrogen in HEMT-type zeolite with cerium cations. This result indicates that the most part of cerium ions could be located at the external surface of H-EMT not inside the main channel.

The acidity of the samples was determined by ¹H MAS NMR spectroscopy. The spectrum of the H-EMT zeolite (Fig. 6 a) presented four peaks at about 1.9, 2.6, 4.4 and 6.7 ppm, corresponding to the silanol groups (SiOH), the AlOH with the Al extraframework, the SiOHAl (Bronsted acid sites) and the ammonium ions, respectively. The peaks in the spectra of the CeH-EMT-21 (Fig. 6b) and CeH-EMT-48 (Fig. 6 c) were attributed to SiOH

(1.6 ppm), probably CeOH (1.8 ppm), AlOH (2.1 ppm) and to SiOHAl (3.1 ppm).

The catalytic activity of zeolite catalyst is related to the acidity, more exactly to the nature of the sites (Bronsted, Lewis), density, acid strength of sites (strong, medium and weak) in the zeolite framework. The ion-exchange process with rare earth is supposed to decrease the total acidity and some new Bronsted sites are formed via the Plank-Hirschler mechanism.^{13,14}

In the present study we investigated the influence of the acidity in toluene methylation at 673 K over CeH-EMT and H-EMT-type zeolites. The reaction of toluene alkylation with methanol is part of the group of electrophilic substitution reactions at the aromatic ring and was reported to proceed through Ely-Rideal mechanism.¹⁵⁻¹⁹ During the alkylation process the xylenes are mainly formed (eq. 1). Besides the primary alkylation, consecutive reactions, such as xylenes isomerization (eq. 2), toluene disproportionation (eq. 3) and toluene polyalkylation (eq. 4) giving trimethylbenzenes and tetramethylbenzenes can also occur.



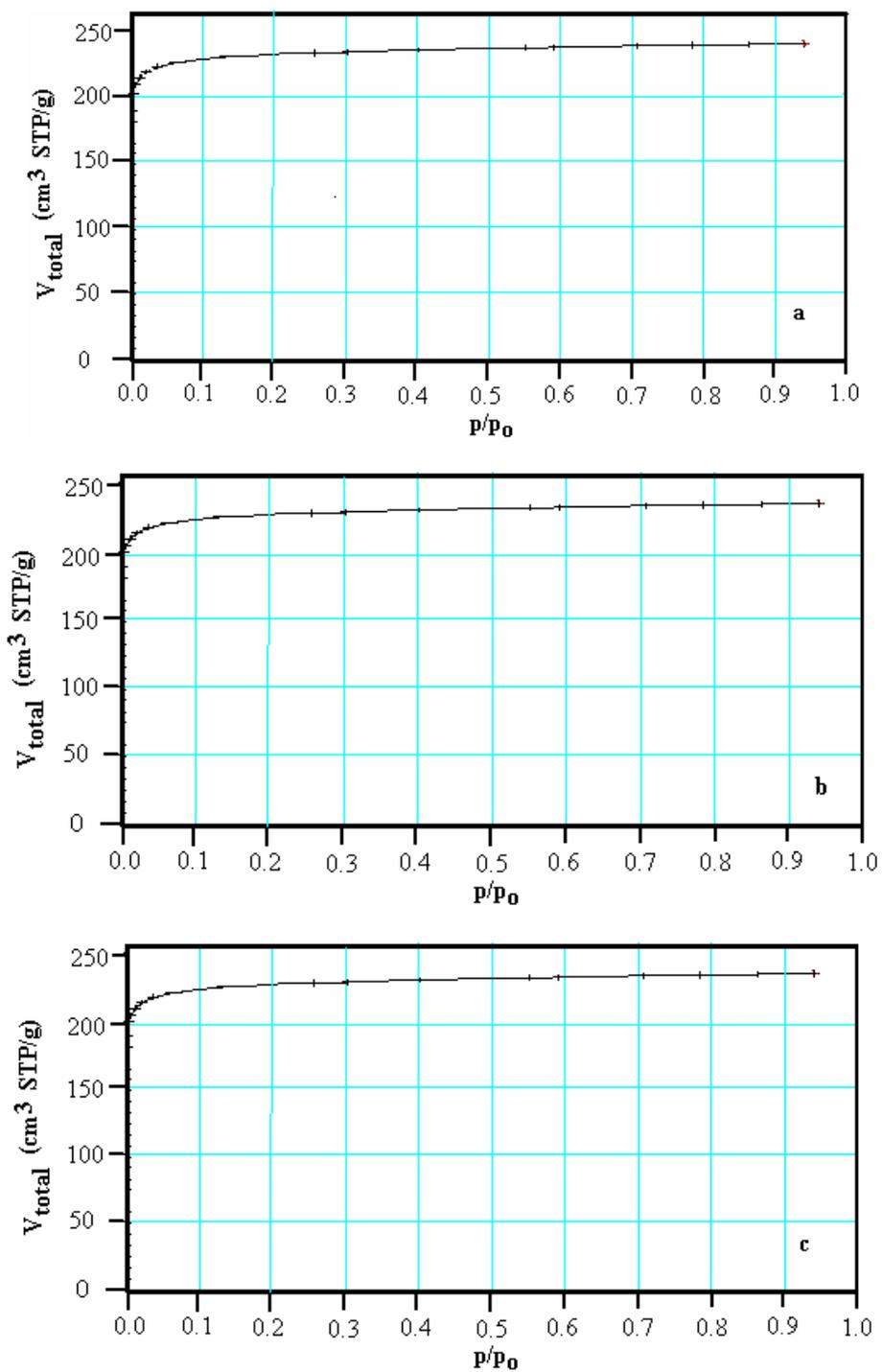
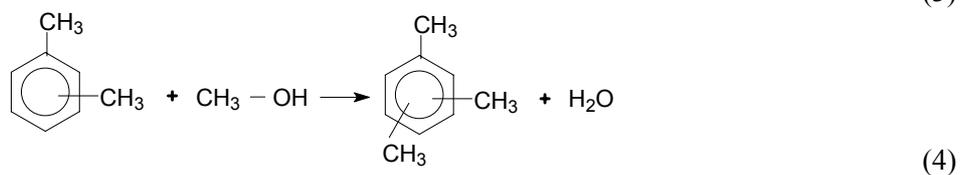
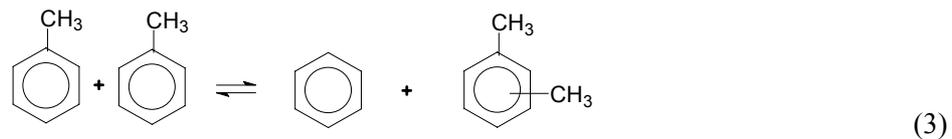


Fig. 5 – N_2 adsorption isotherm on H-EMT (a), CeH-EMT-21 (b) and CeH-EMT-48 zeolite (c).

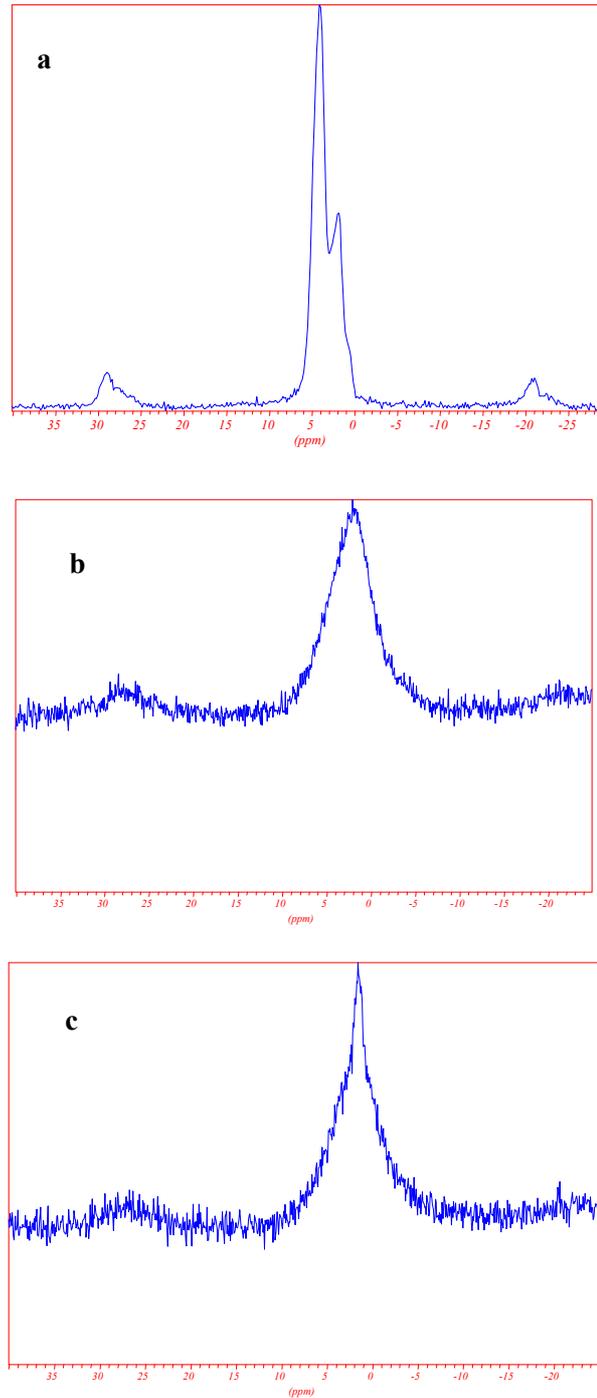


Fig. 6 – ^1H MAS NMR spectra of EMT-type zeolite (a) H-EMT; (b) HCe-EMT-21; (c) HCe-EMT-48.

Alkylation reaction

The catalytic performances of the tested samples were expressed in terms of toluene conversions:
 C_t = total conversion of toluene (% moles):

$$C_t = \frac{T_i - T_f}{T_i} \times 100 \quad (5)$$

where T_i and T_f are the initial and final concentrations of toluene.

C_x = conversion of toluene into xylenes (primary alkylation):

$$C_x = \frac{\sum X_i - B}{T_i} \times 100 \quad (6)$$

where X_i and B are the concentrations of the three xylene isomers and benzene

C_d = conversion of toluene by disproportionation:

$$C_d = \frac{2B}{T_i} \times 100 \quad (7)$$

C_{TMB} = conversion of toluene into trimethylbenzenes (TMB) (secondary alkylation):

$$C_{TMB} = \frac{\sum TMB_i}{T_i} \times 100 \quad (8)$$

where TMB_i are the concentrations of the three trimethylbenzene isomers.

These expressions were established taking into account the material balance of components

involved in eqs. (1-4) and the concentrations of aromatic hydrocarbons which were evaluated from GC analysis.

The conversion of toluene over EMT-zeolite are shown in Fig. 7. It can be seen that all the samples exhibit good activity toward toluene methylation. CeH-EMT-48 zeolite was most active, converting 76% of the total amount of toluene, compared to H-EMT, where the total conversion was 47%. A high selectivity for the ring alkylation of toluene towards xylenes (desired products) was obtained for the samples modified with cerium (Fig. 7). Among these, cerium exchanged zeolite, CeH-EMT-48 has shown high selectivity towards xylenes.

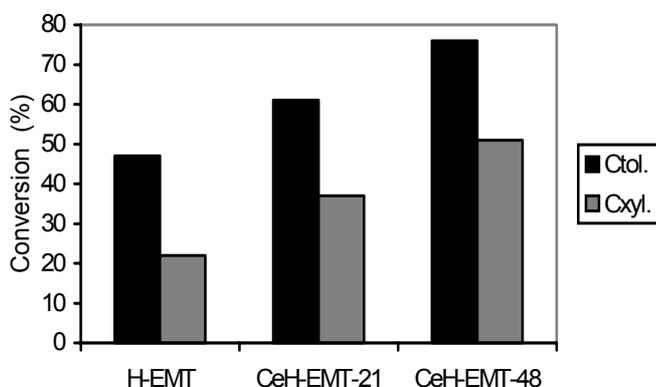


Fig. 7 – Activity of the H-EMT and CeH-EMT zeolite in toluene methylation at 673; T : MeOH = 1:1 (mol/mol).

The difference in behavior of H-EMT and CeH-EMT-48 concerning toluene conversion toward xylenes can be explained taking into account their total acidity. Studies of the acidity of CeH-Y zeolite²⁰ by TPD of ammonia reveals that the total acidity, the weak and the medium acidic sites increases, but the concentration of strong acid sites decreases, compared to H-Y. In cerium ion-exchanged zeolites, the toluene conversion increases with the ion-exchanged degree. The enhanced activity is due to the active centers formed by ion-exchange process. In the case of all the samples, the toluene alkylation with methanol is accompanied by secondary reactions, polyalkylated products, such as TMB and TeMB, possibly due to high acidity. Over CeH-EMT zeolite the toluene disproportionation reaction was diminished and secondary alkylation was negligibly changed compared to H-EMT zeolite.

We can conclude that cerium exchanged zeolite, CeH-EMT, produces maximum amount of the desired products. The difference in behavior of H-EMT and CeH-EMT can be explained taking into account their acidity.

EXPERIMENTAL PART

Catalysts synthesis

The EMT-type zeolite was synthesized according to a slightly modified procedure published by Delprato.²¹ The sodium aluminate (Carlo-Erba 56 % Al_2O_3 , 37 % Na_2O), NaOH (Prolabo, 98 %) and crown ether (18-crown-6, Aldrich, > 99.5 %) were successively added under vigorous agitation to distilled water. The resultant mixture was aged 24 h at room temperature. Finally, the silica sol (Ludox HS 40) was added. The molar composition of the starting mixtures was as follows: 10 SiO_2 : 1 Al_2O_3 : 2.1 Na_2O : 0.5 18-C-6 : 140 H_2O . The crystallization was carried out at 383 K, under autogenous pressure in PTFE autoclaves and static conditions for 11 days. The crystals of the EMT-type zeolite were washed with distilled water, dried at 353 K for 12 h and finally calcined at 723 K for 3 h. The NH_4^+ forms of the sample was obtained by 6-fold ion-exchange with 2M NH_4NO_3 aqueous solution at 353 K for different durations. After the ion exchange, the crystals of the EMT-type zeolite were washed in distilled water and dried at 363 K for 12 h. One part of NH_4^+ exchanged EMT-type zeolite is calcined in air during 3 h at 723 K for obtaining the protonic form, denoted as HEMT. Other part of NH_4^+ exchanged EMT-type zeolite, was converted to the (NH_4^+, Ce^{3+}) EMT-type zeolite by three successive ion exchanges with 0.25, 0.75 M $Ce(NO_3)_3$ solutions for 8 h at 353 K. The exchanged zeolite samples were calcined

under air at 353 K for 3 h for obtaining the (H⁺, Ce³⁺)EMT-form, denoted CeHEMT.

Catalysts characterization

The elemental analysis of the solids was performed by the Service Central d'Analyse of CNRS-Solaize. The crystallinity of the products was determined by X-ray diffraction (Philips diffractometer PW 1800 - CuK α). The surface area was evaluated by means of the t-plot method, from nitrogen adsorption/desorption isotherm performed at 77 K with a Micromeritics ASAP 2100 system. The ²⁷Al MAS NMR and ²⁹Si MAS NMR spectra were recorded on Bruker MSL-300 spectrometer under the following conditions : for ²⁷Al spectra, chemical shift standard Al(H₂O)₆³⁺, frequency = 78.17 MHz; pulse length = 0.7 μ s; pulse angle = $\pi/12$; recycle time = 4 s; spinning rate = 10 KHz; number of scans = 64; for ²⁹Si chemical shift standard : TMS; frequency = 59.63 MHz; pulse length = 5 μ s; pulse angle = $\pi/2$; recycle time 100 s; spinning rate = 4 KHz; number of scans = 290. The ¹H MAS NMR spectra were recorded on a Bruker DSX-400 spectrometer and the single-pulse technique was used under the following conditions: chemical shift standard: TMS; recycle time: 4 s; spinning rate = 2 KHz; number of scans = 8.

Catalytic tests

The alkylation of toluene with methanol was carried out in a pulse-type microreactor coupled with GC. Before reaction, the catalyst was activated or regenerated in air stream at 773 K for 2.5 h, followed by cooling to the reaction temperature in a nitrogen flow. Samples of 0.1 μ l of reagents were injected at constant temperature. Nitrogen was used as a carrier gas (30 ml min⁻¹ flow rate). The reaction products were analyzed on line by GC, using a 1.5 m column packed with 16 % SE-30 + 3 % Benton 34 on Chromosorb W-AWDCMS and a FI detector.

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