

Critical hydroxyl concentration at the frontier between hydrophobic and hydrophilic zeolites

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Introduction

The properties of water confined in hydrophobic zeolite cavities remains a topic of fundamental and applied interests.^{1,2} The estimation at which pressure water condensation (or evaporation) occurs is not obvious as zeolites often contain structural defects which nature and concentration depend on the synthesis process. These defect sites interact with water, and once the number of water molecules in the cavities is increased, water clusters are formed through hydrogen bonding.³ Many types of defect sites can co-exist in all-silica zeolites, mainly internal and external silanol groups. While there is an abundant literature on the nature of defect sites, critical concentrations of these defects which may turn a particular zeolite from hydrophobic to hydrophilic has not been systematically determined.⁴ The objective of this study was to estimate the critical concentration of defects beyond which all silica-zeolites become hydrophilic. A set of all-silica zeolites was prepared, characterized by ²⁹Si NMR, IR and methanol (MeOH) and water (H₂O) sorption. A correlation between water uptake at low pressure and the SiOH concentration has been established and used to estimate a critical SiOH concentration beyond which the zeolite becomes hydrophilic.

Experimental

All-silica zeolites Silicalite-1(OH), Silicalite-1(F), ITQ-13(F), Beta(OH), Beta(F) and Chabazite(F) were prepared using procedures of the literature in alkaline (OH) or fluoride (F) media. They were characterized by ²⁹Si Nuclear Magnetic Resonance (NMR), X-ray diffraction (XRD), N₂ physisorption, diffuse Reflectance FT-IR spectroscopy (DRIFTS) and Scanning Electron Microscopy (SEM). Adsorption of probe molecules H₂O and MeOH were measured at 293,15 K on a BelMax system (BelJapan).

Results

All zeolites exhibit BET surface areas and pore volumes typical of highly crystalline solids. All additional characterization data by XRD, SEM, IR and ²⁹Si NMR are in line with literature results. Major differences between MeOH and H₂O adsorption are observed in the low-pressure part of the isotherms: in most cases, water hardly adsorbs on hydrophobic zeolites while MeOH uptake is significant even at low pressure. The surface affinity for both adsorbates has been quantitatively characterized for all zeolites by the calculation of Henry's constants for

water and methanol vapors at low pressure. In order to correlate the hydrophobic character of zeolites with a density of framework defects, the concentration of silanol groups per unit cell was estimated from i) ^{29}Si NMR spectra and ii) the intensity of the vibrations of free and H-bonded hydroxyls in DRIFTS spectra. Although NMR is sensitive to the environment of Si atoms while DRIFT is sensitive to OH vibrations, the two methods provide similar silanol concentrations. Two major trends regardless of the probe molecules can be observed by plotting Henry's constants for water and MeOH as a function of silanol concentration (Fig. 1). For concentrations $< 2 \text{ SiOH/nm}^2$, Henry's constants are very low (ca. $10^{-6} \text{ mol.g}^{-1}.\text{Pa}^{-1}$) whereas for higher concentrations, Henry's constant markedly increases with the silanol concentration in a linear fashion. We also observe that the Henry's constants of water are systematically inferior to those of methanol when the silanol concentration is below 2 SiOH/nm^2 whereas the opposite trend is observed at higher concentrations. The clear cut of adsorption properties observed for silanol concentration around 2 SiOH/nm^2 , which seems to delimit a frontier between hydrophobic and hydrophilic solids, will be discussed and compared to other experimental and theoretical values of the literature.

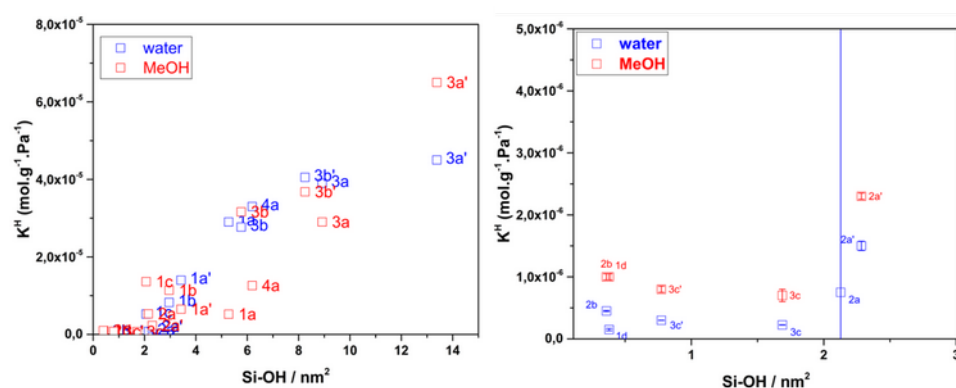


Figure 1 Henry's constants for MeOH and H₂O as a function of the overall silanol density in zeolites (left) with a zoom on the region below 2 SiOH/nm^2 (right)

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- 1) D.H. Olson, W.O. Haag, W.S. Borghard, *Microporous Mesoporous Mater.* 35–36 (2000) 435.
- 2) R. Gläser, J. Weitkamp, *Surface Hydrophobicity or Hydrophilicity of Porous Solids in Handbook of Porous Solids*, F. Schuth, K.S.W. Sing, J. Weitkamp (Eds), Vol. 1, WILEY-VCH Verlag GmbH (2002) pp. 395-431
- 3) J. Stelzer, M. Paulus, M. Hunger, J. Weitkamp, *Microporous Mesoporous Mater.* 22 (1998) 1.
- 4) H. Koller, R.F. Lobo, S.L. Burkett, M.E. Davis, *J. Phys. Chem.* 99 (1995), 12588.