

Single ensemble catalysis: acetylene semi-hydrogenation on indium oxide

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Despite increasing resource scarcity and environmental awareness, industrial hydrogenation catalysts still heavily rely on expensive noble metals such as palladium or platinum modified with toxic selectivity enhancers.¹ Among intensive efforts to address this, one approach involves the untapped potential of metal oxides. In this regard, cerium oxide emerged as an efficient catalyst for the semi-hydrogenation of acetylene,² an important reaction for the purification of olefin streams for downstream polymerization processes. To date, no other metal oxide has been identified that selectively catalyzes this reaction, leaving ample room for a more extensive investigation on the abilities of oxides in hydrogenation catalysis. Here, we have explored the potential of indium oxide to hydrogenate acetylene, uncovering a remarkable 85% selectivity to ethylene at full conversion in continuous-flow tests at ambient pressure (Figure 1a). Detailed analyses by temperature-programmed reduction with H₂, *in situ* diffuse reflectance infrared Fourier transform and Raman spectroscopy, transmission electron microscopy, and density functional theory link the excellent hydrogenation performance with a surface reconstruction during the reaction leading to the creation of well-defined In₃O₅ sites, consisting of an oxygen vacancy, an In trimer and adjacent oxygen atoms, where C₂H₂ and H₂ can co-adsorb and react (Figure 1b). This unusual configuration, which we have named 'single ensemble', comprises a new type of active site in hydrogenation catalysis.

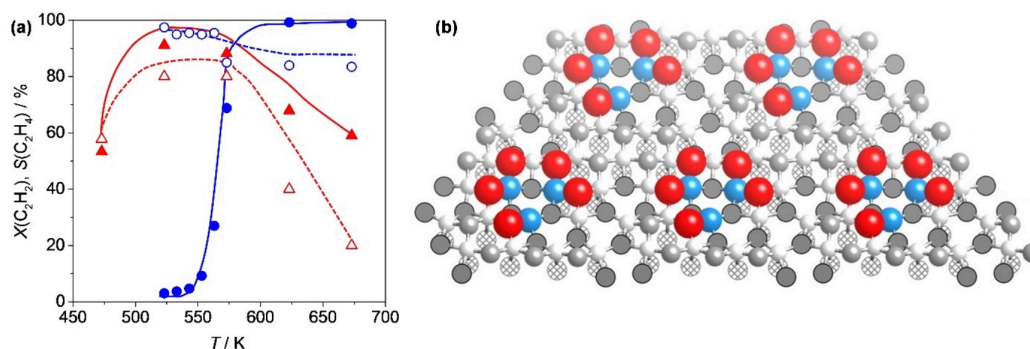


Figure 1 (a) Acetylene conversion (solid symbols) and selectivity to ethylene (open symbols) versus temperature over In₂O₃ (blue) and CeO₂ (red). Conditions: H₂:C₂H₂ = 30, *t* = 1 s, *P* = 1 bar. (b) Oxygen vacancy formation on In₂O₃(111) under reaction conditions leads to the development of In₃O₅ single ensembles. In and O atoms of the ensemble are colored in blue and red, respectively.

[1] G. Vilé, D. Albani, N. Almora-Barrios, N. López, J. Pérez-Ramírez, *ChemCatChem* **2016**, 8, 21.

[2] G. Vilé, B. Bridier, J. Wichert, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2012**, 51, 8620.