Experimental report

01/03/2019

Proposal: 5-23-690 **Council:** 10/2016

Title: CO2 capture on Zeolite A and ZK4with various non-framework cation compositions

Research area: Materials

This proposal is a new proposal

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Samples: K1.6Na5.7Si16.7Al7.3O48
K8.4Na3.6Si12Al12O48
K7.3Si16.7Al.7.3O48
K3.3Na4Si16.7Al7.3O48
K5Na7Si12Al12O48
K4Na8Si12Al12O48

Instrument	Requested days	Allocated days	From	To
D1B	6	6	13/03/2018	19/03/2018
D20	6	0		

Abstract:

In this project, we would like to use the neutron powder diffraction (NPD) technique for studying different compositions of zeolites |NaK|-A and |K|-ZK4 to further quantify the changes in the crystal structures upon adsorption of CO2 sorption. We expect to determine the cation positions in the zeolites and their changes caused by adsorption of CO2.Since neutrons are more sensitive for C (b=6.65 fm) and O (b=5.81 fm) as compared with XRD, we also expect to localize the CO2 molecules in the framework. Ion-exchanged zeolites play a potentially important role in the capture of greenhouse gases (e.g. CO2) and for the upgrading of biogas and natural gas.

Experimental Report for 5-23-690

CO_2 capture on Zeolite A and ZK4 with various non-framework cation compositions

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Zeolite A is known for its potential application for CO_2 capture [1]. In this report we present results of the neutron powder diffraction (NPD) experiment concerning in-situ measurements of the structural changes during CO_2 adsorption in zeolite $|Na_{12-x}K_x|$-A. In particular we were interested in what positions in the zeolite framework are occupied by the adsorbed CO_2 molecules. The results of this experiment were published in Ref. [2].

The NPD experiment was performed on the D1B instrument with a constant wavelength of 2.52 Å and in the range of 2θ: 3 - 120°. Prior to the diffraction measurements the dehydrated samples with different *x* values were loaded and sealed in aluminum containers in a glovebox under a helium atmosphere and mounted to a gas stick. The gas stick was connected to the CO_2 gas-dosing system and placed in the neutron beam. The samples were measured at vacuum, 50, 100, 400, 700 and 1000 mbar of CO_2. The NPD data was analyzed using the Rietveld method [3] and the Topas 5 program [4].

The initial structural model was taken from Ref. [4]. Figure 1 shows an example of the fit of the model to the NPD data for $x = 3$ for the dehydrated sample (a) and after loading of CO_2 at 1000 mbar. From the data analysis, we observe three different positions of adsorbed CO_2 molecules within the large α-cavities in the zeolite structure. Site I of physisorbed CO_2 bridged two cations at neighboring 8-rings and was pulled by Na^+ at 6-ring. This site was filling up most of the capacity of the α-cavities.

The CO_2 molecules at site II are coordinated to a cation in the 8-ring. However, the position differed significantly if the 8-ring site contained Na^+ or K^+. Small Na^+ coordinated the CO_2 molecules near the center of the 8-ring plane whereas large K^+ pushed them away towards the

center of α-cage. 35% of the CO_2 adsorbed on the 8-ring was chemisorbed and formed chemical bonds with the oxygen atoms of the framework as carbonate-like species. Chemisorbed CO_2 as well as different positioning of physisorbed CO_2 were also confirmed by *in situ* infrared spectroscopy. The detected site III was directly attracted by Na^+ at 6-ring, however its occupancy was very low.

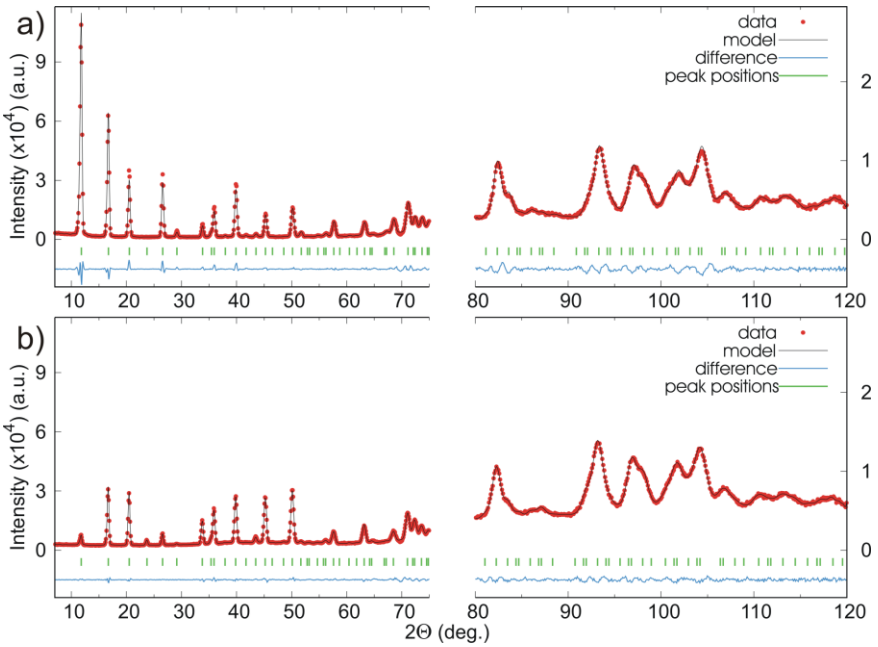

Figure 1: Model fitting to the diffraction data for $|Na_{12-x}K_x|$-A with $x = 3$, for the dehydrated sample (a) and after CO_2 loading at 1000 mbar (b). After [2].

References

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[2] P. Rzepka, Z. Bacsik, S. Smeets, T. Hansen, N. Hedin, D. Wardecki, (2018) *J. Phys. Chem. C*, 122, pp. 27005 – 27015.

[3] H. M. Rietveld (1969) *J. Appl. Crystallogr.*, 2, pp. 65-71.

[4] A.A. Coelho, (2018) *Journal of Applied Crystallography*, 51 (1), pp. 210-218.