

MS30-2-4 In situ characterizations of the selective CO₂ adsorption in free-template nanosized zeolites RHO and CHA

#MS30-2-4

N. Barrier¹, M. Debost¹, J. Grand², P. Boullay¹, E. Clatworthy³, A. Päcklar¹, P. Klar⁴, P. Brázda⁴, N. Nesterenko², J.P. Dath², J.P. Gilson³, L. Palatinus⁴, S. Mintova³

¹Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire de Cristallographie et Science des Matériaux (CRISMAT) - Caen (France), ²Total Research and Technologies, Feluy - Seneffe (Belgium), ³Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS) - Caen (France), ⁴Institute of Physics of the Czech Academy of Sciences - Prague (Czech Republic)

Abstract

Natural gas is a mixture of hydrocarbon gas, mostly containing methane, used as a fossil fuel or source of carbon chain compounds. During one of the natural gas processing steps, methane (CH₄) must be separated from CO₂. One of the methods is to use materials with high adsorption and selectivity as separating membranes. Of the porous materials used as membranes, reduced pore cage type zeolites such as RHO or CHA are very good candidates. Indeed, these porous materials have narrow pores connecting large cages, whose access can be blocked or reduced by the cations (Cs, Li, Na,...) present in their networks. This is the trap-door effect, which gives the material increased selectivity. For example, CO₂ being less voluminous than CH₄, it will have easier access to these pockets.

The influence of different cations has been studied by many research groups.[1] It has a direct impact on the hydrothermal stability of these zeolites. These studies also attributed the high selectivity to the high surface polarity of zeolite RHO, which favours interactions with polar molecules such as CO₂. In addition, it has been found that the high absorption of CO₂ is due to the high pore volume of this zeolite, and not caused by the repositioning of the cations. The increase in the pore volume can be obtained by the synthesis of nanoscale RHO and CHA zeolites, but all the previous studies of the trap-door effect have been carried out on micrometric zeolites.

In this presentation, we will show our results on the CO₂ adsorption/desorption process followed in situ by X-ray (synchrotron and laboratory), neutron and 3D electron diffraction technics. Different free-template CHA [2] and RHO [3] zeolites based on caesium, potassium and sodium whose crystallite sizes vary from 50 to 300 nm have been studied. Our study demonstrates how the cationic distributions in the zeolite framework, or the flexibility of the framework itself influence the CO₂ adsorption-desorption process.

References

[1] (a) M. M. Lozinska, E. Mangano, J. P. S. Mowat, A. M. Sheperd, R. F. Howe, S. P. Thomson, J. E. Parker, S. Brandani, P. A. Wright, *J. Am. Chem. Soc.* 134, 17628 (2012); (b) Y. Lee, J. A. Hriljac, T. Vogt, J. B. Parise, M. J. Edmonson, P. A. Anderson, D. R. Corbin, T. Nagai, *J. Am. Chem. Soc.* 123, 8418 (2001); (c) T. Nenoff, J. B. Parise, G. A. Jones, L. G. Galya, D. R. Corbin, G. D. Stucky, *J. Phys. Chem.* 100, 14256 (1996); (d) J. B. Parise, D. E. Cox, *J. Phys. Chem.* 88, 1635 (1984).

[2] Debost, M.; Klar, P. B.; Barrier, N.; Clatworthy, E. B.; Grand, J.; Laine, F.; Brazda, P.; Palatinus, L.; Nesterenko, N.; Boullay, P.; Mintova, S. Synthesis of Discrete CHA Zeolite Nanocrystals without Organic Templates for Selective CO₂ Capture. *Angew. Chem.-Int. Edit.* 2020, 59 (52), 23491–23495.

[3] Grand, J.; Barrier, N.; Debost, M.; Clatworthy, E. B.; Laine, F.; Boullay, P.; Nesterenko, N.; Dath, J.-P.; Gilson, J.-P.; Mintova, S. Flexible Template-Free RHO Nanosized Zeolite for Selective CO₂ Adsorption. *Chem. Mat.* 2020, 32 (14), 5985–5993.

The trap-door effect for a Cs-RHO zeolite allowing

