Influence of rare earth elements La, Nd and Yb on the acidity of H-MCM-22 and H-Beta zeolites

Angela Martins [a], João M. Silva [a], Carlos Henriques [b],
Fernando Ramôa Ribeiro [b], M. Filipa Ribeiro [b,*]

[a] Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro, 1950-062 Lisboa, Portugal
[b] Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Abstract

The influence of rare earth (RE) elements on the acidic properties of H-MCM-22 and H-Beta was studied by pyridine adsorption followed by infrared spectroscopy (FTIR) and *n*-heptane cracking, as a model reaction.

The zeolites were submitted to ion exchange with rare earth nitrate solutions of La, Nd and Yb. The FTIR spectra of REH-MCM-22 indicate the presence of RE elements inside supercages and in the sinusoidal channels of the zeolite. After pyridine adsorption two additional bands are detected in REH-MCM-22 and REH-Beta, related to pyridine bonded to RE^{3+} cations.

The *n*-heptane cracking reaction shows that the effect of rare earth elements is related not only to the acidity but also with the porous structure of both zeolites. In H-Beta zeolite, the presence of RE elements enhances the acidity of the catalysts. In H-MCM-22 zeolite, the most relevant effect of rare earth elements is on the shape selectivity that becomes more pronounced with the ionic radius of the RE elements. The nature of the coke deposited on the two materials shows distinct profiles that are also related to its porous structure.
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1. Introduction

Rare earth (RE) elements play an important role in the modification of some catalysts, namely faujasites, raising its stability and activity in cracking reactions [1]. The presence of rare earth cations enhances the catalyst activity as a consequence of a higher concentration in Brönsted acid sites because of the hydrolysis of water of solvation of RE^{3+} cations that takes place in the zeolitic cavities [2]. The introduction of rare earth elements also prevents aluminum loss from the zeolite structure, thus resulting in enhanced structural resistance to the severe hydrothermal conditions found in the regeneration step of the FCC [3]. Furthermore, the presence of highly charged cationic species can also modify the acid strength distribution in the zeolite due to the

polarization of OH groups or to an inductive effect on these groups [1].

The influence of rare earth elements on faujasites is well studied, mainly on cracking reactions [3–5], but also in other reactions like hydrogen transfer [6] and isomerization reactions [7,8]. The increase of faujasite catalysts performances led us to study the effect of the introduction of RE elements on other zeolite structures. Nevertheless, there are only a few studies about rare earth influence on other materials like silica [9], alumina [8] and Beta zeolite [10].

MCM-22 zeolite (MWW structure) is a relatively new material, synthesized by the first time in 1990 by Mobil. This material presents an original porous structure, where two independent pore systems exist, both accessible through 10-membered-ring apertures. One of the porous system has sinusoidal channels with 10-MR (4 Å × 5.0 Å). The other pore system comprises large supercages with 12-MR (7.1 Å × 18.4 Å), interconnected by 10-MR channels (4 Å × 5.5 Å). This material combines the characteristics

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* Corresponding author.
  E-mail address: filipa.ribeiro@ist.utl.pt (M.F. Ribeiro).

of both 10 and 12-MR zeolites. Due to this particular pore system MCM-22 has been tested for many kinds of catalytic reactions. Particularly, the potentialities of this zeolite have been tested as an additive for catalytic cracking (FCC) [11], in aromatization of *n*-butane [12], in isomerization of *m*-xylene [13] and in alkylation of benzene [14].

Beta zeolite (BEA structure) was first synthesized in 1967. It has a three-dimensional channel structure with 12-MR with elliptical openings (6.4 Å × 7.6 Å). The pore volume can be compared with that of faujasites. Because of its pore system and high acidity, it is of great potential industrial interest, especially in reactions such as catalytic cracking [15], isomerization [16,17], alkylation [18] and disproportionation [19].

The purpose of this work has been the study of the influence of rare earth elements La, Nd and Yb in the acidic properties of H-MCM-22 and H-Beta. Zeolites acidity is characterized by pyridine adsorption followed by infrared spectroscopy (FTIR) and by the model reaction of *n*-heptane cracking.

2. Experimental

MCM-22 was synthesized according to the method reported by Corma et al. [20], in a way to obtain Si/Al = 15. The as-synthesized form was calcined in air at 500 °C for 4 h. The calcined sample was ion-exchanged three times with 1 M ammonium acetate solution in order to obtain the acidic form, H-MCM-22. H-Beta zeolite was supplied by PQ Corporation with Si/Al = 12.5.

H-MCM-22 and H-Beta samples were submitted to ion exchange with rare earth nitrate solutions of La, Nd and Yb at 80 °C for 3 h in order to obtain RE/Al ratios of 0.3. After the exchange the samples were dried at 100 °C and calcined at 500 °C for 3 h under air flow of 6 L h^{-1} g^{-1} and a heating rate of 5 °C min^{-1}. These samples were named REH-MCM-22 and REH-Beta, with RE = La, Nd or Yb.

Crystallinity of all samples after the ion exchange was evaluated by X-ray powder diffraction, using a Rigaku diffractometer with Cu Kα radiation filtered by Ni. RE element contents (wt.%) were determined by ICP.

The porosity of each sample was determined by nitrogen sorption at −196 °C carried out with an automatic Micromeritics (ASAP 2010) apparatus.

The acidic properties of the samples were studied by pyridine adsorption followed by infrared spectroscopy (FTIR). The infrared spectra were recorded on a Nicolet Nexus FTIR spectrometer (60 scans, resolution 4 cm^{-1}). For IR characterization of the hydroxyl groups and of adsorbed pyridine, the zeolite samples were pressed into 12 mm diameter thin wafers (about 5 mg cm^{-2}) and evacuated at secondary vacuum (10^{-6} mbar) in situ in a IR cell at 300 °C for 8 h. After recording the initial spectrum of the sample (reference), pyridine was adsorbed at 150 °C under an equilibrium pressure of 2.7 mbar. The spectra were recorded

at ambient temperature after degassing the samples for 30 min, at the required desorption temperature (150–550 °C) and using a heating rate of 5 °C min^{-1}. Band intensities were normalized by the sample weight. The background spectrum, recorded under identical operating conditions without sample, was always performed before each spectrum and automatically subtracted.

The catalytic reaction of *n*-heptane cracking was performed in a continuous flow reactor at 350 °C under a total pressure of 1 bar. Before the reaction the catalysts were pre-treated at 500 °C in situ for 10 h under nitrogen flow of 36 L h^{-1} g^{-1}. Experiments were performed for 90 min using a flow of 3 mL h^{-1} of *n*-heptane (molar ratio N$_2$/*n*-C$_6$ = 9) and WHSV = 20.5 h^{-1}. The reaction products were analyzed by an on-line gas chromatograph Hewlett-Packard 6890 series with a flame ionization detector, using a capillary column PLOT-Al$_2$O$_3$/KCl.

The coke analysis was performed by thermogravimetry using a Setaram TG-DSC92 thermobalance. Coked samples were heated under air flow with a temperature increase of 10 °C min^{-1} until 200 °C, maintaining this temperature for 1 h. Afterwards, the temperature was increased again with the same heating rate until 600 °C. The samples were cooled to room temperature and an additional heating cycle was performed under identical conditions to eliminate any fluid transport effect. The weight loss and heat profiles were obtained by subtraction of the two cycle profiles.

3. Results and discussion

3.1. Physicochemical characterization

The XRD patterns of MCM-22 were identical to those reported on literature [20]. After introduction of RE elements the XRD patterns of REH-Beta and REH-MCM-22 maintain the original crystalline structure. The unit cell formula of the samples and the microporous volumes (V_{micorp}), determined by the *t*-plot method, are shown in Table 1. For all samples, the RE contents introduced are always around 10% of the predicted exchange values. For the same ion exchange conditions, NdH-MCM-22 and YbH-Beta present slightly higher contents in RE elements. H-Beta and REH-Beta show very

Table 1
Unit cell composition and microporous volumes for H-MCM-22 and H-Beta samples

Sample	Unit cell formula	V_{micorp} (cm^3 g^{-1})
H-MCM-22	H$_{4.5}$Al$_{4.5}$Si$_{67.5}$O$_{144}$	0.164
LaH-MCM-22	La$_{0.05}$H$_{4.5}$Al$_{4.5}$Si$_{67.5}$O$_{144}$	–
NdH-MCM-22	Nd$_{0.07}$H$_{4.3}$Al$_{4.5}$Si$_{67.5}$O$_{144}$	0.134
YbH-MCM-22	Yb$_{0.04}$H$_{4.4}$Al$_{4.5}$Si$_{67.5}$O$_{144}$	0.135
H-Beta	H$_{4.7}$Al$_{4.7}$Si$_{59.3}$O$_{128}$	0.159
LaH-Beta	La$_{0.04}$H$_{4.6}$Al$_{4.7}$Si$_{59.3}$O$_{128}$	0.157
NdH-Beta	Nd$_{0.05}$H$_{4.6}$Al$_{4.7}$Si$_{59.3}$O$_{128}$	0.155
YbH-Beta	Yb$_{0.10}$H$_{4.4}$Al$_{4.7}$Si$_{59.3}$O$_{128}$	0.158