

Nanoparticulate Pd₃Sn on TiO₂ and ZnO Supports as Catalysts for Semi-hydrogenation: Synthesis and Catalytic Performance

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New catalytic materials and process chemistries are needed to achieve safer processing and future sustainability in a wide range of applications from the chemical industry to environmental remediation. Catalysts are indispensable in fine chemical synthesis, selective hydrogenations, automotive exhaust treatment, and industrial effluent and municipal waste treatment, technological developments in fuel and photovoltaic cells and pollution abatement technologies. It is recognized that novel and robust catalysts, capable of combining high activity with excellent selectivity and substrate compatibility as well as novel reactor concepts are required to ensure atom economy, process efficiency and environmental sustainability in chemical processing.

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It is now recognised that novel and robust catalysts, capable of combining high activity with excellent selectivity and substrate compatibility are required to ensure atom economy, process efficiency and environmental sustainability in chemical processing. Progress made in flow processing and microreactor methodologies also require innovation at the catalyst frontier so that processes can be developed with higher energy efficiency, increased facility of separation and recovery of products. Catalyst materials able to deliver high selectivity and activity control the overall efficiency of a process by avoiding unwanted side-reactions, limiting the presence of unreacted substrates in the product mixture and increasing the conversion per unit time. In particular, the production of fragrances, pharmaceuticals, Active Pharmaceutical Ingredients (APIs), vitamins and agrochemicals, relies on catalysts developed more than 60 years ago and requires significant improvement in terms of both environmental footprint and performance. An example of these catalytic reactions is selective hydrogenation, which involves, for example, the hydrogenation of a carbon-carbon triple bond to a double bond (semi-hydrogenation), avoiding over-hydrogenation to a single bond. Semi-hydrogenation is one of the critical steps in the synthesis of vitamins A and E, the fragrance compound linalool and other important compounds. The semi-hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) is an important starting reaction in industry and is widely used as a model substrate to screen for activity and selectivity of catalyst materials in semi-hydrogenation reactions.

these materials are more active and selective than other platinum-group metals, but their selectivity towards alkene products is still limited due to over-hydrogenation to alkanes and other side reactions such as dimerization and oligomerization reactions. To overcome this, a co-metal is often added to Pd to increase the selectivity. The co-metal can be added to the Pd catalyst as a surface poison, as is the case in the widely used Lindlar catalyst, in which Pd/CaCO₃ is modified by the addition of Pb. However, the use of lead for catalyst modification is subject to increasing environmental concern. Alternatively, a second metal (co-metal) can be incorporated to form a Pd-M alloy, which can take the form of core-shell, or a random or ordered alloy, depending on the synthetic procedure employed. The crystal structure of any resulting compounds formed between the two metals is often overlooked but can be very important. For example, work carried out on intermetallic compounds formed between Pd and Ga has shown that, depending on the stoichiometry and crystal structure of the compound formed between Pd and Ga, drastically different selectivities are achieved in gas phase acetylene hydrogenation. Therefore, achieving phase purity, rather than mixtures of different active compounds present throughout a catalyst, can also be considered of vital importance since different compositions formed between two metals can have different catalytic properties.

Our work on palladium based intermetallic catalyst materials and nanoparticles for selective hydrogenation reactions show that

Many Pd-based alloy (bimetallic) materials have been tested in the literature as selective hydrogenation catalysts, utilising co-metals

such as Ag, Cu, Co, Fe, Zn, Sn, Zr, Ni and Au. When forming an alloy with the second metal, selectivity can be enhanced by two main factors. Firstly, an increase in selectivity can occur due to changes in the electronic structure of Pd brought on by the presence of an additional metal, which can change the relative adsorption energies of alkyne and alkene bonds. This can result in a more favourable adsorption, and hence, the hydrogenation of alkyne, while disfavoring the adsorption and hydrogenation of alkene species. Secondly, alloy formation can reduce the number and size of active site ensembles due to dilution of Pd. This can inhibit secondary reactions that involve different functional groups, or neighbouring reactants to be adsorbed in close proximity to each other. Geometric effects should however have less impact on the semi-hydrogenation of acetylene alcohols as only one functional group is available for hydrogenation, although it may assist in preventing unwanted dimerization reactions from taking place.

The co-metal of interest in this work is Sn, as Sn is known to form a range of compounds with Pd. The Pd-Sn system includes: PdSn, PdSn₃, PdSn₂, α - and β -Pd₃Sn₂, PdSn, Pd₂Sn and Pd₃Sn. We have focused our studies on Pd₃Sn. Catalysts containing Pd-Sn alloys have already been used for electrooxidation, hydrogen peroxide synthesis, water denitration, and in the selective hydrogenations of unsaturated aldehydes, hexa- and butadienes, and gas phase acetylene. In many of these cases, high selectivity is achieved

and attributed to the suppression of the adsorption of certain functional groups to the catalyst due to the altered electronic structure, or to the formation of Pd-Sn bonds by the reduction of active site ensembles. The change in electronic structure of Pd on alloying with Sn has been shown by photoemission data to involve a valence charge transfer from Sn to Pd, and is most prominent when the alloys Pd₂Sn or Pd₃Sn are formed. This charge transfer effect has also been shown to suppress the adsorption of C=C specifically, compared to Pd alone. Furthermore, work carried out on compounds such as PdGa has shown the benefit of isolated Pd sites (ensemble effect) in ordered alloys and intermetallic compounds in favouring the successive, stepwise hydrogenation of the acetylene bond rather than full hydrogenation to alkane.

However, in the current literature on Pd-Sn catalysts, there has been no attempt to characterise the purity of the catalytically active Pd-Sn phase, hence mixtures of Pd/Sn monometallic and/or bimetallic phases are present in the catalyst. This means that it is unclear which phase is responsible for the catalytic performance. Consequently, our work is devoted to studying a range of intermetallic Pd based catalyst materials and alloys, for example, Pd-Sn alloy Pd₃Sn, for selective reduction reactions and this includes an assessment of their purity and crystal structure using a suite of spectroscopic and microscopic techniques, including XRD, HRTEM, SEM, XPS and EDX.