

Adsorption of methanol vapor in ill-crystalized, fully crystalized and hierarchical MFI-type zeolites

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Abstract

A set of MFI-type zeolites was prepared to study the adsorption behavior of methanol in vapor phase. Among the several applications, methanol separation through adsorption process is an interesting topic due to the high-value accessible derivatives (purified methanol, hydrocarbons, olefins). Samples of ill-crystalized (IC), fully crystalized (FC) and hierarchical (HZ) MFI-type zeolites were synthesized and characterized to study the effect of mesoporosity on adsorption of methanol. Equilibrium adsorption measurements of methanol steam on MFI-type zeolites were performed using a vapor sorption analyzer. The experiments were carried out at 313.15 K and pressures from 0.7 of up to 260.0 Torr. The isotherms were fitted using Dubinin–Astakhov (D-A) model. The synthesized samples were compared in terms of adsorption capacities for methanol steam, following the descending order HZ > FC > IC. The increasing of mesopore/micropore volume ratio may improve the adsorption capacity for methanol on MFI-zeolites.

Keywords: Adsorption; Methanol; MFI-type zeolites; Hierarchical zeolites.

1. Introduction

Zeolites are minerals composed of hydrated aluminosilicates with physicochemical properties that give these materials high versatility in the chemical industry. Properties such as a well-defined crystalline structure, microporosity, acid character and high thermal and chemical stability allow their use as catalysts in numerous reactions for industrial applications [1-3]. However, one of these properties, the microporosity, presents itself as a limitation when searching the use of zeolites in reactions involving bulky organic molecules [4,5].

The use of a zeolite-based catalyst for reactions with large organic molecules is difficult, since the reagents or products may have kinetic diameters above the dimensions of the zeolite micropores causing resistance to diffusion by steric hindrance, and eventual coke formation inside the catalyst with consequent deactivation [4,6-8].

An alternative is the use of hierarchical zeolitic materials that present in their structure a

combination of micro- and mesopores obtained by pore engineering methodologies [9,10]. In these materials, the formation of mesopores can occur during the synthesis of the zeolites (bottom-up method) or post-synthesis (top-down method) [11]. The mesopores may then facilitate the formation and diffusion of hydrocarbon molecules with compatible kinetic diameters, conserving the catalytic power that is governed by the kinetics of the mass transfer of such molecules within the pores to the external medium, thus preventing the formation of coke within the catalyst and the eventual deactivation of its active sites [12,13].

In this study the adsorption behavior of methanol in MFI-type zeolites was evaluated. A set of ZSM-5 zeolites samples using ill-crystallized, fully-crystallized, and hierarchical forms was prepared and characterized. The synthesized samples were compared in terms of adsorption capacities for methanol using a vapor adsorption system.

2. Methodologies

2.1. Synthesis of the MFI-type zeolites

The zeolite samples were synthesized based on the method described in the Verified Syntheses of Zeolitic Materials [14] and modified by Silva *et al.* [11], using tumbling at 60 rpm for 15h or 24 h. The desilication procedure was carried out based on the method optimized by Possato *et al.* [15]. The H-form samples were obtained after three consecutive ion-exchange steps using a 0.1 mol.L⁻¹ NH₄NO₃ solution, followed by washing and centrifugation. After that, the samples were calcined in air at 400 °C under a heating rate of 10 °C.min⁻¹ for 3 h.

A set of MFI-type zeolites samples was synthesized and labeled as ill-crystallized (IC), fully-crystallized (FC), and hierarchical zeolite (HZ). The IC sample was obtained by interrupting the crystallization step at 15 h, before reaching the time for total crystallinity (24 h) which the sample is named FC. This fully-grown Na-form zeolite (FC) was then mixed with a 0.2 mol.L⁻¹ NaOH solution (with an OH-/Si mole ratio of 0.8) for 1 h to obtain the hierarchical form, labeled as HZ sample.

2.2. Characterization of samples

Powder X-ray diffraction patterns for fresh and spent catalysts were collected on Rigaku Miniflex 600 diffractometer using Cu K α radiation (40 kV, 15 mA). The X-ray diffractograms were recorded from 5 to 50° with a step of 0.02°. The patterns were analyzed by Rietveld refinement using TOPAS software to obtain the degree of crystallinity (%), the crystallite size (nm), and the unit cell parameters (a, b, c, and volume).

Nitrogen isotherms for fresh and spent catalysts were obtained at 77 K using an ASAP 2420 system (Micromeritics). The samples (~0.200 g) were pretreated for 12 h under vacuum at 350 °C and 80 °C, respectively. The t-plot method calculates the micropore volume and the surface area. The mesopore volume was estimated by the difference between the micropore and the total volume at P/P₀ = 0.98. The adsorption branch was used to calculate pore size distribution (PSD) by the Barrett-Joyner-Halenda (BJH) method since the Tensile Strength Effect of the adsorbate causes the artifact at circa 4 nm when PSD is calculated from the desorption curve [16].

2.3. Equilibrium measurements

The measurements were performed in a manometric vapor adsorption system V Star Quantachrome (Anton Paar). In this system (Fig. 1), the control of the manifold temperature from the vapor source to the sample reduces the possibility of local condensation of the sorbate and guarantees accurate analysis. Prior to each adsorption measurement, the sample was outgassed under ultrahigh vacuum conditions at 150°C for 2 h, and at 300°C for 12h. Methanol adsorption/desorption isotherms and kinetic data were obtained at 40°C.

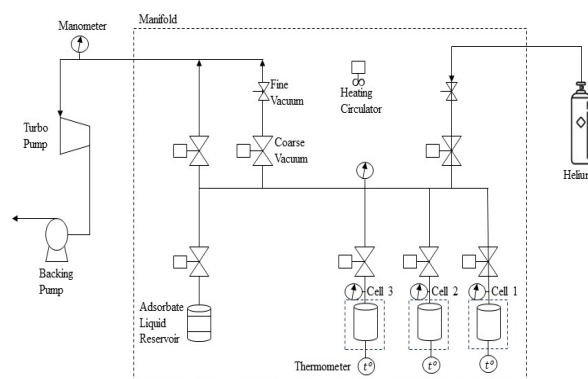


Figure 1. Schematic diagram of the vapor adsorption system.

3. Results and discussions

3.1. Characterization of samples

X-ray diffractograms in Figure 2 and the corresponding Rietveld refinements confirmed that no other crystalline phases were formed, and no amorphous residues were left in the FC sample (Fig. 2b). In turn, the IC sample (Fig. 2a) had a crystallinity of 73 %, corresponding to a partially crystallized ZSM-5 zeolite, as presented by Silva *et al.* [11]. Furthermore, the alkaline treatment for desilication of the FC sample did not lead to loss of the MFI structure (Rietveld refinement, Fig. 2c). It showed only a subtle decrease in the intensities relative to the prominent XDR peaks of the structure without modification in the degree of crystallinity (%) and the unit cell parameters.

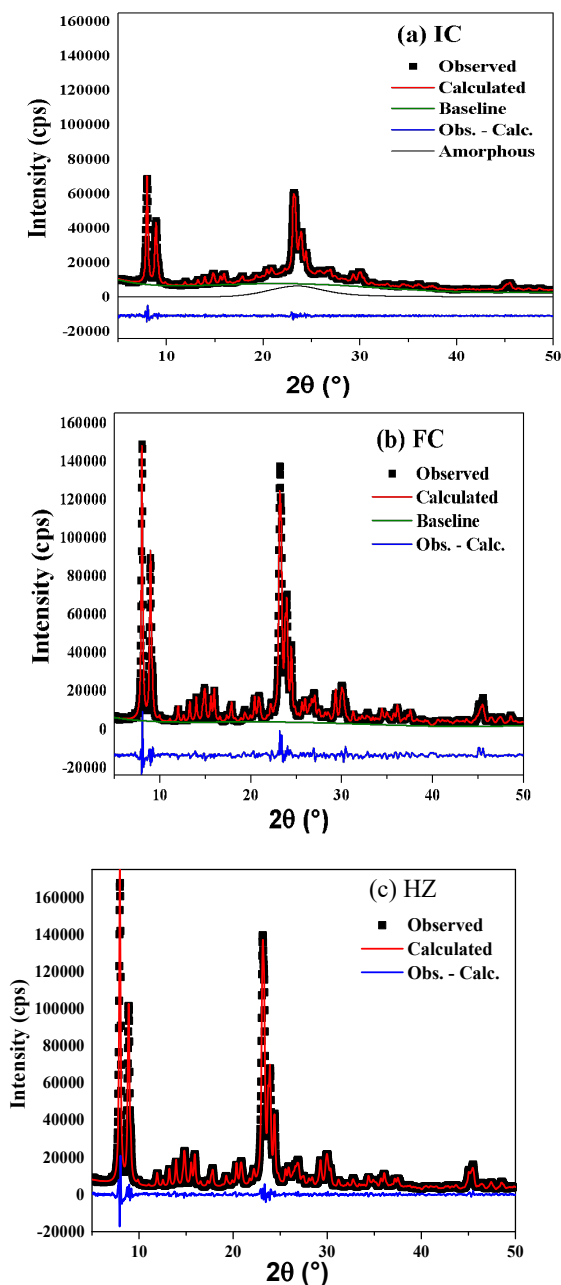


Figure 2. XRD patterns and Rietveld refinements of synthesized samples: (a) IC; (b) FC; (c) HZ; The net results of the Rietveld analyses are shown in red, and the deviations from the measured diffractograms are depicted in blue.

The IC and FC samples had type I nitrogen isotherms at 77 K (Fig. 3), typical of microporous materials. At the same time, hierarchical zeolite (HZ Sample) exhibited the combination of

isotherms of type I and IV, characteristic of micro-mesoporous structures, and a type H4 hysteresis loop, which corresponds to mesopores filling and evacuation of pores subjected to capillary condensation [17]. The external area in Table 1 was calculated through the *t*-plot method. From ill-crystallized (IC) to fully-crystallized zeolite (FC) catalysts, both external area and micropore volume (also in Table 1) increased with crystallization time because of the gradual formation of the microporous structure while the zeolite crystallized.

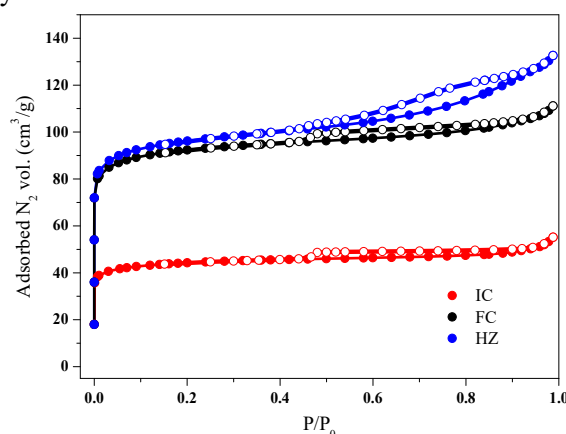


Figure 3. Adsorption (filled) and desorption (open) nitrogen isotherms at 77K.

The pore-size distribution patterns (Fig. 4), estimated by the Barrett Joyner Halenda (BJH) method, revealed mesopores in the hierarchical ZSM-5 zeolites with an average diameter of about 11 nm.

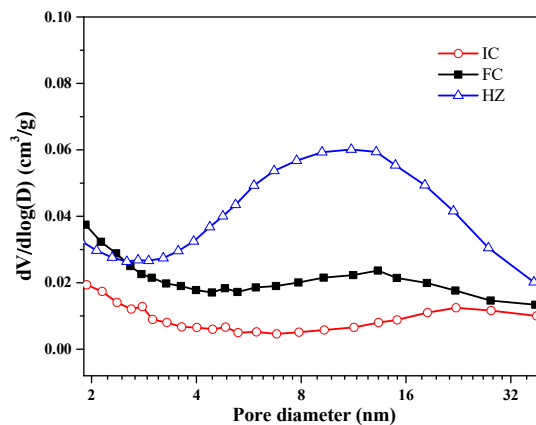


Figure 4. Pore size distributions calculated from the adsorption branch using BJH method.

Upon alkaline treatment, the desilication boosted the surface area, which is related to smaller particles after post-synthesis treatments and mesopore formation. In addition, the hysteresis loop became slightly more distinct, indicating a growing number of mesopores.

Table 1. Textural properties of samples.

Samples	Surface Area (m ² /g)	Micropore vol. (mL/g)	Mesopore vol. (mL/g)	Total pore vol. (mL/g)
IC	139.3	0.066	0.019	0.085
FC	291.1	0.136	0.036	0.172
HZ	304.3	0.132	0.072	0.204

3.2. Equilibrium data

As depicted in Figure 5, at 313.15 K, the adsorption isotherms of methanol may be classified as a combination of types I and II, which means a typical micropore filling at very low P/P_0 region, followed by a middle almost linear section governed by the accessible micropore volume, and then an additional upward curvature as the P/P_0 trends to 1, likely related to multilayer adsorption [18]. Besides, the equilibrium adsorption capability for methanol followed the same pattern observed in their nitrogen isotherms (Fig. 3). In other words, HZ and FC samples obtained a higher adsorbed amount of methanol when compared to IC throughout the pressure range studied. This situation was expected since the total pore volume and surface area have presented the same decreasing order: $HZ > FC > IC$ (Table 2). Numerically, the maximum adsorbed methanol amount for HZ was 4.82 mmol/g, followed by FC and IC with 4.16 mmol/g and 2.77 mmol/g, respectively. The HZ and FC samples had a similar behavior from the beginning of the experiment until $P/P_0 \approx 0.8$, when HZ adsorption presented an abrupt growth promoted by the formation of the mesopores or simultaneous occurrences of multilayer adsorption or capillary condensation

[15,19]. Indeed, as reported in Table 1, the mesoporous volume increased as the micropores collapsed due to the alkaline treatment [15].

Regarding the desorption process, all samples presented a noticeable difference between the adsorption and desorption branches, mainly under high relative pressure. This hysteresis, classified as type H4 [18], is more pronounced in HZ and FC and may be related to their mesoporous volume and surface area.

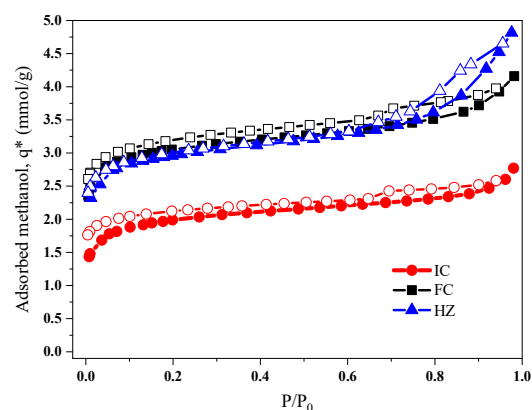


Figure 5. Methanol isotherms for IC, FC, and HZ samples at 40°C. Filled and hollow symbols represent adsorption and desorption branches, respectively.

Table 2. Parameters for Dubinin-Astakhov isotherms of methanol vapor on samples.

Samples	V_0	E , kJ/mol	n	R^2
IC	0.0962	10.15	1.03	0.999
FC	0.1441	13.79	1.00	0.998
HZ	0.1447	11.52	1.00	0.993

As observed in Table 2, which contains the D-A model parameters, the FC sample showed the highest characteristic energy (E), followed by HZ and then IC, with values of 13.79, 11.52, and 10.15 kJ/mol, respectively. These values are similar to the ones reported for the methanol adsorption in other zeolites [18].

4. Conclusion

Samples of MFI-type zeolites were prepared and characterized in this study aiming to evaluate the influence of the mesoporosity on the adsorption of methanol. The results showed that the vapor methanol adsorption has a direct relationship with structural and textural properties of these adsorbents. Among the MFI-type zeolites studied, the HZ sample presented the higher methanol adsorption capacity, followed by FC and IC samples, which suggests that the mesopore/micropore volume has an important role in this process. The H4-type hysteresis observed in HZ and FC samples may be also related to the mesoporous volume. Then, the isotherms were fitted using the D-A model to observe how the samples matched with a model based on the volume filling of micropores.

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