ABSTRACT

Full exploitation of shale resources requires new catalytic techniques to efficiently convert the methane, ethane, and propane found in shale gas to value-added fuels and chemicals. A promising process of converting ethane and propane involves catalytic light alkane dehydrogenation and the subsequent oligomerization of light alkenes. The first part of this work focuses on the examination of the mechanistic details of propane dehydrogenation on Pt-based alloy catalysts, where first principles-based free energy, microkinetic, and degrees of rate control analyses are performed to understand and rationalize the selective propane dehydrogenation using a Pt_3Mn alloy. We show that only the under-coordinated, Mn-decorated Pt sites, represented by a $Pt_3Mn(211)$ surface, are selective to propylene formation, which can be attributed to several key mechanistic details: (1) facile propylene desorption and (2) hindered pathways that are inherently non-selective to propylene and lead to the formation of isomers. These kinetic details can, in turn, be interpreted using the free energy landscapes of propane dehydrogenation on the $Pt_3Mn(211)$ surface, which features a reasonably stronger binding of propylene than those of its isomers. From this study, we extract two selectivity descriptors for propane dehydrogenation: The energetics of propylene desorption versus deep-dehydrogenation, as well as the energetics of the formation of propylene versus its isomers. The properties can be used for designing further improved light alkane dehydrogenation catalysts.

After dehydrogenation, the oligomerization of the light alkenes produces linear alpha olefins with longer carbon backbones. The second part of this work concentrates on ethylene oligomerization using silica-supported, main group metal single sites, which have recently been found to promote ethylene oligomerization with high activity at moderate temperatures and pressures (523 K and 1 atm). We use first principles-based approaches and explore the molecular-level relationship between active site structures and the associated oligomerization mechanisms by developing amorphous, silica-supported Ga^{3+} models from periodic calculations. We show that the three-coordinated Ga^{3+} site promotes oligomerization through a facile initiation process that generates a Ga–alkyl intermediate, followed by a Ga–alkyl-centered Cossee-Arlman mechanism. The strained geometry of a three-coordinated

site enables a favorable free energy landscape with a kinetically accessible ethylene insertion transition state (1.7 eV) and a previously unreported β-hydride transfer step (1.0 eV) to terminate further C–C bond formation. This result, in turn, suggests that Ga^{3+} does not favor polymerization chemistry, while microkinetic modeling confirms that ethylene insertion is the rate-determining step. Further, we show how automated elementary step enumeration techniques can be applied to the Ga^{3+}-silica systems to explore the mechanisms of possible side reactions. The automated exploration results show that the Ga^{3+} is capable of performing three types of elementary steps with relatively low activation energies: C–C bond formation, β-hydride transfer, and α-hydride transfer. The combination of these steps rationalizes the formation of isomers of 1-butene, odd-number oligomers, and coking products observed in experiments. In aggregate, we demonstrate a promising flexibility of main group ions for hydrocarbon transformations and, more generally, highlights the importance of the local geometry of metal ions on amorphous oxides in determining catalytic properties.

In the third part this work, kinetic measurements and first principles calculations are used for probing the mechanistic details of methane activation on the earth-abundant metal nanoparticles. We show that the rate-determining C–H bond activation of methane, occurring typically through oxidative addition on a pure Ni surface, proceeds via a hydrogen abstraction pathway on nanoparticles that incorporates earth-abundant metals, such as Co and Fe. With higher oxophilicity, the catalytic surfaces retain the reactive oxygen atoms that activate the C–H bond of methane with a $[CH_3\text{-}H\text{-}O^*]^\ddagger$ transition state. Since the transition state does not have a surface-stabilized feature, it exhibits higher degrees of freedom, contributing to a low activation free energy. This shift in the C–H bond activation pathway suggests a drastic transition of both the activity descriptor of methane activation, from carbon to oxygen binding energies, as well as the identity of the most abundant surface intermediate, from carbonaceous species to surface oxygen adatoms. The active site tuning and the catalytic involvement of oxygen adatoms can solve the long-standing challenge in the discovery of a stable, coke-resistant methane reforming catalyst: the oxophilic surfaces do not retain coke, leaving the active sites largely free of carbon deposits, thus coking is not an issue.