



Cu/Al₂O₃ catalysts modified with Pd for selective acetylene hydrogenation



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ABSTRACT

A Cu/alumina catalyst has been modified by addition of various quantities of Pd. Characterisation suggests formation of a bimetallic with the surface dominated by Cu. Optimisation of the Cu:Pd ratio (50:1) resulted in a catalyst which combined the properties of Cu and Pd (high ethylene selectivity and activity at low temperature). Using a 3:1 H₂:acetylene feed, >99% acetylene conversion and >70% ethylene selectivity was attained at 373 K, representing a considerable reduction in the temperature necessary to achieve equivalent activity/selectivity over monometallic Cu. Increasing the H₂:acetylene ratio to 10 resulted in >99% acetylene conversion at 363 K as well as enhanced ethylene selectivity (>80%). Enhanced activity of Cu at low temperature is attributed to H₂ dissociation on Pd with spillover onto Cu sites where the reaction takes place. These bimetallic CuPd catalysts offer sufficient activity at low temperature and could represent a replacement to the current industrial PdAg catalysts.

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1. Introduction

Ethylene produced from naphtha crackers can be used for polyethylene production so long as it undergoes a rigorous purification step to remove acetylene impurities. The preferred industrial method involves selective hydrogenation using a Pd catalyst modified with Ag or Au. Achieving high selectivity (i.e. avoiding over-hydrogenation to ethane) is non-trivial and often relies upon the addition of CO as a transient poison since it competes with ethylene but not acetylene for adsorption sites [1,2]. However, such a methodology is far from ideal since the quantity of CO added must be monitored and adjusted to compensate during catalyst deactivation. Traditionally, a selective Pd catalyst was associated with small Pd ensembles which favour acetylene adsorption but limit ethylene adsorption [2]. More recent studies indicate that the interplay between Pd carbides [3–5] and hydrides [6,7] play important roles in governing selective hydrogenation [8–15]. New approaches to improving selectivity in Pd based catalysts include alloying with Ga [16,17] or the adsorption of molecules which act as a selectivity modifier. Examples include sulphur and

phosphorous containing molecules such as diphenyl sulfide [18–20] and triphenylphosphine [21] with selectivity varying depending on the ligand structure suggesting the effect has yet to be fully optimised [22].

Whilst industrial catalysts almost exclusively use Pd as the active metal, a number of other metals such as Cu [23–27], Ni [28–30], Au [31–35], and Ag [36,37] show enhanced alkene selectivity, notably in the absence of CO. Results of density functional theory (DFT) calculations suggest that enhanced selectivity over Au, Ag and Cu is related to the unfavourable adsorption energy of the alkene species [34,38]. Catalysis over a Ni surface may be more complex and involve hydride and/or carbide type species akin to Pd [38]. Despite enhanced selectivity, the use of Cu, Au and Ag is limited since hydrogen dissociation is an activated process and requires the reaction to take place at temperatures approaching 473 K which far exceeds the temperatures required with Pd (298–373 K). For example, the activation energy for H₂ dissociation on a Cu (111) surface has been calculated to be 0.46 eV [39] which is far higher than on Pd (0.20 eV) [40]. When the higher reduction temperature of the Pd free catalysts is also taken into account, it means that these catalysts do not represent ‘drop in’ replacements with existing industrial reactors and some authors acknowledge these limitations [41]. An additional complication is that metals such as Ni and Cu produce greater quantities of acetylene based oligomers (most notably at low temperature) which can again be attributed to a limited supply of hydrogen adatoms and may lead

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to more rapid catalyst deactivation. Interestingly, Bridier et al. [27] demonstrated that the temporary addition of CO to a Cu-hydrotalcite catalyst resulted in a decrease in the formation of oligomers in favour of enhanced alkene selectivity. The observed effect was attributed to a decrease in the size of the Cu ensembles through a combination of surface restructuring and an ensemble dilution effect due to carbon deposition.

To circumvent these problems, a possible solution could involve combining the catalytic properties of Pd with one of the aforementioned selective metals. This would in principle create a catalyst with well dispersed Pd atoms capable of hydrogen dissociation in intimate contact with a second metal upon which the reaction could take place *via* a hydrogen spillover mechanism. A natural choice for the second metal is Cu since it readily forms alloyed particles with Pd [42,43] and some recent reports suggest that the preparation of such a system may be viable for well-defined Cu (111) single crystals [44,45]. The original authors identified isolated Pd atoms as the active site for dissociative H₂ adsorption; however, a recent DFT study suggested that incorporation of Pd atoms into both the surface and subsurface layers reduces the barrier for dissociation [39]. In this study, we report a simple preparation of powdered Cu/Al₂O₃ catalysts promoted with a range of Pd loadings and identify the Cu:Pd ratio which offers optimum activity at low temperature (363 K) whilst offering high selectivity. Some recent reports have demonstrated that CuPd systems can offer enhanced selectivity when Cu is added as a structural modifier to bulk [46] and supported CuPd particles [47,48]. In these cases, the improved selectivity is attributed to a reduction of the Pd ensemble size (in the same manner as Ag acts with Pd) as opposed to the reaction taking place on a Cu surface. It should be noted that catalytic tests described in this report have been performed under conditions selected to attain high selectivity to ethylene whilst removing as much acetylene as possible (i.e. close to 100% conversion). As such extraction of kinetic parameters (reaction rates, TOFs, activation energies) are of limited value given that in some cases rates may not reflect a maximum attainable due to reagent availability. However, such conditions do represent an excellent choice in order to access the propensity of a catalyst to over-hydrogenate acetylene to form ethane.

2. Experimental

10% Cu/Al₂O₃ was prepared by wet impregnation. The Al₂O₃ (Aeroxide-Alu C, Evonik, 100 m² g⁻¹, $\rho = 2.9$ cm³ g⁻¹, particle size estimated as 250 μ m) was pre-wetted with distilled water and the appropriate amount of Cu(NO₃)₂·3H₂O dissolved in distilled water was added dropwise under vigorous stirring. After complete addition, the slurry was stirred for 1 h followed by drying at 393 K and calcination at 673 K for 3 h in a flow of 100 ml min⁻¹. A series of catalysts with different Cu:Pd ratios (Table 1) were prepared by adding the appropriate amount of Pd(NO₃)₂ in a second wetness

impregnation step followed by drying at 393 K and calcination at 673 K for 1 h. A 1.67% Pd/Al₂O₃ catalyst was prepared from Pd(NO₃)₂ using the same method and a 3 h calcination at 673 K for comparison purpose. Bimetallic catalysts are denoted as 'X-CuPd' where 'X' refers to the atomic ratio of Cu:Pd.

Temperature programmed reduction (TPR) experiments were carried out using a TPDRO 1100 instrument with a TCD detector. Profiles were collected in a temperature range of 313–873 K using a heating rate of 5 K min⁻¹. TPR results are presented per gram of sample and hydrogen consumption quantified based on a response factor determined using a CuO standard.

Powder X-ray diffraction (XRD) patterns of the calcined samples were collected using an X'Pert Powder diffractometer supplied by PANalytical. Data were collected in the range 20–60° 2 θ with a step size of 0.03° with a sample acquisition time of *ca.* 10 min.

FTIR of adsorbed CO was performed using a PE Spectrum 100 FTIR spectrometer with sample presented as a 16 mm diameter self-supporting disc. The disc was suspended in a quartz holder and held in a conventional vacuum line which permitted in situ evacuation and gas manipulation. Sample was first heated and reduced in 100 ml min⁻¹ of H₂ for 1 h (323 K for 1.67% Pd/Al₂O₃ and 523 K for all other samples). The sample cell was cooled and evacuated to a pressure of *ca.* 4 $\times 10^{-5}$ mbar. An initial spectrum (25 scans, 4 cm⁻¹ resolution) was collected prior to stepwise introduction of increasing CO overpressures (0.1–80 Torr). Results are presented as difference spectra relative to the initial scan collected prior to exposure to CO. In one case, a 50:50 w/w mixture of 10% Cu/Al₂O₃ and 1.67% Pd/Al₂O₃ (effective metal loading – 5% Cu and 0.84% Pd) was prepared in order to examine how the spectra would appear when the two metals were present in the same disc but as separate metals.

XPS data were collected using a VG Escalab II spectrometer using Al K α radiation (1486.6 eV) and a hemispherical analyser for detection of electrons. The resulting spectra were analysed using CasaXPS peak fitting software and sample charging corrected using C 1s as a reference at 285.0 eV.

All catalyst testing was performed in a Microactivity reference reactor (PID Eng & Tech, supplied by Micromeritics) using 100 mg sample diluted with 400 mg SiC supported in a 9 mm stainless steel reactor. Prior to reaction, samples were reduced in 30% H₂/N₂ for 1 h (323 K for 1.67% Pd/Al₂O₃ and 523 K for all other samples). Reactions were performed at 1 bar pressure with a mixture of 0.6% acetylene/1.8% hydrogen/balance N₂ to give a H₂:acetylene ratio of 3:1 and a space velocity of *ca.* 24,000 h⁻¹. The reactor temperature was varied in intervals from 323 to 423 K with 5 h time on stream (TOS) at each temperature. Analysis of the effluent gas was performed using a PE Clarus 580 GC fitted with an FID and a 30 m \times 0.53 mm elite alumina capillary column. Acetylene conversion was calculated as the amount reacted divided by the amount introduced. Selectivity to ethylene and ethane was calculated as the amount formed divided by the amount of acetylene reacted. Ethylene yield has been calculated as acetylene

Table 1
Nominal metal loadings and Cu:Pd atomic ratio.

Catalyst	Cu (wt%)	Pd (wt%)	Cu:Pd atomic ratio	Estimated CuO crystallite size (nm) ^a
10% Cu/Al ₂ O ₃	10	–	–	23 (^b 24)
100-CuPd	10	0.17	100	23
75-CuPd	10	0.22	75	23
50-CuPd	10	0.33	50	23
25-CuPd	10	0.67	25	23
10-CuPd	10	1.67	10	22
1.67% Pd/Al ₂ O ₃	–	1.67	–	–

^a Estimated from XRD pattern of calcined sample using the Scherrer equation.

^b Sample after second calcination.

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