



# Selectivity in the gas-phase hydrogenation of 4-nitrobenzaldehyde over supported Au catalysts



Noémie Perret<sup>a</sup>, Xiaodong Wang<sup>a</sup>, Thomas Onfroy<sup>b,c</sup>, Christophe Calers<sup>b,c</sup>, Mark A. Keane<sup>a,\*</sup>

<sup>a</sup> Chemical Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, United Kingdom

<sup>b</sup> UPMC Univ Paris 06, Laboratoire de Réactivité de Surface, Case 178, Site d'Ivry-Le Raphaël, 3 rue Galilée, 94200 Ivry sur Seine, France

<sup>c</sup> CNRS-UMR 7197, Laboratoire de Réactivité de Surface, Case 178, Site d'Ivry-Le Raphaël, 3 rue Galilée, 94200 Ivry sur Seine, France

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## ABSTRACT

The effects of Au particle size and support properties have been examined in the gas-phase hydrogenation of 4-nitrobenzaldehyde over Au/ZrO<sub>2</sub>, Au/TiO<sub>2</sub> and Au/Al<sub>2</sub>O<sub>3</sub>. Gold particle size was varied using deposition–precipitation and impregnation syntheses. The catalysts have been characterised in terms of BET area/pore volume, temperature-programmed reduction (TPR), XRD, H<sub>2</sub> chemisorption/TPD, TEM, XPS, and pyridine adsorption FTIR measurements. Reaction exclusivity to 4-aminobenzaldehyde was achieved over Au/ZrO<sub>2</sub> and Au/TiO<sub>2</sub> where a decrease in Au particle size (mean from 7.0 to 4.7 nm) generated a higher turnover frequency. Pyridine adsorption coupled with FTIR analysis has revealed stronger Lewis acidity associated with Au/Al<sub>2</sub>O<sub>3</sub>, which contributes to C=O reduction via the formation of a benzoate intermediate. Selectivity to the alcohol is sensitive to Au size and reaction temperature with 100% 4-nitrobenzyl alcohol selectivity over Au/Al<sub>2</sub>O<sub>3</sub> (mean Au size = 7.8 nm) at 423–443 K. Our results demonstrate the viability of controlling selective –NO<sub>2</sub> and C=O reduction using oxide-supported Au catalysts.

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## 1. Introduction

Functionalised aromatic amines and alcohols are important intermediates in the production of a range of pharmaceuticals, agrochemicals, cosmetics, herbicides, dyes and polymers [1,2]. Amine and alcohol production can be achieved via the catalytic hydrogenation of nitro compounds and aldehydes [3,4]. Selectivity in the targeted reduction of –NO<sub>2</sub> or C=O in the presence of other reactive functional groups (e.g. C=N, C=C, COOH) remains challenging [5,6]. In this study, we examine the feasibility of controlling the selective hydrogenation of 4-nitrobenzaldehyde. Reduction of –NO<sub>2</sub> is more facile than C=O and the amine should be the preferred product [7]. The possible pathways associated with the conversion of 4-nitrobenzaldehyde are presented in Fig. 1, where 4-aminobenzaldehyde (step (I)) and 4-nitrobenzyl alcohol (step (II)) are commercially important compounds [8,9]. This reaction has been studied over soluble metal (Pd [10,11], Ru [8] and Co [12]) complexes and solid transition metal (supported Au, Ru, Ni, Pd and Pt [6,8,9,13–15] and PtO<sub>2</sub>–H<sub>2</sub>O [16]) catalysts in the liquid phase ( $P = 1–50$  bar,  $T = 303–423$  K). There has been only one reported gas-phase application (for 3-nitrobenzaldehyde) over MgO [17]. The reduction of both nitro and carbonyl functions

generates 4-aminobenzyl alcohol (steps (III) and (IV)) as reported for reaction over PtO<sub>2</sub>–H<sub>2</sub>O [16], sol–gel entrapped Pd [18], MgO [17] and Ru/Al<sub>2</sub>O<sub>3</sub> [8]. Moreover, the formation of 4-nitrotoluene can result from either direct attack of C=O (step (V)) or further conversion of 4-nitrobenzyl alcohol (step (VI)) and has been detected in reactions over Au/Fe<sub>2</sub>O<sub>3</sub> and Fe(OH)<sub>x</sub> [13]. Generation of 4-aminotoluene can proceed via steps (VII), (VIII) and (IX). It is well established [6,9,11,16] that 4-aminobenzaldehyde and 4-aminobenzyl alcohol polymerise during hydrogenation with the formation of toxic azoxy compounds. The latter is favoured by the longer contact times that apply in conventional batch processes [11] and should be circumvented in continuous operation. Taking an overview of the literature, 4-aminobenzaldehyde has been the major product with selectivities up to 99% [6,9,10,12,13]. Preferential 4-nitrobenzyl alcohol formation has been demonstrated in reactions involving Ru complex catalysts [8], but the precise source of this selectivity or the means of controlling product distribution remains unresolved.

Studies to date have focused on batch liquid-phase processes where enhanced selectivity in homogeneous catalysis required an alkali additive (KOH) [10,12] and operation under reflux conditions [12]. A switch to heterogeneous catalysis offers advantages in terms of product/catalyst separation while economies of scale favour continuous processes for high throughput. The use of Au catalysts has shown promise in the liquid-phase conversion of 4-nitrobenzaldehyde to 4-aminobenzaldehyde although polymerisation was also

\* Corresponding author.

E-mail address: [M.A.Keane@hw.ac.uk](mailto:M.A.Keane@hw.ac.uk) (M.A. Keane).

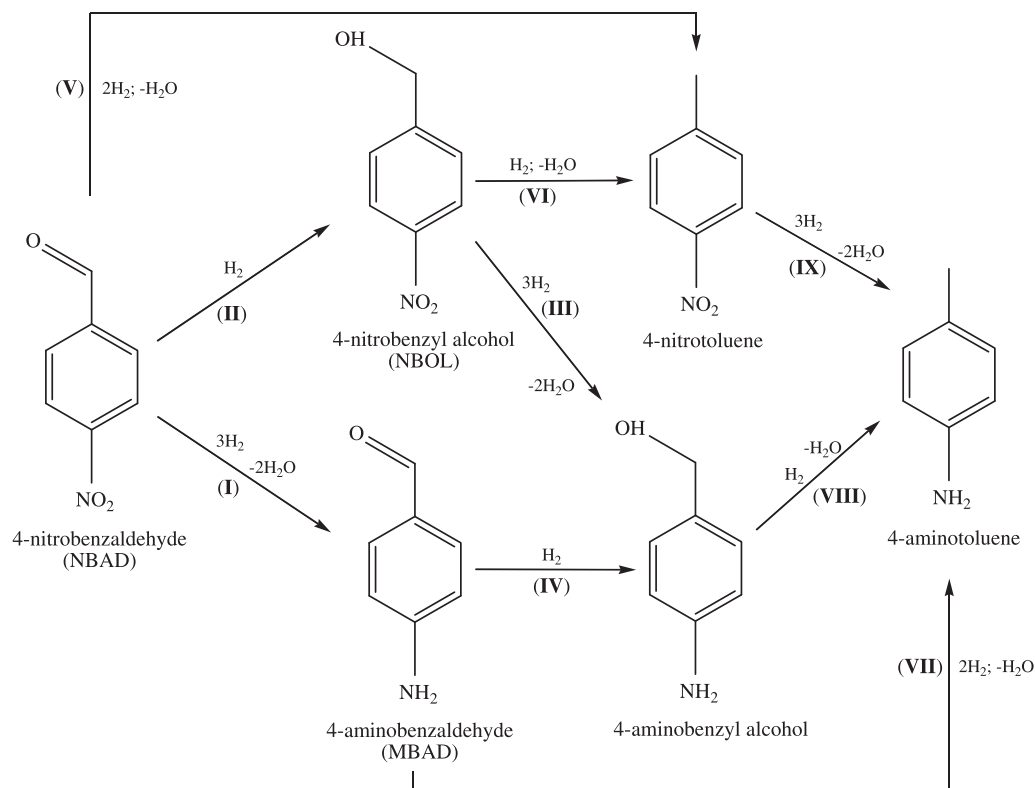


Fig. 1. Possible reaction pathways in the hydrogenation of 4-nitrobenzaldehyde.

observed [6,9,14]. Supported Au has exhibited chemoselectivity in  $-\text{NO}_2$  reduction to  $-\text{NH}_2$  in the presence of other reactive functionalities, e.g.  $\text{C}\equiv\text{N}$  [19],  $\text{C}=\text{C}$  [9], Br [20] and Cl [21]. Baillie and Hutchings [22] first demonstrated  $\text{C}=\text{O}$  activation on Au/ZrO<sub>2</sub>, resulting in enhanced selectivity to crotyl alcohol. This work has led to a number of investigations on the selective hydrogenation of  $\text{C}=\text{O}$  to  $\text{C}-\text{OH}$  [23–33] over Au, but none of these studies have considered the conversion of nitrobenzaldehyde. Previous work has established the importance of the support [26,34–36] and Au particle size [21,37–39] in determining hydrogenation performance. Adopting Au/ZrO<sub>2</sub> as our starting point, we have examined the role of support (TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) and Au size on 4-nitrobenzaldehyde hydrogenation activity/selectivity with a consideration of reaction temperature effects.

## 2. Experimental

### 2.1. Catalyst preparation and activation

The ZrO<sub>2</sub> support was prepared by precipitation of zirconium (IV) oxychloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, ≥99.5%, Aldrich) with aqueous ammonia (35% w/w NH<sub>3</sub>, Fisher). The ZrOCl<sub>2</sub> solution (0.1 M) was added dropwise with vigorous stirring to aqueous ammonia (2.5 M). Temporal pH changes were measured with a crystal-body electrode coupled to a data logging and collection system (Pico Technology), calibrated with standard buffer solutions (pH 7 and 10). The resultant hydrogel was washed with distilled water until the wash water was Cl-free (AgNO<sub>3</sub> test), dried at 373 K for 24 h and calcined in air (20 cm<sup>3</sup> min<sup>-1</sup> g<sup>-1</sup>) at 1 K min<sup>-1</sup> to 673 K for 5 h. Gold (ca. 1% w/w) supported on ZrO<sub>2</sub>, TiO<sub>2</sub> (Degussa) and Al<sub>2</sub>O<sub>3</sub> (Puralox) was prepared by deposition-precipitation (DP) where a suspension (300 cm<sup>3</sup>) of HAuCl<sub>4</sub> (173 mg, 99.999%, Aldrich), aqueous urea (100 cm<sup>3</sup>, 2.8 mol dm<sup>-3</sup>) and support (5 g) was stirred (300 rpm) and heated (1 K min<sup>-1</sup>) to 353 K, which

was maintained for ca. 200 min. Synthesis was conducted in the dark to avoid formation of metallic colloids in solution by photoreduction of Au(III) [40]. As a high residual chloride content (>300 ppm) results in the formation of larger (>20 nm) Au particles [41] and can poison catalytic sites [42], the catalyst precursor was washed repeatedly. Gold on Al<sub>2</sub>O<sub>3</sub> prepared by DP is denoted by AuAl<sub>2</sub>O<sub>3</sub>-1. Alumina-supported Au was also prepared by standard impregnation of Al<sub>2</sub>O<sub>3</sub> with an aqueous HAuCl<sub>4</sub> solution (Aldrich, 7.3 × 10<sup>-3</sup> M, 39 cm<sup>3</sup>) where the slurry was heated at 2 K min<sup>-1</sup> to 353 K and agitated (600 rpm) in a He purge; this sample is denoted by AuAl<sub>2</sub>O<sub>3</sub>-2. The catalyst precursors were dried in He (10 cm<sup>3</sup> min<sup>-1</sup> g<sup>-1</sup>) at 383 K for 3 h and sieved into a batch of 75 μm average diameter. The samples were stored at 277 K under He in the dark in order to prevent Au agglomeration, which can occur when kept in air and in the light [43]. The precursors were activated in 60 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> at 2 K min<sup>-1</sup> to 473 K and passivated in 1% v/v O<sub>2</sub>/He at ambient temperature for *ex situ* analysis.

### 2.2. Catalyst characterisation

The pH associated with the point of zero charge (pH<sub>PZC</sub>) of ZrO<sub>2</sub> was determined by potentiometric mass titration [44]. Three different masses (0.025, 0.050 and 0.075 g) were immersed in 50 cm<sup>3</sup> 0.1 M NaCl to which a known amount of NaOH (0.1 M) had been added to adjust the pH to 11. After stabilisation of the pH (ca. 1 h), titration with HCl (0.1 M) was performed under continuous agitation in He and temporal pH changes measured as described above. Temperature-programmed reduction (TPR), BET surface area, total pore volume, H<sub>2</sub> chemisorption and temperature-programmed desorption (TPD) were measured using the commercial CHEM-BET 3000 (Quantachrome) unit. In TPR analysis, samples (0.2 g) were loaded into a U-shaped Quartz cell (10 cm × 3.76 mm i.d.) and heated in 17 cm<sup>3</sup> min<sup>-1</sup> (Brooks mass flow controlled) 5% v/v H<sub>2</sub>/N<sub>2</sub> at 2 K min<sup>-1</sup> to 473 ± 1 K. The

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