Review of: "The shape of water in zeolites and its impact on epoxidation catalysis"

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Phonon spectroscopic measurements and MD simulations [234] suggest that H_2O molecules form bulk-like three-dimensional structures within 1.3 nm cages of zeolite pores, whereas H_2O molecules coalesce into oligomeric one-dimensional chains when the pore diameter falls below 0.65 nm. Correspondingly, the w_H peak evolves from two components at 3200 and 3400 cm^{-1} to the skin component at 3580 cm^{-1} only. Heating from 304 K to 343 K shift the peak from 3200 to a broad peak centered at 3500 cm^{-1}. The reorganization of these pore-size-dependent H_2O structures during alkene epoxidation catalysis gives rise to entropy gains that increase the turnover rates by up to 400-fold.

Observations clearly indicate the effects of molecular undercoordination [1] and thermal activation [2] on the hydrogen bond (O:H-O) cooperativity and polarizability (HBCP) that shortens and stiffens the H-O bond while lengthens and softens the O:H elongation. Undercoordiantion polarizes the electrons while heating depolarizes water by thermalization. The high reactivity arises from the polarization effect [3].

References

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