Short communication

Propyne hydrogenation: characteristics of a carbon-supported palladium catalyst that exhibits a kinetic discontinuity effect

R. Marshall, G. Webb, S.D. Jackson, D. Lennon*

Department of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK

Abstract

The hydrogenation of propyne over a 1 wt.% Pd/C catalyst that has previously been shown to exhibit a kinetic discontinuity effect for this reaction has been studied under conditions below the transition point to evaluate the characteristics that permit dramatic changes in conversion and selectivity as a function of hydrogen concentration.
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1. Introduction

Recent work from this group investigating propyne hydrogenation over a carbon-supported palladium catalyst showed that the catalyst could be made to switch between two distinct activity regimes by crossing a threshold hydrogen concentration [1]. This behavior was attributed to a kinetic discontinuity effect [2–5]. In order to improve our understanding of the origins of this phenomenon, which can be used to maximize propene yields [1], this communication examines the reaction characteristics of the same carbon-supported palladium catalyst used in the original propyne hydrogenation continuous-flow study [1]. Crucially, this paper only considers the low hydrogen concentration regime, where the hydrogen:propyne concentration does not exceed 3:1. Under these conditions, the catalyst has been shown to operate at low conversions with high propene selectivities [1] and does not exhibit discontinuous behavior. Thus, this paper defines a series of 'benchmark' conditions (reaction profile, order of reaction, activation energies for propyne and propene hydrogenation, catalyst lifetime) against which any increase in propene yield can be evaluated. Furthermore, since previ-

ous studies on this reaction system have indicated variability between catalysts offering similar specifications [6], the performance of an additional Pd/C catalyst prepared by a different procedure has also been examined and its performance is contrasted to that of the original Pd/C catalyst. The catalytic behavior observed with hydrogen:propyne ratios greater than 3:1, where abrupt changes in propene yield occur [1], have also been studied and will be reported elsewhere [7].

Two 1% (w/w) Pd/C catalysts were used for this study (hereafter denoted as Pd/C-1 and Pd/C-2). Pd/C-1 is the catalyst described previously, that was prepared by incipient wetness techniques [1]. Pd/C-2 was prepared by wet impregnation to evaluate the universality of the observations reported for Pd/C-1. Both catalysts used palladium nitrate as the precursor and Norit RX3 (surface area $1100 \, m^2 \, g^{-1}$, pore volume $0.64 \, cm^3 \, g^{-1}$) as the support material. Carbon monoxide pulse chemisorption indicated a palladium dispersion of 11.0 and 7.6% for Pd/C-1 and Pd/C-2, respectively. Assuming the metal particles are spheres of equal diameter, the chemisorption results equate to respective mean particle sizes of 9.7 and 14.1 nm. The catalytic activity towards the gas phase hydrogenation of propyne was measured using a continuous flow microreactor system described elsewhere [1].

* Corresponding author. Tel.: +44 141 330 4372; fax: +44 141 330 4888.
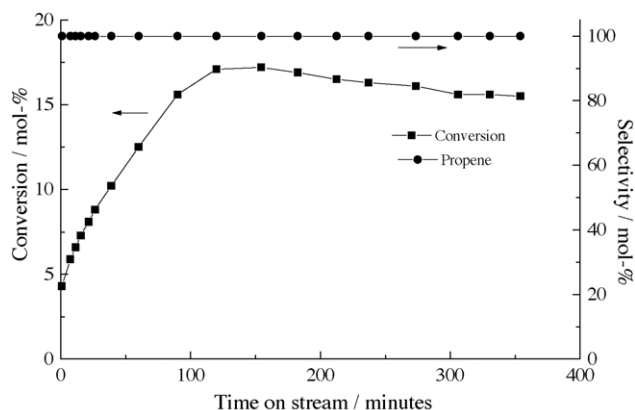 *E-mail address:* d.lennon@chem.gla.ac.uk (D. Lennon).

Fig. 1. Conversion and selectivity as a function of time on stream for Pd/C-1 at 298 K and 2 bar, with a 3:1 hydrogen:propyne molar ratio.

2. Propyne hydrogenation over Pd/C-1

The typical reaction profile for a H_2:C_3H_4 molar ratio of 3:1 is shown in Fig. 1, where catalytic activity can be seen to go through an initial non-steady state regime, during which conversion increases with time on stream. This is attributed to a gradual modification of the catalyst surface by deposition and subsequent conditioning of a hydrocarbonaceous overlayer, which results in the formation of a more active surface [8,9]. After this stage, a relatively modest propyne conversion of ca. 17% is achieved, that progressively diminishes to ca. 15% over a 4 h period. Importantly, during both the non-steady state and steady-state regimes, the only product is propene and there is no evidence for formation of propane or any higher molecular weight C_3 oligomers. Such favourable propene selectivity (100%) matches that reported for an earlier examination of alumina-, zirconia- and silica-supported palladium catalysts operating under an identical hydrogen:propyne ratio in pulse-flow mode [6]. However, these observations contrast with comparable work on silica-supported [8] and alumina-supported [9] palladium catalysts, for which substantial quantities of propane formation are reported. Collectively, the propene selectivity results indicate a wide degree of variability between palladium-based catalysts applied to the hydrogenation of propyne. The chemical parameter responsible for this variability is examined below, although its precise origins in terms of preparative conditions or catalyst composition remains unresolved.

Fig. 2 presents the conversion of propyne as a function of time on stream and increasing hydrogen concentration at 298 K. The reaction order with respect to hydrogen and propyne concentrations was determined at 298 K and found to be respectively 0.93 ± 0.05 and 0.03 ± 0.02. Thus:

$$-\frac{d[C_3H_4]}{dt} = k[C_3H_4]^{0.03}[H_2]^{0.93} \tag{1}$$

which is in general agreement with previous work [6,10]. The activation energy for the reaction with H_2:C_3H_4 molar ratios of 1:1 and 3:1 was determined over the tempera-
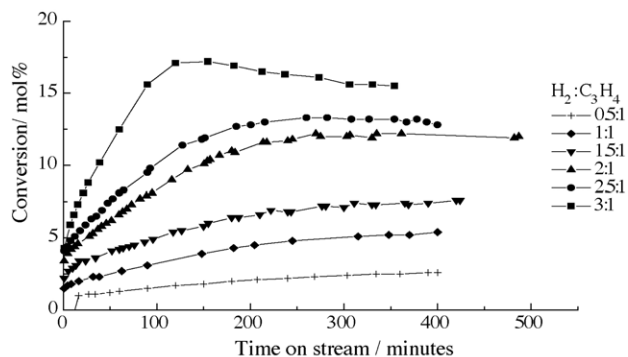

Fig. 2. Propyne conversion as a function of time on stream and increasing hydrogen concentration for Pd/C-1. Reactions were performed for hydrogen:propyne molar ratios of 0.5:1–3:1 at 298 K and 2 bar.

ture range 298–373 K. The apparent activation energies determined from the slope of the Arrhenius plots are 41.6 ± 1.1 and 58.7 ± 0.5 kJ mol^{-1} for the H_2:C_3H_4 molar ratios of 1:1 and 3:1, respectively. These values broadly agree with the range of activation energies previously reported for propyne hydrogenation over palladium catalysts [10,11]. For the reaction with an 1:1 H_2:C_3H_4 mixture, it is interesting to note that even at the highest conversions observed (ca. 63.8% at 373 K), 100% selectivity to propene is maintained. Similarly, for the experiment with a 3:1 H_2:C_3H_4 ratio in the temperature range 298–318 K, conversion increases in line with temperature, with propene being the sole product. However, at 323 K the reaction rate displays a kinetic discontinuity where the conversion increases rapidly to 100% and selectivity to propene decreases to ca. 30% (not shown). As described in Section 1, a detailed analysis of the reaction profiles under those conditions will be presented elsewhere [7].

Fig. 3 presents the activity profile for Pd/C-1 operating with an equimolar hydrogen:propyne ratio over an 80 h period. The low hydrogen concentration was selected to em-
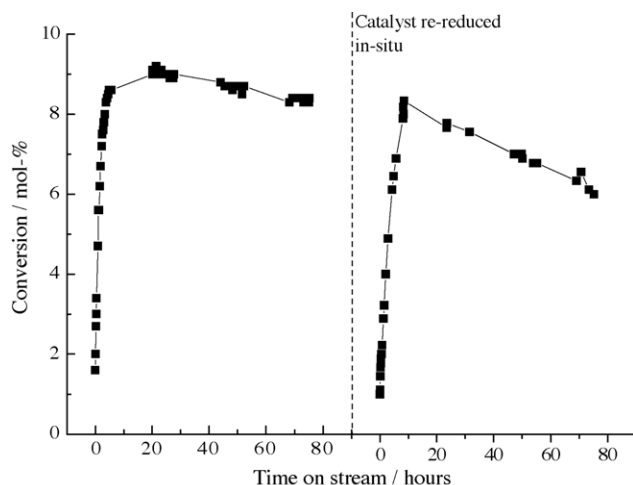

Fig. 3. Propyne conversion as a function of time on stream for Pd/C-1 with an equimolar hydrogen:propyne molar ratio at 298 K and 2 bar. Catalyst re-reduced in situ after 80 h and then reaction performed again using the same conditions.

phasize any deactivation processes apparent with this system. Fig. 3 shows the propyne conversion to progressively increase to a maximum of 9% conversion, which over a 60 h period decreases to 8.0% ($-0.013\%\,\mathrm{h}^{-1}$). In order to evaluate the feasibility of regeneration strategies, the catalyst was re-reduced in situ using the same procedure used for the initial reduction, and the reaction repeated (Fig. 3). Overall, the reaction profile is similar to that observed in the first hydrogenation cycle, however, maximum activity is achieved in a shorter timescale and deactivation is somewhat more pronounced, with the conversion dropping from a maximum of ca. 8.5–6.0% over a 73 h period ($-0.034\%\,\mathrm{h}^{-1}$). Throughout these extended reaction times, complete selectivity to propene was maintained. This observation is consistent with an analysis of the pulse-flow reaction profiles, which show that the processes primarily responsible for deactivation are not directly coupled to the hydrogenation pathways [8].

3. Propene hydrogenation over Pd/C-1

At 298 K and 2 bar (the operating conditions used above), with hydrogen to propene molar ratios ranging from 1:1 to 10:1, no products were detected by GC–MS. For the reaction with $H_2:C_3H_6 = 1:1$ no reaction was observed below 308 K, and an activation energy was determined as $81.6 \pm 1.7\,\mathrm{kJ\,mol}^{-1}$, which is approximately double the value for propyne hydrogenation under similar conditions. The activation energy reported for propene hydrogenation and the information that propene is not hydrogenated at 298 K, accounts for the high selectivity displayed by Pd/C-1 towards propene during propyne hydrogenation. Supported palladium catalysts are normally active for alkene hydrogenation [12] and further investigations are required to establish the actual origins of the elevated energetic barrier for alkene hydrogenation exhibited by this substrate. It is noted that although the inability of Pd/C-1 to hydrogenate propene below 308 K is surprising, it is not unprecedented. Jackson and Casey reported similar behavior using a 1 wt.% Pd/ZrO$_2$ catalyst that was active for propyne hydrogenation but the catalyst demonstrated no activity for propene hydrogenation up to 323 K [6].

4. Propyne hydrogenation over Pd/C-2

Pd/C-2 was tested using an equimolar hydrogen:propyne ratio at 298 K and 2 bar and the results are shown in Fig. 4. This catalyst displays high activity with propyne conversion reaching 100% after a short time on stream, although significantly, selectivity to propene is poor (ca. 35%), with the main product being propane. Interestingly, in further contrast to that seen for Pd/C-1 (Fig. 1), no deactivation is observed. It was not possible to determine an activation energy for the reaction in view of the high activity displayed at the lowest maintainable reactor temperature (298 K). Nevertheless, it is clear from this comparison that the two Pd/C catalysts,
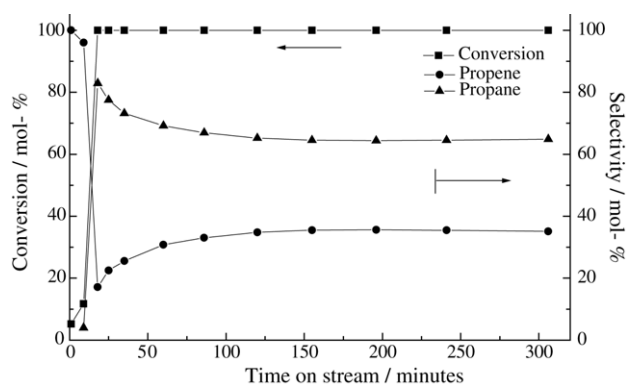
Fig. 4. Conversion and selectivity as a function of time on stream for Pd/C-2 at 298 K and 2 bar, with an equimolar hydrogen:propyne molar ratio.

with similar dispersions, demonstrate significantly different catalytic properties towards propyne hydrogenation.

Figs. 1 and 4 indicate that two carbon-supported palladium catalysts of comparable physical specifications (i.e. metal loading, dispersion and support material) have markedly different reaction profiles. Pd/C-1 exhibits low conversion and high selectivity (5% conversion, 100% selectivity for an equimolar mixture), whereas high conversions and low selectivity are seen with Pd/C-2 (100% conversion, 35% selectivity for an equimolar mixture). Differences in performance for palladium-based propyne hydrogenation catalysts have been reported previously, although the reasons for the different activities have not been directly explored. Specifically, Jackson and Casey report one alumina-supported palladium catalyst to be completely inactive for propyne hydrogenation, whilst another comparable catalyst was active and 100% selective towards propene [6]. The majority of our efforts have concentrated on Pd/C-1, which show it to be representative of other catalysts used to hydrogenate propyne. Thus, given that Pd/C-1 broadly conforms to the physical parameters of other palladium based propyne hydrogenation catalysts, why is Pd/C-1 completely selective to propene production and why does the reaction profile for Pd/C-1 differ so widely from that seen for Pd/C-2?

The propene hydrogenation studies on Pd/C-1 are informative. At 298 K propane formation was forbidden for equimolar and excess hydrogen mixtures. Elevated temperature studies revealed an activation energy of $82\,\mathrm{kJ\,mol}^{-1}$, which defines the energetic barrier that is responsible for the high propene selectivity. This situation is indicative of two distinct active sites. Following on from a rich history of investigations of ethyne hydrogenation, various workers have utilized multiple-site models to relate product distributions from alkyne hydrogenation reactions [13–16]. Previous work from this group has shown that the hydrogenation of propyne over an alumina-supported palladium catalyst can be described within the context of a two-site model, with the sites modified by retained hydrocarbonaceous residues [9]. Specifically, Type I sites are responsible for full hydrogenation of propyne to propane, whereas partial hydrogenation of

propyne to propene occurs at Type II sites [17]. Thus, the ultimate selectivity characteristics of the catalyst are determined by the relative number of Type I and Type II sites present and energetically accessible on the catalyst surface under reaction conditions.

Within the context of the two-site model, the reaction profile for Pt/C-1 (Fig. 1) can be interpreted in terms of only Type II sites being energetically accessible on that catalyst at 298 K. In contrast, both Type I and II sites are energetically accessible at 298 K for Pt/C-2. The small conversion for Pt/C-1 (15% conversion for a hydrogen:propyne mixture of 3:1) is then consistent with there being a small number of Type II sites on the catalyst surface. The importance of hydrogen concentration in influencing product distributions is well established [1,8] and the high conversion observed with Pd/C-2 will require an efficient hydrogen supply, which necessitates a relatively larger area of bare palladium surface (to effect hydrogen dissociative adsorption) than is envisaged for Pd/C-1. In this way, this scenario is moving the hydrocarbonaceous overlayer concept [9] closer to the two-site model recently proposed by Borodskinki for C_2 hydrogenation, which invokes steric hindrance arguments applied to pockets of bare metal surface to describe the composition of the active sites [16]. Further spectroscopic work is required to refine the precise nature of these sites. Nevertheless, the general concepts of a hydrocarbonaceous layer-derived, two-site reaction model seems to successfully rationalise the observed trends and, moreover, establishes that propyne hydrogenation is consistent with the general trends observed for ethyne hydrogenation.

On considering further the possible origins of the two active sites on the palladium crystallites, it is noted that the preparative procedures were different for the two catalysts: Pd/C-1 was prepared by incipient wetness and Pd/C-2 was prepared via wet impregnation. Clearly, further work is required to establish whether the preparative method can be directly linked to the active site distribution. Nevertheless, this work establishes that propyne hydrogenation reaction profiles from carbon-supported palladium catalysts are not readily reproducible, due to the potential for different active site distributions, distinguishable by discrete activation ener-gies. An awareness of these parameters is essential to more fully understand the concept of the kinetic discontinuities in hydrogenation reactions reported for Pd/C-1 [1] and other supported metal catalysts [2–5].

Acknowledgment

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