

Effect of lattice topology on the adsorption of benzyl alcohol on kaolinite surfaces: Quantum chemical calculations of geometry optimization, binding energy, and NMR chemical shielding

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ABSTRACT

We investigate the effect of the lattice topology (ideal hexagonal rings vs. ditrigonal rings) and cluster size of model clusters (three-ring vs. seven-ring clusters) on the nature of benzyl alcohol adsorption on kaolinite surfaces using quantum chemical calculations with an emphasis on the equilibrium configuration, binding energy, and NMR chemical shielding tensors. The optimized structure of benzyl alcohol adsorbed on the tetrahedral layer of kaolinite varies according to the type and size of model cluster. While the calculated binding energy varies with the level of theory and the basis sets used for the calculations, the binding energies between benzyl alcohol and seven-ring clusters are smaller than those between benzyl alcohol and three-ring clusters partly due to the edge hydrogen for the latter. The results also indicate a stronger binding energy between benzyl alcohol and octahedral surfaces than between benzyl alcohol and tetrahedral layers. Although the calculated binding energies for seven-member rings with varying lattice topologies are rather similar, the detailed optimized structures are distinct, demonstrating the effect of lattice topology on the nature of adsorption. The optimized structures and binding energies indicate that an intermediate degree of hydrogen bonding is dominant for the three-member silicate rings and that the interaction between the benzene ring and basal O atoms in the seven-member rings is characterized by a weak hydrogen bond and dispersion force. The calculated ^{17}O isotropic chemical shieldings of some basal O atoms decrease up to $\sim 4\text{--}5$ ppm after the adsorption (with an estimated uncertainty of ~ 2 ppm). Since the high-resolution ^{17}O 3QMAS NMR spectroscopy of layer silicates yielded a resolution of 1–2 ppm for the basal oxygen sites in the layer silicates in previous work, the NMR technique may be useful in exploring the nature of adsorption between organic molecules and silicate surfaces, whereas further computational studies on the effect of the basis sets, the surface coverage, and the types of diverse organic molecules with larger model clusters for surfaces remain to be explored.

Keywords: Kaolinite, benzyl alcohol, quantum chemical calculations, NMR chemical shielding, lattice topology, surface adsorption