MOLECULAR SIMULATION STUDY OF WATER ADSORPTION IN HYDROPHOBIC ZEOLITES

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Introduction

Water exhibits very particular properties due to the hydrogen bonds network. However, in many situations, water is confined to spaces of nanoscopic dimensions, and its properties are considerably modified.

Study of water confinement in hydrophobic environments is of special interest, because of possible applications (waste water treatment), but also because this situation is encountered in biological systems (biological channels or protein cavities).

We have used molecular simulation techniques to investigate structure and thermodynamic properties of water confined in hydrophobic zeolites at the molecular level.

Water intrusion in silicalite-1\textsuperscript{(3,4)}

- Intrusion pressure of about 100 MPa.
- Good agreement between experience and simulation.
- Effect of hydrophilic defects: shift of the intrusion pressure and rounding of the transition.
- Increase of the number of inserted molecules with 4 or 12 defects.
- Evolution of the isotherm type: type V $\rightarrow$ type IV $\rightarrow$ quasi-type I.

Thermodynamic analysis\textsuperscript{(6)}

- Defects W:\n- Weak initial water/zeolite interaction.
- Water/water interaction favoured within the zeolite.

- Defects S:\n- Strong initial water/zeolite interaction $\rightarrow$ pre-adsorption.
- First water molecules localized near the defects.
- Strong anchoring of water molecules close to a defect.

Water intrusion in various zeolites\textsuperscript{(6)}

- Good agreement between experimental and simulation data.
- Hysteresis $\rightarrow$ Two stable states (empty/filled zeolite).
- Hysteresis width depends on activation energy barrier.

Conclusions

- Presence of local hydrophilic defects allows to interpret the variations in water adsorption isotherms of different silicalite-1.
- A unique force field is able to reproduce experimental water adsorption isotherms for various hydrophobic zeolite structures.
- Hysteresis obtained experimentally as well as theoretically can be explained by the thermodynamic potential variations.

Perspectives

- Effect of local hydrophilic defects in ferrierite or in zeolite $\beta$.
- Influence of temperature on adsorption isotherms.
- Study of water confined in other hydrophobic environments.

References

(2) Desbiens, Boutin, and Demachy (2005) JPC B 109, 24071

Monte Carlo simulations:
- Rigid zeolite framework
- Grand Canonical Ensemble
- Bias MC moves

Force field:
- TIP4P water model\textsuperscript{(1)}
- Water/zeolite interactions: van der Waals and electrostatic\textsuperscript{(2,3)}

Local hydrophilic defect:
- Model silanol nest
- 2 sets of parameters: Weakly and Strongly hydrophilic

EXEDOS simulations:
- Wang-Landau algorithm
- Determination of the thermodynamic potential of the system