Adsorption of Pyridine on Model Surfaces of SiO₂, TiO₂ and

ZrO₂ -Ab Initio and Density Functional Studies

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Abstract

Ab *initio* and density functional (DFT) calculations were carried out for the adsorption of pyridine (Py) on model surfaces of SiO₂, TiO₂ and ZrO₂. Cluster models were composed to represent the various test surfaces and the Py adsorption complexes on each surface. The calculations were conducted at Hartree-Fock (HF) and B3PW91 levels with 3-21G*, 6-31G(d) and CEP-121G basis sets, in order to obtain the geometries, electronic structures, vibrational frequencies and adsorption energies of the adsorption complexes formed The calculated adsorption energies were corrected for zero-point vibrational energies (ZPVE) and basis set superposition errors (BSSE). The results favored Py adsorption on SiO₂ solely via hydrogenbonding to isolated and associated silanol groups. Whereas on TiO₂ and ZrO₂ surfaces, Py is further adsorbed via coordination to coordinatively unsaturated (Lewis acid) metal sites. Diagnostic IR absorption frequencies of the normal modes of the ring-breathing (vCCN) vibrations of adsorbed Py were derived for each mode of adsorption, and compared to reported experimental results. Findings of the present work have been shown to help interpreting results of in-situ experiments in which Py is used as an IR probe molecule for acid sites exposed on catalytic metal oxide surfaces.

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