A DFT Study of Mechanism of Selective Oxidation of Propene on Bismuth Molybdate Catalyst

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In this work, we use B3LYP flavor of Density Functional Theory (DFT) to study the oxidation of propene on bismuth molybdates. We use finite model clusters to closely represent the active sites on the surface of BiMoO\textsubscript{x} catalyst. Previous studies have established that bismuth site is responsible for the rate-determining abstraction of \( \alpha \)-methyl hydrogen to form allyl radical. Considering that C-H activation of propene by Bi(III) is very endothermic, and leads to unfavorable reduced Bi(II), we find C-H activation by Bi(V) site, using Bi\textsubscript{4}O\textsubscript{7} as model cluster (Figure 1), to be favorable.

Later steps on doublet surface, such as allyl adsorption onto molybdenum site, 2\textsuperscript{nd} hydrogen abstraction by M=O (Figure 2), and acrolein desorption, are studied using the Mo\textsubscript{3}O\textsubscript{9} model cluster. Adsorption is found to be exothermic and almost barrierless, as expected. Activation energy for 2\textsuperscript{nd} hydrogen abstraction is relatively large, 33 kcal/mol, which might explain the observed lower yield and selectivity of the MoO\textsubscript{3} system once allyl radicals were passed over MoO\textsubscript{3} surface, as compared to the activity of mixed metal BiMoO\textsubscript{x} system. It is suggested that 2\textsuperscript{nd} H abstraction may be assisted with two H\textsubscript{2}O molecules, since first H\textsubscript{2}O molecule is shown to bind to unsaturated Mo site, and thus increase the barrier. Acrolein desorption is barrierless and endothermic, however, a ReaxFF simulation of conversion of propene to acrolein by a MoO\textsubscript{3}-slab shows the reaction to be exothermic, which may correspond to the spectator oxo stabilization present in MoO\textsubscript{3}, as reported in previous studies. Above mentioned reactions are investigated on quartet surface as well.

Figure 1. Transition state for C-H activation of propene by Bi (V).

Figure 2. Transition state for 2\textsuperscript{nd} hydrogen abstraction by Mo (VI).