Using embedded cluster models and the hybrid density functional-molecular mechanics scheme covEPE, we studied computationally various Zn species in ZSM-5 zeolites: Zn2+, [Zn(OH)](+), [Zn(H2O)](2+), and [ZnOZn]2+). The covEPE embedding approach accounts for the flexibility of the zeolite framework and long-range electrostatic interactions. Due to this flexibility of the embedded models, the mononuclear Zn-species in zeolite structures showed more (four) Zn-O contacts or shorter average Zn-O distances compared to the corresponding isolated cluster models. Comparing protonic and Zn-exchanged forms of the zeolites rings suggests that upon Zn-substitution O centers shift farthest, extending bonds in the five-ring and contracting distances in the six-ring. We also calculated energies of two types of formal reactions for exchanging protons in H-ZSM-5 by zinc ions: a reaction with zinc vapor which is exothermic by -73 to -112 kJ/mol and ion-exchange with an aqueous solution of a zinc salt which is exothermic by -33 to -124 kJ/mol; the latter value corresponds to [Zn(H2O)](2+) coordinated at a six-ring. Cluster embedding stabilizes the zinc exchanged form with respect to the protonic one in both types of reactions.
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