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Methylammonium-FAU zeolite: Investigation of the basic sites in base catalyzed reactions and its performance

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ABSTRACT

The basicity of methylammonium-faujasite zeolites (FAU) was evaluated in the Knoevenagel and Claisen–Schmidt condensation reactions and in the alcoholysis of propylene oxide with methanol. The basic character of FAU zeolites (Y zeolite with Si/Al = 2.5 and X zeolite with Si/Al = 1.4) was systematically altered by incorporating cesium and methylammonium cations, which were located in charge compensation sites. In all three reactions, methylammonium-FAU zeolites showed higher specific activity in comparison to cesium-FAU, indicating that these catalysts encompass stronger basic sites. Characterization of the zeolites has shown that ion exchange of sodium by methylammonium cations reduces their micropore volume, however enhances the strength of their basic sites. TPD-CO_2 experiments demonstrated that aluminum rich zeolites possess higher basicity due to higher number of sites. Additionally, XPS (O1s) measurements illustrated that when monomethylammonium cation is present in ion exchange sites, structural zeolite oxygen anions have a higher basic character in comparison to cesium-FAU. This unique result opens news perspectives for application of these highly basic and low-cost methylammonium molecular sieves in base-catalyzed reactions such as Knoevenagel, Claisen–Schmidt condensation and nucleophilic cleavage of propylene oxide with methanol.

1. Introduction

Zeolites have attracted attention recently mainly due to their environmentally benign character and their potential use in fine chemical synthesis [1]. They are interesting materials not only by the properties of the active sites themselves but also by the way these sites are situated inside their microporous structure. In an attempt to profit from the microporosity of zeolites, several researchers have devoted their attention to generated stronger basic sites in zeolites [2,3].

Usually, the basicity of zeolites can be developed by ion-exchange with alkali metal cations [2,3], however these sites present relatively weak basic strength. Intrinsic zeolite basicity is associated with framework oxygen atoms bearing the negative charge and is thus of Lewis type. Decreasing the electronegative character of the non-framework compensating cations the negative charge over oxygen ions is enhanced, i.e. the basicity of alkali-exchanged zeolites increases with the compensating cation size in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ [3,4]. Indeed, this is a way of describing zeolite basicity. According to Barthomeuf [5], the electron density on the oxygen atom depends also on other factors, such as zeolite structure nature and cation location. In this alkali metals sequence, francium (Fr^+) could ensure a higher basicity to zeolites, because it has the lowest known electronegativity. However, this element is the second rarest naturally in occurrence and is a highly radioactive metal. An alternative to incorporate stronger basic sites in the zeolite pores is by decomposing an occluded alkali metal salt. Since cesium creates stronger basic centers than other alkali metals, researchers have focused significant attention on supported cesium catalysts.

Recently we found a new basic zeolite catalyst, comprising ion-exchanged methylammonium cations in Y zeolite (FAU) [6]. These catalysts showed to be six times more active than cesium-Y zeolites in Knoevenagel condensation. This original result indicates that zeolites containing organic cations might have huge potential in various applications, which have not been properly explored. Additionally, ammonium cation adducts are much cheaper than cesium. In this previous work [6], four different cations were evaluated and interestingly, as occurs with the alkali metals, for the same ion exchange degree (IED) the zeolite catalytic activity increases with the size of the organic compensating cation: $NH_4^+ < (CH_3)NH_3^+ < (CH_3)_3NH^+ < (CH_3)_4N^+$. Among the methylammonium cations, the monomethyl cation, $(CH_3)NH_3^+$, showed the highest ion exchange degree (71%) and consequently ensured the highest catalytic activity to the Y zeolite. Another manner of increasing zeolite basicity is by incorporating aluminum in the

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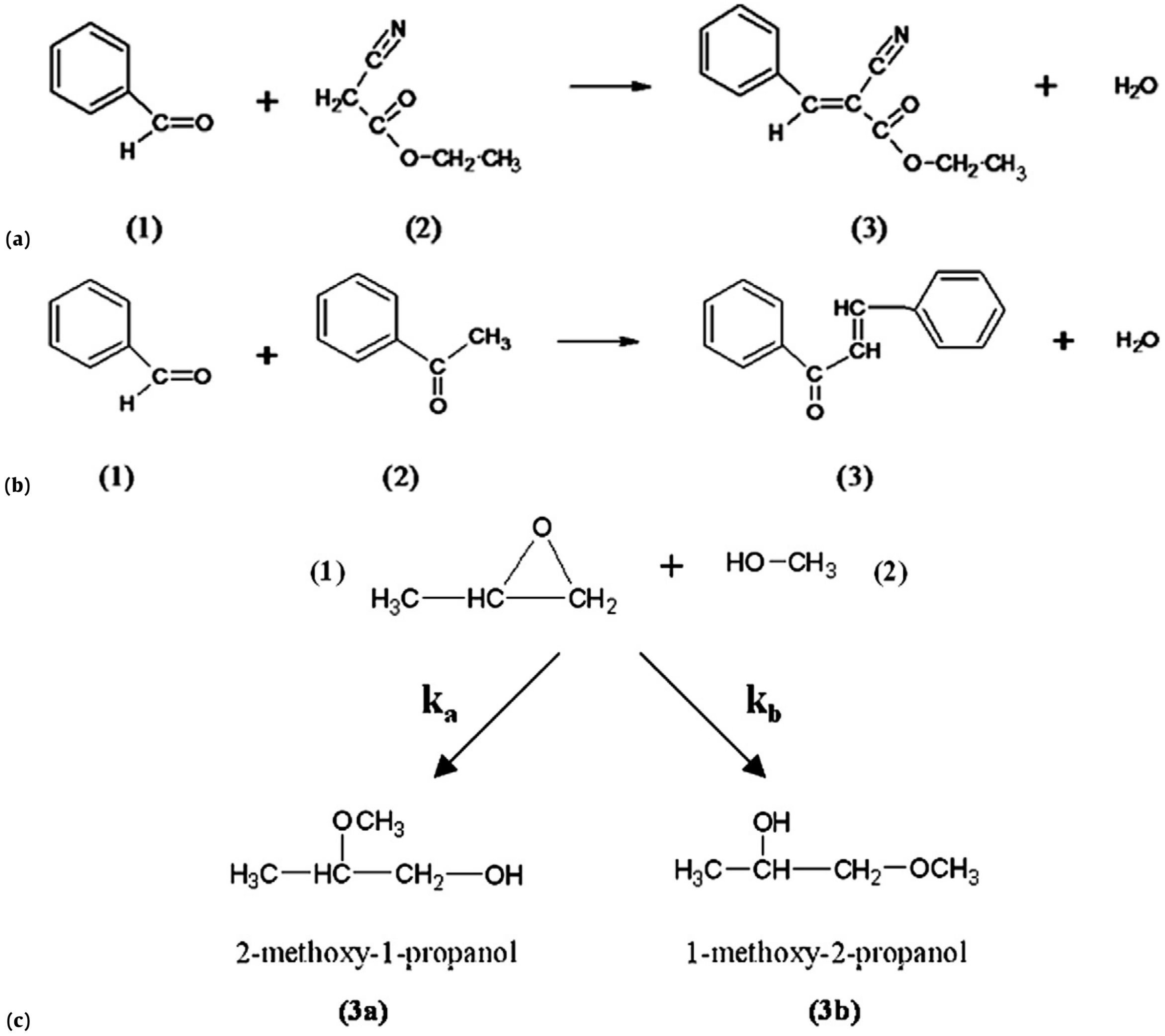

Scheme 1. Reactions studied: (a) Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, (b) Claisen–Schmidt condensation of benzaldehyde with acetophenone and (c) propylene oxide alcoholysis with methanol.

zeolitic framework, because this way negative framework charge density is increased. FAU zeolites with different framework aluminum content and exchanged with methylammonium cations have been tested in the Knoevenagel condensation [7] and the material with higher aluminum content (X zeolite with 1.4 Si/Al ratio) showed a conversion three times superior compared with a zeolite having lower aluminum content (Y zeolite with 2.5 Si/Al ratio). In the context of new materials development for more efficient catalytic processes [8], inorganic–organic hybrid materials offer new and exiting opportunities [9–11]. The main idea when developing these $\mathrm{Me}i^{+}$-FAU hybrid materials ($0 \leqslant i \leqslant 4$ is the number of methyl groups in the alkylammonium cations) was to take advantage of the best properties of each component that forms the hybrid, and trying to eliminate the cesium high costs drawback and obtain materials with superior basicity.

In the present research, we investigate the catalytic properties of methylammonium FAU zeolites in three different base catalyzed reactions (Scheme 1): (a) Knoevenagel condensation, (b) Claisen–Schmidt condensation and (c) propylene oxide (PrO) alcoholysis with methanol.

Knoevenagel condensation is one of the reactions used for carbon–carbon bond formation and has been widely used for the commercial preparation of fine chemistry intermediates [12,13]. This reaction, which is a key step in the commercial production of the antimalarial drug lumefantrine [14], is also largely employed as model reaction for the characterization of catalysts basicity [13]. On the other hand, Claisen–Schmidt condensation is the most useful reaction in the synthesis of chalcones, which represent one of the most rich and omnipresent groups of natural products [15]. In the last few years they have been shown to possess interesting biological properties and can be used as synthetic intermediates in the preparation of several compounds [15]. Finally, the synthesis of glycol ethers over basic catalysts is also an important class of reaction in organic synthesis [16]. There are several methods for the synthesis of propylene glycol ether, however the propylene oxide method is most suitable and commercialized [17,18]. This alcoholysis reaction is actually interesting, because it allows distinguishing between acid and basic catalytic sites [18,19]. The propylene oxide ring might be opened at the C–O bond. In the presence of basic sites, the bond preferentially opens at the least sterically hindered position, leading to most secondary alcohols ($k_b > k_a$, 1-methoxy-2-propanol—Scheme 1). However, acid sites provide most primary alcohols ($k_a > k_b$) [17]. Generally, the use of alcohol reaction network as a test reaction is also proposed because alcohols are expected to give different products depending on the nature of the sites present on the catalyst [20]. The more frequently used and studied model reaction is the conversion of propan-2-ol (isopropanol), assuming that this secondary alcohol dehydrates on acid sites to give propene and is converted in acetone on basic sites [20]. However, the use of propylene oxide alcoholysis with methanol seems to be suitable for our purposes, because for this reaction a very high temperature is not needed and methylammonium-FAU zeolites could be thermally unstable under the temperatures required for conversion of propan-2-ol.

In this work we investigated the diverse properties of methylammonium-FAU zeolites (two different Si/Al ratios) and compared their catalytic properties with those containing cesium. For this comparison we have fixed attention on monomethylammonium and tetramethylammonium cations, i.e. ammonium cations containing one and four carbon atoms. Samples were additionally characterized by nitrogen adsorption/desorption isotherms (micropore volume), elemental analysis, nuclear magnetic resonance of hydrogen (^{1}H MAS NMR). X-ray photoelectron spectroscopy (XPS) and CO_2 temperature programmed desorption (TPD) were used to determine the basicity strength of the catalysts.

2. Experimental

2.1. Obtaining faujasites with different cations

The starting materials were sodium faujasite zeolites (Na/Al molar ratio 1) with two different Si/Al molar ratios: 1.4 (zeolite X, manufactured by Merck) and 2.5 (zeolite Y, manufactured and kindly provided by Zeolyst).

The catalysts were obtained similarly as before [6,7] through three consecutive ion exchanges (6 h each) at 40 °C with 0.5 mol/L solution of the corresponding cation. In this condition, the maximum ion exchange degree (IED) of the corresponding cation was obtained. Then the sample was copiously washed with distilled water and dried at 110 °C overnight. The chlorides of cations used were $CH_3NH_3^+$ (denoted as $Me1^+$), $(CH_3)_4N^+$ (denoted as $Me4^+$) and Cs^+. This last cation was used as a basis for comparison with the monomethyl- and tetramethylammonium cations.

In order to evaluate the effect of methylammonium cation content on catalyst basicity, zeolite Me1-Y containing different IED of cations $Me1^+$ was also prepared according to procedure described elsewhere [6]. In this procedure, the amount of $Me1^+$ cation currently in solution is varied, with the aim of obtaining an ion exchange isotherm.

Ion exchange degree values were obtained in view of residual Na amount in the zeolites samples ($\text{IED\%} = [1 - \text{Na/Al}] \times 100$).

2.2. Knoevenagel and Claisen–Schmidt condensation reactions

Knoevenagel and Claisen–Schmidt condensation reactions (Scheme 1, reactions a and b, respectively) were accomplished in liquid phase without any solvent. To an equimolar mixture of benzaldehyde (4.8 mmol, reactions a and b, compound 1) and ethyl cyanoacetate (4.8 mmol, reaction a, compound 2) or acetophenone (4.8 mmol, reaction b, compound 2), 50 mg of catalyst was added (5 wt%). The reaction mixture was stirred at 60 °C for 3 h for the Knoevenagel condensation and at 140 °C for 6 h for the Claisen–Schmidt condensation. Because acetophenone ($pK_a = 19.1$) is less reactive than ethyl cyanoacetate ($pK_a = 9.2$), a higher temperature was used in Claisen–Schmidt reaction. Condensation reactions were performed in a 2 mL borosilicate glass reactor (GC type tapered flask, with silicon septum). The reactor was coupled in a Teflon lined device, which was immersed in an oil bath equipped with temperature control. This device could accommodate up to 6 reactors at the same time, each one with an individual magnetic stirring, using 4 mm magnetic stir bars. Sampling of the reaction mixture was achieved first by removing the catalyst by rapid centrifugation (3500 rpm for 5 min) and then cooling the liquid product, to be further analyzed by gas chromatograph (GC, Siemens RGC 202). Samples were analyzed on a DB-1 capillary column with a flame ionization detector. The carrier gas was N_2 (1.5 Bar) and the analysis temperature was 230 °C (oven temperature), 220 °C (injector) and 280 °C (detector). The retention times were compared with those of authentic compounds.

2.3. Propylene oxide alcoholysis with methanol

The reaction of propylene oxide with methanol was carried out in a 55 mL Parr-type batch reactor, with the mole ratio of methanol and propylene oxide being 5:1 (15 g of dry methanol and 5.42 g of propylene oxide). Residual water, which could react with propylene oxide and then interfere in reaction analysis, was removed before reaction by treating 1 g of the zeolite sample under vacuum ($<5 \times 10^{-4}$ bar) at 150 °C for 2 h. After that the zeolite was immediately suspended in the reaction mixture. After running at 140 °C for 5 h under magnetic stirring, the reactor was cooled down in an ice-bath. Catalysts were removed from reaction mixture also by rapid centrifugation and the products analyzed in a HP gas chromatograph 6890 series equipped with FS-SE54 capillary column (60 m) and a flame ionization detector. The carrier gas was N_2 (0.8 bar) and the analysis temperature was 250 °C (oven temperature), 250 °C (injector) and 250 °C (detector). The retention times were compared with those of authentic compounds.

3. Characterization

3.1. Micropore volume analysis

Nitrogen adsorption/desorption isotherms were recorded at liquid nitrogen temperature on equipment supplied by Micromeritics (ASAP 2000). Samples were evacuated prior to measurements at 120 °C for 12 h under vacuum of 1×10^{-2} Pa. Micropore volumes were calculated according to the t-plot method [21].

3.2. Elemental analysis

Sodium and aluminum contents in the ion exchanged zeolites were determined using chemical analysis by optical emission spectrometry through inductively coupled plasma (ICP-OES). Carbon, hydrogen and nitrogen contents (mass percentage) were determined on an Elementar Vario EL. Both analyses were done in duplicate.

3.3. Temperature-programmed desorption of carbon dioxide

Temperature-programmed desorption (TPD) of carbon dioxide was performed on CE Instruments TPDRO 1100 series equipment. The Na- and Cs-FAU samples (around 1 g) were first activated at 300 °C for 1 h and subsequently cooled to 80 °C under helium flow. Then the activated materials were saturated with dry gaseous carbon dioxide at this temperature. Physisorbed carbon dioxide was removed by purging the sample under helium flow at 80 °C until a stable baseline was monitored (ca. 1 h). The TPD was performed under helium flow (25 mL/min) by heating the sample from 80 to 600 °C with a heating rate of 10 °C/min. In order to obtain comparable spectra, TPD spectra were plotted dividing the detector signal by sample mass.

3.4. Thermogravimetric analysis (TGA)

Decomposition of organic material and thermal behavior of FAU samples (differential scanning calorimetry—DSC) were evaluated on a Netzsch 209/2/E instrument equipped with a STA 409 controller, and α-Al_2O_3 was used as a reference material. About 10 mg of the zeolites were placed in a platinum pan and heated from room temperature to 1100 °C, at a heating rate of 2 °C/min under air flow.

Table 1
Properties of zeolites used in this work

Cation	V_c (Å^3)[a]	Zeolite	% Ion exchange degree[b]	Anhydrous unit cell formula[c]	Micropore vol. (mL/g)	Temperature of Mei$^+$ decomposition (°C)[d]
Na^+	3.6	Y	0	$Na_{54.8}Y$	0.25	–
		X	0	$Na_{80}X$	0.25	–
Cs^+	20.2	Y	70	$Cs_{38.4}Na_{16.4}Y$	0.20	–
		X	70	$Cs_{56}Na_{24}X$	0.11	–
$Me1^+$	49	Y	71	$(Me1)_{38.9}Na_{15.9}Y$	0.19	266
		X	71	$(Me1)_{56.8}Na_{23.2}X$	0.12	218
$Me4^+$	175	Y	35	$(Me4)_{19.2}Na_{35.6}Y$	0.14	328
		X	15	$(Me4)_{12}Na_{68}X$	0.17	314

[a] Data from Ref. [24].
[b] Ion exchange degree calculated considering residual Na amount.
[c] $Y = (AlO_2)_{54.8}(SiO_2)_{137.2}$; $X = (AlO_2)_{80}(SiO_2)_{112}$.
[d] Peak temperature of maximum decomposition rate.

3.5. ^1H MAS NMR (nuclear magnetic resonance)

^1H magic angle spinning (MAS) NMR spectra were recorded at room temperature with a Bruker DSX 500 spectrometer, using a 4 mm rotors spinning at 10 kHz. $\pi/2$ rad pulses of 0.85 s and a recycle delay of 500 µs were used. To remove residual adsorbed water, samples were treated under vacuum ($<5 \times 10^{-4}$ bar) at 150 °C and carefully transferred to the NMR rotors in a glove box. In the case of Y zeolites, the thermal treatment was done for a period of 5 h, however for X zeolites, which is more hygroscopic, a period of 12 h was necessary to remove all adsorbed water.

3.6. O1s XPS (X-ray photoelectron spectroscopy)

XPS measurements were obtained on VSW HA-100 spherical analyzer using an aluminum anode (Al$K\alpha$ line, $h\nu = 1486.6$ eV). The high-resolution spectra were measured with constant analyzer pass energies of 44 eV, which produce a full width at half-maximum (FWHM) line width of 1.8 eV for the Au($4f_{7/2}$) line. The powdered samples were pressed into pellets and fixed to a stainless steel sample holder with double-faced tape and analyzed without further preparation. The pressure during the measurements was always lower than 2×10^{-8} mbar. Charging effects were corrected by shifting the spectra linearly so that the C1s line had a binding energy of 284.6 eV.

4. Results and discussion

4.1. Ion exchange results and zeolites composition: maximum ion exchange degree

The exchangeable cations in faujasite are usually found at four different crystallographic positions: (I) and (I′), which correspond to cations located inside the small cavities (i.e. hexagonal prisms and sodalite cavities); and positions (II) and (III), which are located in the supercavity [6]. Cations located in this supercavity represent approximately 70% of the cationic sites in the FAU zeolites, and the others 30% to those inside the small cavities. These marks, obtained from crystallographic data and theoretical models, provide an explanation for some results depicted in Table 1. This table shows that the maximum ion exchange degree results (IED) achieved by Cs^+ and $Me1^+$ cations is around 70%, which was expected from their stereo-spatial limitations of exchanging into sodalite and hexagonal prism cavities. Cation $Me4^+$ showed a low IED in zeolite Y (35%), which decreases to 15% when zeolite X is used. These results suggest that the cation $Me4^+$ is submitted to two stereo-special barriers: (1) inaccessibility of hexagonal prisms and sodalite cavities (as occurs to cations $Me1^+$ and Cs^+) and (2) lack of space between the $Me4^+$ cations because they have a spatial diameter higher than the distance between two negative neighboring charges, generated by the zeolite framework aluminum. Zeolite X encompasses a higher framework aluminum density, justifying its lower $Me4^+$ exchange capacity. Previous works have shown that Cs^+ can eventually enter sodalite cavities or hexagonal prisms [22,23], but this is achieved when the sample is dehydrated at elevated temperatures, e.g. 400 °C. Norby et al. [23] showed, by using in situ synchrotron X-ray powder diffraction, that Cs^+ migration to small FAU cavities occurs only at temperatures higher than 300 °C. These conditions cannot be applied to the Me*i*-FAU zeolites, otherwise the alkylammonium cations would decompose. DSC results (differential scanning calorimetry) allowed us to estimate the mean temperature of Mei^+ cation decomposition and these values are depicted in Table 1. Thermogravimetric profiles (TGA) of Me*i*-FAU zeolites showed a broad temperature range for Mei^+ cations decomposition: it started at about 190 °C and continuously increased at about 400 °C. Probably, a broad temperature range was obtained, because thermal analysis is a dynamic method in which the weight loss of a sample is measured continuously as the temperature is changed at a constant rate, and then results are very closely connected with the accompanying experimental conditions. Table 1 shows additionally that Me*i*-FAU samples had the lowest micropore volume, as a consequence of the presence of the voluminous organic cations.

IED values (Table 1) were obtained in view of residual Na amount in the zeolites samples. With the aim of confirming this result, IED was also determined by considering the total amount of alkylammonium cations in these samples. To accomplish this, carbon, hydrogen and nitrogen (CHN) elemental analysis was determined, and the detailed methylammonium-FAU zeolites chemical composition is depicted in Table 2. As the resulting ($Na^+ + Mei^+$)/Al molar ratio is reasonably close to 1, it suggests that the organic cations incorporated into the solid are present in charge compensation sites and not in excess as e.g. occluded chloride salt. Actually, as the exchanging cations are monovalent, cation/aluminum molar ratio should be equal to one in order to maintain the zeolite charge neutrality. This molar ratio was somewhat lower than 1 in Me*i*-X zeolites. This result could be interpreted based on the random experimental error, which one should ascribe from chemical analysis from the different elements (Na, Al, C, H and N). However, one could also interpret that other cation, for example a proton, and therefore not summed to this cation balance, should be present as charge balancing cation. Furthermore, Table 2 also shows that C/N molar ratio is close to 1 and 4, the expected values to the chemical

Table 2
Detailed methylammonium-FAU zeolites chemical composition

Cation	Zeolite	C (wt%)	H (wt%)	N (wt%)	C/N molar ratio	Na^+/Al molar ratio	Mei^+/Al[a] molar ratio	$(Na^+ + Mei^+)$/Al
$Me1^+$	Y	3.08	3.57	3.21	1.1	0.29	0.73	1.02
	X	3.22	4.04	3.80	1.0	0.29	0.65	0.94
$Me4^+$	Y	5.32	3.18	1.63	3.8	0.65	0.36	1.01
	X	2.99	3.31	0.83	4.2	0.85	0.13	0.98

[a] Mei^+: methylammonium cation ($Me1^+$ or $Me4^+$).

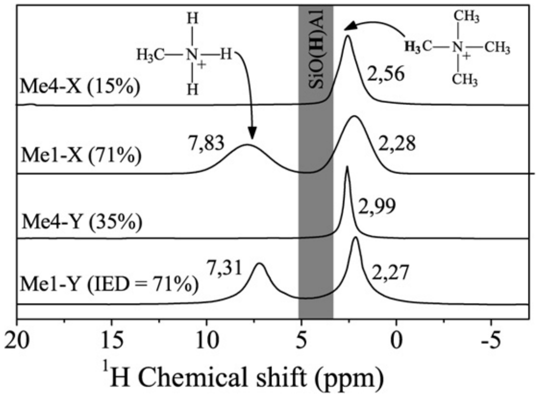

Fig. 1. ^{1}H MAS NMR spectra of FAU zeolites containing methylammonium cations.

composition of the mono and tetramethylammonium cations, respectively.

Ion exchanged Me*i*-FAU zeolites were further analyzed by ^{1}H MAS NMR spectroscopy, with the purpose to identify if H^+ cation were also compensating the negative charge generated by structural aluminum, besides Na^+ and Mei^+. This question came up because Mei^+ cations probably have lower interaction with framework oxygen anion, in comparison to Cs^+, as expected from their large volume (V_c in Table 1). This implies that their interaction with the charged zeolite structure should be weak, indicating that hydrolysis reaction $Mei^+\text{-FAU} + H_2O \rightarrow MeiOH + H^+\text{-FAU}$ could happen. Fig. 1 illustrates ^{1}H MAS NMR spectra of Me*i*-FAU samples and Table 3 the assigned peak positions. Signals assigned to hydrogen from methyl ($-CH_3$) and ammonium (H_3N-) groups are observed. Samples Me1-Y and Me1-X showed signals at around 7.5 and 2.2 ppm, assignable to hydrogen atoms bonded to nitrogen and carbon atoms, respectively. The area below these two peaks showed a relationship of 1:1, which corresponds to $CH_3NH_3^+$ cation chemical composition. On the other hand, samples Me4-Y and Me4-X showed only one signal at 2.95 and 2.56 ppm, respectively, from the hydrogen atoms belonging to the methyl groups. Methylammonium-FAU zeolites did not show any peak around 3–5 ppm, which is assigned to H^+ located in SiO(H)Al bridging groups [25,26], thus supporting the initial supposition that no other cation than Mei^+ or Na^+ is present in the zeolites ion exchange sites. ^{13}C MAS NMR results are depicted in Table 1 and they show that the position of the ^{13}C signal is close to 20 and 54 ppm, for $Me1^+$ and $Me4^+$ cations, respectively. The tendency of the resonance shift from 20 ppm for methyl groups on $Me1^+$ to 54 ppm for methyl groups on $Me4^+$ agrees with the different chemical environment of the carbon atoms [26,27].

4.2. Ion exchange results and zeolites composition: different ion exchange degree of $Me1^+$ in zeolite Y

Fig. 2 shows ion exchange properties of $Me1^+$ cation in zeolite Y. Ion exchange isotherm shape (Fig. 2A) indicates that there is a significant interaction between the cation and the zeolite framework, i.e. for lower molar fraction of $Me1^+$ cation in solution (e.g. 0.2) an IED close to 50% is attained. Fig. 2A also shows that a further ion exchange goes not so easy, because of the increased proximity of the organic cations in the FAU α cavity, as well the inaccessibility of the cationic positions in the smaller β and γ cavities. Fig. 2B shows the micropore volume of Me1-Y as a function of the exchange degree of $Me1^+$ cations, measured by N_2 physisorption. As a consequence of the presence of the alkylammonium cation in zeolite pores, the micropore volume decreases linearly with the exchange degree up to 44% of its original value.

Table 3
^{1}H NMR peak positions

Entry	Sample	Methylammonium cation		Zeolite	
		$-CH_3$[a]	H_3N-	$-SiOH$	$-SiO(H)Al-$
1	Me1-Y (71% ED)	2.27 (20.87)	7.31	ND	ND
2	Me4-Y (35% ED)	2.99 (54.67)	–	ND	ND
3	Me1-X (71% ED)	2.28 (20.68)	7.83	ND	ND
4	Me4-X (15% ED)	2.56 (54.17)	–	ND	ND

[a] In brackets are indicated the carbon peak positions, obtained from ^{13}C NMR.

4.3. Zeolites basic sites characterization by CO_2-TPD and O1s-XPS

The basicity of FAU zeolites was measured by TPD of CO_2. The amount of desorbed CO_2 and the temperature of maximum desorption of CO_2 are the criteria for the concentration and strength of basic sites, respectively. However, in this work this analytical method could be applied only for the zeolites containing sodium and cesium, because methylammonium cations start to decompose in the same region CO_2 desorption is detected (close to 190 °C). Since the desorbed CO_2 and the released amine could not be detected separately, CO_2-TPD profiles of these samples lead to an artificial result. Fig. 3 illustrates CO_2-TPD profiles of four samples, containing sodium and cesium. Low Y aluminum FAU zeolite holds CO_2 desorption temperature peak at 180 °C, thus suggesting the presence of relatively weak base sites in this zeolite. On the other hand, high X aluminum FAU zeolite shows an obvious enhancement of both the desorption area and strength of basic sites (peak at 235 °C) in comparison to Y. Fig. 4 additionally shows that the desorbed CO_2 amount does not depend considerably on the nature of the alkaline cation, meaning that the presence of cesium, instead of sodium cations, does not enhance zeolites basicity significantly. In the case of samples Na-X and Cs-X TPD profile could be deconvoluted in two distinct peaks at 180 °C (peak 1) and 235 °C (peak 2). For sample Na-X area of peaks 1 and 2 corresponded to 59 and 41% of the total area, respectively. On the other hand, for sample Cs-X area corresponded to 51 and 49%, indicating that the presence of cesium increased the amount of basic sites with enhanced basicity. CO_2-TPD quantification was not done, since in this case results would not be very reliable. This is why we preferred a direct comparison of the samples by dividing TPD signals by sample weight (approximately 1 g). In this case detector signal is normalized and samples can be qualitatively compared. CO_2-TPD results on Na- and Cs-FAU zeolites are well known and intensively discussed in literature [28]. Conse-

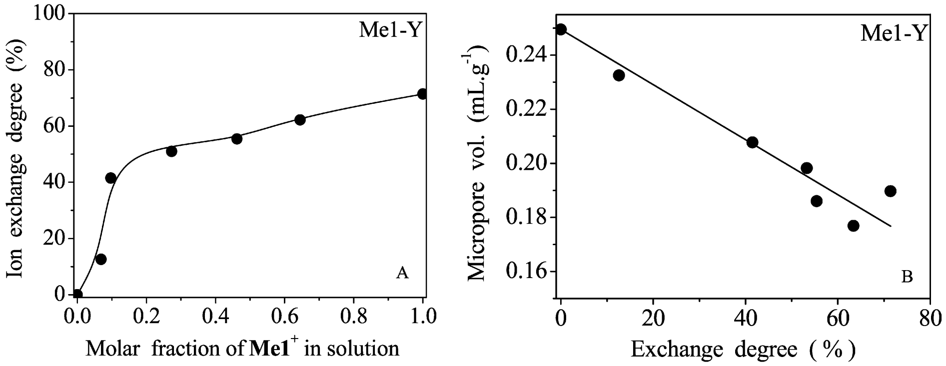

Fig. 2. Sample Me1-Y: (A) ion exchange isotherm and (B) micropore volume as a function of the ion exchange degree.

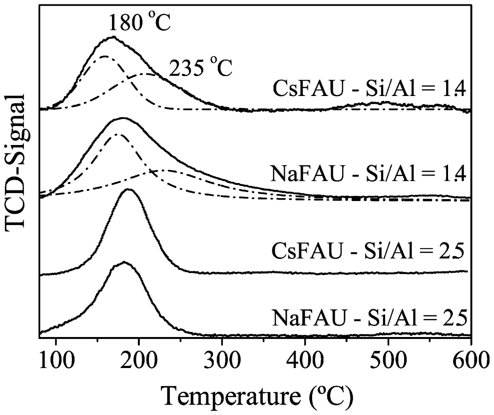

Fig. 3. TPD-CO$_2$ of Na- and Cs-FAU zeolites.

quently, with the purpose of gathering further information about basic strength of methylammonium-FAU samples, O1s XPS experiments were also done.

O1s XPS spectra provide information about electrons binding energy (BE), which can be correlated to oxygen basicity. For zeolites with enhanced basicity, the outermost electrons are less bounded to the oxygen atoms and therefore more available for donation. This means that the ability to share or even to transfer the outermost electrons is increased (low BE). Fig. 4A shows O1s XPS spectra of Y zeolites containing different cations and Fig. 4B the relationship between cation volume and O1s binding energy. XPS is limited to detecting the variation of composition with restricted depth of about 5 to 7 nm into the sample. This is a major limitation and handicap in evaluating bulky particles, as in the case of these zeolites. However, the 1s core level energy (BE-O1s) is a way of determining basicity in zeolites and related aluminosilicates materials [29,30]. O1s XPS has shown a good correlation between oxygen BE and experimental basic properties of zeolites [31,32]. This is an indicative that, in this case, bulky and surface compositions are very close to each other. In this work the surface Si/Al ratio of zeolite Y was around 3, which is close to the value of 2.5 obtained from chemical analysis.

XPS peak shape (Fig. 4A) indicates the presence of only one oxygen component assignable to oxygen bounded to the Y molecular sieve framework [29]. Actually, ^{1}H MAS NMR spectra and CHN analysis revealed that no other cation or contaminant should be present in these samples. When cation Me1$^+$ is present in Y zeolite, O1s binding energy (BE) reaches its lower value (Fig. 4B), indicating that the catalyst Me1-Y possesses higher oxygen basicity in comparison to the Cs-Y catalyst (with the same IED). This can be attributed to the fact that the electronegativity of Me1 cation is lower than that of cesium. Sample Me4-Y (35% of IED) provided a higher BE-O1s value than these two samples (531.80 eV) as a consequence of the lower exchange degree achieved with this most voluminous cation.

Increasing replacement of Na$^+$ cations by less electron acceptor Me1$^+$ ions continuously changed O1s binding energy to lower values (Fig. 5A). O1s BE seems to decrease linearly until 62% of IED and then a strong decrease to 531.22 eV is detected (Fig. 5B). This later behavior can be probably related to a distortion of oxygen bindings due to the complete substitution of sodium ions present in the α cavity of Y zeolite [6], as already observed for other zeolites containing voluminous organic cations [33]. Fig. 5B also shows that compared to the same IED (35%), Me4$^+$ gave lower BE than Me1$^+$ cation, confirming the lower interaction of that more voluminous cation with the oxygen anions of the zeolite framework.

4.4. Knoevenagel and Claisen–Schmidt condensation reactions

Fig. 6 shows the activity of various FAU catalysts (X and Y) for the Knoevenagel (Fig. 6A) and Claisen–Schmidt (Fig. 6B) condensation reactions a and b, respectively, in Scheme 1. The ion

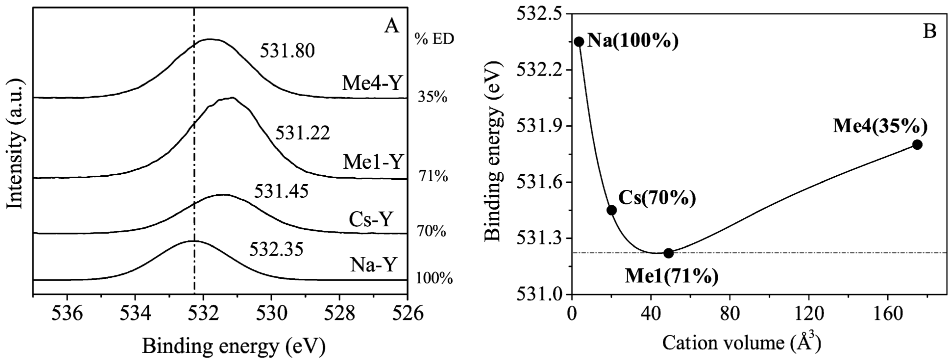

Fig. 4. O1s XPS of Y zeolites (Si/Al = 2.5) containing different cations: (A) O1s line spectra and (B) binding energy *versus* cation volume.

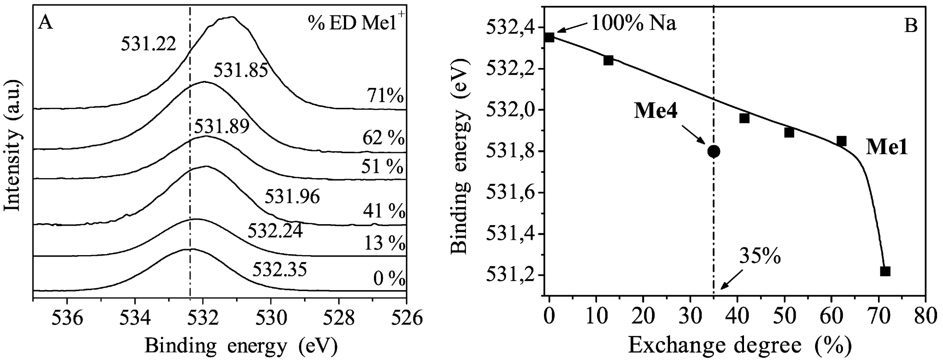

Fig. 5. O1s XPS: (A) spectra of Me1-Y samples (Si/Al = 2.5), with different ion exchange degree of cation Me1$^+$, and (B) binding energy *versus* ion exchange degree (in comparison to zeolite containing maximum IED of cation Me4$^+$).

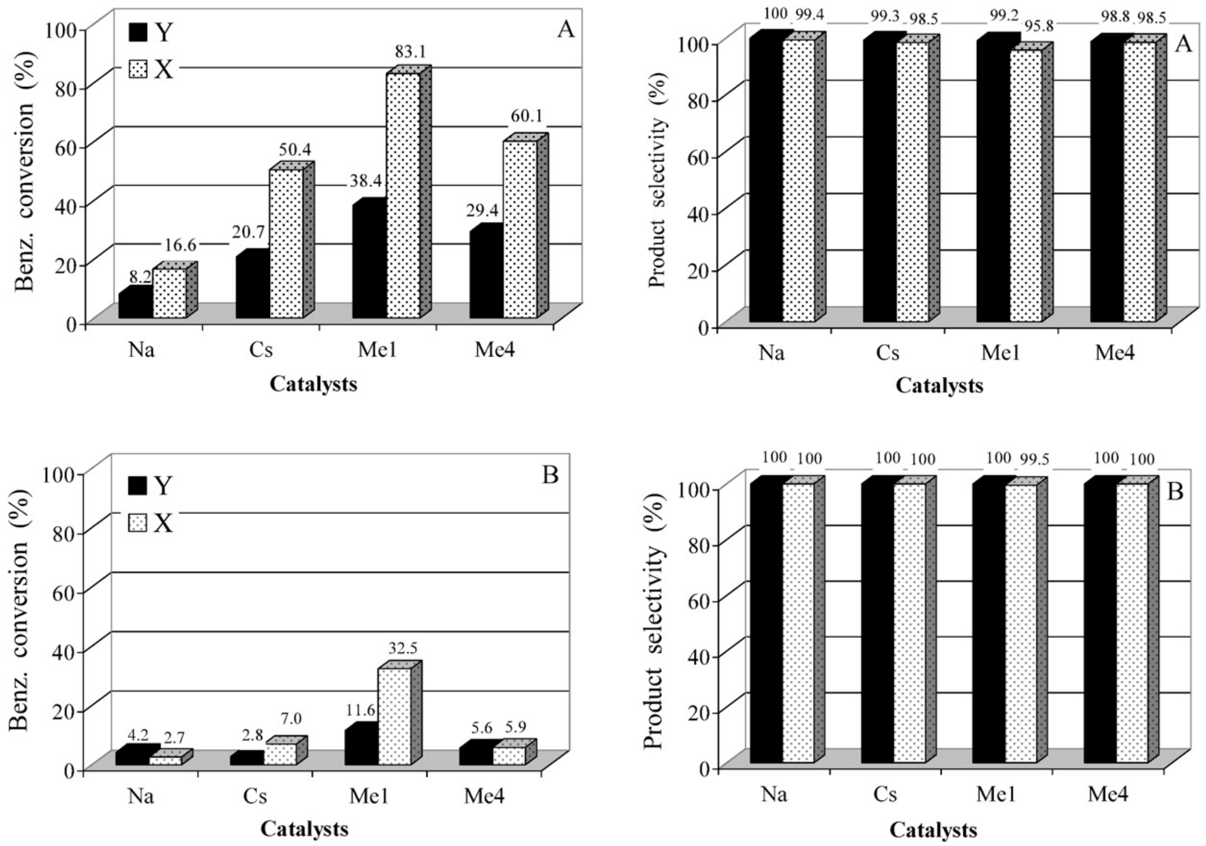

Fig. 6. Catalytic activity of FAU zeolites in (A) Knoevenagel (60 °C, 3 h, 50 mg of catalyst) and (B) Claisen–Schmidt (140 °C, 6 h, 50 mg of catalyst) condensation reactions.

exchanged Cs, Me1 and Me4 FAU zeolites employed in these reactions were those with the highest exchange degrees (Table 1). When benzaldehyde (BA) and ethyl cyanoacetate (ECA) were used as substrates (Fig. 6A), FAU zeolites gave a higher conversion than with acetophenone as methylene component (Fig. 6B). Nonetheless, without any catalyst, Knoevenagel condensation proceeded to give only 3.4% BA conversion. The ion-exchange treatment of original Na-FAU zeolites with various cations caused the change of the catalytic properties of FAU materials; Me1-FAU showed a higher activity in comparison to Cs-FAU. Since Me1 and Me4 decreased the effective micropore volume of FAU zeolites (Table 1) in contrast to Na-form, the narrowed cavities could impose serious restriction on the formation and diffusion of reactants and product. Even though, when bulky cations are used, higher conversions are obtained, as expected from the basicity information provided by the XPS experiments. Fig. 6 also shows how catalysts activities in the condensation reactions over zeolites Y and X vary: for all cations, zeolite X is more active than zeolite Y, as a consequence of its higher basic strength. In order to investigate the catalytic ability of FAU zeolites in reactions demanding stronger basic centers, Claisen–Schmidt condensation was chosen as a test reaction (Fig. 6B). In this reaction, only 2.7% of the condensed product was obtained over Na-X zeolite, but 32.5% was obtained when Me1-X zeolite was used. In both condensation reactions, samples containing cation Me1 showed higher activity in comparison to samples containing Me4 cation, due to their lower IED (35 and 15%, for zeolites Y and X, respectively). Selectivity to the Knoevenagel and Claisen–Schmidt condensation products was close to 100% over all of the catalysts. Neither benzyl alcohol nor benzoic acid was observed from the chromatograms in the reaction products, indicating that the Cannizaro reaction does not take place under these experimental conditions.

Despite the presence of voluminous alkylammonium cations inside FAU zeolite pores, a substantial conversion in Claisen–

Schmidt condensation reaction was observed, when the Me1-X catalyst was used. Because the product contains two benzene groups (Scheme 1, reaction b), it was expected to show a very low activity in all zeolite catalysts, since this bulky product should be formed not at basic sites located preponderating at the internal cavities, but preferentially at the sparse sites present at the zeolite external surface. Nevertheless, a result widely discussed in literature is at this point worthy of emphasis: the naphthalene alkylation with propylene obtained over FAU zeolite [34,35]. Previous experimental results are very surprising with regard to shape selectivity of these zeolite catalysts towards bulky alkylated naphthalene compounds [34]. Contradiction between the expected and obtained results of the naphthalene alkylation with propylene over acid zeolite catalysts can be explained considering that the alkylation and the reactions accompanying alkylation should occur somewhere in the pore entrances [35]. In our case we also expect that somehow the benzaldehyde molecule could react with the adsorbed acetophenone on basic sites near the zeolite pore entrance. In an attempt to increase BA conversion in Claisen–Schmidt condensation, higher amounts of Me1-X and Cs-X catalysts (100 and 150 mg) were used (Fig. 7). Nevertheless, over Me1-X catalyst BA conversion increased only slightly from 32.5 to 37.0% and 40.6%, respectively. This could indicate that external diffusion, across a stagnant film, limited BA conversion. In view of the results of the Knoevenagel reaction, where with the same catalyst (Me1-X) and reactants with similar dimensions to those used in the Claisen–Schmidt reaction (reactions a and b, Scheme 1) conversion close to 100% (Fig. 8A) was reached, diffusion effects are considered less probable. Equilibrium estimation for Claisen–Schmidt reaction showed that at 140 °C a maximum conversion of 46% can be reached. Since the maximum conversion observed is—at 41%—close to equilibrium, an increase in catalyst mass could not contribute significantly to an increase in BA conversion.

Fig. 8 shows the effect of the reaction time on the formation of condensed products catalyzed by Me1- and Cs-X. In the Knoevenagel condensation, the conversion of BA reached 83.1% over Me1-X and 50.6% over Cs-X after 3 h. On the other hand, in the Claisen–Schmidt condensation, the conversion of BA reached 40.6% over Me1-X and 9.9% over Cs-X after 6 h. Selectivity was around 100% for all reaction times. Cs-X catalyst resulted in low benzaldehyde conversion in the Claisen–Schmidt condensation (Fig. 8B) since for this reaction stronger basic sites are required in comparison to Knoevenagel condensation. When Cs-X mass is doubled or tripled, only slight difference in conversion was observed (from 7.0 to 9.9% in Fig. 7), indicating that somehow in this case the contribution of the homogeneous phase reaction might be responsible for the most of the observed conversion.

In order to obtain more insight on the effect of $Me1^+$ cation loading on Knoevenagel conversion reaction, we carried out additional catalytic tests using the samples depicted in Fig. 2A. The activity of Me1-Y zeolites for the Knoevenagel condensation depends on the exchange degree (Fig. 9). Differently from the micropore volume, which decreases monotonically with the exchange degree (Fig. 2B), benzaldehyde conversion in Knoevenagel reaction grows very rapidly (from 2.4 to 38.4%) with no change in selectivity. Regarding the same IED (35%) sample Y containing the more voluminous cation $Me4^+$ clearly showed higher conversion (29.9%), which was expected from its highest basicity, as verified by XPS results. Despite a complex stereo-spatial arrangement of the alkylammonium cation in zeolite pores and reduced micropore volume, the Me*i*-FAU catalysts have an interesting behavior in Knoevenagel and Claisen–Schmidt condensation reactions, pointing out that basic strength of structural oxygen anions are more important in controlling catalyst performance than micropore volume.

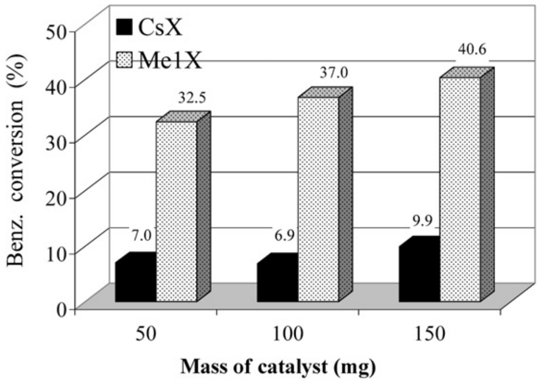

Fig. 7. Activity of Cs-X and Me1-X zeolites with different amount of catalyst in Claisen–Schmidt condensation reaction (140 °C, 6 h).

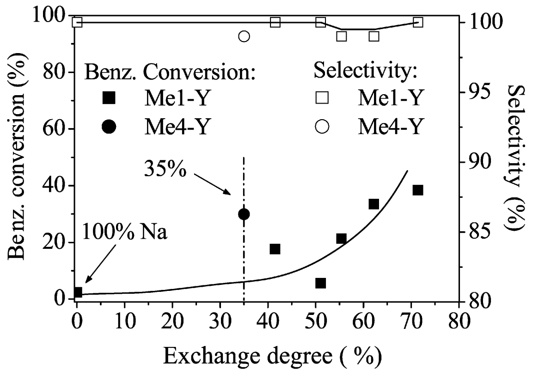

Fig. 9. Activity in Knoevenagel condensation of Me1-Y zeolite with different exchange degree (60 °C, 3 h, 50 mg of catalyst).

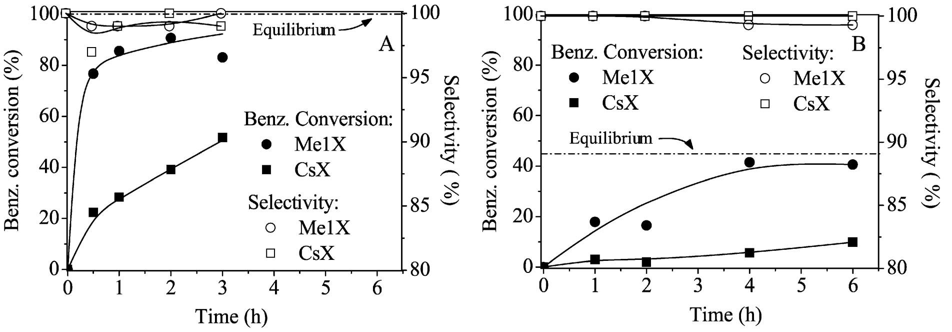

Fig. 8. Comparison of catalytic activity of Cs-X and Me1-X zeolites in different reaction time: (A) Knoevenagel (60 °C, 50 mg of catalyst) and (B) Claisen–Schmidt (140 °C, 150 mg of catalyst) condensation reactions.

Table 4
Me1-Y and Me1-X catalysts used 4 times in Knoevenagel condensation (60 °C, 50 mg of catalyst)

Uses	Me1-Y (IED 71%)		Me1-X (IED 71%)	
	Benzaldehyde conversion (%)	Selectivity (%)	Benzaldehyde conversion (%)	Selectivity (%)
1	38.4	99.2	83.1	95.8
2	39.8	100	83.4	98.1
3	39.0	100	82.5	98.8
4	36.0	100	84.6	98.8

4.4.1. Catalysts recycling in Knoevenagel condensation

Catalyst recycling experiments are important in determining the long term viability of the catalysts. These were performed in Knoevenagel condensation reaction, in a series of Me1$^+$-Y and -X catalyst recycling experiments. After each cycle, catalysts were thoroughly washed with acetone to remove adsorbed products and dried at room temperature. The results of catalyst recycling experiments, depicted in Table 4, demonstrate the reproducibility of the catalytic results: upon repeated use, almost constant conversions of the benzaldehyde were observed (Me1-Y was close to 39% and Me1-X was close to 83%). Selectivity to condensation product is also practically unchanged during recycles. So, alkylammonium-FAU zeolites seem to be an appropriate catalyst for condensation reactions, because they show reasonable activities, very high selectivity and they are stable. Generally, the basic strength and catalytic activity of alkali-exchanged zeolites can be greatly increased by occlusion of alkali metal oxide clusters via impregnation and decomposition of alkali metal compounds [36]. However, although these basic catalysts show great potential in many reactions, their major disadvantage is the reduced stability of the alkali metal oxides to impurities, mostly due to CO_2 poisoning [32]. On the other hand, reactions, which demand temperatures higher than 190 °C will probably limit the application of alkylammonium exchanged zeolites, as TGA results showed that $CH_3NH_3^+$ cations in Me1-X zeolite start to decompose close to 190 °C.

4.5. Propylene oxide alcoholysis with methanol

Commonly, propylene oxide (PrO) methanolysis can be described by equations depicted in Scheme 2. The most preferable conditions would be obtained for the highest content of monopropylene glycol methyl ethers (MPGME, or $CH_3O(PrO)H$, first reaction in Scheme 1c), which is a mixture of isomers 1-methoxy-2-propanol (1M2P) and 2-methoxy-1-propanol (2M1P). In the case of this work the GC analysis gave that the oligomerization degree, n (Scheme 2) was always $\leqslant 2$, probably limited by the zeolite's pore and cavity dimensions, which selectively hinder the formation of more voluminous compounds. Some samples were run for 60 min in GC analysis (the last peak—25 min of retention time—was assigned to $CH_3O(PrO)_2H$) to confirm the absence of higher degree of oligomerization ($n > 2$). However, the sum of the selectivity to all products did not sum 100%, suggesting that part of the propylene oxide is retained inside the zeolite cavities, probably as higher oligomers. Further reactions with oligomerization degree $n > 2$ would give a very complex mixture of isomers having different lengths of oligooxypropylene chain.

When compared to condensation reactions, the addition reaction of propylene oxide (PrO) with methanol had similar behavior on Me*i*-FAU zeolites (see Fig. 9A). For instance, Me1-FAU was found to be also more active than Cs-FAU for the conversion of propylene oxide. Without catalyst, this reaction gave 34.7% propylene oxide conversion, which is roughly close to the result obtained with Na-Y sample (39.4%), indicating that Na-FAU zeolite did not pronouncedly increase reactants consumption, and a possible explanation could be the low basic strength. Concerning the selectivity among the two $CH_3O(PrO)H$ isomers (Scheme 1c), without catalyst 1-methoxy-2-propanol (1M2P) and 2-methoxy-1-propanol (2M1P) molar ratio was 1.4, i.e. almost equivalent amounts of the 1M2P and 2M1P are formed. Interestingly, selectivity toward 1M2P or 2M1P showed to be strongly dependent on catalyst (see Fig. 9B). Then, these results can be interpreted in terms of the relative strength of the conjugated acid–base ion pairs that are present in zeolites: the more active catalysts are also the more selective to the 1M2P isomer. Over sample Me1-X, the isomer 1M2P was selectively produced (molar ratio = 11.0), as a consequence of cation Me1$^+$ low acidity, which does not contribute significantly to 2M1P isomer formation. Sample Na-Y showed a 1M2P/2M1P ratio of 3.4 and sample Na-X of 7.6. Despite both samples comprise only sodium as cation in ion exchange centers, sample Na-X showed higher selectivity towards 1M2P because it encloses higher oxygen basicity, and therefore higher proton-abstracting capacity. As a general result, the catalytic activity (PrO conversion) and isomers selectivity cannot be correlated only with the oxygen anion basicity, but also cation acidity should be considered. Controlling selective production of 1M2P and 2M1P is a very important step in obtaining high-quality glycol ethers. Glycol ethers are versatile molecules and extremely important from an industrial point of view. Catalysts Me*i*-FAU showed excellent results, in providing different acid–basic sites, for obtaining the desired selectivity towards 1M2P and 2M1P isomers. In order to confirm this trend, an acidic sample comprising zeolite Y (denoted as H-Y, with 74% IED) was prepared by thermal decomposition of a NH4-Y zeolite and tested in propylene oxide alcoholysis with methanol. The H-Y zeolite was the most active, presenting a conversion of 98.6% of propylene oxide, but the less selective to the 1M2P isomer: a 1M2P/2M1P ratio of 0.9 was observed (Fig. 9B).

$$CH_3OH + PrO \rightarrow CH_3O(PrO)H \qquad (1^{st}\ \text{reaction})$$

$$CH_3O(PrO)H + PrO \rightarrow CH_3O(PrO)_2H \qquad (2^{nd}\ \text{reaction})$$

$$\overline{CH_3O(PrO)_nH + PrO \rightarrow CH_3O(PrO)_{n+1}H} \qquad (\text{n reactions})$$

Scheme 2. Reactions taking place during propylene oxide methanolysis.

Generally, during propylene oxide methanolysis, dipropylene glycol methyl ether mixture of isomers (DPGME, or $CH_3O(PrO)_2H$ in Scheme 2), is also formed and its content increases with advancement of the reaction. However, on zeolites Me*i*-FAU good selectivity towards $CH_3O(PrO)H$ was obtained and the formation of bulkier products was suppressed (Figs. 9C and 9D). Actually, the aforementioned micropore volume results (Table 1) suggested pore narrowing caused by ion exchange with more voluminous cations (Me1$^+$ and Me4$^+$) and allow explaining the high selectivity towards monopropylene glycol methyl ether isomers (1M2P and 2M1P). Particularly on zeolites Me1-FAU, whose ion exchange degree was of 71%, high selectivity towards the propylene oxide monomer ($CH_3O(PrO)H$) was obtained.

Propylene oxide ring is opened as a consequence of the attachment of a methoxy anion (CH_3O^-), which is formed on the surface of the zeolites. To verify if leaching of the organic cation occurs and if the anion is formed in the reaction system as Me$i^+CH_3O^-$, Me1-Y and Me1-X catalysts were suspended in methanol at 140 °C for 5 h. Then the resulting methanol was analyzed and no basicity was found in the liquid phase (5 mL from the methanol was diluted in 5 mL from deionized water, and 3 drops of the phenolphthalein indicator was added to this test solution and no change in color was observed). This indicates that Me$i^+CH_3O^-$ is not present or the concentration of methoxy anion is not high enough to cause the color of the indicator to change. Me1-Y and Me1-X catalysts

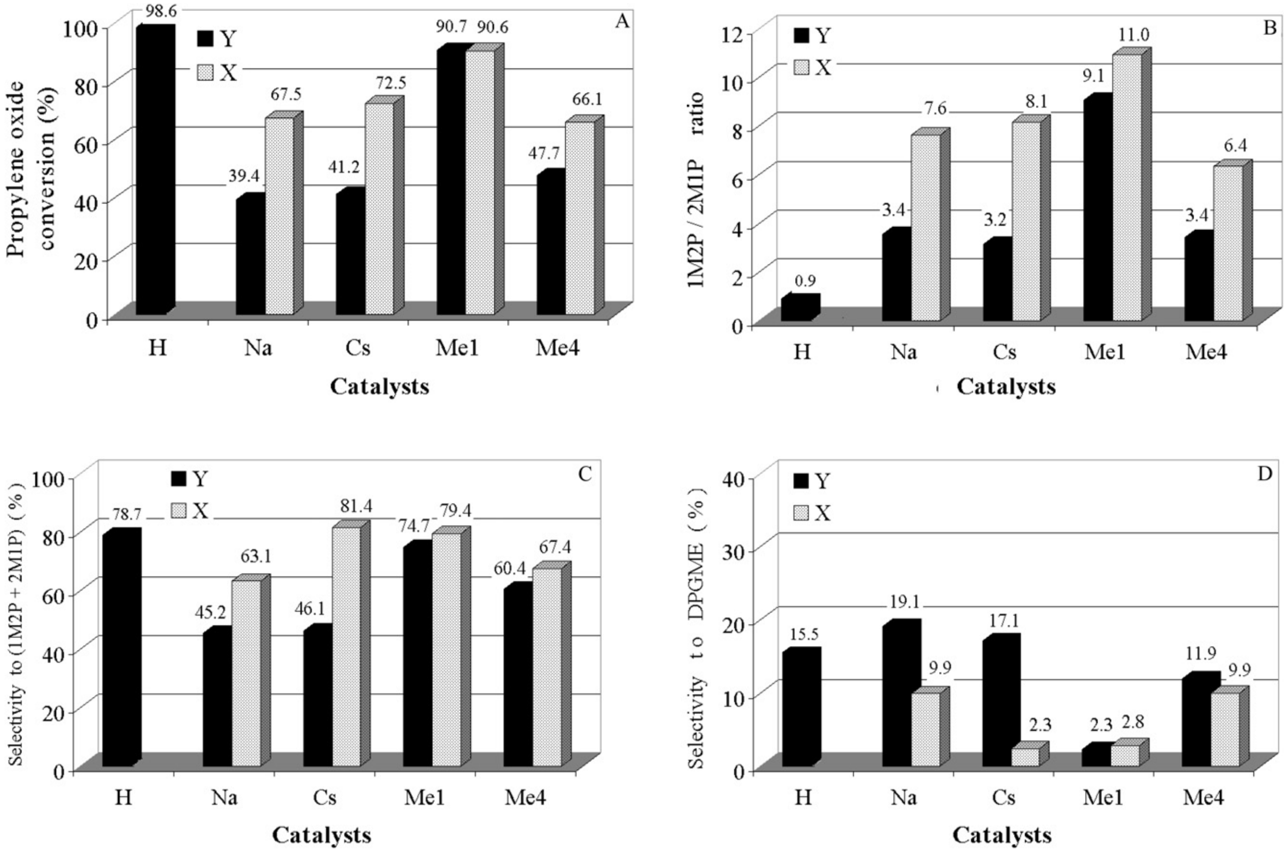

Fig. 10. Catalytic activity of FAU zeolites in propylene oxide alcoholysis with methanol (A) propylene oxide conversion, (B) 1-methoxy-2-propanol (1M2P) and 2-methoxy-1-propanol (2M1P) molar ratio, (C) selectivity to (1M2P + 2M1P, $CH_3O(PrO)H$) and (D) selectivity to dipropylene glycol monomethyl ether ($CH_3O(PrO)_2H$—mixture of isomers).

recovered after this blank experiment were also characterized by thermogravimetry. The results were compared to those of unused catalysts. In both cases, the same mass loss was found. This is a further indication that no leaching occurred, and consequently that no homogeneous catalysis took place.

Tests at 140 °C of the propylene oxide reaction with pure methanol were also done as well as using a methanolic solution of KOH ($K^+CH_3O^-$), 1 mmol/L. Propylene oxide conversion was 34.7% and 49.9%, respectively. On the other hand, using Me1-Y and Me1-X catalysts the obtained conversions were around 90% (Fig. 10). Consequently, if there is no cation leaching and the solid catalysts are much more active then KOH solution, this catalytic reaction is mainly heterogeneous and the catalytic sites are the zeolites framework oxygen anions.

5. Conclusions

Using FAU zeolites containing ammonium cations, whose acidity is lower than cesium, the catalysts activities in condensation reactions increased as a result of their higher basicity. For sodium and cesium containing samples, the increase in cation volume caused only minor increase in specific activity, while further increase in cation volume (alkylammonium cations) caused major enhancement in the catalytic performance in the investigated Knoevenagel and Claisen–Schmidt condensation reactions. The low acidity of alkylammonium cations could also be further confirmed in propylene oxide alcoholysis, where 1-methoxy-2-propanol was selectively produced. Cations in zeolites FAU are present in ion exchange sites, indicating that the observed catalytic results arise exclusively from conjugated acid–base ion pairs.

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