Computational Studies of Catalytic Reactions of Alcohols on Oxide NanoClusters

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Dehydration, dehydrogenation, and condensation reactions of alcohols and diols have been studied on Group 6 transition metal oxides and of ethanol on an Al8O12 cluster model of Î³-Al2O3 to evaluate cluster reactivity at the density functional theory level followed by single point coupled cluster CCSD(T) calculations. All of the reactions proceed by a Lewis acid-base step of the alcohol interacting with the metal center with diol having an additional hydrogen bond to an adjacent oxygen. The dehydration reaction of alcohols on M3O9 proceeds through a dialkoxy intermediate after H2O elimination with Î² hydrogen transfer to a terminal M=O. Dehydrogenation on M3O9 takes place via an Î± hydrogen transfer to an adjacent MVI=O atom or a WVI metal center with redox at the metal for M = Mo and no redox for M = W. Ether formation on M3O9 requires the presence of 3 alcohol molecules with one alcohol sacrificed to form a metal hydroalkoxide, which is a strong gas phase BrÃ¸nsted acid. The conversion of diols (e.g., 1,3-propanediol) on M3O9 clusters is through a metal bisdiolate intermediate (M-OCH2CH2CH2O-M) after two proton transfers to eliminate water with two barriers below reactant asymptote. Ethylene and propylene oxide are generated by breaking C-C bond and C-O bond respectively with nearly identical reaction barriers. The reaction pathway with epoxide formation can produce either acetone or propanal without an additional barrier energy. Dehydration on Al8O12 begins with a stable physisorbed ethanol-cluster complex with a strong Lewis acid-base donor-acceptor bond followed by a Î²-H transfer to a bi-coordinated oxygen atom leading to the formation of ethylene. Dehydrogenation on Al8O12 takes place through a chemisorbed intermediate followed by an Î±-H transfer to the active metal center, which is a proton coupled electron transfer reaction. The addition of a second ethanol on Al8O12 forms two hydrogen bonds with the physisorbed intermediate from the first addition and diethyl ether is generated by an Î±-C transfer from the first to the second ethanol. The computational results agree well with the available experimental data. This work is sponsored by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.