



Effect of support redox character on catalytic performance in the gas phase hydrogenation of benzaldehyde and nitrobenzene over supported gold



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ABSTRACT

A range of oxides (γ -Al₂O₃, TiO₂, ZrO₂, CeO₂, α -Fe₂O₃ and Fe₃O₄) with different redox properties were used to support nano-scale (mean = 2–8 nm) Au and employed in the gas phase hydrogenation of benzaldehyde and nitrobenzene. The catalysts were subjected to TPR, H₂/O₂ titration, H₂ TPD, XRD, TEM/STEM and XPS analysis. The supported Au phase promoted partial reduction of the reducible supports through the action of spillover hydrogen (based on TPD), which generated surface oxygen vacancies (demonstrated by O₂ titration) that inhibit Au particle sintering during catalyst activation. Electron transfer to generate charged Au species (determined by XPS) correlates with support ionisation potential. Higher nitrobenzene hydrogenation (to aniline) TOFs were recorded relative to benzaldehyde where rate increased with decreasing Au size (from 8 to 4 nm) with measurably lower TOF over Au <3 nm. Strong binding of –CH=O and –NO₂ functions to oxygen vacancies resulted in lower hydrogenation rates. Higher temperatures (>413 K) promoted benzaldehyde hydrogenolysis to toluene and benzene. The formation of Au^{δ-} on non-reducible Al₂O₃ favoured selective reduction of –CH=O with full selectivity to benzyl alcohol at 413 K.

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1. Introduction

The selective hydrogenation of benzaldehyde to benzyl alcohol and nitrobenzene to aniline are important in the production of herbicides, dyes, pigments and fine chemicals [1,2]. Conventional batch synthesis delivers low product yields, is energy inefficient and generates significant waste where exclusive reduction of the carbonyl and nitro group is challenging [3]. Continuous gas phase reaction presents a number of advantages including ease of product/catalyst separation and reduced downtime [4]. Supported Au at the nano-scale (<10 nm) exhibits unique selectivity in the hydrogenation of multi-functional reactants although activity is lower compared with conventional transition metals (Pt, Ru, Pd and Ni) [5] due to the limited capacity of Au to chemisorb/dissociate H₂ [6]. Studies to date on the catalytic hydrogenation of carbonyl (acrolein, benzalacetone, cinnamaldehyde and crotonaldehyde) [7,8] and nitro (chloronitrobenzene, nitrostyrene and nitrobenzaldehyde) [9,10] compounds have shown a dependence on the electronic and geometric properties of the Au phase that are influenced by the sup-

port. Smaller Au particles are formed on reducible oxides (e.g. TiO₂ and CeO₂) relative to non-reducible ZrO₂ and SiO₂ [11,12]. Higher turnover frequencies (TOF) with decreasing Au size (2–9 nm) has been reported in the hydrogenation of crotonaldehyde [11,13] and nitrobenzene [14] for Au supported on TiO₂, Al₂O₃ and SiO₂. Okumura et al. [11] observed higher alcohol selectivity (from crotonaldehyde) over Au/TiO₂ than Au/Al₂O₃ and Au/SiO₂. Milone and co-workers [15] proposed that reducible iron oxides promote the formation of electron-rich Au through metal-support electron transfer that favours –CH=O reduction. Rojas et al. [16] concluded that negatively charged Au (on SiO₂) binds the electrophilic carbon in –CH=O facilitating hydrogenation of cinnamaldehyde and benzalacetone.

In nitro group reduction, the high selectivity exhibited by Au/TiO₂ has been attributed to metal-support synergy that promotes –NO₂ activation [17]. Shimizu et al. [18] considered the role of Al₂O₃ acidity/basicity in tandem with coordinatively unsaturated Au to dissociate H₂ to H⁺/H⁻ at the metal/support interface and selectively reduce –NO₂ in the presence of other reactive functionalities. In the hydrogenation of *p*-chloronitrobenzene unwanted hydrodechlorination was reported for Au/Ce_{0.62}Zr_{0.38}O₂ and ascribed to C–Cl scission at oxygen vacancy sites [19]. Selective hydrogenation has been well established for Au catalysts but the

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contribution of the support in modifying Au structure, reactant activation and overall surface reaction mechanism is far from resolved. In this study we compare the catalytic action of Au nanoparticles on oxides (γ -Al₂O₃, ZrO₂, TiO₂, CeO₂, α -Fe₂O₃ and Fe₃O₄) with distinct redox character in the hydrogenation of –CH=O (benzaldehyde) and –NO₂ (nitrobenzene) and correlate performance with catalyst structure. We propose surface reaction mechanisms to account for the role of support reducibility in governing –CH=O and –NO₂ activation and product selectivity.

2. Experimental

2.1. Catalyst preparation and activation

The supports employed in this study were obtained from commercial sources (γ -Al₂O₃ (Puralox, Condea Vista), TiO₂ (P25, Degussa) and CeO₂ (Grace Davison)) or synthesised (α -Fe₂O₃, Fe₃O₄ and ZrO₂) as described elsewhere [12,20]. Supported Au catalysts were prepared by deposition-precipitation using urea (Riedel-de Haën, 99%) as basification agent. An aqueous solution of urea (100-fold excess) and HAuCl₄ ($3\text{--}7 \times 10^{-3}$ M, 400 cm³, Sigma Aldrich, 99%) was added to the support (10–30 g). The suspension was stirred and heated (2 K min⁻¹) to 353 K where the pH progressively increased (to 6.5–8.0) as a result of urea decomposition:



The solid obtained was separated by filtration, washed with distilled water until Cl free (from AgNO₃ test) and dried (2 K min⁻¹) in 45 cm³ min⁻¹ He at 373 K for 5 h. The catalyst precursors were sieved (ATM fine test sieves) to mean particle diameter = 75 μ m and activated at 2 K min⁻¹ to 423–673 K in 60 cm³ min⁻¹ H₂. The catalysts were cooled to ambient temperature and passivated in 1% v/v O₂/He for off-line characterisation.

2.2. Catalyst characterisation

Gold content was measured by atomic absorption spectroscopy (Shimadzu AA-6650 spectrometer with an air-acetylene flame) from the diluted extract in aqua regia (25% v/v HNO₃/HCl). The pH associated with the point of zero charge (pH_{pzc}) of the support was determined using the potentiometric mass titration technique described in detail elsewhere [21]. Temperature programmed reduction (TPR), H₂ chemisorption/temperature programmed desorption (TPD), O₂ chemisorption and specific surface area (SSA) measurements were conducted on the CHEM-BET 3000 (Quantachrome) unit equipped with a thermal conductivity detector (TCD) for continuous monitoring of gas composition and the TPR WinTM software for data acquisition/manipulation. Samples were loaded into a U-shaped Pyrex quartz cell (3.76 mm i.d.) and heated in 17 cm³ min⁻¹ (Brooks mass flow controlled) 5% v/v H₂/N₂ at 2 K min⁻¹ to 423–673 K for supported Au catalysts and to 1073–1273 K for the supports where the effluent gas passed through a liquid N₂ trap. The activated samples were swept with 65 cm³ min⁻¹ N₂ for 1.5 h, cooled to reaction temperature (413 K) and subjected to a H₂ (BOC, >99.98%) pulse (10 μ l) titration procedure. Samples were cooled to ambient temperature, thoroughly flushed in N₂ (65 cm³ min⁻¹) to remove weakly bound H₂ and subjected to TPD (at 50 K min⁻¹) to 873–1173 K with a final isothermal hold until the signal returned to baseline. Oxygen (BOC, 99.9%) pulse (50 μ l) titration at 413 K post-TPR was employed to determine the extent of support reduction where any contribution from Au to total O₂ adsorption is negligible [22]. SSA (reproducible to \pm 8%) was recorded in 30% v/v N₂/He with undiluted N₂ (BOC, 99.9%) as internal standard. At least three cycles of N₂ adsorption-desorption were employed using the standard single point BET

method. Pore volume was measured using the Micromeritics Gemini VII 2390p system. Prior to analysis, samples were outgassed at 423 K for 1 h in N₂. Total pore volume was obtained at a relative N₂ pressure (P/P_0)=0.95. X-ray diffractograms (XRD) were recorded on a Bruker/Siemens D500 incident X-ray diffractometer using Cu K α radiation. Samples were scanned at 0.02 $^\circ$ step⁻¹ over the range 20 $^\circ$ \leq 2 θ \leq 80 $^\circ$ and the diffractograms identified against the JCPDS-ICDD reference standards, i.e. Au (04-0784), γ -Al₂O₃ (10-0425), anatase-TiO₂ (A-TiO₂, 21-1272), rutile-TiO₂ (R-TiO₂, 21-1276), monoclinic-ZrO₂ (M-ZrO₂, 37-1784), tetragonal-ZrO₂ (T-ZrO₂, 50-1089), CeO₂ (43-1002), α -Fe₂O₃ (hematite, 33-0664) and Fe₃O₄ (magnetite, 19-0629). X-ray photoelectron spectroscopic (XPS) analysis was performed on a VG ESCA spectrometer equipped with monochromatised Al K α radiation (1486 eV). The sample was adhered to conducting carbon tape, mounted in the sample holder and subjected to ultra-high vacuum conditions (<10⁻⁸ Torr). Full range surveys (Au 4f_{5/2} and 4f_{7/2} spectra) were collected where the binding energies (BE) were calibrated with respect to the C 1s peak (284.5 eV). The Au 4f spectra were fitted with abstraction of the Shirley background using the Gaussian-Lorentzian function in XPSPEAK 41. Gold particle morphology (size and shape) was examined by transmission (TEM, JEOL JEM 2011) and scanning transmission (STEM, JEOL 2200FS field emission gun-equipped unit) electron microscopy, employing Gatan Digital Micrograph 1.82 for data acquisition/manipulation. Samples for analysis were dispersed in acetone and deposited on a holey carbon/Cu grid (300 Mesh). The surface area weighted mean Au size (d) was based on a count of at least 300 particles according to

$$d = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (2)$$

where n_i is the number of particles of diameter d_i .

2.3. Catalytic procedure

Catalyst testing was carried out at atmospheric pressure, *in situ* after activation, in a continuous flow fixed bed tubular reactor (i.d.=15 mm) at 413–573 K under conditions of negligible heat/mass transport limitations. A layer of borosilicate glass beads served as preheating zone, ensuring the organic reactant was vaporised and reached reaction temperature before contacting the catalyst (10–40 mg). Isothermal conditions (\pm 1 K) were maintained by diluting the catalyst bed with ground glass (75 μ m). Reaction temperature was continuously monitored by a thermocouple inserted in a thermowell within the catalyst bed. Reactants (benzaldehyde (Fluka, \geq 98%), nitrobenzene (Riedel-de Haën, \geq 99%) or benzyl alcohol (Riedel-de Haën, \geq 99%)) were delivered as an ethanolic (Sigma Aldrich, \geq 99%) solution to the reactor *via* a glass/teflon air-tight syringe and teflon line using a microprocessor controlled infusion pump (Model 100 kd Scientific) at a fixed calibrated flow rate. Reactions were conducted in a co-current flow of reactant with H₂ (BOC, >99.98%, 60 cm³ min⁻¹) at GHSV=2 \times 10⁴ h⁻¹. The molar Au to inlet organic molar feed rate (n/F) spanned the range 1.2 \times 10⁻³–3.7 \times 10⁻³ h. In blank tests, passage of each reactant in a stream of H₂ through the empty reactor or over the support did not result in any detectable conversion. The reactor effluent was collected in a liquid nitrogen trap for subsequent analysis using a Perkin-Elmer Auto System XL gas chromatograph equipped with a programmed split/splitless injector and a flame ionisation detector (FID), employing a DB-1 (50 m \times 0.33 mm i.d., 0.20 μ m film thickness) capillary column (J&W Scientific). Data acquisition and manipulation were performed using the TurboChrom Workstation Version 6.3.2 (for

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