



Selective hydrogenation of mixed alkyne/alkene streams at elevated pressure over a palladium sulfide catalyst



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ARTICLE INFO

Article history:

Received 24 July 2017

Revised 28 August 2017

Accepted 2 September 2017

Available online xxxx

Keywords:

Palladium sulfide

Selective hydrogenation

High pressure

Acetylene

Methyl acetylene

Propadiene

ABSTRACT

The Pd₄S phase of palladium sulfide is known to be a highly selective alkyne hydrogenation catalyst at atmospheric pressure. Results presented here demonstrate that high selectivity can be retained at the elevated pressures required in industrial application. For example, in a mixed acetylene/ethylene feed, 100% conversion of acetylene was attained with a selectivity to ethylene in excess of 80% at 18 bar pressure. Similarly, almost 85% selectivity can be obtained with mixed C3 feeds containing methyl acetylene, propadiene, propylene and propane at 18 bar pressure. Using a low loaded sample (0.1 wt% Pd) it was possible to estimate the TOF to be 27 s⁻¹. High selectivity was related to the crystal structure of Pd₄S with the unique spatial arrangement thought to favour Pd atoms acting in isolation from one another. Based on these results, it is proposed that this catalyst could be a potential replacement for PdAg alloys currently used by industry.

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1. Introduction

The selective hydrogenation of acetylene in ethylene rich streams is a key process for the purification of ethylene produced from naphtha cracking [1–4]. A similar purification step is used to remove methyl acetylene and propadiene (collectively referred to as 'MAPD') from propylene streams. In order to achieve the requisite alkene purity, high conversion of the alkyne/alkadiene is necessary (>99.9%) and operation under these challenging conditions inevitably results in hydrogenation of some of the alkene, reducing overall efficiency. The preferred industrial catalyst is a PdAg alloy supported on a low surface area γ -Al₂O₃, where Pd acts as the active component [5–8]. The addition of Ag, as a structural modifier, enhances alkene selectivity [9] by limiting hydride [10] and/or carbide formation which are thought to influence selectivity over monometallic Pd catalysts [11–14]. Even under optimised conditions, CO is often added to limit over-hydrogenation since it adsorbs more strongly than the alkene but less strongly than the alkyne [2]. However, it would be preferable to avoid the use of CO by using more selective catalysts since the amount of CO which

is co-fed needs to be regulated throughout catalyst lifetime. A significant amount of research has been reported in recent years regarding the design of new catalysts for selective alkyne hydrogenation. Numerous strategies have been reported for enhancing the selectivity of Pd catalysts including alloying with alternative metals to Ag [15–26], adsorption of organic modifiers [27–30] and using new types of supports [31–34]. A number of 'Pd-free' catalysts are inherently more selective, although may require operation at higher temperature since hydrogen dissociation is not facile at low temperature [35–42]. This issue can potentially be circumvented by the addition of a dopant [43] or a second metal which facilitates hydrogen dissociation [44–49].

In many reports, there are differences between the experimental conditions used for catalyst testing and those required by industry [1]. For example, some studies hydrogenate the alkyne in the absence of the alkene (i.e., non-competitive conditions) and whilst this can provide useful fundamental information about activity and selectivity, it differs significantly from the true industrial process. Other studies differ in the amount of alkene which is co-fed with the alkyne (competitive conditions) and may or may not include an inert gas as a diluent. The actual composition of the C2 or C3 stream will vary from plant to plant although it is not uncommon for the feed gas to contain as much as a 35-fold excess of alkene relative to alkyne [1,4]. For studies which focus

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on tail-end or back-end hydrogenation (i.e., when a near stoichiometric amount of hydrogen is co-fed relative to the alkyne) variation in feed gas composition seems less significant since over-hydrogenation is ultimately limited by hydrogen availability. Regardless of the feed composition, it is important to report selectivity at high or full conversion. Otherwise, high selectivity may simply be as a result of preferential adsorption of the alkyne (compared with the alkene), meaning that an assessment of whether a catalyst is really prone to over-hydrogenation is not possible. The last and perhaps most significant deviation in testing protocol is the choice of reaction pressure. The vast majority of literature studies are conducted at atmospheric pressure, whereas industrial alkyne reactors typically operate in the pressure range 15–35 bar [1,4]. Bridging this pressure gap is an important step which is often overlooked since retaining selectivity is far more challenging at high pressure when surface coverage will be higher [4].

Very few studies have explored the use of precious metal sulfides as catalysts [50–53], out with the area of hydrotreating [54,55]. Recently, it has been shown that palladium sulfide, or more specifically the Pd₄S phase of palladium sulfide is highly selective for the hydrogenation of alkynes (acetylene and methyl acetylene) and alkadienes (propadiene and butadiene) both under competitive and non-competitive conditions [56–59]. Whilst, optimum selectivity was observed at relatively high temperature (473–523 K), remarkably low alkane formation was observed using reaction conditions which readily allowed for complete alkyne/alkadiene conversion [56]. These results were considered to be highly encouraging and as such catalyst testing was extended to the pressure range used industrially. In this report we demonstrate that it is possible to selectively hydrogenate acetylene/ethylene or MAPD mixtures without significant alkane formation at high pressure and high conversion over a Pd₄S/carbon nanofiber (CNF) catalyst without the need to co-feed CO. In addition, results indicate that Pd₄S/CNF catalyst is both remarkably active (high turnover frequency) and stable. Excellent catalytic performance could be extended to a case where Pd₄S was supported on an alumina pellet suggesting potential as a viable alternative to current industrial PdAg catalysts [5,6,7,8]. The exceptional selectivity is thought to be related to the crystal structure of Pd₄S which results in a uniform type of active site where Pd atoms are spatially isolated.

2. Experimental

2.1. Catalyst samples

Pd₄S nanoparticles supported on acid treated CNF (PR24-HHT, Applied Sciences Inc.) were prepared as described previously [57]. Briefly, catalysts were prepared by incipient wetness impregnation using an aqueous solution of PdSO₄ (1 or 0.1 wt% Pd loading). The sample was stored in this form but subjected to reduction at 523 K in 10% H₂/N₂ for 1 h prior to use. The formation of the Pd₄S phase of palladium sulfide during reduction has previously been verified by high-energy X-ray diffraction [57]. Reduced samples are denoted as 'x Pd₄S/CNF' where 'x' denotes the metal loading (note: unreduced sample is denoted as 'x PdSO₄/CNF'). Whilst the majority of experiments were conducted with 1% Pd₄S/CNF sample it was necessary to use the lower loaded 0.1% Pd₄S/CNF sample to determine a turnover frequency (TOF). For comparison purpose a 1% Pd/CNF sample was also prepared by using PdCl₂ as precursor as described previously [57].

A further sample in a pelletised form was prepared using an alumina extrudate as support (PN 43857, Alfa-Aesar, 100 m² g⁻¹). To prepare this sample, PdSO₄ (0.20 g) was dissolved in aqueous 5% HNO₃ (280 ml) before the resulting solution was poured into a flask containing Al₂O₃ pellets (40 g). The mixture was left for

22 h before the pellets were separated by filtration and washed with ultra-pure water (4 L). This sample is denoted as 'Pd₄S/Pellet' and was determined by ICP-MS as having a metal loading of 0.01 wt% Pd which indicates that not all of the Pd precursor was adsorbed from solution (≈4% uptake, note the remainder of the Pd precursor remains in solution so is not lost and can be used to prepare further batches of catalyst).

2.2. Characterisation

Transmission electron microscopy (TEM) images of the catalysts were measured using a JEOL JEM-2100 field-emission gun electron microscope operated at 200 kV. The sample was ground and ultrasonically suspended in ethanol and then dripped onto a carbon coated copper grid. The mean diameter (*d*) and volume weighted mean diameter (*d_{VW}*) were calculated based on a minimum of 100 particles using the following equations where *n_i* is the number of particles with diameter *d_i*:

$$d(\text{nm}) = \frac{\sum_i n_i d_i}{\sum_i n_i} \quad d_{VW}(\text{nm}) = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3}$$

The acetylene and ethylene uptakes on the catalysts and the evolution of their adsorption heats were recorded in a Tian Calvet heat flow microcalorimeter (Setaram C-80 II) isothermally operated at 303 K and connected to a glass vacuum-dosing apparatus as described in detail elsewhere [60]. Prior to the experiments, 1% PdSO₄/CNF was reduced in H₂ at 523 K for 2 h and then out-gassed at the same temperature for a period of 12 h.

Temperature programmed reduction (TPR) experiments were carried out using a TPDRO 1100 instrument with a TCD detector and 5% H₂/N₂ (20 ml min⁻¹) as reductant. A trap bed was placed between the sample chamber and the detector to remove both moisture and sulfur containing gases. The reduction profile of 1% PdSO₄/CNF was collected by heating from 313 to 523 K using a heating rate of 5 K min⁻¹. Reduced sample (i.e., 1% Pd₄S/CNF) was then subjected to repeated reduction cycles in the same temperature range to determine whether hydride formation/decomposition occurred.

To assess adsorption behaviour of 1% Pd₄S/CNF, sample was exposed to increasing CO overpressures in a quartz cell which permitted FTIR spectra of a self-supporting sample disc to be collected as described in detail elsewhere [44]. No absorption bands could be identified which were associated with adsorbed CO. This result was verified by attempting to collect a CO adsorption isotherm on a Micromeritics 2020-C instrument at 308 K.

2.3. 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 diluted with silicon carbide (Aldrich, 200–450 mesh). Acetylene/ethylene tests were conducted with a mixture of 0.6% acetylene/5.4% ethylene/balance N₂ with 1.8 or 1.2 equivalents of H₂ co-fed relative to acetylene. MAPD tests were conducted with a mixture of 0.85% methyl acetylene/0.65% propadiene/10% propene/1.75% propane/balance N₂. In this case, 1.8 or 1.2 equivalents of H₂ were co-fed relative to the sum of methyl acetylene and propadiene. Analogous tests with Pd₄S/Pellet sample were conducted using the same apparatus but with a 17.5 mm diameter stainless steel reactor.

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 alkyne (and alkadiene if present) reacted divided by the amount introduced. Selectivity to

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