Selective Oxidation on Mixed-Metal Oxides using ReaxFF

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Catalytic selective oxidation of hydrocarbons using mixed-metal oxides (MMO) is of major commercial importance. However, the processes for the direct conversion of saturated hydrocarbons such as propane do not exhibit the selectivity and efficiency necessary for implementation on an industrial scale. We aim to elucidate the mechanism underlying the current propene and propane catalysts and to predict how the catalyst can be optimized to yield better selectivity and activity using computational simulations at realistic reaction conditions. To this end, we developed a ReaxFF reactive force field for use in molecular dynamics (MD) simulations to investigate the structures and reactive dynamics of these complex metal oxide catalysts. The parameters in ReaxFF are derived directly from QM and have been validated to provide good accuracy for a wide variety of reactions. ReaxFF has been used to study the activation and conversion of propene to acrolein by various metal oxide surfaces. Using high-temperature MD-simulations on metal oxides slabs exposed to a propene gas phase, we find that

• Propene is not activated by MoO₃ but it is activated by amorphous Bi₂O₃ to form allyl which does not get oxidized by the surface.

• Propene is activated by Bi₂Mo₃O₁₂ to form an allyl-radical and the hydrogen gets abstracted by a Mo=O bond, which is bridged via an O to a Bi-site.

• Propene is activated over V₂O₅ to form an allyl, which is then selectively oxidized on the surface to form acrolein (Figure 1). The propene reactions on V₂O₅ occur at lower temperatures than on Bi₂O₃ or Bi₂Mo₃O₁₂.

These results are all consistent with experimental observations, encouraging us that such investigations will enhance our mechanistic understanding of catalytic hydrocarbon oxidation sufficiently to suggest modifications for improving reactivity and/or selectivity.

Figure 1. System composition observed during selective oxidation of propene to acrolein on a V₂O₅ surface during MD-simulation.