



# Evolution of palladium sulfide phases during thermal treatments and consequences for acetylene hydrogenation



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## ABSTRACT

Unsupported, bulk phase palladium sulfide has been studied for the selective hydrogenation of acetylene. The sample underwent significant change during thermal pretreatments, the extent of which depends on temperature. Exposure to hydrogen at temperatures of 150 °C or above results in the loss of sulfur from the sample, primarily as hydrogen sulfide. As sulfur is lost, the sample is progressively transformed from a sulfur rich phase (PdS) to a sulfur lean phase (Pd<sub>4</sub>S) via an intermediate phase (Pd<sub>16</sub>S<sub>7</sub>). Reduction at 250 °C produces a material, which contains Pd<sub>4</sub>S as the surface phase, whereas reduction at 350 °C results in a largely pure Pd<sub>4</sub>S phase. Thermal treatments which produce a Pd<sub>4</sub>S surface display excellent catalytic properties. At complete acetylene conversion at 250 °C, ethylene selectivities of 82.8% and 90.0% were obtained under non-competitive and competitive conditions, respectively. Beneficial catalytic properties arise from the uniformity of Pd sites due to the crystal structure of Pd<sub>4</sub>S along with electronic influences on the adsorption/desorption processes arising from sulfur neighbours. No indications of deactivation or significant deposition of carbon were observed over Pd<sub>4</sub>S sample after 50 h on stream.

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## 1. Introduction

A significant proportion of ethylene used for polymerisation is derived from naphtha cracking. This process results in an ethylene stream contaminated with 0.5–2% of acetylene, which can poison the polymerisation catalysts [1–3]. To remove the impurity to an acceptable level (<5 ppm), selective hydrogenation of acetylene is widely employed as it generates additional ethylene and therefore increases profitability [4]. Thermodynamics makes this process viable [5] when both acetylene and ethylene are present, since the adsorption energy of acetylene is generally greater on most surfaces than that of ethylene contributing to preferential adsorption. However, when acetylene concentration is low (i.e., near the 5 ppm requirement), ethylene is free to adsorb resulting in over-hydrogenation to ethane, thereby decreasing process efficiency and profitability. Furthermore, acetylene based oligomerisation results in the formation of green oil (C<sub>x</sub>H<sub>y</sub>), which accumulates on the catalyst surface leading to gradual deactivation [1]. The extent to which deactivation occurs depends on plant design. A ‘front-end’ type reactor is situated upstream of the demethaniser,

and the feed gas contains a large excess of hydrogen. In contrast, a ‘back-end’ type reactor uses a purified gas feed to which a near stoichiometric amount of hydrogen can be added. Deactivation is relatively rapid in hydrogen lean conditions resulting in the need to regenerate more frequently [6]. Despite this limitation, back-end type reactors are the most common plant configuration. Industrial catalysts for this process generally contain Pd as the active component but require the use of Ag as a structural modifier [7] with CO often used to compete with ethylene for adsorption sites to suppress over-hydrogenation [2]. Pd-based catalysts generally demonstrate high activity but limited selectivity in this reaction due to hydride/carbide formation [8–13] with calculations suggesting that the barrier for ethylene desorption is higher than that for over-hydrogenation [14].

A common approach to improve ethylene selectivity over Pd nanocatalysts is to alloy with a second metal such as Ag [15–17], Au [18,19], Cu [20–24], Ni [25], and Zn [26], which dilutes Pd and reduces the ensemble size, and thus inhibits formation of the β-PdH phase [11]. In recent literature, the idea of ‘Pd active site isolation’ has become popular and typically contributes to enhanced alkene selectivity [27]. Well defined intermetallic PdM compounds (M = Ga, In, Cu) fall within this category and favour the enhancement of selectivity but at the expense of activity [28–30]. Moreover, the effectiveness with which the costly precious metal

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component is used (i.e., fraction exposed at the surface) is generally low. Some progress has been made towards making nanosized intermetallic catalysts to overcome this limitation [31]. A more effective use of Pd has been demonstrated in single atom alloys (SAA's) where a high proportion of Pd atoms are actually surface atoms. In some cases the Pd atoms in SAA's are assigned as the active site, [32,33] whereas in others they act as a site for hydrogen dissociation with spillover onto the alloy component where a selective reaction can take place [34–36]. There are also a growing number of reports which indicate that surface modifiers can influence selectivity in alkyne hydrogenation. In this regard, both sulfur [37–39] and phosphorous [40–42] containing compounds have been shown to be effective. Interestingly, with diphenyl sulfide as modifier, it was possible to decompose the organic component of the modifier, retain the sulfur atoms and still suppress ethylene hydrogenation activity [37].

Despite the surge in the number of approaches to enhance performance in alkyne hydrogenation, a number of challenges still remain, perhaps the most pertinent of which is enhanced resistance to deactivation. Therefore the search for improved catalyst formulations now extends beyond metal based catalysts with metal oxides such as  $\text{CeO}_2$  [43,44] and  $\text{In}_2\text{O}_3$  [45] showing promise, albeit at elevated temperature unless doped with other components [46]. Recently, metal sulfides, or more specifically, supported palladium sulfide nanoparticles have been shown to be an excellent hydrogenation catalyst [47,48] with performance attributed to the formation of the  $\text{Pd}_4\text{S}$  phase and isolation of the active Pd sites [49,50]. Whilst these reports focused on a supported  $\text{Pd}_4\text{S}$  phase, it was hinted that similar results could be obtained with a bulk phase palladium sulfide powder [49]. Reports of sulfur being beneficial in heterogeneous catalysis are still somewhat limited [51]. Herein, results are presented which demonstrate how a PdS powder evolves and changes with thermal pre-treatment to yield a highly selective alkyne hydrogenation catalyst. Detailed characterisation by XRD, TPR, TEM, EDX, XPS and XAS create an understanding of how the phase composition and crystal structure impacts upon catalytic performance. The deposition of carbon over  $\text{Pd}_4\text{S}$  sample after 50 h reaction were investigated by TPO-MS. Whilst a bulk phase PdS powder does not represent an efficient use of the expensive Pd component, it does serve as an excellent material for creating links which reinforce our understanding of how and why supported sulfide phases are selective in alkyne hydrogenation.

## 2. Experimental

### 2.1. Samples

Palladium sulfide powder was purchased from Alfa-Aesar (12,674, 99% purity on a metal basis). Sample which was used as received is referred to as 'fresh palladium sulfide'. Portions of the as received sample were subjected to a reduction treatment in a 20%  $\text{H}_2/\text{N}_2$  mixture (200 ml  $\text{min}^{-1}$ ) for 1 h at 50, 150, 250 or 350 °C in the reactor. Samples are denoted as R50, R150, R250 or R350 to reflect the reduction temperature.

### 2.2. Catalyst testing

Gas phase hydrogenation reactions were performed in a continuous flow, fixed-bed microreactor (9 mm diameter, Microactivity Reference, supplied by Micromeritics) using catalyst (20 mg) diluted with silicon carbide (Aldrich, 200–450 mesh). Single reagent tests were conducted with a mixture of 1.2% acetylene/balance  $\text{N}_2$  with 2 equivalents of  $\text{H}_2$  co-fed relative to acetylene. Multi reagent tests were conducted in a mixture of 0.6% acetylene/5.4%

ethylene/balance  $\text{N}_2$  flow with 2 equivalents of  $\text{H}_2$  co-fed relative to acetylene and a space velocity of 800,000  $\text{h}^{-1}$  based on mass of catalyst. In a typical experiment, a catalyst was tested in the temperature range 50–250 °C with 25 °C increments with 5 h time on stream (TOS) at each temperature to ensure quantitative measurement of raw conversion/selectivity data were reproducible.

The gas composition at the reactor outlet was determined by GC-FID (PE Clarus 580) using an elite alumina capillary column. Conversion was calculated as the amount of acetylene reacted divided by the amount introduced. Selectivity to ethylene and ethane were calculated as the amount formed (i.e., ethylene out – ethylene in) divided by the amount of acetylene reacted. For multi reagent tests a negative ethylene selectivity implies that a fraction of the ethylene co-fed to the reactor also undergoes hydrogenation to ethane. Acetylene is known to form oligomers under reaction conditions. Whilst analysis permitted detection of C4 and C6 products, it was deemed more appropriate to evaluate oligomer selectivity based on a carbon balance [6], since higher molecular weight oligomers may remain adsorbed on the surface, as measured by TPO-MS.

### 2.3. Characterisation

Surface area of samples was measured using a Micromeritics Tristar 3000 instrument using  $\text{N}_2$  as adsorbate. Samples were first pre-treated by heating to 200 °C for 2 h in a flow of  $\text{N}_2$ . X-Ray Diffraction (XRD) patterns of samples were measured in the range of  $2\theta = 20\text{--}85^\circ$  using an X' Pert powder diffractometer (PANalytical) fitted with a PIXcel1D detector, using  $\text{Cu K}\alpha$  radiation and a step size of  $0.013^\circ$  ( $\approx 15$  min acquisition time). The phase compositions were determined by Rietveld refinement using the software HighScore Plus [52].

Temperature programmed experiments were conducted using a TPDRO 1100 instrument with a TCD detector. The effluent gas stream was then passed into an Eco-Sys portable mass spectrometer (European Spectrometry Services) to determine the gas composition. Temperature programmed reduction (TPR) was conducted by heating a fresh palladium sulfide sample in the temperature range 40–350 °C using a heating rate of 5 °C  $\text{min}^{-1}$  in a mixture of 5%  $\text{H}_2/\text{N}_2$ . Temperature programmed desorption (TPD) was conducted by first performing a TPR to 150 °C, followed by cooling to 40 °C in the same 5%  $\text{H}_2/\text{N}_2$  mixture. The gas was then switched to  $\text{N}_2$  and sample heated from 40 to 350 °C using a heating rate of 5 °C  $\text{min}^{-1}$ . TPR and TPD results are presented per gram of sample and hydrogen consumption quantified based on a response factor determined using a  $\text{CuO}$  standard. Temperature programmed oxidation (TPO) was also performed in the range 40–500 °C using a ramping rate of 5 °C  $\text{min}^{-1}$  using a 5%  $\text{O}_2/\text{He}$  gas mixture.

High Resolution Transmission Electron Microscopy (HR-TEM) images were collected using a JEOL JEM-2100 instrument. The particle size and lattice fringes were characterised by analysis of the collected images. The morphology, structure and elemental composition of the samples were examined in several zones using a Zeiss Supra 55 Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyser.

X-Ray Photoelectron Spectroscopy (XPS) of samples was performed using a Thermo Fisher Scientific K-alpha + spectrometer. Samples were analysed using a micro-focused monochromatic Al X-ray source (72 W) over an area of approximately 400  $\mu\text{m}$ . Data were recorded at pass energies of 150 eV for survey scans and 40 eV for high resolution scan with 1 eV and 0.1 eV step sizes respectively. Charge neutralisation was achieved using a combination of low energy electrons and argon ions. The resulting spectra were analysed using Casa XPS peak fitting software and sample charging corrected using the C 1s signal at 284.8 eV as reference.

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