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Palladium–bismuth intermetallic and surface-poisoned catalysts for the semi-hydrogenation of 2-methyl-3-butyn-2-ol

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ABSTRACT

The effects of poisoning of Pd catalysts with Bi and annealing in a polyol (ethylene glycol) were studied on the semi-hydrogenation of 2-methyl-3-butyn-2-ol (MBY). An increase in the Pd:Bi ratio from 7 to 1 in the Bi-poisoned catalysts decreased the hydrogenation activity due to blocking of active sites, but increased maximum alkene yield from 91.5% for the Pd catalyst to 94–96% for all Bi-poisoned Pd catalysts, by decreasing the adsorption energy of alkene molecules and suppressing the formation of β-hydride phase. Annealing of the catalysts induced the formation of intermetallic phases and decreased its activity due to sintering of the catalytic particles and low activity of intermetallic compounds. Langmuir–Hinshelwood kinetic modelling of the experimental data showed that poisoning of Pd with Bi changed the relative adsorption constants of organic species suggesting ligand effects at high Bi content.

1. Introduction

Semi-hydrogenation or selective hydrogenation reactions aim to transform triple-bonded molecules into double bonded ones, and constitute critical steps in the synthesis of a vast array of fine chemicals including vitamins, fragrances, drugs and many other products with a worldwide production of more than 1000 t a year [1,2]. However, traditional hydrogenation catalysts including supported nanoparticles of Pd and Pt usually lead to low catalyst selectivity. To overcome the problem, the catalysts are usually modified with reversible and irreversible adsorbates which introduce ligand (electronic) effects that change the relative adsorption energies and selectively block the active sites responsible for side-reactions [3,4].

The catalyst modification is performed by surface poisoning and alloying. For example, active sites of Pd in Pd–Ag alloys are isolated, which decreases the rate of oligomerization, while silver induces ligand effects changing the adsorption energies facilitating desorption of alkenes [5,6]. Often, carbon monoxide (a reversible adsorbate) is added to the acetylene feedstock to increase selectivity by competing with alkene molecules for adsorption sites [7,8]. Lindlar catalyst, an industrial standard for semi-hydrogenation, employs lead as an irreversible adsorbate and quinoline as a reversible adsorbate. Metals such as Cu have been extensively studied as irreversible adsorbates [9,10] while sulphur- and nitrogen-containing polymer modifiers combine the functions of reversible and irreversible adsorbates [11,12]. However, the increase in selectivity brought about by modifiers is usually counterbalanced by the decrease in activity [2,10,13], so industrial semi-hydrogenation catalysts should combine an optimal level of catalyst poisoning to improve selectivity while minimising decrease in activity. Moreover, other considerations such as catalyst price, the environmental footprint of catalyst synthesis and the overall economy of the catalytic process should be considered. In this respect, Lindlar catalyst is still the main catalyst used by industry because of its high activity, selectivity and ease of preparation. However, there are a number of problems associated with the use of Lindlar catalysts including the toxicity of lead compounds and that an additional separation step is required when quinoline is used.

In order to address these problems, bimetallic Pd-based catalysts are being studied to improve selectivity and to mitigate environmental problems associated with the use of lead in Lindlar catalyst. Highly selective Pd–Zn alloys were shown to form in

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Pd/ZnO catalysts during hydrogenation [14–17] while many other bimetallic systems have been studied and theoretically evaluated [4,18]. However, from an industrial point of view, the synthesis of an industrial semi-hydrogenation catalyst should be scalable, hence many catalytic systems that require expensive metallorganic precursors for their synthesis and very carefully controlled reaction conditions cannot compete with Lindlar catalyst. A rather recent trend in catalysis is the study of the intermetallic compounds, which can be defined as electrically conductive compounds of metals, but the most interesting properties for catalytic applications might be precisely defined structural order and electronic properties different from that of initial metals [19]. For example, palladium–gallium intermetallic compounds have been reported to be very selective in acetylene hydrogenation [20]; however, recent data show that Pd_2Ga intermetallic compounds oxidise quickly in liquid-phase hydrogenation even under carefully controlled laboratory conditions due to the high oxygen affinity of Ga [21].

Therefore, in an attempt to identify promising catalysts, considering their performance and the ease of synthesis, we have confined our attention in this study to easily reducible heavy metals. Lead, the adsorbate in Lindlar catalyst, has two neighbours in the periodic table: thallium and bismuth. Palladium-based catalysts modified with either one of these metals showed very high selectivity in hydrodechlorination reactions [22], but considering the extremely high toxicity of thallium, palladium–thallium catalysts cannot be considered as a promising alternative to Lindlar catalyst. In contrast to lead, the toxicity of bismuth is significantly lower [23–25], which makes it a promising catalyst for industrial applications in the semi-hydrogenation in the synthesis of fine chemicals.

Palladium–bismuth systems have been studied in oxidative acetoxylation reactions and Pd_3Bi intermetallic compounds have been found to be the most selective [26,27]. Promotion of Pd with Bi was found to increase the selectivity to the partial oxidation of glucose to gluconic acid [28–30]. Similarly, in hydrogenation reactions, intermetallic compounds of Pd and Bi were identified as promising highly selective catalysts [31–33]. Anderson and co-workers studied a Pd catalyst selectively poisoned with Bi and demonstrated the preferential adsorption of Bi on step sites, which had little effect on 1-hexyne hydrogenation, but decreased the rates of subsequent 1-hexene isomerisation reactions [34,35]. To the best of our knowledge, intermetallic compounds of palladium and bismuth have not been tested in semi-hydrogenation reactions. These catalysts could potentially combine the advantages of Pd–Ga intermetallics with low toxicity and ease of synthesis of bismuth-modified catalysts.

The aim of the study was to investigate the effects of Bi-poisoning and intermetallic formation of Pd catalysts on the semi-hydrogenation of 2-methyl-3-butyn-2-ol (MBY), an important industrial intermediate used in the synthesis of fine chemicals and vitamins [1,36,37].

2. Experimental

2.1. Catalyst preparation

Pd/SiO_2 catalyst with the Pd nominal loading of 5% was prepared by dissolving palladium (II) acetate ($Pd(Oac)_2$, 98%, Aldrich) in the calculated amount of toluene (99%, VWR chemicals) to fill the pores of amorphous fumed silica (Alfa Aesar, BET specific surface area of 200 $m^2\,g^{-1}$). The slurry was dried in a rotary evaporator, calcined in a tube furnace at 400 °C for 2 h and reduced in hydrogen at 150 °C for 1 h. Amorphous silica and high Pd loading were deliberately chosen to allow for analysis by X-ray diffraction.

The catalyst obtained was poisoned with Bi. Pd/SiO_2 catalyst (about 700 mg) was placed into a 50 mL flask and 2% acetic acid (20 mL) in distilled water was added. Then the calculated aliquot of a 20 mM $Bi(NO_3)_3$ solution in 2% acetic acid was added under stirring to obtain the catalysts with Pd/Bi ratios of 1/1, 3/1 and 7/1 assuming that all Bi was reduced from the solution. The dispersion was stirred for 16 h at 80 °C in hydrogen atmosphere. The catalysts were centrifuged, washed with water (2 × 40 mL), acetone (3 × 30 mL), and dried in a rotary evaporator at 80 °C. After cooling of the samples in the rotary evaporator to room temperature, the vacuum pump was turned off, slowly admitting air to the catalyst over a period of about 2 h to passivate the surface. The catalysts were packed into vials and kept under a nitrogen atmosphere to prevent further oxidation. The surface-poisoned catalysts obtained were named Pd_7Bi/SiO_2, Pd_3Bi/SiO_2 and Pd_1Bi/SiO_2 to reflect the nominal Pd:Bi ratio.

Each Bi-poisoned catalyst was annealed in ethylene glycol to induce the formation of intermetallic phases adapting the polyol method [38]. The catalyst (400 mg) was placed into a round-bottom flask and 50.0 mL of ethylene glycol (99%, Fisher Scientific) was added under stirring. Air from the flask was displaced by a flow of nitrogen for 5 min; the slurry was heated, refluxed at 196 °C for 20 min, and cooled in nitrogen flow. The catalysts obtained were centrifuged, washed, passivated as per Bi-poisoned Pd catalysts, and named as $Pd_1Bi(t)/SiO_2$, $Pd_3Bi(t)/SiO_2$ and $Pd_7Bi(t)/SiO_2$.

Unsupported nanoparticles of Pd–Bi intermetallic compounds were obtained using the polyol method annealing Pd and Bi precursors in the presence of polyvinylpyrrolidone (PVP, Sigma–Aldrich) [38]. $Pd(Oac)_2$ (50 mg) and $Bi(NO_3)_3{\cdot}3H_2O$ (the amount was calculated to obtain Pd:Bi molar ratios of 1:1 and 1:2) were dissolved in 75 mL of ethylene glycol under sonication, PVP (250 mg) was slowly added under stirring. After 30 min, $NaBH_4$ (300 mg, 98%, Sigma–Aldrich) was added and the solution was heated and refluxed under nitrogen flow for 20 min. When the slurry was cooled, the dispersion was diluted with 50 mL methanol, centrifuged, washed with water (2 × 30 mL), methanol (2 × 30 mL), acetone (2 × 30 mL) and left in 20 mL of acetone. The dispersion obtained was sonicated for 10 min and 15 mL were used to impregnate silica (800 mg) giving raise to $PdBi(im)/SiO_2$ and $PdBi_2(im)/SiO_2$ catalysts.

Lindlar catalyst (Pd poisoned with Pb supported on $CaCO_3$) was purchased from Aldrich and used as received without the addition of quinoline.

2.2. Characterisation

Powder X-ray diffraction (PXRD) measurements were performed using an Empyrean X-ray diffractometer equipped with a monochromatic Kα-Cu X-ray source and a PIXcel linear detector. The scanning was performed in 2θ range of 20–85°, step length 0.0390°, and step time 25 min. Silica-supported catalysts were packed into conventional powder holders, while the dispersion of the intermetallic nanoparticles in acetone was dropwise added on a silicon zero-background sample holder.

Scanning electron microscopy (SEM) study was performed on a Zeiss EVO 60 instrument equipped with energy-dispersive X-ray spectrometer (EDX) Oxford Instruments Inca System 350 under the pressure of 10^{-2} Pa and electron acceleration voltage of 20 kV. Catalyst powder was applied on carbon adhesive mats and carbon-coated before the study.

Transmission electron microscopy (TEM) study was performed using a Jeol 2010 instrument equipped with an energy-dispersive X-ray spectrometer (EDX) produced by Oxford Instruments. For the study, the materials were dispersed in ethanol under sonication and a few droplets of the dispersion were applied on carbon-coated copper grids. TEM study was performed from 5–8 regions for every sample to obtain representative data.

Elemental analysis was performed using a Perkin Elmer Optima 5300DV emission inductively coupled plasma spectrometer. The