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Pd_3Sn nanoparticles on TiO_2 and ZnO supports as catalysts for semi-hydrogenation: Synthesis and catalytic performance

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ABSTRACT

The two catalysts Pd_3Sn/TiO_2 and Pd_3Sn/ZnO were prepared via a one-pot procedure based on the "polyol method" with the addition of a capping agent (polyvinylpyrrolidone) to control the particle size distribution. The same procedure was used to prepare Pd/TiO_2 and Pd/ZnO for comparison. All four catalysts showed high activity and selectivity for the selective hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) in the liquid phase under identical conditions. However, Pd_3Sn/TiO_2 and Pd_3Sn/ZnO show selectivities to alkene significantly higher than that of the Pd catalysts. Specifically, the selectivity increases from 96.4% to 97.4% on TiO_2 support, and 96.2% to 97.6% on ZnO support, at 90% conversion. Transition electron microscopy shows nanoparticles evenly dispersed on the support, with mean particle sizes as low as 4.1 (± 0.8) nm when Sn is incorporated into the catalyst. Unsupported Pd_3Sn was prepared using the same method and characterised by powder X-Ray diffraction followed by the Rietveld refinement. Pd_3Sn was found to be single-phase and isostructural to Pd metal with a face centred cubic unit cell.

1. Introduction

Highly selective, active and environmentally-friendly catalysts are of prime importance for many areas of chemistry. In particular, the production of fragrances, pharmaceuticals, 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 [1].

The semi-hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) (Fig. 1) is an important starting reaction in industry [2] and is widely used as a model substrate to screen for activity and selectivity of catalyst materials in semihydrogenation reactions [3,4].

Palladium-based catalysts in semi-hydrogenation reactions are active and more selective than other platinum-group metals [5], 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 [6]. 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 [7], in which $Pd/CaCO_3$ is modified by the addition of Pb. However, the use of lead for catalyst modification is subject to increasing environmental and product poisoning concerns [8].

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 [9]. 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 [10]. Therefore, achieving phase purity, rather than mixtures of the various

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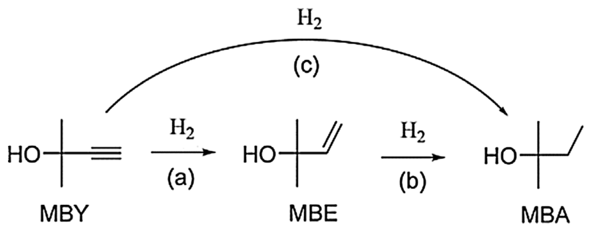

Fig. 1. Reaction scheme of the hydrogenation of MBY to MBA. (MBY = 2-methyl-3-butyn-2-ol, MBE = 2-methyl-3-butene-2-ol and MBA = 2-methylbutan-2-ol.) For a selective semi-hydrogenation, steps (b) and (c) should be avoided.

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.

Many Pd-based alloy (bimetallic) materials have been tested in the literature as selective hydrogenation catalysts, utilising co-metals such as Ag [11,12], Au [13–15], Bi [8,16–18], Co [19], Cu [20,21], Fe [22,23], Ni [23,24], Sn [25], Zn [26–29], Zr [30]. 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 disfavouring the adsorption and hydrogenation of alkene species [31]. Secondly, alloy formation can reduce the number and size of active site ensembles due to dilution of Pd [9,32]. 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 dimerisation reactions from taking place.

The co-metal of interest in this work is Sn, because Sn is non-toxic and is known to form a range of compounds with Pd. Known Pd-Sn binary alloys include $PdSn_4$, $PdSn_3$, $PdSn_2$, α- and β-Pd_3Sn_2, PdSn, Pd_2Sn and Pd_3Sn. We have focused our studies on Pd_3Sn, which is isostructural to Pd and hence makes for a better comparison to the catalytic performance of monometallic Pd.

Catalysts containing Pd-Sn alloys have already been used for electrooxidation [33,34], hydrogen peroxide synthesis [35], water denitration [36–38], and in the selective hydrogenations of unsaturated aldehydes [39,40], hexa- and butadienes [41–43], and gas phase acetylene [44]. In many of these reactions, high selectivity is achieved and attributed to the suppression of the adsorption of certain functional groups onto 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 Pd_2Sn or Pd_3Sn are formed [45]. This charge transfer effect has also been shown to suppress the adsorption of C=C specifically, compared to Pd alone [40]. 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 [10,46–48].

However, in the current literature on Pd-Sn catalysts, there has been no attempt to achieve purity of the catalytically active Pd-Sn phase, hence mixtures of Pd/Sn monometallic and/or bimetallic phases are present in the catalyst [33,34,37–40,44]. This means that it is unclear which phases are responsible for any improved catalytic performance compared to monometallic Pd.

The aim of this work was to study the Pd-Sn alloy Pd_3Sn and assess the purity and crystal structure of the material. Furthermore, Pd_3Sn/TiO_2 and Pd_3Sn/ZnO catalysts were prepared and showed enhancement in the catalytic performance compared to Pd/TiO_2 and Pd/ZnO catalysts in the semi-hydrogenation of MBY.

2. Experimental

2.1. Materials

The metal precursors used in the catalyst preparation were palladium(II) acetylacetonate (99%, Aldrich) and tin(II) acetyl acetate (99.9%, Aldrich). Zinc oxide (99.9%, 200 mesh powder, Alfa Aesar) and titanium(IV) oxide, rutile phase (powder, < 5 μm, ≥99.9%, Aldrich) was used as support and polyvinylpirrolidone (PVP) (average mol. Wt. 40,000 g mol^{-1}, Sigma-Aldrich) was used as a capping agent. Acetone (laboratory reagent grade, Fischer Chemical), ethanediol (laboratory reagent grade, Fischer Chemical), *n*-hexane (GPR grade, VWR Chemicals) and deionised water were used as solvents without any pretreatment. For the hydrogenation reactions, butan-1-ol (analytical reagent grade, Fisher Scientific) was used as internal standard for GC analysis. All chemicals were used as purchased.

2.2. Catalyst preparation

The method used for the preparation of the catalysts was adapted from a polyol method used by Cable and Shark [49] for the preparation of Pt_3Sn.

Firstly, appropriate stoichiometric amounts of the metal precursors, palladium acetylacetonoate and tin acetate, each in 100 mL ethylene glycol, were combined into the reaction vessel and either ZnO or TiO_2 support was added alongside PVP as capping agent (10 monomer mol% of total Pd and Sn). The amount of the support used was calculated to achieve 2 wt% Pd loading. The mixture was stirred under nitrogen gas flow at room temperature for at least 30 min to displace air before heating at reflux (469 K) for 1 h. The mixture was cooled and the resulting brown/grey solid was obtained from the reaction mixture by centrifugation at 3500 rpm, washing alternately with acetone and deionised water (3 × 30 mL each) and dried at 353 K in air for 1 h to yield a grey powder. The catalysts are stored in a vacuum desiccator until use.

Unsupported Pd_3Sn for structural characterisation was prepared using the same method with exclusion of the support and PVP.

2.3. Catalyst characterisation

Powder X-ray diffraction (PXRD) was carried out using a PANalytical Empyrean X-ray diffractometer using monochromatic Cu Kα1 radiation and line PIXcel detector, scanning in the 2θ range of 20–120°, step size 0.105° and step time 12,000 s. Results were recorded using the instrument's built-in software. Rietveld refinement was performed using GSAS software with the EXPGUI interface [50].

Samples for transmission electron microscopy (TEM) were dispersed in ethanol using an ultrasonic bath and a drop of dispersion was deposited onto carbon-coated copper grids. Images were obtained using a Gatan Ultrascan 4000 digital camera with Digital Micrograph software, attached to a Jeol 2010 TEM instrument running at 200 kV. Nanoparticle size distributions were obtained studying 3–5 TEM microphotographs obtained from different areas of the catalyst sample, measuring the diameter of a total of 200–400 individual nanoparticles using Gatan Digital Micrograph software.

The total uptake of CO was measured with a Micromeritics AutoChem 2910 apparatus. Prior to a measurement, the catalyst was reduced in hydrogen with the following programme: flushing with helium at room temperature for 10 min, reduction in hydrogen at 573 K (10 K/min) for 120 min, flushing with helium at 573 K for 30 min and then returned to ambient temperature.

Palladium and tin content of the catalysts were determined using a Perkin Elmer Optima 5300DV emission inductively coupled plasma

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