

0.1 Title

Periodic density functional theory calculations of methanol and vanadium oxide aggregates on cerium oxide: geometrical and electronic structures, vibrational properties, and reactivity.

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First-principles spin-polarized DFT + U calculations will be performed for the investigation of the structure, electronic and vibrational properties and the reactivity of vanadia and methanol on ceria model catalysts. Calculations will be performed on periodic structures using the VASP program. First we will identify the thermodynamically stable monomeric and aggregated species on large unit cells. We will evaluate the reactivity of the systems using reactivity descriptors, the oxygen defect formation and the hydrogenation reaction energies. Then the coadsorption of methanol and dissociated methanol with vanadia on ceria surfaces will be considered. Further on we will investigate the possible minimum energy paths for the oxidation in the presence of vanadia species of methanol to formaldehyde. The role of the ceria support and of the vanadia structures is a key aspect of the enhanced activity observed for ceria supported vanadia in certain oxidation reactions. The reaction energies, as well as the determination of the electronic, thermodynamic and vibrational properties will be studied. The transition states will be determined and analyzed in detail. The activation barriers and thermodynamic and kinetic data will be calculated for all of the elementary steps.