FULL PAPER

Density functional theory investigation of structure, stability, and glycerol/hydrogen adsorption on Cu, Cu—Zn, and Cu—ZnO clusters

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Abstract

Extensive density functional theory calculations are performed to analyze the structure and activity of Cu and Cu—Zn/Cu—ZnO clusters containing up to 10 Cu/Zn atoms. The minimum-energy structures of Cu—Zn and Cu—ZnO clusters are found by doping minimum-energy pure Cu clusters with Zn atom(s) and ZnO molecule(s), respectively, followed by energy minimization of the resultant clusters. Odd-even alteration in properties that determine cluster stability/activity is observed with cluster size, which may be attributed to the presence/absence of unpaired electrons. The difference in behavior between Zn/ZnO doping can be interpreted in terms of charge transfer between atoms. Charge transfers from Zn to Cu in the Cu—Zn clusters and from Cu and Zn atoms to O atom in Cu-ZnO clusters, which implies that the Cu atom acts as an electron acceptor in the Cu—Zn clusters but not in the Cu—ZnO clusters. Finally, the adsorption energies of glycerol and hydrogen on Cu—Zn/Cu—ZnO clusters are computed in the context of the use of Cu—Zn/Cu—ZnO catalysts in glycerol hydrogenolysis. Glycerol adsorption is generally found to be more energetically favorable than hydrogen adsorption. Dual-site glycerol adsorption is also observed in some of the planar clusters. Fundamental insights obtained in this study can be useful in the design of Cu—Zn/Cu—ZnO catalysts.

KEYWORDS

catalysis, copper-zinc clusters, DFT, glycerol adsorption, mixed oxides

1 | INTRODUCTION

Alloys of more than one metal have been of interest to mankind since prehistoric days as they provide the means to attain desired synergistic behavior using a proper combination of constituents. With recent advances in material synthesis and nanotechnology, newer applications of such materials have emerged. For instance, in the area of catalysis, a large variety of bimetallic catalysts has been reported that often exhibit enhanced properties such as stability, selectivity to desired products, resistance to poisoning/deactivation, etc. compared to single-metal catalysts formed by their respective constituents.[1–3] Besides, the addition of a second, cheaper metal is also often an economical choice when dealing with expensive metals. Such catalysts are of tremendous interest in emerging areas of hydrogen production,[4,5] CO_x utilization,[6] water treatment,[7] biomass conversion,[8] etc.

The experimental design of bimetallic catalysts using the trial and error method is a costly and time-consuming affair, which may benefit from theoretical knowledge of metal-metal interactions and charge transfers in a bimetallic system. Although detailed quantum chemistry calculations of bulk catalysts containing thousands of atoms are far from feasible with current computational capabilities, two plausible alternatives exist.