MS30 Advanced porous materials : MOFs, COFs, SOFs....and what else?

MS30-03

A combined experimental and theoretical approach to interpret the anomalous thermal behaviour of Pb-exchanged zeolite (STI)

G. Cametti [1], D. Roos [1], S.V. Churakov [2], D. Prieur [3], A.C. Scheinost [3]

[1]Institute of Geological Sciences, Baltzerstrasse 1+3, 3012 - Bern (Switzerland), [2]Paul Scherrer Institut, Forschungstrasse 111, 5232 - Villigen (Switzerland), [3]The Rossendorf Beamline at the European Synchrotron Radiation Facility (ESRF), Avenue des Martyrs 71, 38043 - Grenoble (France)

Abstract

Pb-exchanged zeolites are of interest because of their applications in environmental-related issues and in industrial processes. The thermal stability of these materials is an important aspect to consider if the retaining capacity of the incorporated heavy metals has to be assessed. In our recent study, we characterized and determined the crystal structure of a natural zeolite stellerite (with **STI** framework type), exchanged with Pb^{2+} [1] and we further investigated its thermal behaviour as a function of increasing temperature [2]. It was found that Pb-STI showed an anomalous thermal behaviour with respect to the natural counterpart and the other metal-exchanged zeolites with **STI** framework type [3]. In particular, after an initial contraction of the unit-cell volume (-3.5%), accompanied by dehydration, the framework expands (+2%) and adopts a structural topology equivalent to that observed at room temperature. Thus, in contrast to natural stellerite and to the Cd-, Ag-, and Na- exchanged forms [4,5] no breaking of the tetrahedral bonds is observed upon heating and, most important, the thermal stability significantly increased.

The interpretation of the mechanism, which leads to the change from negative to positive thermal expansion during the dehydration process, is still unclear and complicated by: i) the occurrence of different extraframework (EF) species (i.e. Pb^{2+}, $Pb(OH)^{+}$ and H_2O), and ii) their severe disorder within the voids. In this contribution, different hypotheses and eventual reactions occurring upon heating were experimentally and theoretically tested to shed light on the observed anomalous dehydration behaviour.

The following scenario were considered: i) dehydration of the structure, i.e. loss of H_2O without any further reaction. ii) dehydration accompanied by hydrolysis of the water molecules according to the reaction $H_2O \rightleftharpoons OH^- + H^+$ [6]. iii) loss of H_2O and subsequent formation of Pbx(OH)x or PbxOx clusters. iv) oxidation of Pb^{2+} in Pb^{4+}, according to the reaction $Pb^{2+} + 2\,H_2O \rightleftharpoons Pb^{4+} + 2OH^- + H_2(g)$ [7].

The best agreement between experimental data and theoretical predictions was observed for models iii) and iv). However, we did not have any experimental evidence of Pb oxidation. The Pb-L3 XANES spectra of Pb-stellerite collected from 25 to 400°C showed the expected increase of thermal disorder with increasing temperature, but no change of local symmetry or oxidation state during the dehydration process. For model (iv), the formation of different kind of clusters ($Pb_2(OH)_2$, Pb_2O_2, $Pb_4(OH)_4$, etc.) was tested. The best agreement between model and observation corresponds to a structure with 33% of Pb forming $Pb_4(OH)_4$ clusters, located inside the bigger cavity of stellerite (Fig. 1).

References

[1] Roos, D., Scheinost, A. C., Churakov, S. V., Nagashima, M., Cametti, G. (2021) On the nature of Pb species in Pb-exchanged zeolite stellerite (STI): a combined experimental and theoretical study. Microporous and Mesoporous Materials, 327, 111444.

[2] Roos, D. (2021) Crystal structure and thermal stability of STI and LEV zeolites after Pb^{2+} incorporation. Master Thesis, University of Bern, Switzerland, 59 pp.

[3] Arletti, R., Mazzucato, E. Vezzalini, G. (2006) Influence of dehydration kinetics on T-O-T bridge breaking in zeolites with framework type STI: The case of stellerite. American Mineralogist, 91, 628-634.

[4] Cametti, G., Scheinost, A.C., Giordani, M. Churakov, S.V. (2019) Framework modifications and dehydration path of a Ag^+-modified zeolite with STI framework type. Journal of Physical Chemistry C, 123, 13651-13663.

[5] Cametti, G., Scheinost, A. C., Churakov, S. V. (2019) Structural modifications and thermal stability of Cd^{2+}-exchanged stellerite, a zeolite with STI framework type. Journal of Physical Chemistry C, 123, 25236-25245.

[6] Albuquerque, R. Q., Calzaferri, G. (2007) Proton activity inside the channels of zeolite L. Chemistry a European Journal, 13, 8939-8952.

[7] Ronay, C., Seff, K. (1985) Crystal structure of Pb_6-A and $Pb_9(OH)_8(H_2O)_3$-A. Zeolite A ion exchanged with Pb_{2+} at pH 4.3 and 6.0 and evacuated. Journal of Physical Chemistry, 89, 1965-1970.

Fragment of the simulated Pb-STI structure showing