Basic activity of Y zeolite containing alkylammonium cations in Knoevenagel condensation

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ABSTRACT

This paper compares the catalytic activity of Y zeolite containing alkylammonium cations in the Knoevenagel condensation. For steric reasons, the exchange of Na^+ for alkylammonium cations was restricted to the faujasite supercavity, and the degree of ion exchange decreased with the radius of the organic cation. The basicity of the catalysts was analyzed using X-ray photoelectron spectroscopy (XPS) and the Knoevenagel condensation reaction, with good correlation obtained between the results of the two methods. The best catalytic activity was observed for the Y zeolite exchanged using the butylammonium cation. The better performance of this catalyst was attributed to increased accessibility of the reactants to the catalytic sites.

1. Introduction

Base catalyzed condensation reactions are important for the preparation of a wide variety of organic compounds and key intermediates in the manufacture of pharmaceutical and fine chemical products [1]. The replacement of liquid bases by solid base catalysts has the advantages of decreasing corrosion and environmental contamination, while allowing easier separation and recovery of the catalysts [1]. Furthermore, many organic reactions catalyzed by liquid bases require a stoichiometric amount of the catalyst [2]. Particularly, the Knoevenagel condensation reaction can be catalyzed by solid bases possessing very different basic strength; it can be used as a probe reaction to compare the basic character of various solids [3]. Commercially this reaction was carried out using various homogeneous base catalysts such as piperidine, amines, ammonia, and ammonium salts, which are corrosive, toxic, non-reusable and also produce neutralization waste [4]. A number of heterogeneous base catalysts have been reported in literature for Knoevenagel condensation reaction such as NaX faujasite zeolite exchanged with cesium cation [5], alkali earth oxide supported on alumina [6], magnesium oxide [7] zeolites exchanged with methylammonium cations [8–10] and other cations [11].

Zeolites exchanged with methylammonium cations showed higher catalytic activity in the Knoevenagel condensation than zeolites exchanged with cesium cation. Binding energy values of the

1s oxygen electron, obtained by X-ray photoelectron spectroscopy (XPS), confirmed that methylammonium cations have provided basic sites stronger than cesium [12]. Although the methylammonium cations have provided stronger basic sites, the catalytic activity of the site was strongly affected by steric hindrance. That is, the voluminous organic cations in confined spaces, such as micropores and cavities of the zeolite, can prevent access of the reactants to the catalytic strong basic sites or the diffusion of reactants and products through these pores [12].

As a development of the earlier studies [8–12], the objective of this work was to evaluate the influence of linear alkylammonium ions with even number of carbons present in Y zeolite, on its catalytic activity in the Knoevenagel condensation.

2. Materials and methods
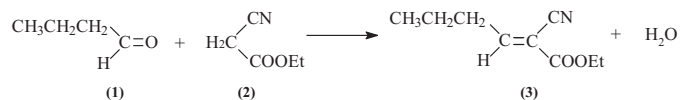
2.1. Ion exchange isotherms

The catalysts were preparing using commercial zeolites NaY (Zeolyst) with Si/Al molar ratios equal to 2.5. These Si/Al ratios mean that 29% of the tetrahedra in these zeolite consisted of aluminate anions. Ion exchange isotherms were obtained at 40 °C, using the procedure described previously [13]. Sodium ions present in zeolite were ionically exchanged by the following ammonium cations: trimethylammonium, tetramethylammonium, propylammonium and butylammonium.

Ion exchange solutions were prepared with sodium chloride and alkyl ammonium chloride. The followings salts were using to prepare the ion exchange solution: trimethylammonium chloride

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Table 1
Nomenclature used for samples.

Cation	Y zeolite
$(CH_3)_3NH^+$	Me_3Y
$(CH_3)_4N^+$	Me_4Y
$CH_3-CH_2-CH_2NH_3^+$	Pr_1Y
$CH_3-CH_2-CH_2-CH_2NH_3^+$	Bu_1Y

Scheme 1. Knoevenagel condensation.

Fig. 1. Ion exchange isotherms at 40 °C of the Na^+ by trimethyl-, tetramethyl-, propyl- and butylammonium cations.

(Fluka, 98%) and tetramethylammonium chloride (Aldrich, 98%). For the other cations linear alkyl ammonium salts were prepared by acid–base titration of amines (Aldrich, 98%) with hydrochloric acid corresponding to the equivalence point.

Each ion exchange solution was prepared using the amounts of the salts required to maintain isotonic conditions and a constant total cation concentration of 0.05 mol/L. The zeolite mass used resulted in a total cations ratio $R = (C^+ + Na^+)/Al$ in the liquid phase equal to 4. In order to obtain catalysts with a maximum degree of exchange, three consecutive exchanges were performed with the organic cation solution, corresponding to a single concentration of 0.5 mol/L. 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).

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 a pressure of 0.1 mbar. The specific micropore volume in the different samples was determined by extrapolating the volume adsorbed at different pressures, using the t-plot method [14].

X-ray photoelectron spectroscopy (XPS) analyses were performed using a VSW HA-100 spherical analyzer, equipped with an Al K-α source ($h\nu = 1486.6$ eV), at a pressure less than 2×10^{-8} mbar. The loading effects were adjusted by linear displacement of the spectrum, so that the C1s signal had a binding energy equal to 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 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 was 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 7%.

Under the reaction conditions used, the Knoevenagel condensation was always 100% for compound 3 (Scheme 1).The turnover frequency of some selected base catalysts was estimated at zero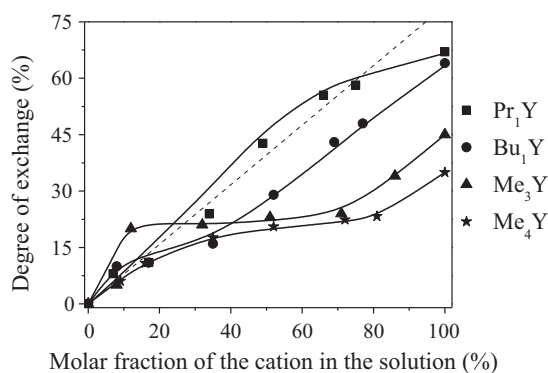 reaction time. To do this, the Knoevenagel condensation was performed under the same conditions as above, but using 20 mL of the reaction mixture in a 50 mL jacketed reactor fitted with a reflux condenser. To determine the conversion as a function of time, a sample was analyzed by gas chromatography, as above, every 5 min during a period of 1 h. An exponential curve was then adjusted to the points, and the initial reaction rate was obtained by derivation of the curve at zero reaction time.

3. Results and discussion

3.1. Ion exchange isotherms

Fig. 1 shows the isothermal ion exchange, at 40 °C, of the sodium cations in the Y zeolite by the trimethyl-, tetramethyl-, propyl- and butylammonium cations. The horizontal axis indicates the molar percentage of the organic cation in the aqueous solution at equilibrium (S_E), and the ordinate axis corresponds to the molar percentage of the organic cation in the zeolite (Z_E). The figure also shows a dotted line that corresponds to a hypothetical nonselective ion exchange; in other words, where S_E and Z_E are equals.

It was observed that in all the isotherms, even when the aqueous solution practically contained only the ammonium cations in equilibrium with the solid, i.e., $S_E \cong 100$, the percentage of this cation in the zeolite was always less than 70% ($Z_E < 70$). That is, the alkylammonium cations were unable to replace all the sodium cations in the zeolite. According to Breck [15], at near-ambient temperatures ion exchange is limited because it is difficult for the cations in the solution to access the sites inside the hexagonal prisms and sodalite cavities. Consequently, under these conditions, the ion exchange is limited to the cations located in the supercavities of the faujasite.

The Me_3-NaY and Me_4-NaY systems exhibited non-selective isotherms, indicating low interaction of the ammonium cations with the zeolite framework. This profile is typical of ion exchange involving high volume cations [13].

The exchange isotherms of Pr_1-NaY and Bu_1-NaY systems exhibited sigmoidal profile. This profile indicates that the selectivity varies with the concentration of linear alkylammonium cation-exchange in solution. Furthermore, the presence of inflection points indicates competition between two or more sites by exchangeable cations [13].

The points at which the isotherms intersect the diagonal indicate a change in selectivity. Note that the Y zeolite is not selective to the Pr_1^+ values until $S_E = 0.5$ from that concentration. For Bu_1^+, Y zeolite is selective in $S_E \leq 0.1$ and from that concentration becomes nonselective. This result indicates that the selectivity of Y zeolite decreases with increasing carbon number.