Tuning thermal expansion and mechanical properties by high pressure insertion of guest molecules

Frederico ALABARSE (Elettra Sincrotrone Trieste, IT),
Benoît BAPTISTE (IMPMC, UMR7590-CNRS, Sorbonne Université, IRD, MNHN, FR)
Julien HAINES (ICG, Université de Montpellier, CNRS, ENSCM, FR)

Abstract

Zeolites are aluminosilicates built up of corner-sharing TO_4 (T = Si, Al, ...) tetrahedra, which form a network of pores with typical diameters between 3 and 8 Å. These microporous materials are used at a large scale for applications in, for example, catalysis, adsorption, separation, and ion exchange. If zeolites are compressed in the presence of fluids containing atoms or molecules small enough to enter the pores, pressure-induced guest insertion can be observed. This can provide important information on the maximum possible filling of these porous materials and can be of interest in the fields of CO_2 capture[1-3] and hydrogen storage[4,5]. Guest insertion also strongly modifies the phase stability and the mechanical properties, such as compressibility and thermal expansion, of filled as compared to empty-pore zeolite. The rhombohedral, zeolite chabazite (CHA) with small 3.7 Å pores based on 8-membered rings of tetrahedra, is a promising candidate for CO_2 capture[3] due to the small difference between the pore size and the kinetic diameter of CO_2 (3.3 Å) and the loading of CO_2 has been studied, stabilizing its structure up to 12 GPa with a high degree of filling[3]. The aluminophosphate $AlPO_4$-17, with the hexagonal, erionite structure (ERI), space group $P6_3/m$ and cell parameters a and c of 13.1113 Å and 15.3600 Å, respectively,[6] is another example of a zeolite-type material with even smaller 3.4 Å, 8-membered ring pores, which are even closer to the kinetic diameter of CO_2, differing from chabazite in the stacking sequence of 6-membered rings in the c-direction (AABBCC for CHA and AABAAC for ERI). This material could be expected to have a very promising CO_2 and H_2 capture performance. Anhydrous $AlPO_4$-17 has been found to exhibit a very strong Negative Thermal Expansion (NTE) coefficient, *the highest known for an oxide*, of -35.1×10^{-6} K^{-1} over the temperature range of 18-300 K [7], and complete pressure-inducing amorphisation (PIA) near 2.5 GPa in non-penetrating pressure transmitting media [6]. Structural studies on insertion in $AlPO_4$-17 at high pressure (HP) shed light on deactivation of PIA on this system: recently we have performed the insertion of Ar, N_2 and O_2 on $AlPO_4$-17 (see ref. 8) and on the study of its structural behavior to HP and low T (see ref. 9). Accurate isobaric scans at low T were performed and analysis from the data were able to precisely locate the inserted molecules and determine the structure of O_2-filled $AlPO_4$-17 at HP. Thermal expansion was measured precisely at 0.38 GPa by synchrotron powder XRD. Spectacular results were obtained: whereas the overall volume thermal expansion only exhibits a small change with respect to empty $AlPO_4$-17 at ambient pressure, the expansion along the a direction decreases almost to zero and the expansion along c increases by a factor of 7 [9]. Very recently we were able to perform HP CO_2 insertion on $AlPO_4$-17, measured by synchrotron XRD single crystal under HP and high-T, being able to localize the guest molecules. Now, on-going experiments are investigating the structural response of $AlPO_4$-17 to pressure, temperature and guest insertion by using H_2 and He as penetrating PTM. In this Invited Talk we will present the latest obtained results and perspectives.

References

[1] J. Haines, O. Cambon, C. Levelut, M. Santoro, F. Gorelli, G. Garbarino, *Deactivation of pressure-induced amorphization in silicalite SiO_2 by insertion of guest species*, J. Am. Chem. Soc. **132**, 8860 (2010).
[2] B. Coasne, J. Haines, C. Levelut, O. Cambon, M. Santoro, F. Gorelli, G. Garbarino, *Enhanced Mechanical Strength of Zeolites by Adsorption of Guest Molecules*, Phys. Chem. Chem. Phys. **13**, 20096 (2011).
[3] G. Bera, P. Botella, J. Pellicer-Porres, D. Diaz-Anichtchenko, D. Errandonea, O. Gomis, R. Oliva, J. Ibañez, F. Alabarse, S. Valencia, F. Rey, A. Otero-de-la-Roza, D. Santamaria-Perez, *Structural stability and adsorption behaviour of CO_2-loaded pure silica CHA and ITW zeolites upon compression*, Micropor. Mesopor. Mater. **380**, 113317 (2024).
[4] W. Xu, X.-D. Liu, M. Peña-Alvarez, H.-C. Jiang, P. Dalladay-Simpson, B. Coasne, J. Haines, E. Gregoryanz, M. Santoro, *High-Pressure Insertion of Dense H_2 into a Model Zeolite*, J. Phys. Chem. C, **125**, 7511 (2021).
[5] M. Santoro, J. Rouquette, M. Fabbiani, F. Di Renzo, B. Coasne, W. Dong, K. Glazyrin, J. Haines, *Strong Swelling and Symmetrization in Siliceous Zeolites due to Hydrogen Insertion at High Pressure*, Angew. Chem.-Int. Edit. **63**, e202406425 (2024).
[6] F. Alabarse, G. Silly, J.-B. Brubach, P. Roy, A. Haidoux, C. Levelut, J.-L. Bantignies, S. Kohara, S. Le Floch, O. Cambon, J. Haines, *Anomalous Compressibility and Amorphization in $AlPO_4$-17, the Oxide with the Highest Negative Thermal Expansion*, J. Phys. Chem. C, **121**, 6852 (2017).
[7] P. Attfield, A.W. Sleight, *Exceptional Negative Thermal Expansion in $AlPO_4$-17*. Chem. Mater **10**, 2013-2019 (1998).
[8] F. Alabarse, B. Baptiste, Y. Guarnelli, B. Joseph, J. Haines, *Strongly Modified Mechanical Properties and Phase Transition in $AlPO_4$-17 Due to Insertion of Guest Species at High Pressure*, J. Phys. Chem. C, 127, **29**, 14528–14533 (2023).
[9] F. Alabarse, B. Baptiste, B. Joseph, J. Haines, *Tuning Negative Thermal Expansion in $AlPO_4$-17 by Insertion of Guest Molecules* J. Phys. Chem. Lett., **13**, 9390−9395 (2022).