

UV-Raman fingerprint of Brønsted sites in MFI zeolites

Alessandro Damin,¹ Matteo Signorile,² Francesca Bonino,² Silvia Bordiga²¹ Department of Chemistry, University of Torino, Via P. Giuria 7, 10125-Torino (Italy), and NIS Centre
alessandro.damin@unito.it² Department of Chemistry, University of Torino, Via P. Giuria 7, 10125-Torino (Italy), and NIS Centre

Zeolites (general formula SiO_2) are an important class of crystalline porous and high surface area tecto-silicates widely adopted in catalysis.¹ Some of them can be obtained by substituting part of $\text{O}_4\text{Si(IV)}$ framework atoms with Al(III) atoms, so that a negative charge is generated which can be balanced by the presence of H (so generating strong acidic Brønsted sites) or other positive counterions. In their acidic form, zeolites are largely exploited in refinery and petrochemical processes, such as the evergreen FCC (Fluid Catalytic Cracking)² or the increasingly important MTH (Methanol To Hydrocarbons).³ Unfortunately, at reaction condition a progressive leaching of Al atoms from framework position occurs, with a concomitant loss of the associated Brønsted acidity.⁴ This process, commonly known as dealumination, can be considered as the main cause of the irreversible deactivation of acidic zeolite catalysts.

Vibrational spectroscopy has been often applied in the characterization of acid zeolites: infrared spectroscopy allows to give a clear picture on the nature of the Brønsted acid sites and their interaction with probes and reactants,⁵ while Raman spectroscopy is useful in measuring the framework (i.e. collective) vibrational modes.⁶ Nowadays most of the vibrational fingerprints of zeolites have been univocally interpreted, allowing the application of the related spectroscopies to the detailed studies of zeolites structures, reactivity as well as of their dealumination. With respect to the infrared one, the Raman characterization of zeolites usually involved much simpler approaches and experimental setups: apart from some pioneering studies, most of the experiments were carried out in air, i.e. without considering the effect of hydration of the samples and their interaction with environmental molecules.

In the present work a detailed UV-Raman characterization of a set of H-MFI zeolites with variable atomic Si/Al ratio is presented. A new vibrational feature (located at 745 cm^{-1}) was detected: interestingly such peak is present only when samples are carefully activated. Moreover its intensity is quantitatively related to the Al content of the framework through a direct law. On these basis, the signal has been provisionally attributed to the Brønsted moiety. The assignment was further confirmed by means of exchange experiments (with deuterium, sodium and ammonium), proving the relevant contribution of the Brønsted proton in this peculiar vibration. Finally, by applying a steaming-like treatment (known to be able to induce de-alumination), the observed decrease in the mode intensity was related to the leaching of Al atoms out of the framework, i.e. to the destruction of a fraction of the former Brønsted sites population. In this regard, the monitoring by UV-Raman of such signal could represent an useful marker in detecting steaming and/or reaction induced de-alumination in acidic zeolites.

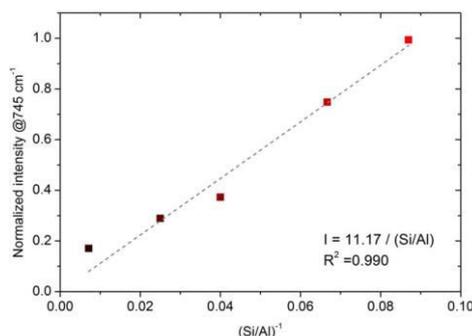


Figure 1: Intensities of the 745 cm^{-1} band vs. the reciprocal of Si/Al ratio in the H-MFI samples.

References

- [1] C. Martinez, A. Corma, A., *Coord. Chem. Rev.* **255**, 1558 (2011).
- [2] E.T.C. Vogt, B.M. Weckhuysen, *Chem. Soc. Rev.* **44**, 7342 (2015).
- [3] M. Bjorgen, S. Svelle, F. Joensen, J. Nerlov, S. Kolboe, F. Bonino, L. Palumbo, S. Bordiga, U. Olsbye, *J. Catal.* **249**, 195 (2007).
- [4] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Prieto, J. Bilbao, *Energy Fuels* **18**, 1640 (2004).
- [5] A. Zecchina, G. Spoto, S. Bordiga, *Phys. Chem. Chem. Phys.* **7**, 1627 (2005).
- [6] P.K. Dutta, K.M. Rao, J.Y. Park, *J. Phys. Chem.* **95**, 6654 (1991).