



Palladium sulphide – A highly selective catalyst for the gas phase hydrogenation of alkynes to alkenes



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ABSTRACT

A particular palladium sulphide phase (Pd₄S) supported on carbon nanofibers is shown to be one of the most selective alkyne hydrogenation catalysts reported to date. Propyne and ethyne (in the absence of the corresponding alkene) can be converted in the gas phase to the corresponding alkene with 96% and 83% selectivity at 100% alkyne conversion. A bulk phase PdS powder (pre-reduced at 523 K) also demonstrated excellent performance (79% ethene selectivity). Other bulk phase metal sulphides (Ni₂S₃ and CuS) were tested and whilst the nickel analogue was found to be active/selective the performance was poorer than observed with either supported or unsupported Pd sulphide. Exceptional alkene selectivity extends to mixed alkyne/alkene feeds using the Pd₄S/CNF catalyst – 86% and 95% alkene selectivity for C3 and C2 mixes, respectively. This report opens up exciting possibilities for using metal sulphides as highly selective hydrogenation catalysts.

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1. Introduction

C₂–C₄ alkenes are widely produced from naphtha cracking, although this produces alkene streams which contain small quantities of alkynes. Purification of the alkene is necessary before it can be used for polymerization since alkynes can poison the Ziegler–Natta catalysts used downstream [1–3]. The preferred method of purification is selective catalytic hydrogenation of the alkyne (and alkadienes if present) since this can yield additional alkene, making the process more profitable [4]. In principle, this is feasible since the alkyne generally adsorbs more strongly than the alkene, leading to preferential hydrogenation of the carbon–carbon triple bond. However, avoiding alkene hydrogenation is challenging once high alkyne conversion has been reached (requirement of <5 ppm alkyne remaining). Industrially, selective alkyne hydrogenation can be carried out in two ways depending on plant design and these are referred to as front-end or tail/back-end and vary primarily, with respect to the amount of hydrogen available [1,5]. A front-end unit is placed upstream of the demethanizer meaning that the alkene stream contains a large excess of hydrogen (and methane). In contrast, a tail-end reactor is located after separation of CH₄/H₂

meaning that a near stoichiometric amount of hydrogen can be added relative to the alkyne. Irrespective of plant design, CO can be used to moderate alkene selectivity since it competes with the alkene for adsorption sites in the absence of the alkyne [2]. This is far from ideal since the amount of CO needs to be regulated in real time to avoid ‘alkyne slip’ and changes over catalyst lifetime.

Academic research in this area is rife, with many fundamental studies enhancing our understanding of factors which promote over-hydrogenation. For example, over Pd catalysts, both experimental and theoretical studies have demonstrated that the interplay between hydride and carbide phases governs alkene hydrogenation [6–12]. The preferred industrial catalyst is a PdAg alloy supported on an alumina carrier and studies have shown that alloying limits hydride formation and enhances alkene selectivity [13], although deactivation due to oligomer formation/carbon deposition is still a problem. A number of new approaches in this area show promise. The use of S [14–18] and P [19] based ligand modifiers has been shown to enhance alkene selectivity for Pd catalysts with improved performance retained at moderate pressure [16]. Ceria has been shown to be a highly selective catalyst for ethyne/propyne hydrogenation, although primarily under front-end conditions with a large excess of hydrogen [20,21]. The use of ceria also appears restricted to moderately high temperatures unless the structure is doped with Ga [22]. An increasing number of studies indicate that the selectivity of a Pd based catalyst can

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be enhanced by diluting ensemble size, perhaps to the point of Pd atom isolation [23]. A number of different bimetallic systems appear feasible in this regard, including PdCu [24–26], PdGa [8,27,28] and PdZn [29] and in some cases a decrease in the strength of alkene adsorption is reported to be the cause of reduced alkene hydrogenation [29]. The use of metal–metal spillover to activate more selective but less active metals has also been widely studied [30–34]. For example, isolated Pd atoms within a Cu surface can act as sites for hydrogen dissociation and this spillover methodology has been successfully applied to the selective hydrogenation of ethyne [25,35–37] as well as propyne/propadiene mixtures [38]. Nanostructured AuPd bimetallic catalysts (defect rich nanoflowers and core–shell structures) have also been studied and show significantly different performance than either metal in isolation [39,40].

Transition metal sulphides are widely exploited in industry as hydrotreating catalysts because they offer stability under harsh conditions, resistance to sulphur/poisons and dissociate H₂ readily [41–44]. In general, these catalysts are based on sulphided Mo or W but contain additional promoters such as Ni or Co. Sulphided platinum group metals (PGMs) are typically overlooked for this process due to their high cost, despite RuS₂ offering higher activity than Mo or W analogues [42]. Reports of other sulphided PGMs as catalysts are scarce, although a few recent articles hint that Pd sulphide may be useful for alternative reactions where more subtle transformations are required (i.e., chemoselectivity) or where avoiding consecutive reactions are imperative (i.e., selective hydrogenation) [45–49]. In this article, we report that palladium sulphide, or more specifically the Pd₄S phase offers outstanding performance as a selective hydrogenation catalyst. The gas phase hydrogenation of ethyne or propyne are used as test reactions in order to demonstrate remarkably high selectivity can be retained under challenging condition of complete alkyne conversion as well as with mixed alkyne/alkene feeds which mirror the conditions encountered in industry. In addition, this may provide insight into why organic sulphur modifiers can enhance the performance of Pd catalysts [14].

2. Experimental

Pd₄S supported on carbon nanofibers (PR24-HHT, Applied Sciences Inc.) was prepared as described previously [47,50]. Briefly, the catalyst was prepared by incipient wetness impregnation using PdSO₄ as the metal salt and has a nominal Pd loading of 1 wt%. Additional experiments were performed with commercially available bulk phase metal sulphide powders – PdS (Aldrich, 1001044315, 19 m² g⁻¹), Ni₂S₃ (Aldrich, 1001189015, 0.43 m² g⁻¹) and CuS (Alfa Aesar, 42925, 1.0 m² g⁻¹).

High-energy X-ray diffraction (HEXRD) data were collected at the ID15A beamline at the ESRF-The European Synchrotron with a wavelength of 0.17750 Å (69.85 keV), using a Perkin Elmer area detector and a sample-detector distance of 650 mm. Transmission electron microscopy (TEM) images of the catalyst 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 before TEM images were generated. The mean diameter (*d*) of the Pd particle size was calculated based on a minimum of 100 particles, using the following equation where *n_i* is the number of particles with diameter *d_i*:

$$d \text{ (nm)} = \frac{\sum_i n_i d_i}{\sum_i n_i}$$

To compare with particle size determined by XRD the volume-weighted average diameter was estimated by the following equation:

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

Gas phase hydrogenation reactions were performed at 1 bar in a continuous flow, fixed-bed microreactor (9 mm diameter, Microactivity Reference, supplied by Micromeritics) using 50 mg catalyst diluted with 200 mg silicon carbide (Aldrich, 200–450 mesh). Prior to testing, all catalysts were reduced by heating to 523 K in 10% H₂/N₂ for 1 h. 5 h time on stream was permitted for tests where temperature (323–523 K) or H₂/reactant ratio (1.8–14.2) was varied, to ensure performance was stable. For such experiments, conversion/selectivity is reported at the end of each 5 h period. The majority of single reagent tests were performed with 0.6% ethyne/balance N₂ or 0.85% propyne/balance N₂ mixtures using a gas hourly space velocity of ≈60,000 h⁻¹. The Pd₄S/CNF catalyst was found to be very active meaning it proved necessary to test under extreme conditions in order to observe any deactivation. For this purpose, a reaction was performed with a 4.8% ethyne/1% methane/balance N₂ mixture (where methane served as internal standard) using a very high space velocity of approximately 750,000 h⁻¹. To put this into perspective, operation under the second set of condition results in exposure of the catalyst to ca. 100 fold more ethyne during the same time period. Multi reagent tests were performed with 0.6% ethyne/5.4% ethene/N₂ or 0.85% propyne/0.65% propadiene/10% propene/1.75% propane/N₂ mixtures and performance evaluated for up to 24 h to verify longer term stability. For the complex C3 mixture the H₂ excess was calculated assuming both propyne and propadiene as reactants. 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 alkene and alkane was calculated as the amount formed divided by the amount of alkyne reacted. For single reagent experiments, selectivity to oligomers (C4+ alkene/alkadienes, typically with even numbers of carbon atoms) [51,52] was calculated based on a carbon balance. In all tests reported here, high or complete alkyne conversion was achieved meaning that evaluation of kinetic parameters is not appropriate [35]. However, conditions of high alkyne conversion are hugely beneficial for accessing a catalysts tendency for over-hydrogenation and as such as deemed as appropriate (i.e., industrial alkyne conversion must reach >99.9% conversion and retain high alkene selectivity).

3. Results & discussion

3.1. Preparation and characterization

A number of different palladium sulphide phases are known to exist (i.e., PdS, Pd₁₆S₇, Pd₃S and Pd₄S) [46]. Given that each phase may have different catalytic properties, it is imperative to work with pure phases as far as possible. In this work, PdSO₄ was impregnated onto carbon nanofibers (CNF) and exclusively converted into Pd₄S nanoparticles by reducing at 523 K following a procedure previously reported [47,50] – denoted as ‘Pd₄S/CNF’ throughout the manuscript. The formation of the correct phase was confirmed by HEXRD (Fig. 1) with good agreement between the observed 2θ values and those of a reference pattern for Pd₄S (JCPDS 73-1387, 2θ = 4.15, 4.37, 4.45, 4.60 and 4.81 for the most intense peaks). Representative high resolution TEM images of the Pd₄S/CNF catalyst are presented in Fig. 2 along with the particle size distribution. The majority of particles were observed to be 1–4 nm in size, although with a small number of larger particles (>10 nm) apparent. The particle size distribution determined from TEM gave a mean particle diameter of 4.6 nm (Table 1). Whilst this type of average is generally used in catalysis, the volume-weighted

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