

The Synthesis of Fine Chemicals Using Novel Catalysis

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Received: March 14, 2017; Accepted: March 15, 2017; Published: March 17, 2017

The preparation and development of new catalyst materials for selective activation of specific organic functional groups is critical in the fine chemicals industry. Intermetallic nanoparticle catalyst materials supported on micron-sized materials have recently increased in prominence and use as highly selective catalyst materials for carbon-carbon transformations including selective hydrogenation reactions. These reactions constitute critical steps in the manufacture of a vast array of fine chemicals including vitamins, pharmaceuticals, fragrances, cosmetics and nutritional substances. The selective reduction of 2-methyl-3-butyn-2-ol, for example to yield 2-methyl-3-buten-2-ol, avoiding over saturation to butyl alcohol, is an important step in the synthesis of vitamins A and E. On the other hand, the partial reduction of acetylenes to ethylenes in general, are also crucial in industrial polymerization reactions such as the manufacture of polyethylene or polystyrene, since even trace amounts of acetylene can poison the polymerisation reaction, demonstrating the importance of catalyst selectivity on this and similar reactions, which have been widely carried out for many decades, conventionally, using bulk metals such as Pd, supported on materials such as oxides (alumina, titania, etc.) or carbon materials.

Bulk Palladium as the active species in hydrogenation catalysis is incredibly active; however it has limitations in its selectivity to partial hydrogenation reactions due to its high saturation with hydrogen leading to over-hydrogenation and other side reactions such as oligomerisation. The addition of poisons or inactive co-metals to reduce the amount of adsorbed hydrogen, or to reduce the size of active site ensembles to exclude side reactions that require more space is commonplace. The use of "poisoned" catalysts such as the widely used Lindlar catalyst in which the initial Pd on CaCO₃ catalyst is further modified by the addition of lead and quinoline is one effective way of overcoming the selectivity problem.

These studies show that the addition of Pb did not alter the morphology, nor the electronic properties of Pd in the catalyst and thus it was proposed that the mechanism by which Pb improves the selectivity of the catalyst must be by simple blockage of certain active sites on the atomic scale. By alloying Pd with other metals, the electronic effects that influence the adsorption/desorption properties of hydrogen and reactants can have a large effect on the selectivity of hydrogenation reactions. Alongside the electronic effects, however, lie the same effects of reducing the size of active site ensembles that have already been attributed to the selectivity of the Lindlar catalyst. This is achieved


by simple dilution of the Pd atoms present in the material. Such materials have been investigated extensively as selective hydrogenation catalysts using co-metals such as Pb, Ag, Cu and Co. The drawback to these materials however is that even with a Pd content as low as 30%, it is impossible to completely diminish the presence of significantly large ensembles of Pd atoms when randomly distributed in a solid solution. Furthermore, assuming the co-metal is significantly less active than Pd, the greater the extent of dilution, the greater the loss in catalytic activity.

These drawbacks are being addressed in our work focusing on a new or novel generation of intermetallic catalyst materials which are being synthesized, designed and developed to combine high selectivity with activity. Intermetallic compounds are different from alloys in that they have a partially ordered crystal structure within which all of the Pd atoms can potentially be isolated from each other completely in terms of space and coordination. It has been shown that isolated Pd atoms when present as adatoms on another metal surface can dramatically change the hydrogenation characteristics compared to either metal alone and act as hydrogen dissociation sites causing spill over of hydrogen atoms to the less active metal.

Although the Pd is incorporated in a very different way in intermetallic compounds such as PdGa, the same isolation concept can be found here and it stands to reason that in addition to acting as adsorption and reaction sites for the

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Citation: Ibhadon AO, Johnston SK. The Synthesis of Fine Chemicals Using Novel Catalysis. Synth Catal. 2017, 2:1.

organic reagents in question, the same hydrogen dissociation and spill over effects may apply wherein the intermetallic compounds PdGa and Pd₃Ga₇ were first shown as highly active and selective hydrogenation catalysts. These were prepared by melting together stoichiometric amounts of each metal followed by milling to obtain particles. Before achieving sufficiently high activity in the hydrogenation of acetylene, the particles had to be subjected to chemical etching in ammonia to remove the Ga₂O₃ surface layer formed during the milling procedure and expose active Pd atoms at the surface. These catalysts were shown to exhibit similarly high activity compared to reference catalysts of Pd/Al₂O₃ and Pd₂₀Ag₈₀ and, crucially, higher selectivity and thermal stability. The higher selectivity of PdGa was attributed to the concept of active site isolation since all of the active Pd atoms in the structures were coordinated only to Ga with no neighbouring Pd atoms.

In addition to remarkable activity and selectivity many of these compounds exhibit, another important feature of intermetallic compounds is their increased stability compared to conventional metal catalysts. This increased stability is perhaps due to the partially covalent nature of the bonding as opposed to the metallic bonding in elemental Pd. This inhibits the subsurface chemistry that is attributed to the deactivation of elemental Pd over time in catalytic reactions. The roles of structure, order and crucially, active site isolation, have been proposed as crucial factors in selective catalysts for acetylene hydrogenation from the development of the Lindlar catalyst many decades ago, to the recent work on intermetallic compounds where active site isolation has come to the forefront of considerations in the development of new catalyst materials.