

## Faujasites exchanged with alkylammonium cations applied to basic catalysis

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## ABSTRACT

NaX and NaY faujasites (with Si/Al ratios of 1.3 and 2.5, respectively) were subjected to different degrees of ionic exchange with linear monoalkylammonium cations containing between 1 and 6 carbon atoms. The products were characterized using X-ray diffraction (XRD), nitrogen physisorption, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). The Knoevenagel condensation was used as a model reaction to characterize the activity and accessibility of the catalytic sites. Ionic exchange isotherms showed that only the sodium cations present in the supercavities were exchangeable for the alkylammonium ions. The XPS results showed that the monoalkylammonium cations increased the basicity of the sites of both faujasites, with the basicity increasing with the length of the carbon chain. The catalytic activity in the Knoevenagel condensation was governed by three factors: the degree of exchange, the aluminum content, and the water content of the zeolites.

## 1. Introduction

The Knoevenagel condensation reaction (Scheme 1) is widely used industrially for the synthesis of various pharmaceutical products. The reaction is usually catalyzed by organic bases, such as pyridine or piperidine [1,2]. There are several difficulties associated with the use of homogeneous catalysts, including the presence of undesirable secondary reactions, the generation of large volumes of effluents, and difficult recovery of the catalyst [1–3]. In attempts to mitigate these problems, several studies have investigated a new type of heterogeneous catalyst with basicity enhanced by the presence of organic cations in the zeolite composition [4–7]. Advantages of these catalysts used to replace homogeneous catalysts include environmental benefits, due to reduced volumes of effluents, as well as cost savings, since fewer separation steps are required in the process.

The basicity of zeolites is due to the presence of the aluminate anion  $[\text{AlO}_4]^-$  in the framework. The basic sites are associated with the structural oxygen atoms close to the cations that compensate for the negative charge [8]. The acid-base properties of zeolites can be classified according to the Lewis model, whereby the lower the acidity of the cation the higher is the basicity of the anion associated with it. When the compensation cation is weakly electronegative, the charge density of the oxygen increases sufficiently to generate basic properties. In the case of zeolites, a higher concentration of aluminum atoms in the

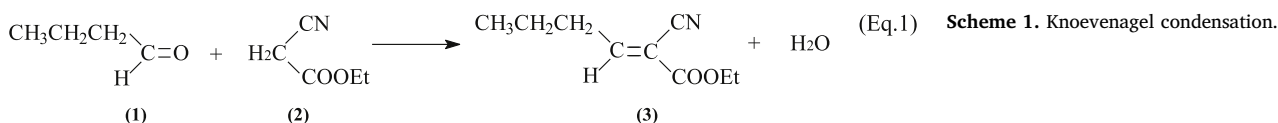
framework results in higher basic strength of the oxygen atoms [8].

One way to increase the basicity of a zeolite is to compensate the anions with lower electronegativity inorganic cations, such as cesium. However, a less expensive way to enhance zeolite basicity, reported by Cardoso et al. [4], is to use ionic exchange with organic cations. Firstly, investigation was made of ion exchange of the sodium form of Y zeolite using methylammonium cations with different numbers of methyl groups. It was found that the ionic exchange reached equilibrium in around 50 min, with steric hindrance being the limiting factor of the reaction, restricting the ion exchange to the supercavities [4]. In addition, the maximum degree of exchange decreased according to the volume of the cation. Subsequently, the properties of these catalysts with different degrees of exchange were compared with the properties of X zeolite containing the same cations. Catalyst basicity was investigated by X-ray photoelectron spectroscopy (XPS) and by using the Knoevenagel condensation reaction, with good correlation between the results obtained by the two methods [5,6]. The best catalytic activity was found for the faujasite with higher content of aluminum (X zeolite), exchanged with the monomethylammonium cation [6]. These modified zeolites showed higher basicity, compared to those containing cesium, the cation that up to now has provided these materials with the highest basicity [4–6]. The better performance of this catalyst, compared to those containing alkylammonium cations with several methyl groups, was attributed to the combination of two factors, namely basicity and

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the accessibility of the basic sites [6].

Given this background, the aim of the present work was to evaluate the basicity of X and Y zeolites exchanged with linear monoalkylammonium cations with different carbon chain lengths.

## 2. Experimental

### 2.1. Ion exchange isotherms

The catalysts were preparing using commercial zeolites: NaX (Merck), and NaY (Zeolyst), with Si/Al molar ratios of 1.4 and 2.5, respectively. These Si/Al ratios mean that 42% and 29%, respectively, of the tetrahedra in these zeolites consist of aluminate anions. Ion exchange isotherms were obtained at 40 °C after 6 h of reaction, using the procedure described by Colella [9]. Sodium ions present in the zeolites were exchanged by linear alkylammonium cations of the type  $(\text{C}_n\text{H}_{2n+1})\text{NH}_3^+$ , where n is the number of carbons of the linear chain.

The ion exchange solutions were prepared using the chloride salts of the cation exchangers. Commercial methyl- and ethylammonium salts were used (Fluka, 98%). For the other cations, linear alkylammonium salts were prepared by acid-base titration of amines (Aldrich, 98%) with hydrochloric acid until the equivalence point.

Each ion exchange solution was prepared with different NaCl and  $\text{C}^+\text{Cl}$  proportions, where  $\text{C}^+$  corresponds to alkylammonium used. The total ion concentration of the solutions was kept constant at 0.05 M by the addition of NaCl in the required amounts. Each experimental point of the isotherm corresponds to a new ion exchange procedure, instead of consecutive exchanges. But, to obtain maximum ion exchange points (molar fraction equal to 1.0), three consecutive ion exchanges were performed with an alkylammonium cation solution corresponding to a concentration of 0.5 M. Ion exchange degrees were established through chemical analyses made in duplicate, for Na and Al elements present in the solid. Table 1 shows the nomenclature employed for the catalysts, according to the organic cation and the zeolite used.

### 2.2. Characterization of the zeolites

The sodium and aluminum concentrations in the zeolites were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Thermogravimetric measurements were performed with an SDT 2960 analyzer (TA Instruments), using a heating rate of 10 °C/min, under a 40 mL/min flow of  $\text{N}_2$ . Prior to analysis, the samples were hydrated for 24 h in a saturated atmosphere above a concentrated aqueous solution of  $\text{CaCl}_2$ .

X-ray diffractograms of the zeolites were obtained using a Shimadzu XRD-6000 diffractometer, with Cu K- $\alpha$  radiation (40 kV, 40 mA), a

nickel filter, and a goniometer scanning speed of 0.5°/min. To determine the unit cell parameter ( $a_0$ ), 15 wt% of elemental silicon was mixed with the sample, as an internal standard. This mixture was previously hydrated for 24 h under an atmosphere in equilibrium with a concentrated aqueous solution of  $\text{CaCl}_2$ . The  $a_0$  values were calculated using UnitCell software [10], considering the reflection peaks (220), (311), (331), (440), (533), (642), and (660). For the NaX zeolite, these crystallographic planes correspond to 2 $\theta$  angles of 10.00, 11.73, 15.43, 20.07, 23.31, 26.65, and 33.59°, respectively. The UnitCell program estimates results with errors on the order of  $4.34 \times 10^{-4}$  nm and 95% confidence.

The materials were characterized by nitrogen physisorption, using an ASAP-2020 instrument (Micromeritics). To remove physisorbed water, the samples were pretreated for 2 h at 110 °C and pressure of 0.1 mbar. The micropore specific volumes of the samples were determined by extrapolating the volume adsorbed at different pressures, using the t-plot method [11].

X-ray photoelectron spectroscopy (XPS) analyses were performed using a VSW HA-100 spherical analyzer equipped with an Al K- $\alpha$  source ( $h\nu = 1486.6$  eV), at a pressure less than  $2 \times 10^{-8}$  mbar. The loading effects were adjusted by linear displacement of the spectrum, so that the Cls signal had a binding energy of 284.6 eV. The high-resolution spectra were obtained with constant pass energy of 44 eV, which produced a half width of 1.8 eV for the Au 4f7/2 line.

The Knoevenagel condensation (Scheme 1) was performed in 2-mL batch reactors. For these yield tests, a reaction mixture containing equimolar amounts (4.8 mmol) of butyraldehyde (Reagent 1) and ethyl cyanoacetate (Reagent 2) was prepared and diluted in the same total volume of toluene as solvent. About 1 mL of this mixture and 3 wt% of catalyst were placed in the vial and maintained under stirring at 50 °C for 1 h. The reaction product was analyzed using a Varian gas chromatograph fitted with a DB-1 capillary column and a flame ionization detector. For quantitative analysis of the reaction components, linear fittings were constructed from the experimental data using the internal standards method. The results gave a confidence interval of 93%. Under the reaction conditions used, the Knoevenagel condensation was always 100% towards ethyl-2-cyano-3-butylacrylate (compound 3, Scheme 1).

The chemical stabilities of the catalysts were determined by their reuse under standard reaction conditions. After each reaction, the catalysts were washed with acetone and then dried in an oven.

To confirm that homogeneous catalysis does not occur, Knoevenagel condensation was performed under the conditions described above but for only 20 min so that the reagents were not fully consumed. After 20 min of reaction, the catalyst was removed from the reaction medium by filtration and the liquid phase was allowed to react for further 40 min under the same reaction temperature. After 40 min without catalyst, the reaction mixture was analyzed by gas chromatography and the results show that there was no further increase of the condensation product. Therefore, it can be concluded that leaching of the alkylammonium cations to the liquid phase did not occur.

The turnover frequency of selected basic catalysts was estimated at zero reaction time. To do this, the Knoevenagel condensation was performed under the same conditions as above, but using 20 mL of the reaction mixture in a 50-mL jacketed reactor fitted with a reflux condenser. In order to determine the conversion as a function of time, a sample was analyzed by gas chromatography, as described above, every 5 min during a period of 1 h. An exponential curve was then fitted to the points and the initial reaction rate was obtained by extrapolation of the curve to zero reaction time.

**Table 1**

Nomenclature used for the samples according to the alkylammonium cation and zeolite used.

| Cation                                                                                 | X zeolite | Y zeolite |
|----------------------------------------------------------------------------------------|-----------|-----------|
| $\text{Na}^+$                                                                          | NaX       | NaY       |
| $\text{CH}_3\text{NH}_3^+$                                                             | MeX       | MeY       |
| $\text{CH}_3\text{-CH}_2\text{NH}_3^+$                                                 | EtX       | EtY       |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{NH}_3^+$                                     | PrX       | PrY       |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{NH}_3^+$                         | BuX       | BuY       |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{NH}_3^+$             | PeX       | PeY       |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{NH}_3^+$ | HeX       | HeY       |

**Table 2**

Distributions of the crystallographic sites per unit cell for the NaX and NaY zeolites [12].

| Site type | NaX (sites) | (%) | NaY (sites) | (%) |
|-----------|-------------|-----|-------------|-----|
| I         | 16          | 19  | 16          | 29  |
| II        | 32          | 37  | 32          | 57  |
| III       | 38          | 44  | 8           | 14  |
| Total     | 86          | 100 | 56          | 100 |

### 3. Results and discussion

#### 3.1. Ion exchange isotherms

The profiles of the isotherms for ionic exchange between the sodium cations of the zeolite and the ammonium cations dissolved in the aqueous phase, as well as the maximum degrees of exchange achieved, were governed by the zeolite structure, the type of ammonium cation, and the location of the exchangeable sites. According to Breck [12], the faujasite sodium cations can be located at three types of sites: type I, within the hexagonal prisms and the sodalite cavities; type II, on the external part of the large cavity, near the six-member rings; and type III, on the external part of the large outer cavity, near the four-member rings. Table 2 shows the distributions of the types of sites for zeolites X and Y [12], from which it can be seen that the main difference between the two zeolites was in the number of type III sites, which accounted for 43% of the sites in the X zeolite and 14% of the sites in the Y zeolite.

The access diameters of sodalite cavities and supercavities are 0.22 and 0.80 nm, respectively [13]. From comparison of these values with the ionic radius of the methylammonium cation (0.245 nm), it could be concluded that the sodium cations present in the sodalite cavities, and consequently in the hexagonal prisms, were inaccessible to the linear alkylammonium cations used in this work. Hence, the ionic exchange was restricted to the supercavities [13–15].

Fig. 1 shows the isothermal ion exchange of the sodium cations present in the X and Y faujasites by the linear alkylammonium cations, at 40 °C. The horizontal axis indicates the molar percentage of the cations in the aqueous solution at equilibrium ( $S_E$ ), and the ordinate axis corresponds to the molar percentage in the zeolite ( $Z_E$ ). The continuous curves with filled symbols refer to the X zeolite, and the dotted curves with open symbols refer to the Y zeolite. Also shown are dotted lines corresponding to hypothetical non-selective ion exchange; in other words, where  $S_E$  and  $Z_E$  are equal.

The values of  $Z_E$  obtained for  $S_E \sim 100\%$  corresponded to the maximum degrees of exchange (MDE) achieved for these zeolites. It can be seen from Fig. 1(a–f) that it was not possible to achieve total ionic exchange of the sodium cations with any of the exchanger cations, since for  $S_E \sim 100\%$ , the MDE value was always  $< 100\%$ . It was also apparent that the MDE values decreased with increasing size of the linear chain, indicating that the ionic exchange was limited by steric effects. Similar results have been reported previously for the ionic exchange of methylammonium cations with faujasite zeolites [4–6,14].

The maximum degree of exchange obtained experimentally decreased slightly with increase of the linear chain up to five carbons (Fig. 1). However, for the X zeolite, from the  $Pe^+$  cation to the  $He^+$  cation, the maximum degree of exchange decreased sharply, from 63% to 45%. This was because the length of the  $He^+$  cation (1.24 nm) is approximately the same as the internal diameter of the supercavities (1.24 nm) [13], which hindered ionic exchange of the sodium cations present on the opposite face.

The ion exchange isotherms (Fig. 1) showed a Langmuir profile for the Na–EtY pair, indicating that zeolite Y presented strong and selective interaction with these organic cations [9]. The Na–MeY and Na–PrY pairs presented selective isotherms that approximate the thermodynamic equilibrium model. The main reason for these isotherms to

deviate from the Langmuir profile is that Langmuir's theory assumes homogeneity of adsorption sites, whereas most adsorptions exhibit heterogeneity of adsorption sites [16]. For the other pairs, the ionic exchange showed sigmoidal type isotherms; these occur when the selectivity of the zeolite towards the exchanger cation depends on the fraction of this cation in the solution ( $S_E$ ). For the X zeolite, the isotherms crossed the diagonal at  $S_E$  values of around 30% (Fig. 1(a–f)). Hence, up to these molar contents, the X zeolite showed moderate selectivity towards the organic cations. After this point, the selectivity reverted to the sodium cation [13,15]. According to Breck [12], the presence of an inflection point indicates that the cations can occupy more than one type of exchangeable site, with the selectivity being different for each site. For the X zeolite, this point corresponded to the  $S_E$  concentration at which ionic exchange at the type III sites started.

Sherry [17], using inorganic cations, found that ion exchange occurred more easily first at type III sites, then at type II sites, and finally at type I sites. With longer carbon chains, steric hindrance makes ionic exchange difficult, resulting in decreased selectivity of the zeolites towards the organic cations. For the X zeolite, this point corresponded to the  $S_E$  concentration at which ionic exchange at the type II sites began.

The X zeolite presented sigmoidal type isotherms for the  $Me^+$ ,  $Et^+$ , and  $Pr^+$  cations, while the Y zeolite showed selective type isotherms. The inflection point observed in the sigmoidal profiles occurs when there is competition between sites [9]. As sites of type I are inaccessible to the alkylammonium cations, the competition in X zeolite must occur between sites of type II and III. This competition did not occur in the case of the Y zeolite, due to the presence of a much smaller number of type III sites. These results are in agreement with those observed by Theng et al. [13].

The content of Al is higher in X zeolite than in Y zeolite, resulting in a greater density of negative charges and higher affinity of the surface for less electronegative cations. Since the electronegativity of alkylammonium cations decreases with the length of the carbon chain, the relative selectivity of the X zeolite consequently increased accordingly.

#### 3.2. $N_2$ physisorption

The micropore volumes of the X and Y zeolites were calculated using the t-plot method [8] applied to the nitrogen physisorption isotherms of the samples. The isotherms were typical of microporous material, as shown in Fig. S1 (Supplementary Material) for the Y and X zeolites that showed the maximum degrees of exchange with the alkylammonium cations.

Fig. 2 shows curves of the micropore volume ( $V_m$ ) plotted as a function of the number of moles of sodium cation sites exchanged by alkylammonium cations ( $\eta$ ), for the Y and X zeolites. The values of  $\eta$  were calculated assuming that the total numbers of moles of exchangeable sites present in the Y and X zeolites were 6279 and 7591  $\mu\text{mol/g}$ , respectively [13]. For both zeolites, the micropore volume decreased as  $\eta$  increased, with the reduction being greater for the Y zeolite than for the X zeolite. It was also observed that for the maximum degree of exchange, the micropore volume decreased with increasing length of the carbon chain, except in the case of the  $He^+$  cation. This was because the length of the  $He^+$  cation (1.24 nm) is close to that of the supercavity (1.24 nm) [13], which hindered advance of the ion exchange reaction. Consequently, there was a smaller number of moles of exchanged sites ( $\eta$ ) and a larger micropore volume.

In order to estimate the effect of the steric hindrance on the catalytic activity, for each alkylammonium cation, pairs of zeolites Y and X containing similar numbers of alkylammonium cations were selected. In order to maximize this effect, between the pairs of zeolites Y and X with similar numbers of alkylammonium cations, those with the highest number of alkylammonium cations were chosen. Table 3 lists the zeolites that met these criteria, where the numbers within parentheses indicate the degrees of exchange. The results showed that for each cation, the decrease in micropore volume ( $V_m$ ) was greatest for the Y

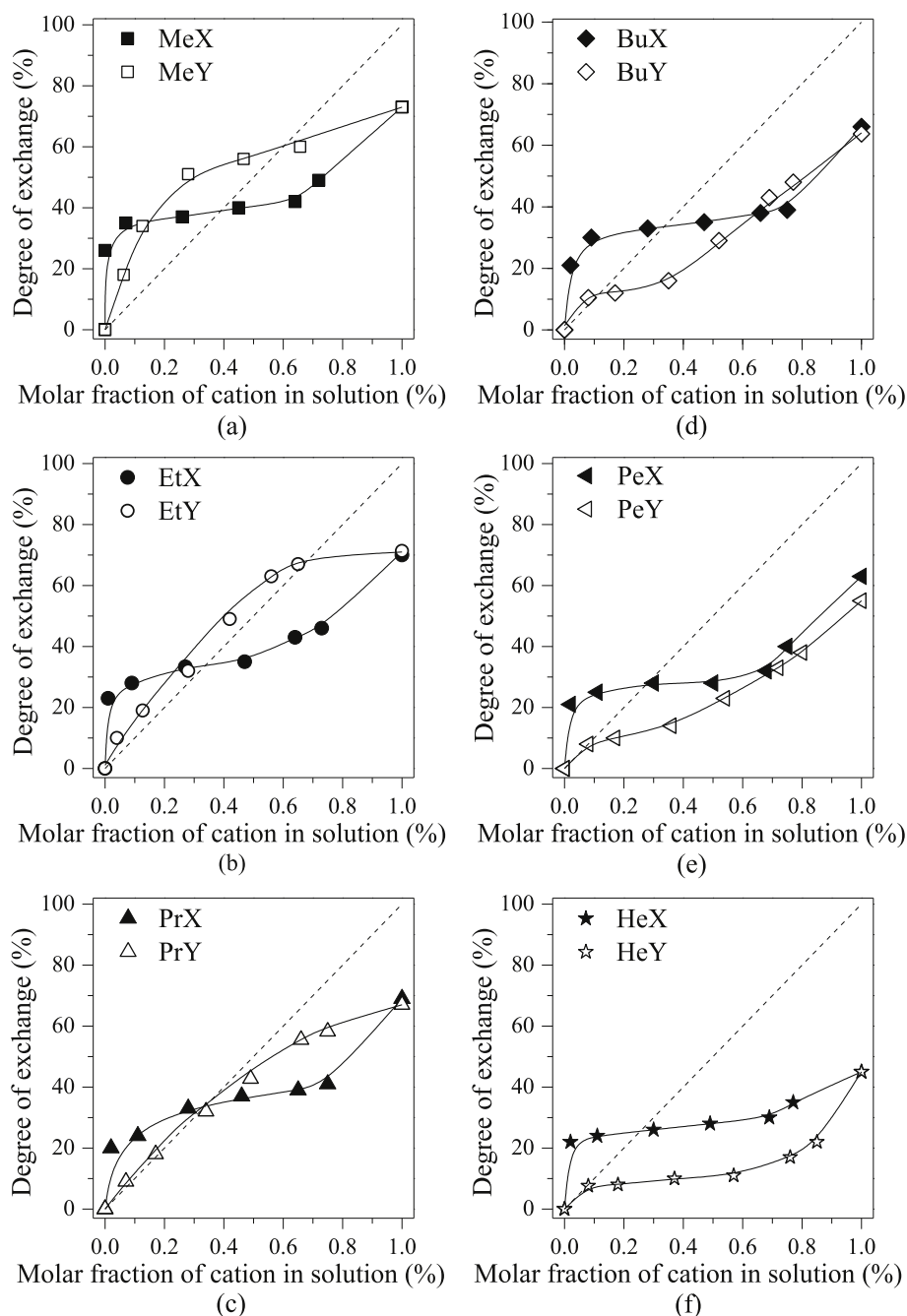


Fig. 1. Isotherms for ionic exchange of the NaY and NaX zeolites with alkylammonium cations.

zeolite, because it possessed 6.5% more type II sites (located in the supercavity), compared to the X zeolite, with the ionic exchange being concentrated at this type of site.

### 3.3. X-ray diffraction analysis

Fig. 3(a and b) shows X-ray diffractograms in the  $2\theta$  region between  $23^\circ$  and  $28^\circ$  for the Y and X zeolites in the sodium forms and with the maximum contents of alkylammonium cations. The peaks related to planes (622) and (624) are shown in this  $2\theta$  range. The full diffractograms are provided in Fig. S2 and Table 1S shows the values of the angles  $\theta$  of planes 622 and 624 (Supplementary Material). Comparison of the diffractograms for the sodium forms of the zeolites with those for the zeolites containing alkylammonium cations revealed a shift towards smaller  $2\theta$  angles. It could also be seen that this shift increased

according to the carbon chain length of the alkylammonium cation. According to the Scherrer equation these changes to smaller angles are due to the expansion of the unit cells [18].

Fig. 4 shows the values of the unit cell parameters ( $a_0$ ) as a function of the number of carbon atoms of the Y and X zeolites. The zeolites containing alkylammonium cations were those that presented the highest degrees of exchange (indicated by the numbers within parentheses). For both faujasites (X and Y), there was a tendency for  $a_0$  to increase according to the length of the carbon chain, suggesting that expansion of the unit cells of these zeolites was due to the greater volume of the alkylammonium cations.

In the case of the X zeolite containing cations with up to three carbon atoms, it was found that the unit cell size increased slightly with increasing length of the carbon chain. The unit cell size then remained almost constant for the zeolite containing cations with four and five

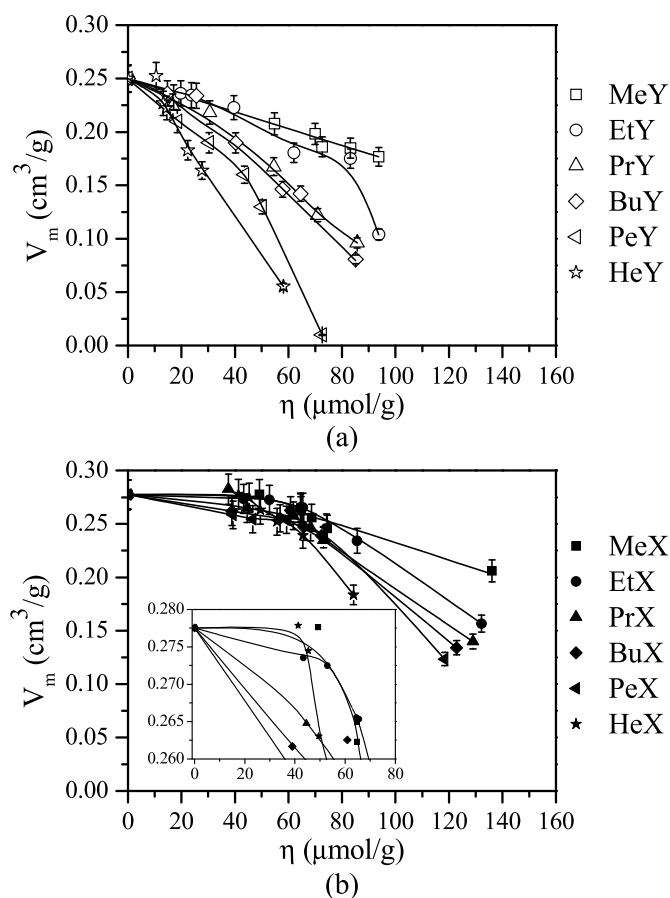


Fig. 2. Micropore volume as a function of the number of moles of exchanged sites: (a) Y zeolite and (b) X zeolite.

Table 3

Number of moles of sodium cation sites exchanged by alkylammonium cations ( $\eta$ ) and Micropore volumes ( $V_m$ ) of the Y and X zeolites.

| Sample  | $\eta$ ( $\mu\text{mol/g}$ ) | $V_m$ ( $\text{cm}^3/\text{g}$ ) | Sample  | $\eta$ ( $\mu\text{mol/g}$ ) | $V_m$ ( $\text{cm}^3/\text{g}$ ) |
|---------|------------------------------|----------------------------------|---------|------------------------------|----------------------------------|
| NaY     | —                            | 0.25000                          | NaX     | —                            | 0.27751                          |
| MeY(56) | 74.0                         | 0.18600                          | MeX(40) | 74.5                         | 0.24585                          |
| EtY(63) | 83.2                         | 0.17510                          | EtX(46) | 85.7                         | 0.23413                          |
| PrY(58) | 76.6                         | 0.12200                          | PrX(41) | 76.1                         | 0.23459                          |
| BuY(50) | 66.0                         | 0.13042                          | BuX(35) | 65.8                         | 0.24456                          |
| PeY(55) | 72.6                         | 0.01000                          | PeX(40) | 74.3                         | 0.23699                          |
| HeY(45) | 59.4                         | 0.05541                          | HeX(35) | 65.4                         | 0.24347                          |

carbon atoms. It can also be seen from Fig. 4 that a lower maximum degree of exchange was obtained for the  $\text{He}^+$  cation, compared to the  $\text{Bu}^+$  and  $\text{Pe}^+$  cations, probably due to steric effects. Consequently, this cation caused a smaller expansion of the unit cell.

For the Y zeolite, the unit cell parameter showed almost no increase following exchange with the  $\text{Me}^+$  and  $\text{Et}^+$  cations, suggesting that there was sufficient space for their accommodation within the large faujasite cavities. However, when the carbon chain length was increased ( $\text{Pr}^+$  and  $\text{Bu}^+$  cations), there were substantial increases in the unit cell values. Further increase of the carbon chain length ( $\text{Pe}^+$  and  $\text{He}^+$  cations) resulted in a less pronounced change in the unit cell size, suggesting that the capacity to accommodate larger cations was reaching its maximum limit. This was reflected in the maximum degree of exchange, which decreased to 45% for the  $\text{He}^+$  cation (Fig. 1).

### 3.4. Thermogravimetric analysis

Thermograms and their derivatives for the X and Y zeolites

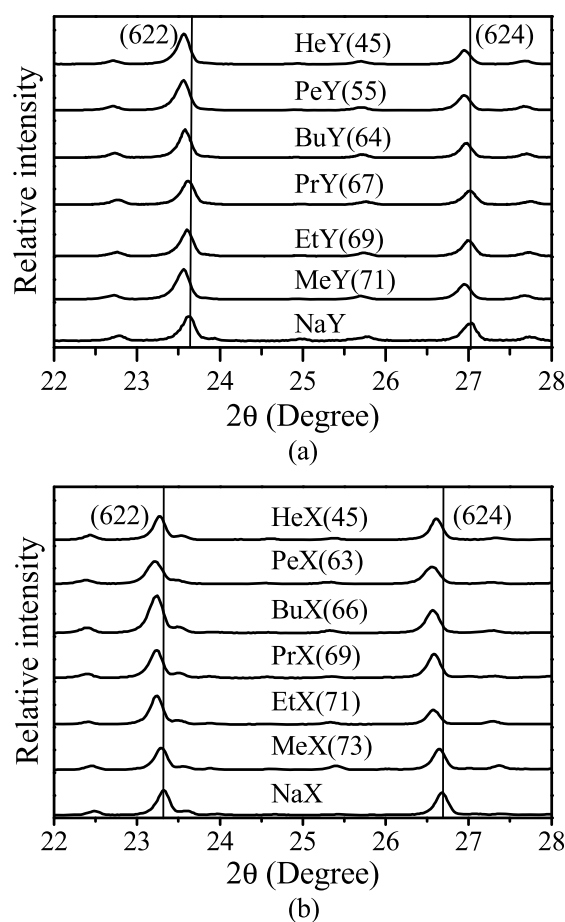


Fig. 3. X-ray diffractograms of the zeolites with the maximum degrees of exchange with linear alkylammonium cations, in the  $2\theta$  region between  $22^\circ$  and  $28^\circ$ : (a) Y zeolite and (b) X zeolite.

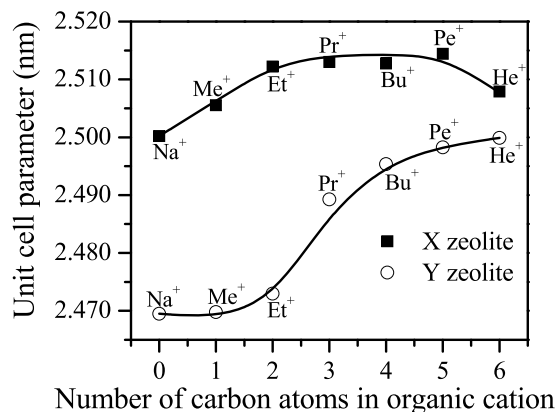


Fig. 4. Unit cell parameter as a function of the number of carbons in the alkylammonium cations.

containing the alkylammonium cations (C1–C6) are shown in Fig. S3 (Supplementary Material). For each cation, the zeolite studied was the one that showed the highest degree of exchange.

The results of the thermogravimetric analyses are summarized in Table 4, showing the percentage mass loss for each temperature interval as defined according to the observations. For both the Y and X zeolites, mass loss between 25 and  $250^\circ\text{C}$  could be attributed to removal of physisorbed water, while mass loss between 250 and  $480^\circ\text{C}$  was associated with decomposition of the alkylammonium cations [4]. At temperatures above  $480^\circ\text{C}$ , the X zeolites containing the alkylammonium

**Table 4**

Temperature ranges for mass losses of the zeolites containing alkylammonium cations.

| Zeolite | Mass loss (%) |                |          |
|---------|---------------|----------------|----------|
|         | 25–250 °C     | 250–480 °C     | > 480 °C |
| NaY     | 20.0          | — <sup>a</sup> | —        |
| MeY(71) | 14.8          | 7.60           | 3.17     |
| EtY(69) | 14.0          | 11.1           | 2.30     |
| PrY(67) | 14.7          | 12.6           | 2.18     |
| BuY(64) | 9.40          | 15.8           | 2.14     |
| PeY(55) | 9.42          | 15.7           | 1.49     |
| HeY(45) | 9.34          | 14.9           | 1.33     |
| NaX     | 25.0          | —              | —        |
| MeX(70) | 13.5          | 10.7           | —        |
| EtX(70) | 12.3          | 14.2           | —        |
| PrX(69) | 10.7          | 17.3           | —        |
| BuX(66) | 9.00          | 20.0           | —        |
| PeX(63) | 7.00          | 23.0           | —        |
| HeX(45) | 6.00          | 16.0           | —        |

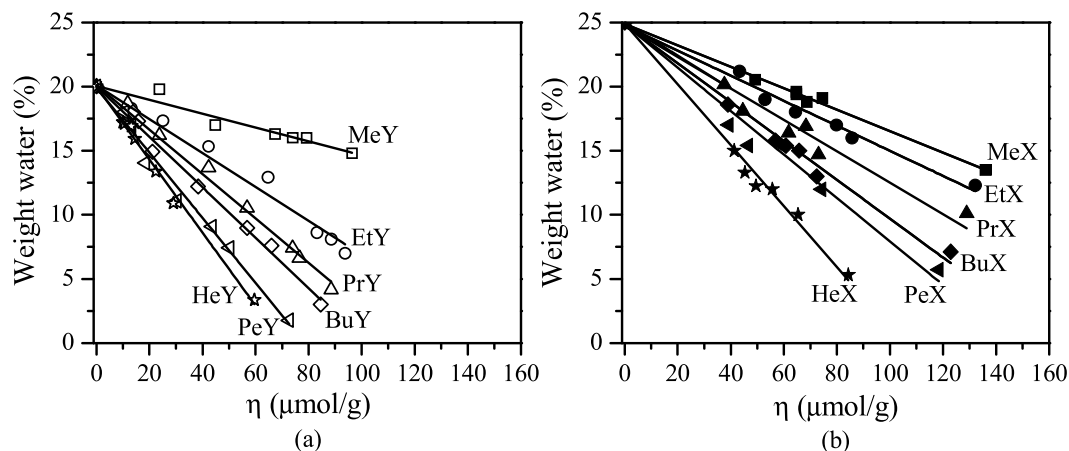
<sup>a</sup> No mass loss.

cations showed no mass loss. In contrast, the Y zeolites showed mass losses with maxima at 680 °C, due to dehydroxylation of the protonated sites formed after desorption of the corresponding amine [19]. The X zeolites presented no dehydroxylation in this region, because the high aluminum content in the framework led to low stability of the protonated sites, so this decomposition occurred in the second region, together with desorption of the alkylamine [4].

Fig. 5 shows the mass losses of water from the X and Y zeolites as a function of the type of alkylammonium cation and the number of sites exchanged ( $\eta$ ). For the same degree of exchange, the water mass loss decreased with increasing length of the carbon chain, because the alkylammonium cations are less hydrophilic than the sodium cation [20], with the hydrophobicity increasing in line with the length of the carbon chain.

### 3.5. X-ray photoelectron spectroscopy

The XPS results for line 1s of the oxygen of some of the Y and X zeolites are shown in Figs. 6 and 7. The oxygen electron binding energy,  $E_b[O1s]$ , is indirectly indicative of the basic strength. The lower the  $E_b[O1s]$  binding energy, the greater is the availability of electrons, and consequently the greater the Lewis basicity of oxygen. Although all oxygen atoms are potential basic sites, in zeolites only those belonging to the aluminate anions possess sufficient basicity for catalytic activity [8].



**Fig. 5.** Mass losses of water as a function of the number of moles of exchanged sites per gram: (a) Y zeolite and (b) X zeolite.

In order to characterize the basicity of the zeolites used in this study, deconvolution was applied to the XPS spectra for zeolites containing different cations, as shown in Figs. 6 and 7. For each alkylammonium cation, selection was made of the Y and X zeolites with similar numbers of moles of exchanged sites (the same pairs shown in Table 3).

To perform the deconvolution of the spectra, it was considered that they originated from the signals of the oxygen atoms belonging to four different environments: curve A, attributed to oxygens of the aluminate anions compensated by alkylammonium cations [6], denoted MAIO in Table 5; curve B, attributed to aluminate anions compensated by sodium cations, denoted NaAlO [21,22]; curve C, attributed to SiOSi bonds [21,22]; and curve D, attributed to silanol SiOH groups [23]. The deconvoluted spectra reflecting the chemical environments were compared with the exchange degrees determined by chemical analysis. Therefore, the areas of the A and B curves are consistent with the contents of the sodium and alkylammonium cations in the zeolites. Table 5 shows the  $E_b[O1s]$  energy values for each of these environments, determined from the deconvolutions.

The  $E_b[O1s]$  binding energies of the oxygen atoms belonging to the aluminate anions of the X zeolite, linked to the alkylammonium cations (column MAIO, Table 5), were the same for the  $Me^+$  and  $Et^+$  cations. For the cations with three or more carbon atoms,  $E_b[O1s]$  decreased by around 0.20 eV, indicative of increased basicity for this group of cations. Differently, for the Y zeolite,  $E_b[O1s]$  decreased with increase of the carbon chain up to the  $Pe^+$  cation, reflecting a continuous increase of basicity. Comparison of the two zeolites in terms of the  $E_b[O1s]$  values, for the MAIO environment of the same cation, revealed that the binding energy was lower for the X zeolite than the Y zeolite. As observed by Barthomeuf [24,25], this indicated that due to the higher content of aluminum atoms, the basic sites in the X zeolite were stronger than in the Y zeolite.

For the other oxygen environments (NaAlO, SiOSi, and SiOH), the  $E_b[O1s]$  values did not vary significantly. Similar behavior was observed for zeolites Y and X exchanged with methylammonium cations with different numbers of methyl groups [5,6]. These results assisted in the elucidation of catalytic activity (discussed below).

### 3.6. Knoevenagel condensation

Fig. 8 shows the ethyl-2-cyano-3-butylacrylate yields obtained in the Knoevenagel condensation between n-butyraldehyde and ethyl cyanoacetate (compound 3, Scheme 1), as a function of the number of alkylammonium cations in the Y and X zeolites. Table 6 compares the yields of compound 3 for zeolites Y and X (the same pairs shown in Table 3), indicating (in parentheses) the approximate numbers of moles of exchanged sites per gram of zeolite ( $\eta$ ). Table 6 also shows the

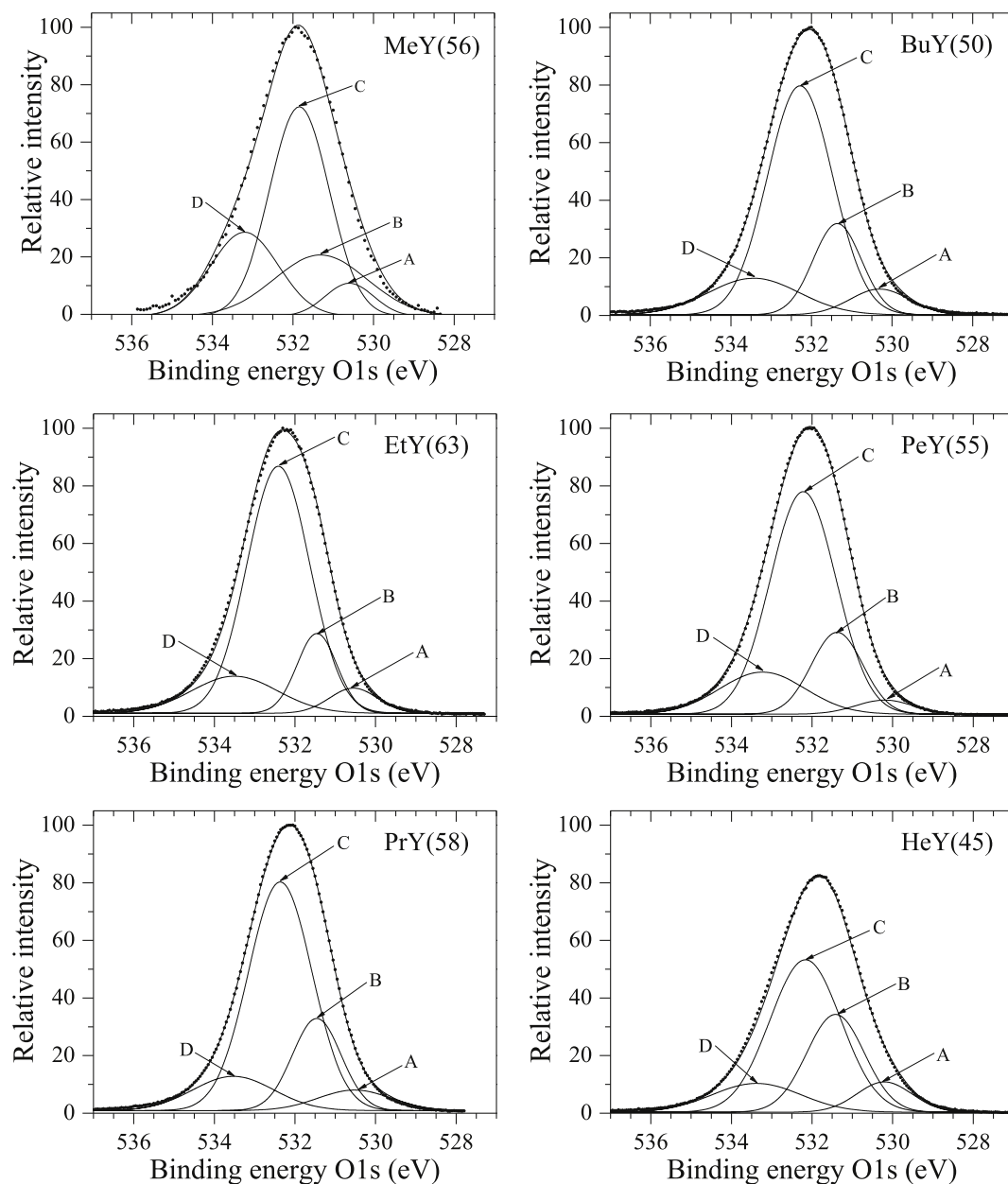


Fig. 6. XPS spectra of some of the Y zeolite samples. The dotted lines represent the measured photoemission spectra.

percentages of water present in the zeolites (obtained from Fig. 5).

As shown in Table 5, the  $E_b[\text{O}1s]$  binding energy values were lower for the X zeolites than for the corresponding Y zeolites, suggesting that the basicity of the former should be higher. In practice, the yields of the catalytic reaction (Table 6) showed that the basicity, as measured by XPS, affected the catalytic properties of the zeolites, although the influence was not always the same. The MeX, EtX, and PrX zeolites were much more active than the corresponding Y zeolites. However, when the carbon chain length of the organic cation was increased to butylammonium, the activity of BuY increased substantially and approached that of its homolog, BuX, despite the latter having superior basicity. A similar effect was observed when the chain length was increased to pentylammonium, with the activity increasing even further for the PeY zeolite and becoming equal to that of the PeX zeolite, which also had superior basicity. Finally, when the cation chain length was increased to hexylammonium, the activities of the two zeolites were reversed, with the HeY zeolite being more active than the HeX zeolite, despite that fact that according to the XPS analyses, the basicity of HeX was higher than

that of HeY.

The variable influence of basicity (as estimated by XPS) on the product yield suggested that more than one factor affected the catalytic activities of the zeolites. For similar systems [4–6], a possible effect has been suggested to be due to the steric hindrance induced by alkylammonium cations with different chain lengths. However, this would not be consistent with the results shown in Table 6, because in the case of the Y zeolites, the activity increased with the length of the chain, when the opposite effect would be expected. Another possibility could be increased hydrophobicity of the zeolite surface with increasing length of the alkylammonium cation chain, as indicated in Fig. 5. Greater hydrophobicity of the zeolite surface should influence the reaction shown in Eq. (1), due to higher affinity of the reactants for the regions of the catalytic sites, as well as expulsion of the water formed in the reaction, hence shifting the equilibrium in favor of formation of compound 3. As shown in Table 6, the water content of the Y zeolites decreased much more rapidly, compared to the X zeolites, hence explaining the increase in activity of the former as the alkylammonium

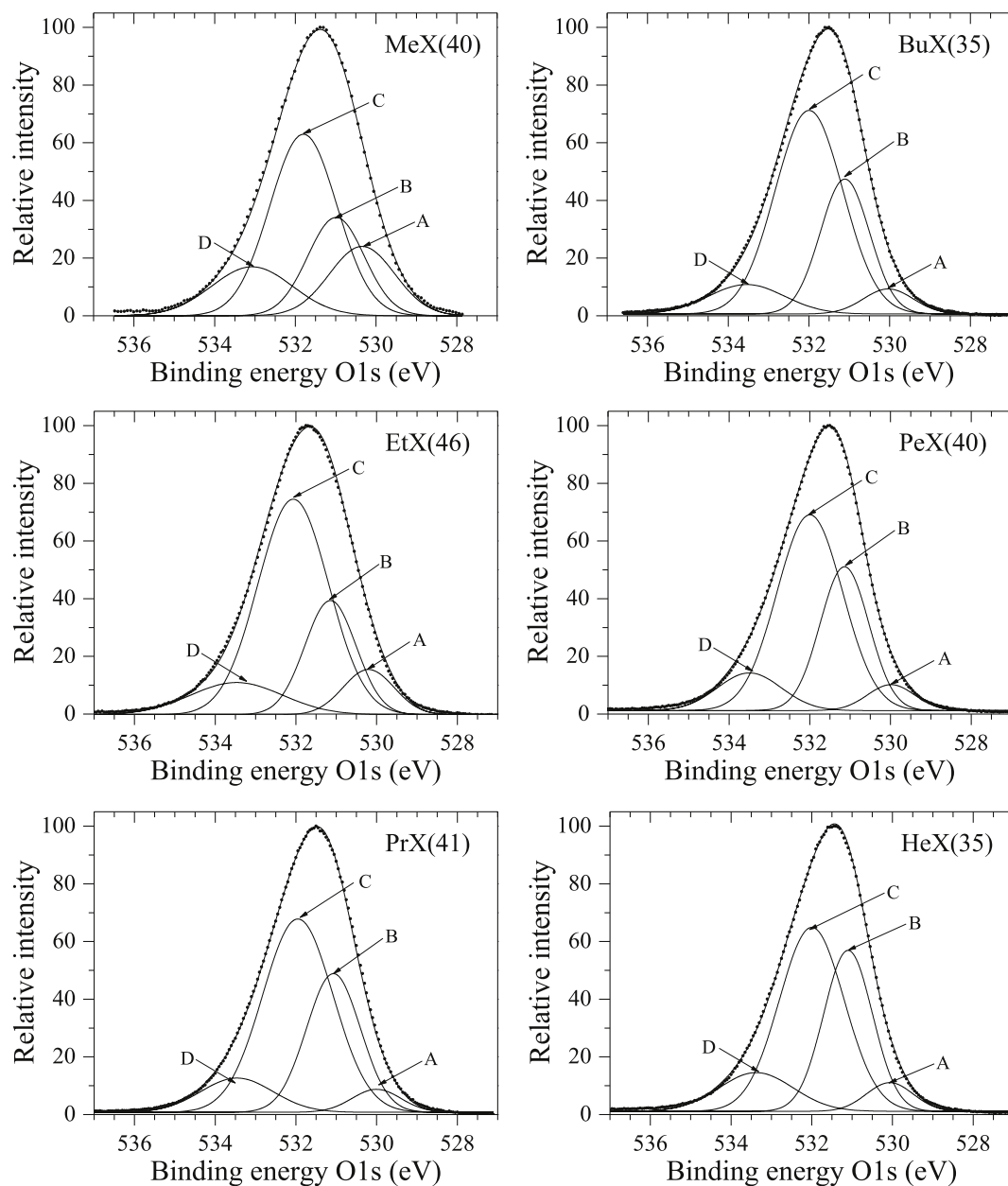


Fig. 7. XPS spectra of some of the X zeolite samples. The dotted lines represent the measured photoemission spectra.

**Table 5**

O1s Binding energies of the zeolites obtained from deconvolution of the XPS spectra.

| Y zeolite | E <sub>b</sub> [O1s] (eV) <sup>b</sup> |       |       |       | X zeolite | E <sub>b</sub> [O1s] (eV) <sup>b</sup> |       |       |       |
|-----------|----------------------------------------|-------|-------|-------|-----------|----------------------------------------|-------|-------|-------|
|           | MAIO <sup>a</sup>                      | NaAlO | SiOSi | SiOH  |           | MAIO <sup>a</sup>                      | NaAlO | SiOSi | SiOH  |
| NaY       | –                                      | 531.3 | 532.0 | 533.1 | NaX       | –                                      | 531.0 | 531.8 | 532.9 |
| MeY(56)   | 530.6                                  | 531.3 | 531.8 | 533.2 | MeX(40)   | 530.2                                  | 531.0 | 531.8 | 533.0 |
| EtY(63)   | 530.5                                  | 531.4 | 532.4 | 533.5 | EtX(46)   | 530.2                                  | 531.1 | 532.1 | 533.5 |
| PrY(58)   | 530.4                                  | 531.4 | 532.3 | 533.4 | PrX(41)   | 530.0                                  | 531.1 | 532.0 | 533.5 |
| BuY(50)   | 530.3                                  | 531.4 | 532.3 | 533.4 | BuX(35)   | 530.0                                  | 531.1 | 532.0 | 533.5 |
| PeY(55)   | 530.2                                  | 531.4 | 532.2 | 533.2 | PeX(40)   | 530.0                                  | 531.1 | 532.0 | 533.5 |
| HeY(45)   | 530.2                                  | 531.4 | 532.3 | 533.4 | HeX(35)   | 530.0                                  | 531.1 | 532.0 | 533.4 |

<sup>a</sup> M = Me<sup>+</sup>, Et<sup>+</sup>, Pr<sup>+</sup>, Bu<sup>+</sup>, Pe<sup>+</sup> and He<sup>+</sup>.

<sup>b</sup> Error = ± 0.1 eV.

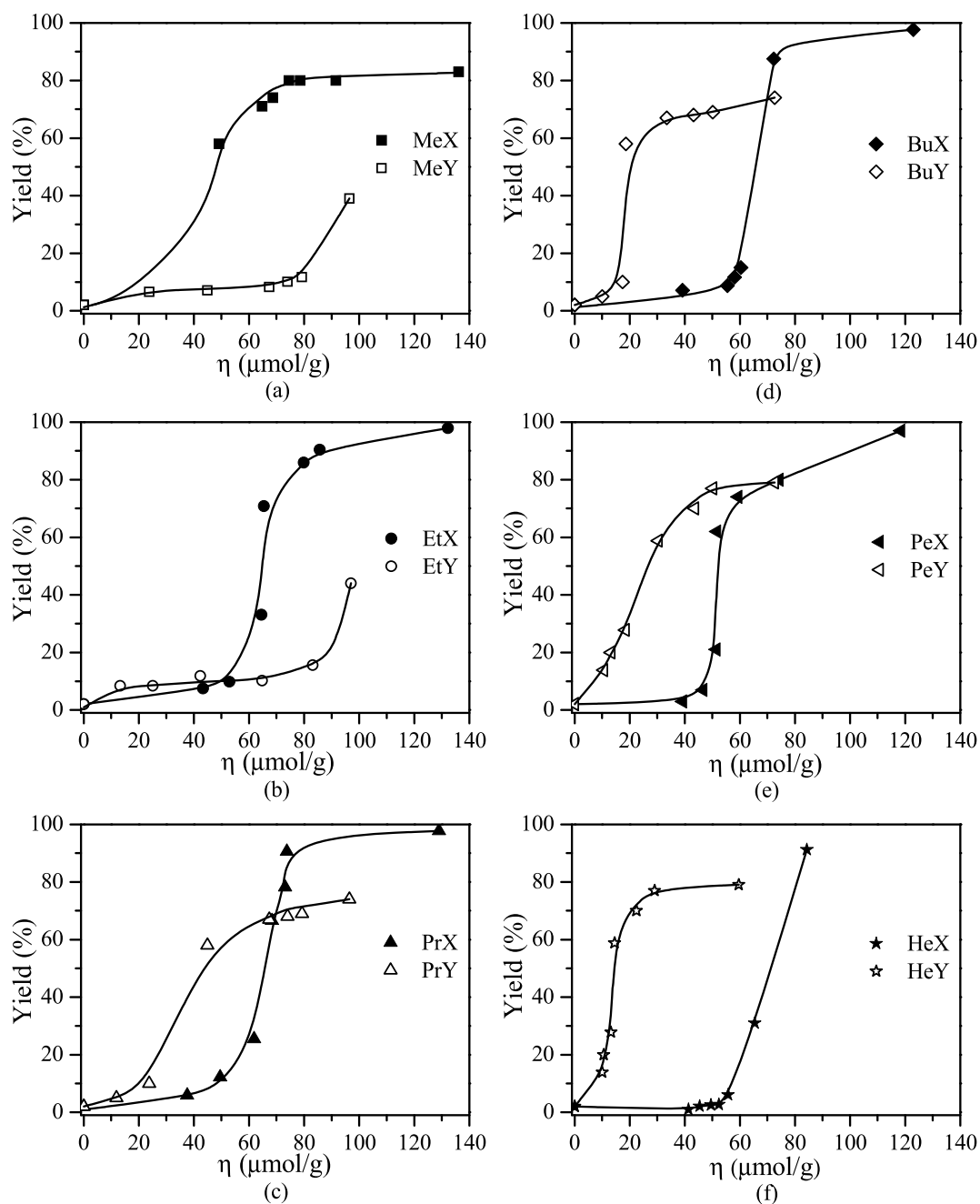


Fig. 8. Yields of compound 3 (Scheme 1) as a function of the exchanged sites number for Y and X zeolites.

Table 6

Catalytic yields and percentages of water in the zeolites.

| Sample  | Wt. H <sub>2</sub> O (%) | Yield (%) | Sample  | Wt. H <sub>2</sub> O (%) | Yield (%) |
|---------|--------------------------|-----------|---------|--------------------------|-----------|
| MeY(56) | 16.0                     | 10        | MeX(40) | 19.1                     | 80        |
| EtY(63) | 8.60                     | 16        | EtX(46) | 16.0                     | 90        |
| PrY(58) | 6.62                     | 15        | PrX(41) | 15.1                     | 91        |
| BuY(50) | 7.60                     | 69        | BuX(35) | 15.0                     | 88        |
| PeY(55) | 1.77                     | 79        | PeX(40) | 12.0                     | 80        |
| HeY(45) | 3.34                     | 79        | HeX(35) | 10.0                     | 31        |

cation chain length increased.

Table 7 shows the turnover frequency (TOF) values for some of the X zeolites in the Knoevenagel condensation between butyraldehyde and ethyl cyanoacetate. In calculation of the TOF for each sample, the number of framework sites in the X zeolite was assumed to be

Table 7

Turnover frequency (TOF) values of the basic sites for the Knoevenagel condensation reaction of butyraldehyde with ethyl cyanoacetate.

| Sample  | η (μmol/g) | TOF (min <sup>-1</sup> ) |
|---------|------------|--------------------------|
| PrX(39) | 73.1       | 75.6                     |
| PrX(69) | 129        | 30.1                     |
| BuX(66) | 123        | 23.8                     |

1400 μmol/g. It was also assumed that only alkylammonium cations were associated with the basic catalytic sites for this reaction. The TOF values decreased with increase in the number of moles of exchanged sites (η) for zeolites PrX(39) and PrX(69), suggesting that steric effects acted to decrease the catalytic activity. Zeolites PrX(69) and BuX(66) possessed approximately the same number of moles of exchanged sites,

with TOF values of 30.1 and 23.8 min<sup>-1</sup>, respectively, further evidencing that steric effects decreased the catalytic activities of the zeolites.

#### 4. Conclusions

Ion exchange isotherms showed that the location of the alkylammonium cations in the zeolites was restricted to the supercavities. The ion exchange reaction was limited by steric effects, which increased with increasing length of the carbon chain.

The incorporation of alkylammonium cations in the X and Y faujasites led to expansion of the zeolite frameworks. The intensity of this expansion showed dependence on the carbon chain length of the organic cation and the degree of exchange. In parallel with changes in the framework parameters, the exchange of cations tended to reduce the micropore volumes of the zeolites.

Deconvolution of the catalyst XPS spectra identified four oxygen environments in the structures, including those associated with the alkylammonium cations (M-AlO). The aluminate anion was responsible for most of the basicity of the zeolites. Due to the higher aluminum content of the X zeolite, the E<sub>b</sub>[O1s] binding energy was smaller than for the Y zeolite. The E<sub>b</sub>[O1s] value decreased with the carbon chain length of the organic cation. The lower E<sub>b</sub>[O1s] values obtained for the X zeolite suggested that the active sites were more basic.

The performance of the X and Y zeolites containing alkylammonium cations in the Knoevenagel condensation was the result of a combination of factors, namely the basic strength of the sites, steric hindrance and hydrophobicity. For cations with up to three carbon atoms, the basic strengths of the sites of the X zeolites overcame the steric hindrance and resulted in higher yields. However, for cations with longer chains, the steric effects and greater hydrophobicity of the Y zeolite led to higher yields for this reaction.

Under the reaction conditions employed, the X zeolites with the maximum degrees of ionic exchange for the ethyl-, propyl-, butyl- and pentylammonium cations provided yields of around 98%, the maximum achieved with these catalysts.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2019.03.024>.

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