

Abstract

The acidic zeolite H-FER with Si:Al ratios of 71, 35 and 8 was investigated employing a periodic DFT model, as well as cluster models and the CCSD(T) level of theory. The computational study of the H-FER in a high silica form (Si:Al = 71) accompanied by the investigation of the interaction of the CO and N₂ probe molecules with the H-FER sample was supplemented with the experimental data obtained from the variable temperature infrared spectroscopy (VTIR).

The H-FER samples with different Si:Al ratios were characterized by the structure, location and relative stabilities of the Brønsted acid groups. Relative stability of these sites was found to be dependent on Si:Al ratio, which is the main factor dictating the relative concentration of Brønsted acid sites having different types of local configuration. The number of AlO₄ tetrahedra sharing an oxygen with the SiO₄ tetrahedron involved in the Brønsted acid site determines the Si-O(H)-Al angle, O-H stretching frequency and deprotonation energy (and hence acid strength).

Furthermore, the theoretical results obtained for the CO and N₂ interaction with the H-FER were found to be in a good agreement with the experimental VTIR data. Several types of hydrogen-bonded OH...CO and OH...N₂ complexes were characterized, formed by interaction between the adsorbed molecules and the Brønsted acid OH groups of the zeolite. CO or N₂, forming linear complexes with OH groups pointing towards a sufficiently ample void space, show the largest adsorption enthalpy which was found to be in the (approximate) range of -25 to -29 kJ mol⁻¹ for CO and -15 to -19 kJ mol⁻¹ for N₂. Less stable OH...CO and OH...N₂ complexes can be formed when either the Brønsted acid OH group is involved in intra-zeolite hydrogen bonding or when the free space available is too small to allow formation of linear complexes without previous re-location of the proton of the OH group involved.