Palladium assisted copper/alumina catalysts for the selective hydrogenation of propyne, propadiene and propene mixed feeds

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HIGHLIGHTS

- Pd assists Cu by providing a site for hydrogen dissociation at low temperature.
- Full propyne conversion observed at temperatures below 393 K.
- High selectivity achievable with mixed feeds containing propyne/propadiene/propene.
- >85% propene selectivity achieved at 99% conversion at only 383 K.

GRAPHICAL ABSTRACT
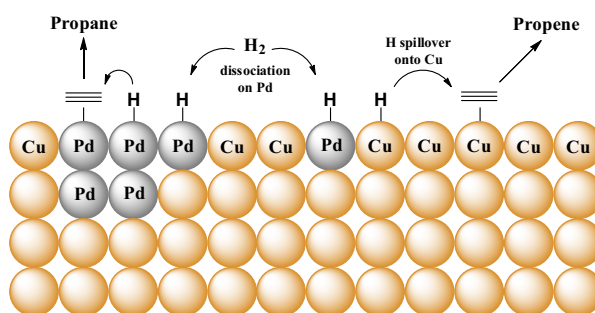
ABSTRACT

A series of copper rich catalysts with different Cu:Pd atomic ratios were screened for the selective hydrogenation of propyne. Sample with 50:1 Cu:Pd ratio exhibited high propene selectivity, yet could be operated at temperatures far lower than typically observed for Cu only catalyst. It is believed that Pd facilitates reaction at Cu sites by promoting hydrogen dissociation at low temperature, followed by spillover onto Cu where the reaction occurs selectively. Catalyst testing with propyne alone showed that full conversion could be achieved at only 383 K with greater than 70% selectivity to propene. Industrially relevant tests were also conducted with a mixed C3 feed containing propyne, propadiene, propene and propane which is unique given that most literature studies fail to consider that propadiene is also an impurity which must be removed during selective hydrogenation of C3 cuts from naphtha crackers. Under such conditions and at only 383 K, propene selectivity of around 90% was achievable at >99% conversion. The option to operate at such low temperature, in the absence of CO, makes 50-CuPd sample an interesting alterative to current industrial catalysts.

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1. Introduction

Naphtha crackers produce alkene streams with contain alkyne and alkadiene impurities which need to be removed before the alkene can be utilised for polymerisation processes [1–3]. The preferred purification route is selective hydrogenation since this, in principle, converts an impurity into a valuable product. However avoiding over-hydrogenation is not simple and can rely upon the use of CO as a competitive adsorbate to hinder alkene adsorption which would otherwise lead to alkane formation. Whilst CO is a transient selectivity modifier, too high a concentration can reduce catalyst activity leading to alkyne/alkadiene slip. As such, it is necessary to regulate the amount of CO used in real time as catalyst

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activity varies with lifetime, which is far from ideal. A number of studies have explored the reasons why a Pd catalyst may or may not be selective through both surface science and computational approaches. Results indicate that formation of a Pd-hydride phase [4–8] is detrimental to achieving high alkene selectivity and this in turn may be influenced by the role of Pd-carbides [7–10]. Importantly, alloying with a second metal such as Ag may hinder hydride formation leading to enhanced selectivity [11]. Industrial catalysts reflect these results and typically use low loaded PdAg catalysts (supported on 2–6 mm α-Al$_2$O$_3$ pellets) with Pd acting as the active site for hydrogenation at temperatures below 393 K [12].

Several strategies have been explored in an attempt to prepare more selective catalysts but improvements often rely on a compromise between enhanced selectivity and changes to process conditions (i.e., operation at lower pressure or operation/activation at higher temperature). For example, monometallic catalysts such as Cu [13–17], Ni [16,18–20], Ag [21,22] and Au [23–26] exhibit high inherent alkene selectivity but suffer from a significant energy barrier which limits hydrogen dissociation rates meaning that reactions must be performed at elevated temperatures (473–523 K). Similarly, bimetallic and trimetallic catalysts such as PdGa [27,28], AuAg [29], NiZn [30] and CuNiFe [31,32] offer high selectivity but require activation/use at high temperature. Metal-free CeO$_2$ [33–35] has been shown to offer high alkene selectivity but limited activity at temperatures employed industrially unless doped with Ga or In [36]. Interestingly, CeO$_2$ offers best performance when a large excess of H$_2$ is used relative to alkyne (typical front-end conditions) whereas more industrial reactors now operate with a stoichiometric amount of hydrogen (typical back or tail-end conditions). The performance of monometallic Pd catalysts has been shown to be greatly improved by the addition of organic sulphur [37–40] and phosphorous [38,40,41] based modifiers through a surface template effect which creates sites that favour alkyne adsorption but hinder alkene adsorption (although limiting hydride formation also appears significant). Such catalysts can operate at low temperature and retain high selectivity at 10 bar pressure [40] but only when CO is co-fed using triphenylphosphine as modifier [41]. Alternative methods of improving performance of Pd catalysts for acetylene hydrogenation have been recently reviewed [42].

Two other catalyst formulations – NiAu and CuPd demonstrate promise since they offer high selectivity and activity at industrially relevant temperatures. Nikolaev and co-workers have shown that low loaded NiAu/Al$_2$O$_3$ catalysts offer high activity/selectivity at temperatures around 357 K but no report of tests at higher pressures have been reported to date [23,43]. CuPd catalysts have been shown to offer excellent performance for acetylene hydrogenation at 373 K [44] under both non-competitive (no alkene co-fed) and competitive (alkene co-fed) conditions, although tests indicated a drop-off in performance was likely at elevated pressure [45]. In the case of CuPd catalysts it is thought that Pd acts to promote hydrogen dissociation with spillover onto Cu where hydrogenation takes place [46–49] – therefore marking these catalysts somewhat unique when compared with most bimetallic catalysts reported for alkyne hydrogenation where Pd acts as both the site for hydrogen activation and reaction (Note: a similar approach has been reported for AuPd catalysts [50]). Importantly both NiAu and CuPd catalysts demonstrated high alkene selectivity in the absence of CO, representing an improvement compared with PdAg catalysts. In the case of CuPd catalysts surface composition/catalytic performance could be improved further by using CO induced surface segregation [51].

In this study, the use of CuPd catalysts for purification of C3 alkyne and alkadiene streams is described. Simple single reagent (propyne) tests are used to discriminate between catalysts of different Cu:Pd atomic ratios. Subsequently, the best catalyst (50:1 Cu:Pd ratio) is tested under competitive conditions using a complex C3 mixture containing propyne, propadiene, propene and propane. This is somewhat unique since almost all studies involving propyne hydrogenation fail to consider the propadiene that is also present as an impurity in C3 streams produced from naphtha cracking.

2. Materials and methods

2.1. Synthesis of catalysts

Bimetallic copper–palladium catalysts were prepared by a sequential impregnation method as described previously [44]. Briefly, 10% Cu/Al$_2$O$_3$ was prepared by impregnation using Cu(NO$_3$)$_2$·3H$_2$O and Aeroxide Alu-C Al$_2$O$_3$ (Evonik, 100 m^2 g^{-1}) followed by calcination at 673 K. Bimetallic samples were prepared by addition of an appropriate amount of an aqueous solution of Pd(NO$_3$)$_2$ to Cu/Al$_2$O$_3$, followed by calcination at 673 K again, to yield materials with different Cu:Pd atomic ratios (Table 1). A monometallic 1.7% Pd/Al$_2$O$_3$ sample was prepared as a reference and contains the same nominal Pd loading as 10-CuPd sample.

2.2. Catalytic testing

All catalyst testing was performed in a Microactivity reference reactor (PID Eng & Tech, supplied by Micromeritics) in a 9 mm inner diameter stainless steel reactor tube following sample reduction (1 h, 30% H$_2$/N$_2$, 323 K for 1.7% Pd/Al$_2$O$_3$, 523 K for Cu/Al$_2$O$_3$ and CuPd samples). Effluent gas from the reactor was sampled and analysed online using a Perkin-Elmer Clarus 580 GC equipped with an FID detector and a 30 m × 0.53 mm elite alumina capillary column. In general, tests were conducted at 1 bar pressure, temperature varied in the range 323–398 K and 5 h time on stream was allowed at each temperature. All catalyst testing was conducted with fine powder samples (<250 μm size). Given that the particle size is significantly smaller than the reactor size, the thickness of any boundary layer should be negligible as determined by application of the Mears criterion [52]. The effect of internal mass transfer was considered using the Weisz–Prater criterion [53] which was met assuming the diffusivity of the gas mixture was at least 2.2×10^{-7} m^2 s^{-1}. It should be noted that no literature data on diffusivity was available for a comparable C3 mixture, although the necessary diffusivity falls well below the value reported by Asplund [54] for an acetylene/ethylene mixture (3.3×10^{-7} m^2 s^{-1}). Some data was determined at temperatures in excess of that necessary to achieve 100% conversion. This reaction data is excluded when calculating reaction rates or activation energy barriers since the rate will be limited by reactant availability. However data collected under these conditions is illustrative of the ability of the catalysts to avoid over-hydrogenation and also mirrors the industrial process where high selectivity must be obtained at conversion in excess of 99.95%.

Non-competitive conditions were used to screen catalysts using a mixture of 0.85% propyne/2.6% hydrogen/balance N$_2$ to give a H$_2$:propyne ratio of 3:1 and a space velocity of 24,000 h^{-1}. Propyne

Table 1
Characteristics of metal loaded catalysts.

Sample name	Cu/wt (%)	Pd/wt (%)	Cu:Pd atomic ratio
10% Cu	10	–	–
1.7% Pd	–	1.7	–
10-CuPd	10	1.7	10
25-CuPd	10	0.7	25
50-CuPd	10	0.3	50
75-CuPd	10	0.2	75