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CO_2 adsorption in different mesoporous ZSM-5 zeolites prepared with biomass

The adsorption of CO_2 over porous materials seems to be the best solution to reduce the emissions of this gas into the atmosphere, that has been steadily increasing in the past few decades. With this process, it is possible to both adsorb the excess of CO_2 present in the atmosphere as well as adsorbing CO_2 from industrial wastes to avoid its emission. This can be achieved using different materials, such as amine-based compounds, activated carbons and zeolites. Moreover, the waste of biomass industry is also a concern among scientists, due to possible contamination of soils and water reservoirs. In this way, we present herein a comparative study of CO_2 adsorption over different types of mesoporous zeolites prepared in the presence of biomass using post-treatment methods. The biomass selected was lignin from Russian wood waste, and its treated form (oxidized lignin). In this way, both CO_2 and biomass waste are valorized, providing solutions for these two problems. The influence of the synthesis procedure in the zeolite crystallinity, type of pore created, and adsorption capacity was investigated. It was observed a constant crystallinity even when mesopores were created in the zeolite structure. Moreover, it was also observed an increased performance in the adsorption process when high mesopores size was present. By comparing these results with pristine commercial zeolite, we aim to provide useful insights on the factors that may influence the CO_2 adsorption capacity over zeolites. With this new information, it may be possible to provide further strategies for adjusting their properties to obtain the better outcome of the process.

Keywords: *CO_2 adsorption, zeolite, mesoporous zeolites, hierarchical porosity, adsorption capacity.*

Introduction

The incessant release of CO_2 in the atmosphere has already started to influence the world as we know. The increased number of floods, droughts, hurricanes, deicing of the polar calottes, among other disasters, have been attributed to the increase of the global temperature caused by an increased concentration of CO_2 in the atmosphere [1–3].

With the continuous use of industries and processes that emit this gas, scientists have started to worry about the future of our planet. With that in mind, several researchers have devoted their studies into strategies to adsorb CO_2 into materials that can be then easily desorbed and converted. Among those, amine-based scrubbing remains the most mature technology currently applied in industry [4–6]. However, this process is associated to high implementation costs and hazardous by-products, being necessary to develop alternative methods for adsorption of CO_2. Several authors have proposed the use of layered double hydroxides, a family of hydrotalcites compounds, as a material with high performance at both low and high temperatures [7–10]. On the other side, porous carbons materials have proven to be highly competitive to other compounds due to their tunable pore and surface textures, moderate heat of adsorption, and less sensitivity to the presence of water in the gas stream [11–13]. Recently, manifold researchers have reported the use of zeolites for this purpose. Several studies showed a great potential towards these materials due to their capture capacity, low regeneration temperatures and high stability overall several adsorption-desorption cycles [14–17]. In a previous work of our group [18], it was verified that the creation of mesopores by simple desilication treatment did not enhance the capacity, although it was observed an influence concerning the type of cation used and the concentration of Al-atoms in the framework.

Inspired by this and other works of the group Louis et al. that valorise the use of biomass in the synthesis of zeolites [19–21], we present a strategy to introduce mesopores on the zeolite structure by recrystallization of the framework in the presence of biomass. The type of biomass studied was lignin and the oxidized form of lignin with functional groups capable to interact with the zeolite structure. These new materials were tested in the CO_2 adsorption, and we aim to give insights on the influence of the type of mesoporosity in CO_2 capture.

Experimental

Preparation of the samples

Commercial ZSM-5 zeolite (CBV3020E, Si/Al = 15, Zeolyst), herein named Z0, was submitted to several treatments for the creation of additional porosity. The typical procedure consisted in the mix of 300 mg of catalyst with 30 mL of 0.1 M of NH_4OH (ammonium hydroxide) for 10 min at room temperature. Then 0.1 g of oxidised lignin (LO) or lignin (L) was added to the previous solution and mixed for 5 min. The gels were, then, transferred to an autoclave and placed in an oven at 150°C for 10h. The samples were named Z1-LO and Z1-L, respectively to samples prepared with oxidised lignin and lignin. Both types of biomass were kindly provided by the Department of Chemistry of the Saint-Petersburg State University.

A third sample named Z2-LO was first submitted to a pre-treatment with 15 mL of 0.2 M of NaOH at 65°C for 30 min. The powder was filtrated, washed, dried, and mixed with 30 mL of 0.1 M of TEAOH (tetraethylammonium hydroxide) for 10 min at room temperature. 0.1 g of LO was later added for 5 min, and the gel was transferred to an autoclave at 150°C for 10h.

All the samples were filtrated, washed, dried, and calcined at 550°C for 15h, with a heating ramp of 1h to eliminate the biomass and to obtain the sodium-form of the catalysts.

Characterization

Powder X-ray diffraction (XRD) patterns of zeolites were acquired using a Bruker D8 (Cu Kα) diffractometer operated at 40 kV and 40 mA. XRD patterns were recorded in the 2θ = 5–60° range with a step size of 0.05°. SEM images were acquired in a JEOL FEG-6700F microscope working at a 9 kV accelerating voltage. The textural properties were analyzed by means of nitrogen physisorption using Micromeritics ASAP 2420 equipment. Samples were pre-treated *in-situ* at 200°C under vacuum prior to the analyses. Surface areas were determined using the BET method and pore size distributions were obtained using the adsorption branch of the isotherms (BJH method).

Adsorption of CO_2

Thermogravimetric sorption of CO_2 on zeolites was measured using a TGA analyzer (Q500 TA Instrument). All solids were first calcined in a muffle furnace at a temperature comprised between 400 and 600ºC for 5 h, before transferring the samples to the TGA analyzer. To avoid any error, the test was done immediately after the first calcination. Finally, the samples were further calcined *in situ* for 1 h in N_2 prior to the measurement. CO_2 adsorption experiments were carried out at 1 atm with a constant flow of CO_2 (40 mL min^{-1}) at 35°C.

Results and discussion

Textural properties

Fig. 1 shows the diffraction patterns of the samples prepared. Z0, the pristine commercial zeolite, exhibits peaks typically associated to MFI structure. It is also observed a high crystallinity, and a pure phase. Upon treatment and recrystallization, it seems there is some loss of crystallinity. This has been previously reported and considered quite common, since the zeolite was subjected to a partial dissolution of its framework to originate additional pores [22, 23]. Once can also conclude that the recrystallization step was not totally efficient in the recrystallization of the zeolite structure.

In general, the samples prepared with oxidised lignin exhibit lower crystallinity than the one prepared with sole lignin. Also, the process involving two steps, case of Z2-LO, reduces considerably this parameter.

To verify the efficiency of these processes in the creation of additional porosity, nitrogen adsorption-desorption was performed on the samples. Fig. 2 shows Type I isotherms of nitrogen physisorption for the samples Z0, Z1-LO and Z1-L with an associated H4 hysteresis loop. This is typical of microporous materials such as zeolites. The loop describes the behaviour of a wide range of narrow slit-like nanopores [24]. However, for the samples Z2-LO, although the isotherm can be attributed to a Type I, the hysteresis loop describes the presence of mesopores.

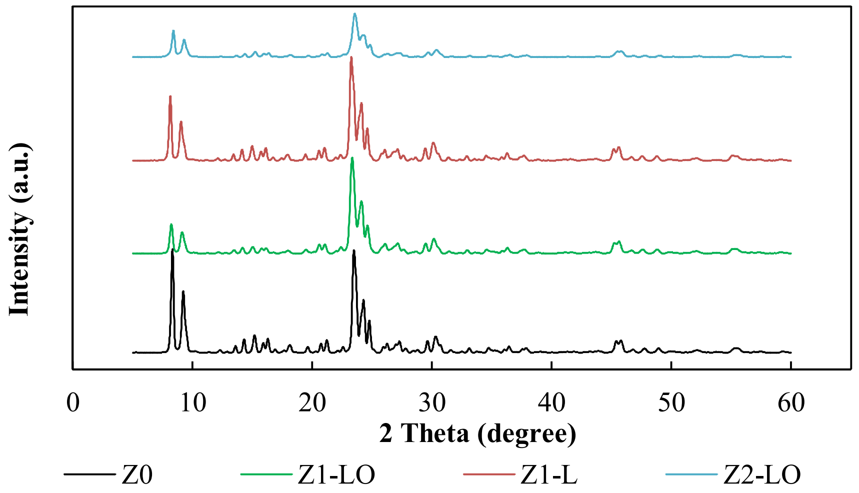

Fig. 1. XRD patterns of the pristine zeolite and mesoporous samples

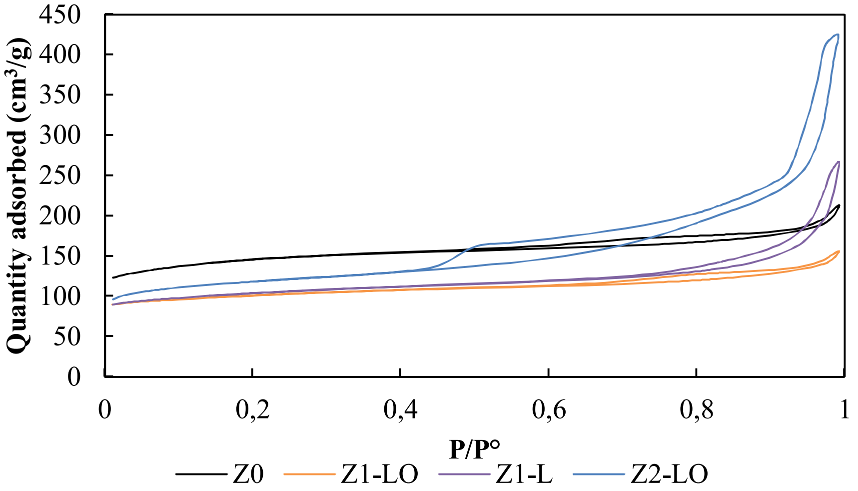

Fig. 2. Isotherms of N_2 adsorption-desorption of the samples in study

The pore profile obtained by the BJH method is present in Fig. 3. Z0 exhibits pores around 3.5 and 6.5 nm that are associated to intercrystalline mesopores, commonly present in nanocrystals. For Z1-LO, the peak at 3.5 nm is maintained while the second peak is shifted to 7.5 nm, suggesting that the use of oxidised lignin in the first method allowed a slight increase of the pore size. Similarly, Z1-L exhibits characteristic pores around 3.5 nm, but two additional pore sizes appear: 12 and 51 nm. It seems that the post-treatment was successful in the creation of mesopores in the zeolite. This was also observed to Z2-LO with a peak around 13 and 32 nm, although in this case a very evident peak at 3.5 nm is observed. It seems that the last method with oxidised lignin creates mesopores maintaining the microporous structure of the zeolite intact unlike the other samples.

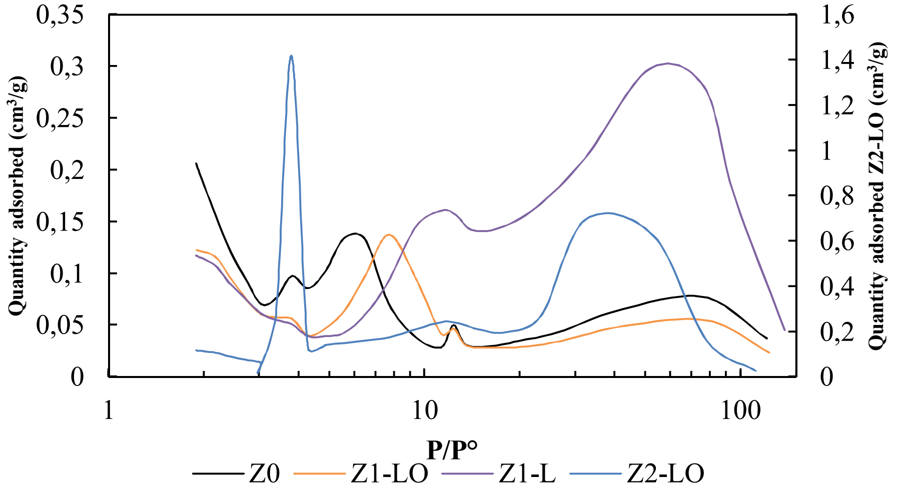

Fig. 3. BJH pore profile of the samples in study

To summarize the results obtained by nitrogen adsorption-desorption, the main parameters are present in Table. All the samples had a reduction of the specific and external surface area relatively to pristine zeolite, due to the creation of additional mesopores. However, the microporous structure seems to further decrease for Z2-LO, the sample with higher nitrogen intake, that can be associated to higher amount of mesopores present in the structure. In fact, the determined pore volume is the highest of all samples, although they suffered a reduction of the microporous volume relatively to Z0. This has been observed in previous studies, that suggest the dissolution of the framework by treatment with a base destroys partially the micropores. For Z1-LO this meant a large loss of pore volume, which may indicate that the recrystallization step was not efficient, and so the dissolved zeolite structure did not recrystallize.

Specific surface area (S_{BET}), external surface area (S_{ext}), microporous surface area (S_{micro}), total pore volume (V_{pore}) and microporous volume (V_{micro}) of the samples in study obtained by N_2 adsorption-desorption

Sample	S_{BET} (m²/g)	S_{ext} (m²/g)	S_{micro} (m²/g)	V_{pore} (cm³/g)	V_{micro} (cm³/g)
Z0	479	181	298	0.30	0.15
Z1-LO	331	108	222	0.22	0.11
Z1-L	341	127	214	0.37	0.11
Z2-LO	391	162	229	0.47	0.11

SEM image in Fig. 4, *A* show the nanocrystals of the commercial zeolite Z0, proving the presence of pores around 3.5 and 6.5 nm associated to intercrystalline mesoporosity. Upon treatment, these crystals seem to be partially destroyed which justifies the decrease of crystallinity. It is also visible some mesopores in the majority of these crystals, that were created by the dissolution and further recrystallization of the framework in the presence of biomass.

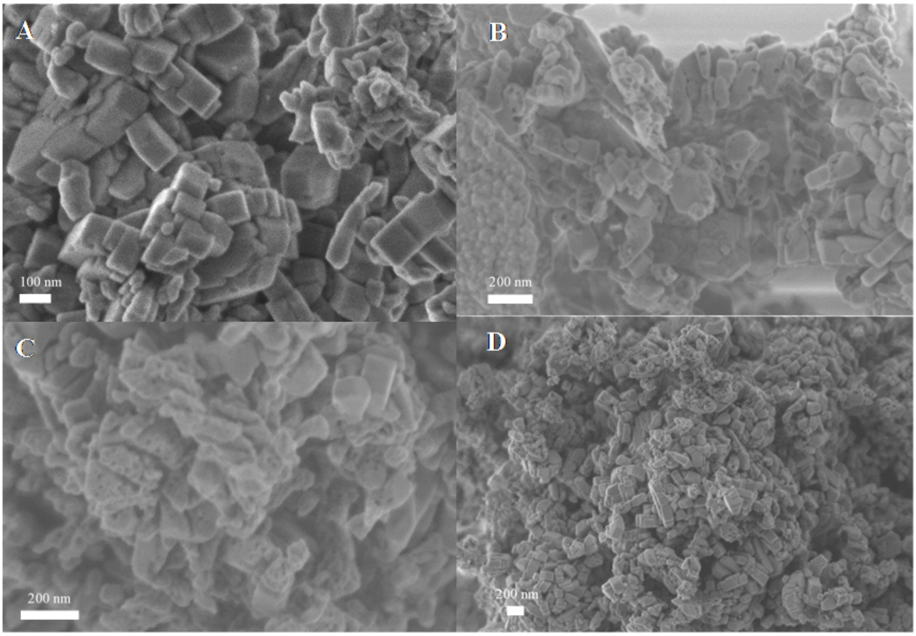

Fig. 4. SEM images of as-synthesised samples: *A* – Z0; *B* – Z1-LO; *C* – Z1-L; *D* – Z2-LO

CO_2 adsorption

In the previous section, it was verified the creation of additional porosity in the ZSM-5 zeolite by different methods and by different types of biomass. As mentioned earlier in this paper, it is our aim to investigate the influence of mesopores in the adsorption of CO_2. The results are present in Fig. 5.

The capacities obtained for Z0, Z1-LO, Z1-L and Z2-LO were 0.76, 0.69, 0.73 and 0.94 mmol/g, respectively. It is observed an initial fast (around 1 min) CO_2 uptake since this molecule does not present diffusional constrains. Then, there is a diffusional control effect which is translated by a slow CO_2 uptake. This process may be associated to physisorption between CO_2 molecules and not interactions between active sites and molecules. The samples Z1-LO and Z1-L had a decrease of CO_2 adsorption capacity comparing with Z0 leading to the conclusion that the presence of mesopores little influences this phenomenon. However, this was not the case for Z2-LO.

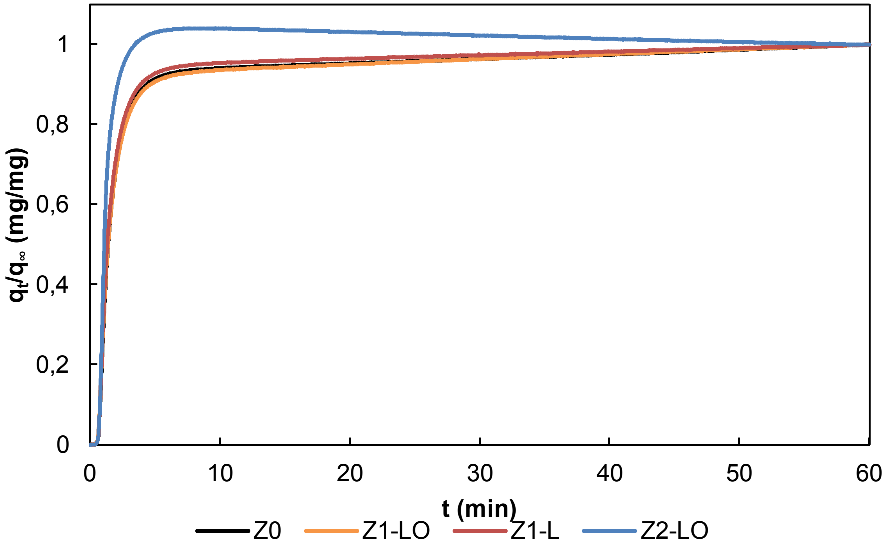

Fig. 5. CO_2 adsorption curves of the samples (y axis as quantity of CO_2 adsorbed at determined time t divided by the quantity of CO_2 adsorbed at the saturation point). Closer look into the near saturation moment

This samples presents two interesting observations: a quick CO_2 adsorption followed by a slower weight decrease until it reaches saturation; and higher adsorption capacity than Z0. The first indicates that lower diffusional constrains allows the uptake of a higher amount of CO_2, however a small fraction of these molecules are weakly adsorbed on the zeolite surface, leading to their desorption with the continuous passage of flow. This was also observed by C. Megías-Sayago et al. [18] when studying CO_2 adsorption in zeolites and layered double hydroxide materials. The higher capacity can be attributed to a higher pore volume that was not present in the remaining samples. By having more space in the zeolite surface, the molecules are capable to interact between each other, by physisorption phenomenon, creating layers of adsorbed CO_2 molecules. Also, it seems that lower crystallinity does not affect this parameter.

Conclusion

The synthesis of mesoporous zeolites by post-treatment methods was successfully achieved. By dissolution of the zeolite framework with a base and recrystallization in the presence of biomass, it was possible to create additional porosity in the zeolite structure. It was also assessed that the type of method and biomass used led to different final characteristics, in terms of crystallinity and textural properties. The influence of these parameters was investigated in CO_2 adsorption. It was observed that only one sample presented higher performance than pristine zeolite, which was related to lower diffusional constrains upon the initial uptake of CO_2 molecules. Higher pores on the zeolite structure allowed the formation of additional CO_2 adsorbed layers, increasing its adsorption capacity.

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