

Computational Studies of Transition Metal Oxide Clusters as Models of Catalysts

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Transition metal oxides (TMOs) form an important class of materials widely employed as industrial catalysts and catalyst supports. We use density functional theory (DFT) and coupled cluster (CCSD(T)) methods to study the molecular structures, acid-base chemistry, electronic properties, and reactions of group IVB $[(\text{MO}_2)_n, \text{M} = \text{Ti, Zr, Hf}; n = 1-4]$ and VIB $[(\text{MO}_3)_n, \text{M} = \text{Cr, Mo, W}; n = 1-6]$ TMO clusters. Calculated electron affinities of these clusters were compared with those from anion photoelectron spectroscopic measurements. CCSD(T) provides excellent electronic affinities for these clusters. Benchmark studies of DFT show that the B88-P86 and PW91-PW91 exchange-correlation functionals yield the best electron affinities for the MO_3 and $(\text{MO}_3)_2$ clusters. Total atomization energies (TAEs) were calculated at the CCSD(T)/CBS (complete basis set) level for the monomers and dimers, and were used to obtain their heats of formation. For the trimers and tetramers, heats of formation were obtained from the normalized clustering energies (NCEs), which were shown to have significantly less basis set dependence than the TAEs. DFT benchmarks show that the PBE1PBE functional yields the best NCEs for these clusters. The group VIB TMO clusters were used as models for catalysts in the oxidative dehydrogenation reaction of methanol to produce formaldehyde. Potential energy surfaces (PES) for the reactions of these clusters with water and methanol were calculated up to the CCSD(T)/CBS level. DFT calculations of the PES were carried out to assess the performance of various functionals. Our studies show that the catalytic processes can be divided into a Lewis-acid base addition, proton transfer to a μ -oxo group, and an endothermic reduction. The catalyst is regenerated by an exothermic oxidation. Reduced metal oxide clusters such as M_3O_8 were predicted to have many low-lying electronic states, which could play an important role in the catalytic reaction. The calculated electronic affinities of the M_3O_8 cluster for $\text{M} = \text{Cr}$ and W are in good agreement with those measured by anion photoelectron spectroscopy.