Dokumenttyp: Journal Article

Autor(en) des Beitrags: Aleksandrov, H. A.; Shor, E. A. I.; Shor, A. M.; Nasluzov, V. A.; Vayssilov, G. N.; Rosch, N.

Titel des Beitrags: CATIONIC ZINC SPECIES IN ZSM-5 ZEOLITES: STRUCTURE AND STABILITY FROM EMBEDDED CLUSTER MODELING

Abstract: Using embedded cluster models and the hybrid density functional-molecular mechanics scheme covEPE, we studied computationally various Zn species in ZSM-5 zeolites: Zn\(^{2+}\), \([\text{Zn(OH)}](^+)\), \([\text{Zn(H}_2\text{O)}](^2+)\), and \([\text{ZnOZn}](^2+)\). 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 \([\text{Zn(H}_2\text{O)}](^2+)\) coordinated at a six-ring. Cluster embedding stabilizes the zinc exchanged form with respect to the protonic one in both types of reactions.

Kongresstitel:
This work was supported by Deutsche Forschungsgemeinschaft via SPP 1155, Fonds der Chemischen Industrie (Germany), the Bulgarian National Science Fund (National Center of Advanced Materials UNION), the Siberian Branch of the Russian Academy of Sciences (Integration projects no. 79), and the Presidium of the Russian Academy of Sciences (Project no. 51 of the Priority program no. 27). E.A. Ivanova Shor gratefully acknowledges an individual grant of the Russian Science Support Foundation.