

Resonant Raman Spectroscopy and computational methods for the study of Ti-zeolites interacting with probe molecules

Alessandro Damin¹, Matteo Signorile¹, Francesca Bonino¹, Valentina Crocellà¹, A. Bernhard², F. Schmidt², Heiko Morell², Carlo Lamberti¹, Silvia Bordiga¹

¹ Dipartimento di Chimica-Centro Interdipartimentale NIS-Università di Torino, alessandro.damin@unito.it

² Evonik Resource Efficiency GmbH, Rodenbacher Chaussee 4, 63457 Hanau, Germany

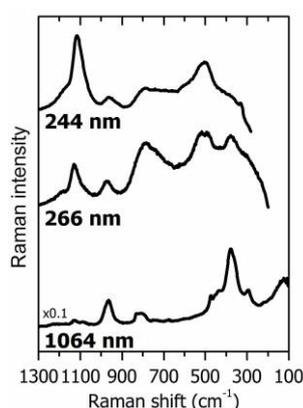


Figure 1: Raman spectra of perfect TS-1 recorded adopting different exciting laser lines.

Ti-zeolites (in which few Ti atoms substitute Si atoms in framework positions) are an important class of materials widely adopted in the field of catalysis of partial oxidation reactions by hydrogen peroxide. Among them, Ti-silicalite (TS-1) is the most important [1] and it is currently the subject of an intense research activity. It has been stated in the past that the highest activity is reached when Ti atoms (the catalytic active centers of TS-1) possess a "perfect" tetrahedral environment, forming four well defined equivalent Ti-O-Si bonds. "Perfect" TS-1 presents peculiar electronic and vibrational features, as well documented in the past [2,3]. In particular, Raman spectra (see Fig. 1) recorded in Resonant conditions (*i.e.* by adopting exciting laser lines quite near to the energy of electronic transitions involving the Ti center), but not in controlled atmosphere, evidenced the presence of a very intense signal located at 1125 cm⁻¹. Such peak has been assigned to the symmetric combination of Si->O->Ti normal mode involving the four Si-O-Ti bonds of the Ti containing tetrahedron. In order to shed further light on vibrational features of Ti containing zeolites (in particular on TS-1), and to improve the degree of knowledge of such materials, we adopted in the last years a combined experimental and computational approach. On experimental side, new set-up for recording Raman spectra in controlled atmosphere on both activated samples and contacted by probe molecules (PM) from the gas-phase have been designed and tested; thanks to this, and through the combined use of different exciting laser lines, it was possible to exploit the Resonance effect for both bare (244 nm, Raman Lab-NIS in Torino) and PM-contacted (266 nm, IUVS-Elettra in Trieste) TS-1 and to follow how Ti-involving vibrations are modified by the presence of extra ligands such as NH₃ and H₂O. On the computational ground, we perform a new set of calculations (by exploiting computational facilities available at CINECA and the CRYSTAL code), substantially improving, with respect to our past calculations [2,4], the model adopted for simulating TS-1: indeed **a**) the silicalite (MFI) framework (96 independent Si sites if P1 symmetry is concerned) has been used (at variance with respect to [4], where CHAbazite framework was chosen) and **b**) just one Si atom has been substituted for Ti (final [Ti]/[Ti+Si] ratio 0.01), in this way building a model quite near to the real system (P2₁/n and [Ti]/[Ti+Si] ratio of about 0.01). Relative stability for Ti substitution at the 24 independent T_n (n=1...24) sites of P2₁/n TS-1 has been initially investigated, finding five most stable sites in a 5 kJmol⁻¹ energy range. NH₃ and H₂O adsorption has been then investigated, resulting a favored process ($\Delta G_{ads} < 0$), as experimentally verified: the computed ΔH_{ads} (-81.7 kJmol⁻¹ for the NH₃ mono-adduct and -56.7 kJmol⁻¹ for the H₂O) one are quite near to the measured heat of adsorption as reported in [5]. Finally, the computed vibrational features well reproduced the observed behavior after NH₃ and H₂O dosages, further confirming the goodness of the adopted computational approach.

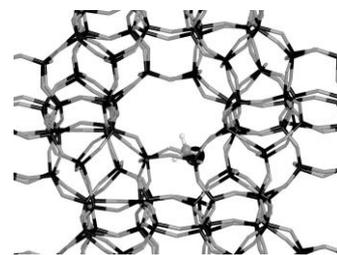


Figure 2: pictorial representation of Ti containing site in TS-1 and interacting with NH₃ molecule.

References

- [1] Notari B., in: D.D. Eley, W.O. Haag, B. Gates (Eds.) *Advances in Catalysis*, Elsevier Academic Press Inc, San Diego, (1996).
- [2] Ricchiardi G., Damin A., Bordiga S., Lamberti C., Spanò G., Rivetti F., Zecchina A., *J. Am. Chem. Soc.* **123**, 11409 (2001).
- [3] Bordiga S., Damin A., Bonino F., Zecchina A., Spanò G., Rivetti F., Bolis V., Prestipino C., Lamberti C., *J. Phys. Chem. B* **106**, 9892 (2002).
- [4] Signorile M., Damin A., Bonino F., Crocellà V., Lamberti C., Bordiga S., *J. Comput. Chem.* **37**, 2659 (2016).
- [5] Bolis V., Bordiga S., Lamberti C., Zecchina A., Carati A., Rivetti F., Spanò G., Petrini G., *Langmuir* **15** 5753 (1999).