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Increased performance of Pt-based catalysts in the catalytic dehydrogenation of propane

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Propylene plays a key role in petrochemical industry for its use in polypropylene production. The conventional source for light alkenes is steam cracking, but this high-temperature process (>1000 K) is not selective and cannot satisfy the growing demand. For this reason, alternative pathways such as on-purpose catalytic propane dehydrogenation have been investigated. However, this highly endothermic reaction, operated at 800-900 K, is sensitive to deactivation reactions. Higher selectivity and activity and minimal coke formation can be achieved by promoting the typical Pt catalyst with another element such as Ga [1]. Additionally, co-feeding hydrogen, which inhibits coke formation, can be used to enhance catalyst performance [2].

Thermodynamic and kinetic data of the propane dehydrogenation reaction were obtained using periodic DFT calculations. Geometries and electronic energies at 0 K were calculated using the Vienna Ab initio Simulation Package (VASP). The optPBE vdw-DF functional was used to take non-local interactions into account, such as van der Waals forces. The Pt(111) and $Pt_3Ga(111)$ surfaces are modeled by a four layered slab and are represented using a 4×2 unit cell, corresponding to typical catalyst coverage. Thermodynamic and kinetic data at relevant temperatures (873 K) have been calculated using statistical thermodynamics and transition-state theory.

To investigate the role of Ga-promotion on the catalytic activity, the energetics of the dominant reaction path towards propylene have been compared on Pt(111) and $Pt_3Ga(111)$. All considered intermediates adsorb more strongly on $Pt_3Ga(111)$ than on Pt(111), only propylene adsorbs as strongly on both surfaces. Furthermore, lower reaction barriers are calculated on $Pt_3Ga(111)$ and, hence, higher catalytic activity for propane dehydrogenation can be expected using Ga-promotion, which is in agreement with experiment [1]. C-C scission reactions and deep dehydrogenation reactions are responsible for coke formation and catalyst deactivation. The favored C_3 species on the surface is 1-propylidyne and this hydrogen-lean species can be considered to be the main coke precursor. Calculations point out that, with respect to gaseous propylene, 1-propylidyne is 46 kJ/mol less strongly bonded to the $Pt_3Ga(111)$ surface than on the Pt(111) surface. It can be concluded that Ga-promotion of Pt is likely to decrease coke formation and enhance catalyst lifetime, as also observed experimentally [1].

Finally, microkinetic simulations have been performed at 873 K and atmospheric pressure with varying hydrogen feed pressures (from 0.0 to 0.25 bar H_2, fixed C_3H_8 pressure of 0.2 bar). Simulations confirm that co-feeding hydrogen leads to hydrogenation of deeply dehydrogenated species on the surface and, hence, higher catalyst steady-state activities.

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