



Palladium phosphide nanoparticles as highly selective catalysts for the selective hydrogenation of acetylene



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ABSTRACT

Pd₃P and PdP₂ phases of ca. 4 nm particle diameter were prepared on a TiO₂ support by an impregnation route. Data from the hydrogenation of acetylene under both non-competitive and competitive conditions showed that PdP₂/TiO₂ exhibits enhanced selectivity and stability relative to Pd₃P. Furthermore, the selectivity produced over PdP₂ (84% ethylene selectivity @ 100% acetylene conversion) compares favorably with recently reported materials. XPS and CO-IR measurements reveal that the incorporation of P helps to break up contiguous Pd sites. This in turn is thought to affect the adsorption and desorption of reactants/products and thus improves selectivity. This work reveals that the incorporation of P into Pd materials could be regarded as a promising approach to develop new and improved Pd-based catalyst by creating a means to control the nature of the active sites.

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1. Introduction

Ethylene is a key intermediate and product in the petrochemical industry with the majority being used for polyethylene production. Traditionally, it has been produced from steam cracking of naphtha [1–4]. However, the emergence of a plentiful supply of low cost ethane from shale gas means that steam cracking of ethane is growing in popularity [5,6]. Both approaches tend to produce undesired unsaturated hydrocarbons which can poison polymerization catalysts unless removed down to low ppm levels. For example, naphtha cracking yields 0.5–2% of acetylene [1,4]. The preferred method for reducing acetylene to an acceptable level is selective hydrogenation since this yields additional ethylene and therefore maximizes the profitability.

Supported Pd catalysts are commonly employed in these processes but exhibit unsatisfactory selectivity and stability unless, for example, alloyed with a second metal [3,4]. Alloying is thought to serve multiple functions. Firstly, it breaks up contiguous Pd sites, which have a greater barrier for desorption of ethylene relative to that of hydrogenation [7,8]. Secondly, alloying limits hydrogen migrating into the bulk of Pd to form palladium hydride with good

evidence linking hydride formation to over-hydrogenation [9–14]. Industrially, Ag is the most commonly utilized metal for alloying, although a number of alternatives have been reported in the literature [15–19]. In some cases the role of the second metal is merely structural, although in other examples the second metal (i.e., Cu) may play an active role in the catalytic mechanism [20–25]. Even though alloying enhances selectivity, it is not uncommon to co-feed CO as a competitive adsorbate to limited ethylene adsorption at high levels of acetylene conversion [3]. The difficulty with this latter approach is that the amount of CO added must be regulated in real-time to avoid deactivating the catalyst to an extent where ‘acetylene slip’ occurs [2,3,26].

In recent years a number of alternative approaches to control selectivity have been reported which include using sulfur and phosphorous molecules as selectivity modifiers [27–30], inter-metallic compounds [31–33], metal oxides such as CeO₂ [34,35] and In₂O₃ [36] or site-isolated Pd atoms constrained within a C₃N₄ host [37]. All of these examples are similar in that the environment around the active site is both uniform and well-defined. Inspired by success using sulfur compounds to enhance the selectivity of Pd catalysts, recently attention was given to palladium sulfide (specifically the Pd₄S phase) where exceptionally promising results were obtained which were attributed in part to a ‘site isolation’ effect [38–40]. Albani et al. subsequently published a molecular level understanding for Pd₃S/C₃N₄ as a catalyst and attributed

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the stellar performance to site-isolated Pd trimers [41]. In that work, Pd₃S and Pd₄S are compared and shown to be similar, yet subtly different.

Encouraged by the performance of palladium sulfide attention was turned to palladium phosphide materials which have already attracted considerable interest in magnetic [42], electronic [43,44], optics [45,46], energy storage [47,48] and catalytic applications [49,50] but are less well studied than the analogous nickel phosphides [51]. In terms of heterogeneous catalysis, this class of materials offers fascinating properties such as tunable composition (i.e., Pd₁₅P₂ to PdP₃ phases known to exist) and controllable crystallinity. For example, several studies have shown that metal phosphides (e.g., NiP [52,53], CoP [54,55] and RhP [56]) are highly active towards hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of petroleum feedstocks. Moreover, Ni–P nanoparticles have recently been explored for the chemoselective hydrogenation of phenylacetylene [57]. However, there are few reports in the case of palladium phosphide [58], particularly with regards to the selective hydrogenation of acetylene. Herein, the synthesis of two TiO₂ supported palladium phosphides with different Pd/P ratios are described. Detailed characterisation showed that either Pd₃P or PdP₂ phases were formed with selectivity linked to the unique active site arrangement created by incorporation of P.

2. Experimental

2.1. Materials

Chemical reagents including PdCl₂ (Johnson Matthey), NaCl (Fisher Scientific), NH₄H₂PO₂ (Alfa Aesar) and P25 TiO₂ (Aldrich) were purchased and used without further purification. Deionized water (electrical conductivity < 10⁻⁶ S cm⁻¹) was used in all the experimental steps.

2.2. Synthesis of TiO₂ supported Pd_xP_y catalysts

Palladium phosphide catalysts with different Pd/P ratios were prepared by an impregnation method [59]. Firstly, Pd/TiO₂ (2 or 10 wt% Pd) was prepared by wet impregnation using PdCl₂ dissolved in 1 mol L⁻¹ aqueous HCl. A slurry was formed (2 g of TiO₂) and stirred for 2 h before being dried at 120 °C. Next, Pd/TiO₂ was impregnated with phosphorous by adding an aqueous solution of 1 mol L⁻¹ NH₄H₂PO₂ with stirring for 2 h followed by drying at 70 °C, to give samples with nominal Pd/P molar ratios of 3:1 and 1:2. The materials were then reduced in 20% H₂/N₂ (25-ml min⁻¹) at 500 °C for 4 h with a heating rate of 10 °C min⁻¹. Samples are denoted as 2 or 10% Pd_xP_y/TiO₂ where x and y denote the palladium phosphide stoichiometry/phase (either Pd₃P or PdP₂).

2.3. Catalyst characterisation

X-ray Diffraction (XRD) patterns were recorded on an X'Pert powder diffractometer (PANalytical) fitted with a PIXcel1D detector using Cu K α radiation ($\lambda = 0.154$ nm) at $2\theta = 20$ – 85° with a step size of 0.013° . The phase compositions were determined by Rietveld refinement using HighScore Plus software [60]. The particle size and structure of samples were determined using a JEOL JEM-2100F high-resolution transmission electron microscope (HRTEM) combined with energy dispersive X-ray spectroscopy (EDX) to examine composition. Elemental analysis for Pd was performed using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectrometer (ICP-AES). Temperature-programmed reduction and oxidation experiments (TPR and TPO, respectively) were performed on a TPDR0 1100 instrument with a thermal conductivity detector (TCD). The sample (100 mg) was loaded in the

bottom of quartz reactor. TPR profiles were collected in a temperature range of 30–250 °C using a heating rate of 5 °C min⁻¹ and 5% H₂/N₂ as the reductant gas (20 ml min⁻¹). The hydrogen consumption was quantified based on a response factor determined using a high purity CuO standard. Carbon deposition was analyzed by conducting TPO-MS experiments. Used catalyst samples were heated in 5% O₂/N₂ (20 ml min⁻¹) from room temperature to 600 °C with a heating rate of 10 °C min⁻¹. In situ diffuse reflectance Fourier Transform Infrared (DRIFT) spectroscopy of adsorbed CO was obtained with a Bruker Tensor 27 instrument with a resolution of 4 cm⁻¹. Samples were first treated at 250 °C in N₂ for 30 min, before being cooled to room temperature and evacuated to ca. 10⁻⁴ mbar before a background was recorded. Then the samples were exposed to a 99.9% CO flow for another 30 min. A spectrum was then obtained after further evacuation to ca. 10⁻⁴ mbar. X-ray photoelectron spectra (XPS) of samples were measured to obtain the surface atomic ratios from a Shimadzu AXIS Supra X-Ray Photoelectron spectrometer equipped with an Al K α anode. The C1s peak at 284.6 eV was used as the reference.

2.4. Selective hydrogenation of acetylene

Gas phase hydrogenation reactions under non-competitive and competitive conditions were conducted in a Microactivity Reference fixed-bed microreactor (9 mm diameter) at 1 bar pressure using catalyst (50 mg) diluted with SiC (200 mg, 200–450 mesh, Aldrich). Non-competitive reactions were carried out in a flow of 1.2% acetylene/balance N₂ with 2 equivalents of H₂ co-fed relative to acetylene. The competitive tests were performed in a mixture of 0.6% acetylene/5.4% ethylene/balance N₂ with 2 equivalents of H₂ co-fed relative to acetylene. The reactor temperature was varied from 50 to 225 °C in 25 °C increments with 5 h time on stream (TOS) at each temperature in order to access catalyst stability. Prior to reaction, samples were re-reduced in 10% H₂/N₂ at 250 °C for 2 h (60 ml min⁻¹). The product distributions were determined by gas chromatography (PE Clarus 580) with a flame ionization detector using an elite alumina capillary column. Conversion is defined as the amount of acetylene reacted divided by the amount introduced. Product selectivity is defined as the amount formed (i.e., ethylene_{out} – ethylene_{in}) divided by the amount of acetylene reacted. Negative selectivity indicates that a fraction of the ethylene in the feed is over-hydrogenated to ethane. Selectivity to oligomers was calculated from a carbon balance (100 ± 2%) assuming that the sum of alkene, alkane and oligomers selectivity equaled 100% [22,23].

3. Results and discussions

3.1. Catalytic performance under competitive and non-competitive conditions

The catalytic performance of the 2% loaded samples were first evaluated using experiments with acetylene as the sole hydrocarbon in the feed gas (Fig. 1). At 50 °C, the P:Pd ratio appeared to have an impact on the initial activity with the Pd₃P phase being more active than PdP₂. Analysis of the absolute Pd loading by ICP (Table S1) suggested that this effect was more likely associated with the nature of the phosphorous phase as opposed to the amount of Pd present in the samples. In terms of selectivity at 50 °C, the most active sample, 2% Pd₃P/TiO₂, produced ethylene and ethane in similar amounts (ca. 40%) whereas 2% PdP₂/TiO₂ exhibits higher selectivity to ethylene (55%) with oligomers (35%) and ethane (20%) as minor products. The product distribution over PdP₂/TiO₂ may imply that under these conditions hydrogenation is less prominent or that acetylene coverage is high which promotes

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