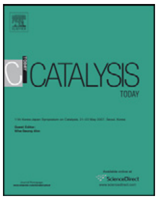
Catalysis Today 203 (2013) 146–152

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod



Selective suppression of disproportionation reaction in solvent-less benzyl alcohol oxidation catalysed by supported Au–Pd nanoparticles

Enhong Cao[a,b], Meenakshisundaram Sankar[c], Ewa Nowicka[c], Qian He[d], Moataz Morad[c], Peter J. Miedziak[c], Stuart H. Taylor[c], David W. Knight[c], Donald Bethell[e], Christopher J. Kiely[d], Asterios Gavriilidis[a,b,*], Graham J. Hutchings[c,**]

[a] Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK
[b] Materials Chemistry Centre, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[c] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK
[d] Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-3195, USA
[e] Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK

ARTICLE INFO

Article history:
Received 2 November 2011
Received in revised form 2 May 2012
Accepted 14 May 2012
Available online 17 July 2012

Keywords:
Gold palladium catalysts
Alcohol oxidation
Benzyl alcohol oxidation

ABSTRACT

Disproportionation of benzyl alcohol has been identified as the source of toluene formation in the solvent free oxidation of benzyl alcohol using supported gold palladium catalysts. There is a slight increase in the disproportionation reaction, and hence the toluene selectivity, when this reaction is performed in a continuous mode using a micro-packed bed reactor when compared to the same reaction performed in a conventional glass stirred batch reactor. Oxidation and disproportionation reactions respond slightly differently to the changes in reaction parameters, like oxygen concentration and pressure, when a micro packed bed reactor was used instead of a conventional glass stirred reactor. When MgO supported gold–palladium catalysts were used for this reaction, the toluene selectivity reduced substantially at the cost of conversion.

1. Introduction

Selective oxidation of alcohols, using molecular oxygen, has received considerable attention in the recent past due to its potential application in the production of intermediates in the fine chemicals and fragrance industries [1–3]. Many heterogeneous catalysts have been reported to be active for this transformation and recently supported gold nanoparticles have been shown to be highly effective [4–6]. With respect to gold catalysis, it is known that this reactivity is due to small gold nanoparticles; their interface with the supporting matrix is also important [7–10]. Recently, we reported a twenty five fold increase in turnover frequency for the oxidation of alcohols by adding small amounts of palladium to supported gold catalysts and we showed that they can be used for the solvent-free aerobic oxidation of alcohols [11]. Subsequently bimetallic gold–palladium catalysts have been utilized for the oxidation of a wide range of substrates including aliphatic alcohols, polyols and alkyl aromatics [12–14]. Benzyl alcohol has long been used as a model substrate for selective oxidation [15–17]. Earlier investigations on the solvent-free aerobic oxidation of this substrate using supported gold–palladium catalysts resulted in the detection of many products, including toluene, benzoic acid, benzyl benzoate and dibenzyl ether, besides the desired product benzaldehyde [15–18]. A detailed knowledge of the origins of these products is crucial to fine-tune the catalyst to obtain the most important product, benzaldehyde, in high yield by suppressing the formation of by-products. Benzaldehyde and benzoic acid are formed by the sequential oxidative dehydrogenation and further oxidation of benzyl alcohol. Dibenzyl ether is formed by the dehydration of benzyl alcohol, and benzyl benzoate is reported to be formed either via hemi-acetal from benzaldehyde or by the esterification of benzoic acid by the substrate; benzyl alcohol [12,18,19]. There has been a long debate on the origin of the other major by-product: toluene [12,20–22]. Baiker *et al.*, proposed hydrogenolysis of benzyl alcohol as the origin of toluene but many other groups proposed a disproportionation mechanism of benzyl alcohol as the origin of toluene [12,20–22]. Disproportionation of benzyl alcohol results in an equimolar mixture of benzaldehyde and toluene as shown in reaction (1).

$$2PhCH_2OH \rightarrow PhCHO + PhCH_3 + H_2O \qquad (1)$$

---

* Corresponding author at: Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK.
** Corresponding author. Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, 8 UK.
E-mail addresses: a.gavriilidis@ucl.ac.uk (A. Gavriilidis), Hutch@cf.ac.uk (G.J. Hutchings).

0920-5861/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2012.05.023

Since benzaldehyde is formed by both oxidation as well as disproportionation reactions, it becomes difficult to study this disproportionation reaction under aerobic conditions, where both oxidation as well as disproportionation reactions are active [23]. Recently we reported a methodology to quantify these two reactions separately, even under such aerobic conditions [23]. Based on this methodology, we found that the oxidation and disproportionation reaction could have different active sites in the supported gold palladium catalysts; metal sites for the oxidation reaction and metal–support interface sites for the disproportionation reaction. We have also demonstrated that by changing the support, we can either switch-on or switch-off this disproportionation reaction and thus toluene formation [12,23]. All the above mentioned results were obtained in a conventional glass stirred reactor (GSR) operated in a batch mode. Industrially, reactions operated in a continuous mode are more attractive and many catalytic reactions display a change in product selectivity when operated in continuous-flow conditions when compared to batch mode operation.

For gas–liquid–solid multiphase reactions, packed-bed flow reactor systems have the advantages of simplifying the process by eliminating separation of liquid products and solid catalyst. Performing these reactions continuously over a longer time period permits insight into the stability of the catalyst, by comparison of its performance using conventional batch reactor or autoclave. For most multiphase reactions, where mass transfer can be a limiting factor, micro-reactors offer improved overall reaction rates and reactor performance when compared with conventional macro-reactors [24–26]. The small channel of the micro-reactor enables efficient gas–liquid mixing and sufficient gas–liquid–solid contact, leading to improved mass transfer in the packed catalyst bed. For highly exothermic reactions, uniform temperature control throughout the reactor can be easily achieved by virtue of the high surface-to-volume ratio [27]. The small internal reactor volume also lowers the consumption of raw materials, thereby improving both safety and economy.

In an attempt to understand the effect of using such micro-reactors on the two reactions of interest; the oxidation and disproportionation reactions of benzyl alcohol using supported gold–palladium nanoalloys, we have compared the outcomes from these reactions under various reaction conditions in two different reactors; namely, conventional glass stirred batch reactor (GSR) and a micro packed bed reactor (MPBR) and report the results obtained herein.

2. Experimental

2.1. Catalyst preparation

For the preparation of 1%(Au–Pd)/TiO_2 and 1%Au–Pd/MgO catalysts, aqueous solutions of $PdCl_2$ (Sigma Aldrich) and $HAuCl_4 \cdot 3H_2O$ (Sigma Aldrich) of the desired concentrations were prepared. Polyvinyl alcohol (PVA) (1 wt% aqueous solution, Aldrich, MW = 10,000, 80% hydrolysed) and an aqueous solution of $NaBH_4$ (0.1 M) were also prepared. To a mixed aqueous $PdCl_2$ and $HAuCl_4$ solution of the desired concentration, the required amount of a PVA solution (1 wt%) was added (PVA/(Au + Pd) (wt/wt) = 1.2); a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/(Au + Pd) (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilized by adding the solid support [TiO_2 (Degussa, P25), MgO (BDH)] and acidified to pH 1 by concentrated sulphuric acid under vigorous stirring in the case of TiO_2, acid was not added when MgO was used as the support. The amount of support material required was calculated so as to have a total final metal loading of 1 wt% with a metal ratio of 1:1 molar. After 2 h, the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight under static air. The filtrate solution was checked for the presence of Au and Pd. It was found that there were no metal ions in the filtrate, indicating that all the metals are immobilized on to the support.

2.2. Catalyst characterisation using scanning transmission electron microscopy

The 1%(Au–Pd)/TiO_2 and 1%Au–Pd/MgO catalysts have been extensively studied previously [23,28,29,18] and it has been found that particle size and composition are important factors and for that reason we extend these studies by scanning transmission electron microscopy (STEM). Samples for examination by TEM were prepared by dry dispersing the catalyst powder onto a holey carbon film supported by a 300 mesh copper TEM grid. STEM high angle annular dark field (HAADF) images and X-ray energy-dispersive spectra (XEDS) of individual nanoparticles were obtained using an aberration corrected JEOL 2200FS STEM operating at 200 kV and equipped with a Thermo Scientific Inc. Si(Li) detector for XEDS.

2.3. Catalytic performance in a glass stirred reactor (GSR)

Benzyl alcohol oxidation was carried out in a Radleys carousel reactor using a 50 mL glass stirred reactor. In a typical reaction, the requisite amount of catalyst and substrate were charged into the reactor at room temperature which was then purged with the required gas (O_2, He or air) three times before the reactor was sealed using a Teflon screw threaded cap. The reactor was always connected to the gas line to ensure that any gas consumed was replenished. The pressure was measured using a gauge fitted to the inlet line. There was no change in the pressure during the course of the reaction. The reactor with the reaction mixture was loaded into a preheated heating block, which was maintained at the reaction temperature. The reaction was started by switching on the stirring inside the reactor with a magnetic bar at 1000 rpm. After a specific time, the stirring was stopped and the reactor was immediately cooled in an ice bath. After cooling for 10 min, the reactor was opened carefully and the contents were centrifuged. An aliquot of the clear supernatant reaction mixture (0.5 mL) was diluted with mesitylene (0.5 mL) for GC analysis. It was established that no reaction occurred in the absence of the Au–Pd catalyst or in the presence of the catalyst support alone. Mass transfer was found not to be rate-limiting at a stirring speed of 500 rpm or above. The turnover numbers for individual reactions; oxidation (TON_O), disproportionation (TON_D) and the total turnover number TON_{Tot} were calculated using the following equations [23]:

$$TON_D = \frac{2 * mol_{tol}}{mol_{metal}}$$

$$TON_O = \frac{mol_{PhCHO}\text{-}mol_{tol}}{mol_{metal}}$$

$$TON_{Tot} = \frac{mol_{phCH_2OH}\text{converted}}{mol_{metal}}$$

2.4. Catalytic performance in a micro-packed bed reactor (MPBR)

The micro-packed bed reactor chips were made of silicon and glass with an overall size of 23 mm × 23 mm [18]. The dimension of the reaction channel was 0.6 mm (*W*) × 0.3 mm (*H*) × 190 mm (*L*). The prepared catalyst powder was pelletized and the desired particle size (53–63 μm) fraction was obtained by crushing and sieving. The catalyst was then introduced into the reaction channel through