

Evaluation of the acid properties of aluminosilicate MCM-22 material synthesized under static conditions

MEIRY G. F. RODRIGUES¹, ANTONIELLY S. BARBOSA¹, ANA C. F. CORIOLANO²,
EDJANE F. B. SILVA³, ANTONIO S. ARAUJO^{3*}

¹Federal University of Campina Grande, Academic Unit of Chemical Engineering, 58109-970, Campina Grande PB, Brazil

²Potiguar University – Laureate International Universities, Av. Nascimento de Castro 1597, 59056-450, Natal RN, Brazil

³Federal University of Rio Grande do Norte, Institute of Chemistry, 59078-970, Natal RN, Brazil

The hydrothermal synthesis of MCM-22 zeolite was carried out using silica, sodium aluminate and hexamethyleneimine, under static conditions at 150 °C for a period of 10 days, followed by washing with deionized water, drying overnight and calcination at 650 °C. The obtained material was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The XRD analysis evidenced that MCM-22 presented a well defined MWW structure. The FT-IR spectrum confirmed the efficiency of the hexamethyleneimine as an organic template used to direct the structure of the MCM-22 zeolite under static conditions. The SEM image indicated that the particles are spherical in shape, with a diameter of ca. 10 µm. The acid properties of the MCM-22 zeolite, as determined by n-butylamine adsorption, were investigated in the temperature ranges of 105 to 300 °C and 300 to 525 °C, relative to medium and strong acid sites, respectively.

Keywords: *crystal structure; synthesis of zeolites; porous materials; MCM-22*

© Wrocław University of Technology.

1. Introduction

The MCM-22 material is a synthetic high-silica zeolite, which crystallizes as very thin plates [1]. Due the presence of active acid sites on its surface, this crystalline aluminosilicate material can be a very promising heterogeneous acid catalyst for some industrial applications, such as oil refining and petrochemical processes, like alkylation and isomerization.

From a structural point of view, the MCM-22 material presents a complex porosity, containing both medium and large pores [2]. According to International Zeolite Association, the MCM-22 presents MWW structure with two independent pore systems [3]. One of them is defined by two-dimensional sinusoidal 10-membered-ring channels (0.40 × 0.59 nm). The other pore system consists of large supercages with a free inner diameter of 0.71 nm, which is circumscribed by 12-membered rings [4–6].

The MWW structure can be built using units of 36T atoms (T = Si or Al). The T36-unit resembles a "half-cage" (or 12-ring cup) consisting of cylindrical 6-ring band closed at one side by a 6-ring, to which two T2-dimers and two T atoms are bonded (or built from four 6-1 units and one 1-6-1 unit) [7, 8]. The one-dimensional Periodic Building Unit is obtained when T36-units, related by a mirror plane perpendicular to "a", are connected into columns along "c" through double 6-ring and single T–T bonds, as can be seen in Fig. 1.

A typical preparation of the MCM-22 materials basically needs a solvent, an organic template and silica under stirring. The as-synthesized materials present a layered structure, and after calcination, the template is removed from the pore systems of the layered-MCM-22 by subsequent silanol condensation, giving rise to a MCM-22 zeolite structure, as shown in the Fig. 2.

In the current work, MCM-22 has been synthesized under static hydrothermal conditions using hexamethyleneimine as an organic template.

*E-mail: araujo.ufrn@gmail.com

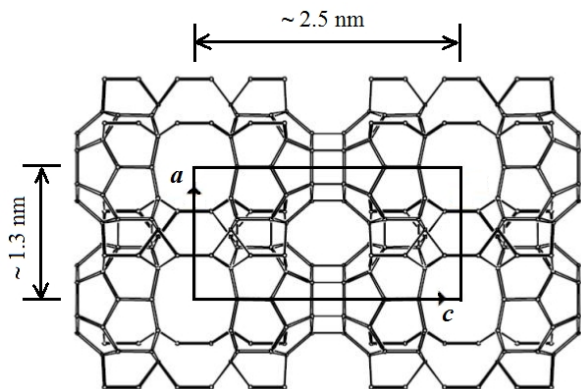


Fig. 1. Unit cell of MCM-22 zeolite viewed along the "a" and "c" axis.

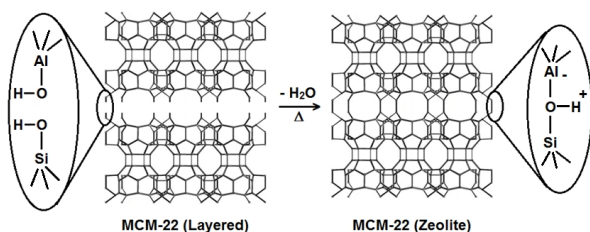


Fig. 2. Conversion of layered structure MCM-22(L) to the aluminosilicate MCM-22(Z) zeolite, and subsequent generation of a protonic acid sites.

The acidity of the material was investigated using *n*-butylamine as a molecular probe. This measurement was carried out by thermogravimetry method in order to determine the amount and strength of the active sites in specific temperature ranges.

2. Experimental

The MCM-22 zeolite was prepared by a thermal treatment of a specific aluminosilicate precursor. This precursor was obtained according the following procedure: a mass of 3.11 g of anhydrous sodium aluminate (50 to 56 % Al_2O_3 , 40 to 45 % Na_2O , Riedel-deHaën) and 1.93 g of sodium hydroxide (97 % Merck) were dissolved in 415 g of deionized water. The obtained solution was stirred for 15 min. Then, 25.4 g of hexamethyleneimine (HMI) (99 % Aldrich) was added dropwise under vigorous stirring. A mass of 30.7 g of silica (Aerosil 200, Degussa) was added to the mixture

and the slurry was vigorously stirred for additional 30 min. After that, the gel was transferred to an autoclave and heated at 150 °C for 10 days, without stirring, or under static condition. Then, the autoclave was quenched in cold water, and the obtained material was washed with deionized water and centrifuged until a $\text{pH} \leq 9$, and dried at 70 °C. In this step, the obtained material presented a layered structure, being signed as MCM-22(L). The second step consisted in the calcination of the layered material, MCM-22(L), at 650 °C for 7 h, under air atmosphere, in order to obtain the zeolite material, called then MCM-22(Z).

The X-ray diffraction (XRD) analysis of the MCM-22(L) and MCM-22(Z) samples was carried out using Shimadzu XRD 6000 equipment using $\text{CuK}\alpha$ radiation at 40 kV and 30 mA, with a goniometric velocity of 2° min^{-1} and 2θ ranging from 2 to 50° . The Fourier transform infrared (FT-IR) spectra of the MCM-22(L) and MCM-22(Z) samples were obtained by the KBr method, with a concentration of ca. 7 % in mass. The measurements were accomplished using a spectrophotometer AVATAR TM360 FT-IR, wavelengths ranging from 4000 to 400 cm^{-1} , and resolution of 4 cm^{-1} . The scan electron micrograph (SEM) was obtained using a microscope Philips XL 30 EDAX, equipped with an X-ray energy dispersion spectrophotometer (EDS) to investigate the composition of the material before and after the calcination.

The determination of the acidity was accomplished according the procedure previously reported [9–13]. For this measurement, the calcined sample (0.1 g) was firstly activated at 400 °C, under nitrogen gas flowing at 60 mL min^{-1} for two hours. Then, the sample was exposed to the vapors of *n*-butylamine at 95 °C, for a period of one hour, for the complete saturation of the acid sites of the MCM-22(Z) sample. A mass of ca. 10 mg of the sample, previously saturated with *n*-butylamine, was transferred to a thermobalance (DuPont 910, TA-2000) and heated from room temperature up to 900 °C, at a heating rate of $10^\circ \text{ C min}^{-1}$, using nitrogen as a carrier gas, at the same flowing conditions. The total acidity was defined as the

absolute mass of base desorbed from the acid sites of the catalyst, expressed in mmol g^{-1} in specific temperature ranges.

3. Results and discussion

The X-ray patterns of the materials: MCM-22(L) precursor and MCM-22(Z) are presented in Fig. 3. The XRD patterns of both samples are in agreement with those already reported, suggesting that high crystalline material was obtained [1]. One distinct difference between the two samples is observed in the range of $2\theta = 12$ to 25° , where the X-ray patterns of MCM-22 zeolite is characterized by some sharp and separated peaks. Another region that distinguishes MCM-22(L) from MCM-22(Z) is observed in the range of $2\theta = 26$ to 29° .

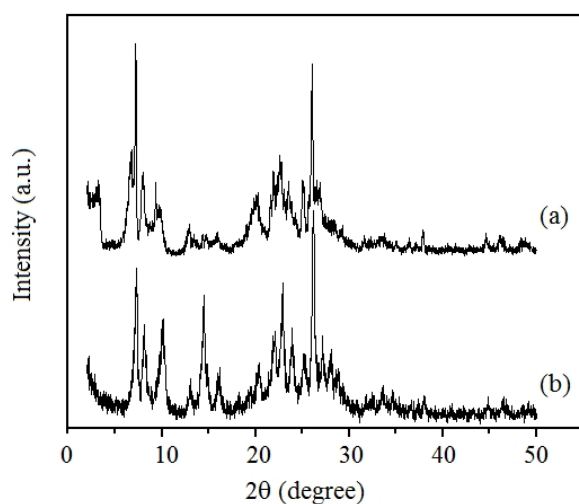


Fig. 3. X-ray diffractograms of the samples: (a) MCM-22(L) precursor and (b) MCM-22(Z) material synthesized under static conditions.

The X-ray pattern of the layered MCM-22(L) presents two peaks centered at $2\theta = 26.07$ and 26.60° , whereas the zeolite MCM-22(Z) is characterized by four sharp peaks, at $2\theta = 26.23$; 27.14 ; 28.08 and 28.84° . The position of the reflections (001) and (002) in the MCM-22(L), located respectively at $2\theta = 3.25$ and 6.71° disappeared during the calcination process, suggesting a lamellar structure. This is a clear indication that the c-parameter of the unit cell decreased and became more

regular, as can be visualized in the Fig. 1 and 2. Other peaks located at $2\theta = 7.20$; 25.11 and 26.07° practically remain unchanged, indicating that the structural changes involve only the "c" axis.

The infrared spectra for the samples are shown in Fig. 4. From FT-IR of MCM-22(L), the presence of bands related to the symmetrical and asymmetrical stretching of the O-H connections in the MCM-22(L) precursor sample was verified. The band at 786 cm^{-1} refers to the external symmetrical stretching, while the band at 1237 cm^{-1} refers to the external asymmetric stretching. Also, peaks in the range of hydroxyl groups, in the range of 3800 to 3500 cm^{-1} , and nitrogen of HMI template, at ca. 3200 cm^{-1} , as indicated in the FT-IR spectra, were observed.

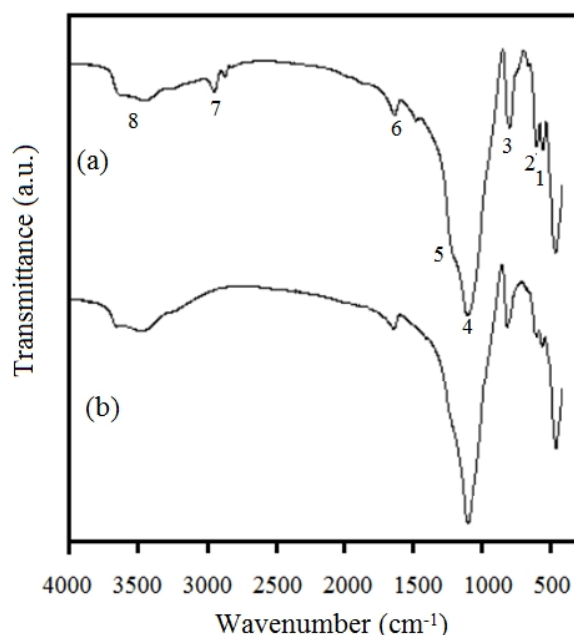


Fig. 4. Fourier transform infrared spectra of: (a) as-synthesized MCM-22(L); and (b) MCM-22(Z) zeolite after calcination. The wavenumbers of the peaks identified in the spectra are: (1) 550 ; (2) 594 ; (3) 786 ; (4) 1095 - 1070 ; (5) 1384 ; (6) 1626 ; (7) 3200 and (8) 3500 - 3800 cm^{-1} .

The bands at 1095 and 1070 cm^{-1} region correspond to internal asymmetric stretching, and the bands at 594 and 550 cm^{-1} are attributed to the presence of double rings in the MCM-22(L)

structure. At 1626 cm^{-1} the band is ascribed to the angular deformation of the N–H bond of the hexamethyleneimine template. The band centered at 1384 cm^{-1} indicates the presence of the amine functional group (HMI).

According to the scanning electron micrograph, the MCM-22(Z) shows the structure whose fine particles grow into spherical structures, resulting from the agglomeration of these particles, with a depressed central region, as shown in Fig. 5. The spheres are approximately $10\text{ }\mu\text{m}$ in diameter, showing some fracture along the "c" axis, probably due to the elimination of organic template (HMI) during the calcination.

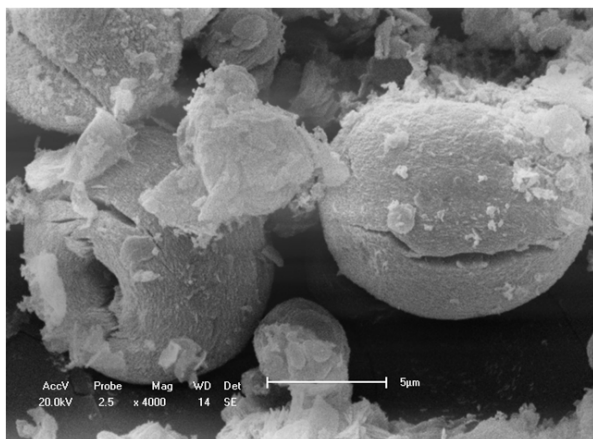


Fig. 5. Scanning electron micrographs of the MCM-22(Z) material after calcination.

From the results of elementary chemical analysis, by EDS, it was confirmed that both the layered and the zeolite materials showed high concentration of silica (SiO_2) and low concentration of alumina (Al_2O_3) in the zeolite structure, with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 11.5 and 11.3 for MCM-22(L) and MCM-22(Z), respectively, characteristic of the MWW structure. After calcination, a small reduction of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was observed, but it remained nearly unchanged. This could be attributed to the static conditions used in the hydrothermal method.

Acidic properties of the calcined material, MCM-22(Z), were examined on the basis of the TG/DTG curves for thermodesorption of n-butylamine as shown in Fig. 6. The activity of

a zeolite is a function of the nature, density and strength of the acid sites. The acidity of the zeolite is generated by neutralization of a negative charge of a unit cell by cations or protons. The n-butylamine is a relatively strong base, with $\text{pKb} = 3.23$, and it is commonly used to determine the total acidity, because it reacts with all acid sites on the zeolite surface. It is considered that the amine molecules enter the pores of the zeolite to interact with all the acid sites, and the number of acid sites was determined from the amount of a base required to reach the saturation point. The decomposition of n-butylamine by the medium and strong acid sites was considered.

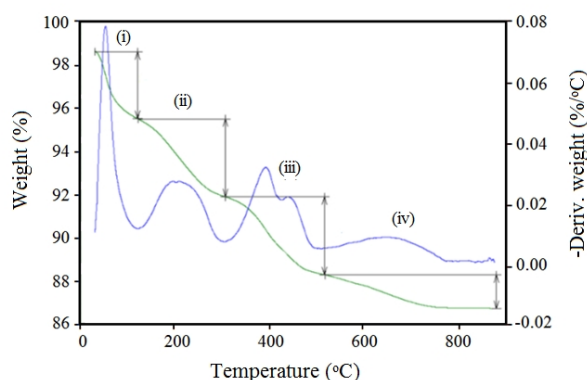
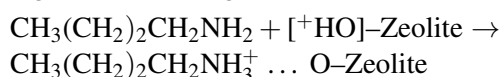
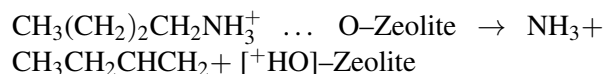


Fig. 6. TG/DTG curves for the calcined material MCM-22(Z) with adsorbed n-butylamine.

The TG/DTG curves show four weight losses in the following temperature ranges: (i) room temperature to $105\text{ }^{\circ}\text{C}$ – referring to desorption of n-butylamine physically adsorbed on the zeolite surface; (ii) 105 to $300\text{ }^{\circ}\text{C}$ – representing the medium acid sites, ca. $3.6\text{ }\%$ or 0.356 mmol g^{-1} , and (iii) from 300 to $525\text{ }^{\circ}\text{C}$ – attributed to the strong acid sites, with approximately $3.7\text{ }\%$ or 0.425 mmol g^{-1} .

During the step (ii), it is proposed that the n-butylamine molecules interact with the medium acid sites in the zeolite $[\text{H}^+\text{O}]\text{-Zeolite}$, forming the butylammonium ion on the zeolite surface. Then, this ion dissociates to butane and ammonia, according to Hoffman degradation, as follows:





At high temperatures (step (iii), where the acid sites are strong), it is proposed that primary amines were converted into diamines, $[\text{CH}_3(\text{CH}_2)_2(\text{CH}_2)]_2\text{NH}$, inside the pores of the zeolite, which is observed in the TG/DTG curves. It is suggested that the formation of diamines should occur in the bulk of the MCM-22 zeolite. However, for calculation of the total acidity of the material, it was assumed that one molecule of n-butylamine adsorbs selectively on one acid site. The last step of weight loss (iv) was related to degradation of carbonaceous residues deposited in the micropores of the material.

The zeolite consists of a three dimensional network of TO_4 tetrahedra ($\text{T}=\text{Si}$ or Al). Bronsted acids are generated when silicon with formal valence of four, is replaced by an atom of lower valence. In aluminosilicate zeolites, the most common is the replacement of Si^{4+} by Al^{3+} . The acid site is attached by a proton to the oxygen atom connected to silicon and aluminum atoms, resulting in a chemically stable bond, with oxygen becoming three coordinated (Fig. 2). The Si-O and Al-O have considerable covalency, resulting in a relatively weak OH bond. The OH stretch frequencies of the Bronsted acidic protons vary in the range of 3650 and 3550 cm^{-1} , and the silanol, Si-OH , at frequency of 3745 cm^{-1} . The frequency of approximately 1050 cm^{-1} can be assigned to the in-plane bending mode of Bronsted acidic protons

4. Conclusions

The crystalline phase of the MCM-22 was successfully obtained by the hydrothermal treatment of a reactive hydrogel of silica and alumina in presence of hexamethylenimine, under static conditions and subsequent thermal treatment of the layered precursor, MCM-22(L). This phase was identified from X-ray diffraction by the presence of the (001) and (002) peaks, which represent the lamellar structure. This material, submitted to calcination, resulted in a crystalline material, the MCM-22 zeolite, whose X-ray diffraction patterns

present a better definition in terms of characteristic peaks. The FT-IR analysis confirmed that the MCM-22(L) precursor presented all bands characteristic of a material consisting of intercalated layers of organic substances and water. Scanning electron microscopy images of MCM-22 zeolite revealed its spherical shape with ca. $10\text{ }\mu\text{m}$ in diameter. Medium and strong acid sites were evidenced in the obtained material, as determined from thermogravimetry, using n-butylamine as a molecular probe. From the acid sites density of the material, a strong/medium acidity ratio of ca. 1.2 was obtained, suggesting that the aluminosilicate MCM-22 material synthesized according to the static condition is very promising for application as catalyst in reactions that need strong acidity to proceed, such as hydrocarbon cracking, alkylation and disproportionation of aromatics.

Acknowledgements

The authors acknowledge the support from the Agência Nacional do Petróleo, Gas Natural e Biocombustíveis (ANP/PRH-25), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). One of us (MGFR) acknowledges the UFCG and PPGQUFRN for the post-doctoral fellowship.

References

- [1] LAWTON S.L., FUNG A.S., KENNEDY G.J., ALEMANY L.B., CHANG C.D., HATZIKOS G.H., LISSY D.N., RUBIN M.K., TIMKEN H.K.C., STEUERNAGEL S., WOESSNER D.E., *J. Phys. Chem.*, 100 (1996), 3788.
- [2] CORMA A., CORELL C., FERNES V., KOŁODZIEJSKI W., PEREZ-PARIENTE J., *Zeolites*, 15 (1995), 576.
- [3] DELITALA C., CADONI E., DELPIANO D., MELONI D., MELIS S., FERINO I., *Micropor. Mes.*, 110 (2008), 197.
- [4] KUMAR G.S., SARAVANAMURUGAN S., HARTMANN M., PALANICHAMY M., MURUGESAN V., *J. Mol. Catal. A-Chem.*, 272 (2007), 38.
- [5] MIHALYI R.M., LAZAR K., KOLLAR M., LONYI F., PAL-BORBELY G., SZEGEDI A., *Micropor. Mes.*, 110 (2998), 51.
- [6] AGUILAR J., PERGHER S.B.C., DETONI C., CORMA A., MELO F.V., SASTRE E., *Catal. Today*, 133 (2008), 667.
- [7] CHOI S.H., CORONAS J., LAI Z.P., YUST D., ONORATO F., TSAPATIS M., *J. Membrane Sci.*, 316 (2008), 145.
- [8] RIGOREAU J., LAFORGE S., GNEP N.S., GUISET M., *J. Catal.*, 236 (2005), 45.

- [9] FERNANDES V.J., ARAUJO A.S., FERNANDES G.J.T., *J. Therm. Anal. Calorim.*, 56 (1999), 275.
- [10] CORIOLANO A.C.F., SILVA C.G.C., COSTA M.J.F., PERGHER S.B.C., CALDEIRA V.P.S., ARAUJO A.S., *Micropor. Mes.*, 172 (2013), 206.
- [11] ARAUJO A.S., FERNANDES V.J., GIOLITO I., ZINNER L.B., *Thermochim. Acta*, 223 (1993), 129.
- [12] ARAUJO A.S., DINIZ J.C., SILVA A.O., MELO R.A.A., *J. Alloy. Compd.*, 250 (1997), 532.
- [13] JACOBS W.P.J.H., JOBIC, H., VAN WOLPUT, J.H.M.C., VAN SANTEN, R.A., *Zeolites*, 12 (1992), 315

Received 2914-07-16

Accepted 2014-11-07