MS6 – P3: Methanol adsorption at High Pressure in MFI- Zeolites

Davide Comboni[a,b], G. Diego Gatta[a], Paolo Lotti[a], Marco Merlini[a], Pagliaro F.[a], Catizzone E.[c], Migliori M.[c], Giordano G.[c] Michael Hanfland[d]

[a]*Dipartimento di Scienze della Terra, Università degli Studi di Milano,* [b]*Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia,*[c]*Department of Environmental and Chemical Engineering, University of Calabria,* [d]*ESRF- European Synchrotron Radiation Facility,*
diego.gatta@unimi.it

In some olefins-production processes, MFI-zeolites are currently used as catalysts, representing an appealing alternative to the high-energy demanding Steam Cracking process, from which the 95% of the total worldwide olefins production relies[1,2]. Furthermore, MFI zeolites have been used in the methanol-to-olefins (MTO) synthesis process, to obtain olefins directly from methanol, thus bypassing oil as raw precursor. At ambient conditions, only the surfaces of the zeolite crystallites are believed to be active in the methanol-to-olefins process. However, pressure can enhance methanol adsorption in the structural cavities of zeolites[3], thus enhancing the active surface directly in contact with methanol. This may bear a significant impact in the industrial applications of this zeolite as a catalyst: a "cold" intrusion of methanol into the zeolite cavities might pave the way to ultimately increase the efficiency of the MTO conversion process. In this study, we synthesized and investigated, by *in situ* synchrotron powder-XRD experiments with a diamond-anvil cell, the high-pressure behaviour of six MFI-zeolites with different chemical composition (Na-Al-MFI, Na-Fe-MFI, Na-B-MFI, H-Al-MFI, H-B-MFI, and Silicalite-1-MFI). Consistently with previous studies[4], all the synthesized zeolites are monoclinic (space group $P2_1/n11$) at ambient pressure. A monoclinic-to-orthorhombic ($P2_1/n11$-to-*Pnma*) phase transition (MOPT) was reported to occur at $P > 1$ GPa in MFI-zeolites. On the basis of the *in-situ* X-ray diffraction data, we ascertain that: *i*) all the MFI zeolites compressed in *silicone oil* (acting as non-penetrating fluid) have overall the same bulk compressibility, *ii*) methanol penetrate through the structural voids (leading to an apparent lower compressibility, Fig. 1) and, among the different zeolites, the magnitude of the adsorption phenomenon is different, *i.e.* it is governed by the different chemical composition, *iii*) the MOPT is influenced by the chemical composition of the zeolites and by the absorption of methanol. The experimental findings of this study represent the first step to select the optimal chemical composition of a potential MFI-catalyst for the MTO conversion process operating at high-pressure conditions.

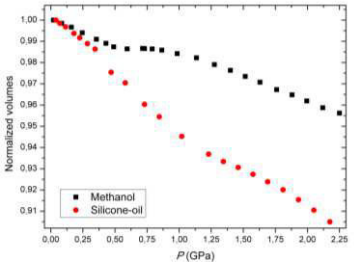

Figure 1. High-pressure evolution on the unit-cell volume of the synthesized H-B-MFI, compressed in methanol (*black squares)* and in silicone-oil (*red spheres*).

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