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1. Introduction

The use of bimetallic catalysts is attracting increased research interest¹ due to their enhanced activity,^{2,3} selectivity⁴ and resistance to poisoning⁵ in comparison with the corresponding mono-metallic systems. This has been exploited in commercial applications, notably Pd–Zn in hydrogen production,⁶ Pd–Au in vinyl acetate synthesis,⁷ Cu–Zn in methanol production⁸ and Fe–Cr in the water gas shift reaction.⁹ This study focuses on Au–Pd formulations, which to date have been used in the synthesis of hydrogen peroxide,¹⁰ NO₂ decomposition,¹¹ hydrodesulphurisation (of thiophene and dibenzothiophene),¹² hydrodechlorination (of trichloroethene),¹³ oxidation (of glycerol,¹⁴ CO,¹⁵ benzyl alcohol, cinnamyl alcohol, 2-octen-1-ol and *n*-octanol)¹⁶ and hydrogenation (of 1,3-butadiene,^{17,18} benzaldehyde,⁵ naphthalene and toluene,^{19,20}

Selective gas phase hydrogenation of nitroarenes over Mo₂C-supported Au–Pd

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We report the first synthesis of Mo₂C-supported Au and Au–Pd catalysts (nominal Au/Pd = 10 and 30) obtained from colloidal nanoparticles stabilised by polyvinyl alcohol (PVA). Equivalent Au/Al₂O₃ and Au–Pd/Al₂O₃ were prepared and served as benchmarks. Residual PVA was removed by thermal treatment in N₂, which was monitored by thermogravimetric analysis. The catalysts were characterised in terms of temperature-programmed reduction (TPR), BET surface area, H₂ chemisorption, powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) measurements. The reduced catalysts exhibited an equivalent metal particle size range (1–8 nm) and mean size (4–5 nm). The carbide samples showed greater H₂ chemisorption capacity than the Al₂O₃ systems where inclusion of Pd enhanced H₂ uptake. XPS measurements suggest electron transfer from Al₂O₃ to Au while the Au binding energy for the carbide samples is close to that of the metallic Au reference. The catalysts were tested in the gas phase hydrogenation of nitrobenzene, *p*-chloronitrobenzene and *p*-nitrobenzonitrile and delivered 100% selectivity to the target amine in each case. Inclusion of Pd served to increase selective hydrogenation rates where Au–Pd/Mo₂C outperformed Au–Pd/Al₂O₃, a response that is attributed to increased surface hydrogen.

acetylene,²¹ allyl alcohol² and cinnamaldehyde²²). Improved performance relative to monometallic Pd and Au catalysts has been attributed to ensemble, ligand or geometric effects.^{23,24} Prior studies have established chemoselectivity for supported Au in targeted -NO2 reduction of functionalised nitrocompounds.²⁵⁻²⁸ Reaction exclusivity is important in minimising waste and addressing the sustainability gap in non-selective processes using standard (Pd,²⁹ Ru (ref. 30) or Ni (ref. 31)) transition metal catalysts. However, hydrogenation rates delivered by supported Au fall below those achieved with non-selective metal catalysts.³² It is now crucial to increase selective hydrogenation rates to address the key commercial consideration of productivity that combines activity and selectivity. Gold activation of H₂ is the limiting step due to the high energy barrier for dissociative adsorption.³³ We have explored the use of Mo₂C as a support that can chemisorb H₂ and increase surface concentration, leading to higher hydrogenation rates.34 We demonstrated higher selective hydrogenation rates over Au/Mo₂C than those over Au/Al₂O₃ but further improvements are required in Au/Mo₂C synthesis directed at decreasing the Au particle size as a critical variable that governs H₂ activation.³³ Preliminary data³ established that addition of Pd to Au on Al₂O₃ (prepared by depositionprecipitation) increased the hydrogenation activity but lower selectivities were recorded at higher Pd loading (Au/Pd < 20).

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We have now examined the viability of Mo₂C-supported Au-Pd to elevate rates while retaining selectivity in the hydrogenation of nitroarenes.

The challenge in supported bimetallic synthesis is to exert control over surface composition and size/dispersion.³⁵ To date, supported Au-Pd catalysts have principally been prepared by impregnation (incipient¹⁹ and wet^{3,5,17}) and (co)-deposition.^{3,10,17,36,37} The synthesis procedure influences the ultimate metal loading, morphology and structure^{10,21} where surface segregation and formation of isolated Au and Pd particles can occur.³ The use of Au-Pd catalysts has been largely focused on Au addition to modify the catalytic properties of Pd, where Au/Pd $< 1.^{21}$ This study takes the opposite approach with Pd inclusion directed at increasing selective hydrogenation rates. A range of oxides (Fe₂O₃,³⁷ TiO₂,³⁸ ZrO₂¹⁰ and MgO¹³) have been used as Au-Pd supports with the predominance of $Al_2O_3^{3,13,17,19,20,37}$ and $SiO_2^{13,20,21,36,39}$ as carriers. In this study, we report the first preparation of Au- Pd/Mo_2C (Au/Pd \geq 10) using colloidal polyvinyl alcohol (PVA), which provides a protective layer around the metal nanoparticles preventing agglomeration in solution to generate small supported metal particles.⁴⁰ The use of "protecting" agents (polyvinyl pyrrolidone (PVP)¹² and PVA^{14,16}) to minimise nanoparticle aggregation has been applied in the synthesis of supported Au,⁴¹ Pd (ref. 42) and Au-Pd.^{14,16} We examine the catalytic action of Au-Pd/Mo₂C in the hydrogenation of nitroarenes (nitrobenzene, p-chloronitrobenzene and p-nitrobenzonitrile) where Au-Pd/Al₂O₃ prepared using the same method served as a benchmark.

2. Experimental

2.1 Chemicals

Gold(m) chloride hydrate (HAuCl₄·xH₂O, 99.999%), palladium tetraamine dinitrate (Pd(NH₃)₄(NO₃)₂, 99.99%) and polyvinyl alcohol (PVA, 87–89%) were obtained from Aldrich, while molybdic acid (H₂MoO₄, 99%) and NaBH₄ (>99%) were acquired from Merck and Fluka, respectively. All gases were of high purity (99.9%) and supplied by BOC or Air Liquide. The nitro-reactants (nitrobenzene, *p*-chloronitrobenzene and *p*-nitrobenzonitrile, Aldrich (\geq 98%)) and solvent (1-butanol, Riedel-de Haen, 99.8%) were used as-received without further purification.

2.2 Catalyst preparation

β-Mo₂C was synthesised *via* temperature-programmed carburisation of H₂MoO₄ (2 g) in 20% v/v CH₄ in H₂ (340 cm³ min⁻¹). The temperature was ramped at 1 K min⁻¹ to 973 K, maintained for 1 h and decreased to ambient temperature under H₂ with sample passivation in 1% v/v O₂/He (30 cm³ min⁻¹) for 1 h. The passivation step was necessary to circumvent autothermal oxidation upon contact with air.⁴³ Gold and gold–palladium catalysts were prepared according to a colloidal method developed by Prati *et al.*⁴⁴ for carbon supports and adopted for use with Al₂O₃. Gold was incorporated using

an Au sol that was deposited on Mo₂C (or Al₂O₃) with a nominal loading of 1% w/w as reported previously.18 Aqueous solutions of HAuCl₄ (6 cm³, 2.5×10^{-2} M) and PVA (1.5 cm³, $2.3 \times$ 10^{-6} M; Au/PVA = 50) were added to 200 cm³ distilled water with vigorous agitation for 3 min, then a freshly prepared solution of NaBH₄ (4.5 cm³, 0.1 M) was added (NaBH₄/Au = 3) with a resultant colour change from light yellow to red, indicating reduction of Au^{3+} to Au^{0} . The sol was acidified to pH = 2 with H₂SO₄ (0.1 M) and 3 g of support was added to the mixture, which was maintained under vigorous stirring at ambient temperature for 2 h; water was removed using a rotary evaporator. Bimetallic synthesis followed an equivalent protocol where 1% w/w Au/Mo₂C (or Au/Al₂O₃) was suspended in 200 cm³ distilled water to which a known amount of PVA solution $(2.3 \times 10^{-6} \text{ M}; \text{Pd/PVA} = 80)$ was added under vigorous stirring with subsequent addition of $Pd(NH_3)_4(NO_3)_2$ (4.7 \times 10⁻³ M; nominal Au/Pd = 10 or 30). Hydrogen (50 cm³ min⁻¹) was then bubbled into the reactor for 2 h to reduce Pd on the supported Au colloids. The mixture was stirred for further 16 h and water was removed by rotary evaporation. The resultant solid was washed repeatedly and dried under vacuum at ambient temperature. The samples were heated (2 K min⁻¹) in 600 cm³ min⁻¹ N₂ to 773 K for 1 h to remove the stabilising agents, cooled to ambient temperature and subjected to thermal reduction in 100 cm³ min⁻¹ H₂ to 773 K (at 2 K min⁻¹). Upon cooling, the samples were passivated as above for off-line analysis. The bimetallic catalysts are labelled as Au-Pd/Mo₂C (or Al_2O_3)-X, where X represents the nominal Au/Pd molar ratio (= 10 or 30).

2.3 Catalyst characterisation

Au, Mo, Cl and Al contents were measured by inductively coupled plasma (ICP) atomic emission spectroscopy (CNRS Centre of Chemical Analysis, Vernaison). Carbon content was determined using an Exeter CE-440 elemental analyser after sample combustion at 1873 K. Temperature-programmed reduction (TPR), BET surface area and H₂ chemisorption were a commercial CHEM-BET 3000 measured using (Quantachrome) unit. The passivated samples were loaded into a U-shaped Quartz cell (10 cm × 3.76 mm i.d.) and heated in 17 cm³ min⁻¹ (Brooks mass flow controller) 5% v/v H_2/N_2 at 2 K min⁻¹ to 523 ± 1 K, which was held for 1 h. The effluent gas passed through a liquid N2 trap and H2 consumption was monitored by TCD with data acquisition/manipulation using the TPR Win[™] software. The samples were swept with 65 cm³ min⁻¹ N₂ for 1.5 h, cooled to ambient temperature and subjected to H₂ chemisorption using a pulse (10 µl) titration procedure. BET surface area was determined (post-TPR) in 30% v/v N₂/He using pure N₂ (99.9%) as an internal standard. At least three cycles of N2 adsorption-desorption in the flow mode were conducted to determine the total surface area using the standard single point method. BET area and H₂ chemisorption measurements were reproducible to within ±3% and the values quoted represent the mean.

Powder X-ray diffractograms (XRD) were recorded on a Bruker/Siemens D500 incident X-ray diffractometer using Cu K α radiation. The samples were scanned at 0.02° per step over the range $20^\circ \le 2\theta \le 85^\circ$ and the diffractograms were identified using JCPDS-ICDD reference standards, i.e. Au (Card No. 04-0784), Pd (05-0681), B-Mo₂C (11-0680) and δ-Al₂O₃ (16-394). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were conducted using an SDT Q600 simultaneous TGA/DSC analyser (TA Instruments) that measured temporal mass and heat flow as a function of temperature. Samples were swept with air/N₂ (100 cm³ min⁻¹) and ramped (10 K min⁻¹) from ambient temperature to 373 K with an isothermal hold (for 1 h) and subsequent heating to 773 K. Transmission electron microscopy (TEM) was performed using a JEOL 2010 electron microscope operating at 200 kV. Samples for analysis were crushed and homogeneously dispersed in ethanol by ultrasonication and a drop of the suspension was deposited on a carbon-coated copper grid and evaporated. Up to 200 individual Au particles were counted for each catalyst and the mean metal particle sizes are given as the surface areaweighted average (d) according to

$$d = \frac{\sum_{i}^{n} n_i d_i^3}{\sum_{i}^{n} n_i d_i^2} \tag{1}$$

where n_i is the number of particles of diameter d_i . XPS spectra were collected on a SPECS (Phoibos MCD 150) X-ray photoelectron spectrometer using an Al K α (hv = 1486.6 eV) X-ray source. The binding energies (BE) were calibrated with respect to the C–C/C–H component of the C 1s peak (BE = 284.7 eV). Spectral processing was performed using the Casa XPS software package.

2.4 Catalytic procedure

Reactions were carried out at 493 K and 1 atm, immediately after catalyst activation in H₂ (60 cm³ min⁻¹, 2 K min⁻¹ to 523 K, held for 1 h) in a continuous flow fixed bed vertical glass reactor (i.d. = 15 mm, l = 600 mm). The catalytic reactor and operating conditions to ensure negligible heat/mass transport limitations have been fully described elsewhere.⁴⁵ A layer of borosilicate glass beads served as a preheating zone, ensuring that the organic reactants were vaporised and reached the reaction temperature before coming into contact with the catalyst. Isothermal conditions (±1 K) were ensured by diluting the catalyst bed with ground glass (75 μ m). The reaction temperature was continuously monitored with a thermocouple inserted in a thermowell within the catalyst bed. The reactant (nitrobenzene, p-chloronitrobenzene or *p*-nitrobenzonitrile) in butanol (as the carrier) was delivered via a glass/Teflon air-tight syringe and Teflon line using a microprocessor-controlled infusion pump (Model 100, kd Scientific) at a fixed flow rate. A co-current flow of the organic component and H_2 (400 \leq H_2 /nitroarene \leq 2500) was maintained at GHSV = 2×10^4 h⁻¹ with an inlet nitroarene flow (*F*) in the range 0.06–0.38 mmol h⁻¹; the molar Au (n_{Au}) to *F* (*i.e.* n_{Au}/F) spanned the range 2 × 10⁻³–6 × 10⁻² h. In a series of blank tests, passage of each reactant in a stream of H₂ through the empty reactor did not result in any detectable conversion. The reactor effluent was frozen in a liquid nitrogen trap for subsequent analysis, which was conducted using a Perkin-Elmer Auto System XL gas chromatograph equipped with a programmed split/splitless injector and flame ionisation detector, employing a DB-1 (50 m × 0.20 mm i.d., 0.33 µm film thickness) capillary column (J&W Scientific). Repeated reactions with different samples from the same batch of catalyst delivered raw data that were reproducible to within ±6% with a carbon balance ≥95%. Taking *p*-nitrobenzonitrile as an example, fractional hydrogenation (x_i) was obtained from

$$x_{i} = \frac{\left[p\text{-nitrobenzonitrile}\right]_{in} - \left[p\text{-nitrobenzonitrile}\right]_{out}}{\left[p\text{-nitrobenzonitrile}\right]_{in}}$$
(2)

where selectivity (S_i) to *p*-aminobenzonitrile (*p*-ABN) is given by

$$S_{i}(\%) = \frac{[p\text{-aminobenzonitrile}]_{out}}{[p\text{-nitrobenzonitrile}]_{in} - [p\text{-nitrobenzonitrile}]_{out}} \times 100 \quad (3)$$

3. Results and discussion

3.1 Catalyst characterisation

It has been shown that calcination in air (at 773 K) is effective in removing residual PVA following the synthesis of bimetallics on alumina.¹⁸ Oxidative treatment is not applicable in the case of Au-Pd/Mo₂C as the support can undergo deep oxidation with irreversible structural modification at high temperatures. We examined the feasibility of thermal treatment in N2, taking Au-Pd/Al2O3-10 and Au-Pd/Mo2C-10 as representative samples. TGA-DSC analysis of Au-Pd/Al₂O₃-10 for treatment in air (A) and N_2 (B) resulted in equivalent profiles (Fig. 1). The endothermic response at 328 K (from DSC) is due to the loss of physisorbed water while the exothermic mass loss at higher temperature (T > 400 K) can be attributed to the removal of PVA. The overall change in mass converged (at ca. 6% w/w) in both cases, suggesting equivalence for treatment in air and N2. Thermal treatment of Au-Pd/ Mo_2C-10 in N_2 showed comparable behaviour (Fig. 1(C)) with low and high temperature endothermic and exothermic mass losses. We accordingly applied the same thermal treatment (in N₂ to 773 K) for both alumina and carbide samples. Gold loadings were close to the nominal (1% w/w) value with Au/ Pd atomic ratios approaching the target 30 and 10 in the bimetallic systems (Table 1). Moreover, the Mo/C ratios were close to 2, confirming the synthesis of a Mo₂C phase with no significant contamination by surface free carbon, which can occlude Mo₂C active sites and lower the activity.⁴⁶

The temperature-programmed reduction (TPR) profiles of $Au-Pd/Al_2O_3-10$ and $Au-Pd/Mo_2C-10$ are presented in Fig. 2.



Fig. 1 TGA (solid line) and DSC (dashed line) profiles generated in the pre-treatment of (A) Au-Pd/Al₂O₃-10 in air, (B) Au-Pd/Al₂O₃-10 in N₂ and (C) Au-Pd/Mo₂C-10 in N₂; 100 cm³ min⁻¹ gas flow at 10 K min⁻¹ to 373 K (held for 1 h) and then to 773 K.

As the metal component was reduced by NaBH₄ during preparation, there was no detectable TPR response for Au–Pd/ Al₂O₃-10 (Fig. 2(I)). The TPR signal recorded at 437 K for Au– Pd/Mo₂C-10 (II) can be ascribed to the removal of the passivation layer from the carbide support. This is facilitated by the Pd component with a lower T_{max} at lower Au/Pd (Table 1). The BET surface area of the carbide systems showed a decrease from 57 to 34 m² g⁻¹ with increasing metal loading that was not evident for the Al₂O₃ samples. The XRD profile of the latter (taking Au-Pd/Al₂O₃-10 as a representative (Fig. 3(I)) presented peaks characteristic of δ -Al₂O₃.⁴⁷ The signal at 2θ = 77.5° can be assigned to Au (311) but the intensity is too weak to allow any meaningful determination of Au particle size from standard line broadening. The XRD pattern of Au-Pd/Mo₂C-10 (Fig. 3(II)) is consistent with that of hexagonal β -Mo₂C, showing characteristic peaks due to (010), (002), (011), (012), (110), (013) and (112) planes. There was no detectable signal for bulk oxide (MoO₃ or MoO₂), indicating that the precursor had been fully converted to carbide and that passivation resulted in superficial (rather than bulk) oxidation. Gold detection is hampered by overlap with XRD peaks due to the carbide support but the absence of an Au (200) peak at 44.5° suggests a well-dispersed Au phase. There was no detectable diffraction peak due to Pd (notably at 40.1° (111)) in the Au-Pd samples but the Pd loading was too low for detection. The formation of bimetallic nanoparticles has been established in an earlier study using IR spectroscopy coupled with CO adsorption for Au-Pd/Al₂O₃ prepared by the same method.¹⁸ Villa et al. have proposed the generation of bimetallic Au-Pd particles on activated carbon when PVA is used as a protecting agent.48 The presence of isolated Pd atoms surrounded by Au atoms in bimetallic Au-Pd particles is a critical feature of various catalytic reactions using goldpalladium catalysts (*e.g.* hydrogenation¹⁸ and oxidation⁴⁴). The IR spectra (not shown) obtained for the Au-Pd/Al₂O₃ samples are identical to the ones reported in a previous study.¹⁸ However, it was not possible to characterise the Au-Pd/Mo₂C systems using the same technique because of strong absorption by the dark Mo₂C material. At this juncture, we assume that the results obtained for the aluminasupported catalysts are applicable to the Mo₂C systems.

Gold particle size is important in hydrogenation applications⁴⁹ where particles <5 nm are intrinsically more active in the gas phase hydrogenation of p-chloronitrobenzene and *m*-dinitrobenzene³² and butadiene.⁵⁰ Representative TEM images (of Au-Pd/Al₂O₃-10 (A) and Au-Pd/Mo₂C-10 (B)) are presented in Fig. 4(I), where well-dispersed pseudo-spherical particles in the 1-8 nm size range (Fig. 4(II)) can be observed. An essentially equivalent mean metal size (4-5 nm) was obtained for all the Al₂O₃- and Mo₂C-supported systems. Previous Au/Mo₂C synthesis by deposition-precipitation (with urea) generated an appreciably wider size range (4-20 nm) and larger mean size (13.4 nm).³⁴ Application of PVA as a stabilising agent was effective in generating homogeneously dispersed nanoparticles. Hydrogen dissociation on supported Au has a higher activation energy barrier than that on conventional hydrogenation metals (Pd, Pt and Ni)49 and is dependent on Au coordination where dissociation is facilitated at edge and corner sites associated with smaller Au particles (<10 nm).³³ Ambient temperature H₂ chemisorption on Au/ Al₂O₃ was low and is in agreement with previous reports.^{28,51} Inclusion of Pd resulted in a significant increase in H₂ uptake that was enhanced at lower Au/Pd ratios as observed for catalysts prepared by deposition-precipitation.³⁴ The higher H₂ chemisorption capacity exhibited by the carbide systems

	Au (% w/w)	Molar ratio		BET	TPR	Particle size (nm)		H ₂	BE XPS (eV)	
		Au/Pd	Mo/C	area $(m^2 g^{-1})$	T _{max} (K)	Range	Mean (d)	chemisorption (µmol g ^{−1})	Au 4f _{7/2}	Mo 3d _{5/2}
Au/Al ₂ O ₃	0.94	_	_	104	_	1-8	5.4	0.4	83.0	_
Au-Pd/Al ₂ O ₃ -30	0.97	27	_	100	_	1-8	4.6	0.7	_	_
Au-Pd/Al ₂ O ₃ -10	0.95	9	_	101	_	1-7	4.5	1.2	83.0	
Mo ₂ C	_	_	1.95	57	500	1-7	_	0.4	_	228.4
Au/Mo ₂ C	0.81	_	1.95	42	493	1-7	4.3	1.0	84.2	228.4
Au-Pd/Mo ₂ C-30	0.87	32	2.00	38	476	1-7	4.2	1.5	_	_
Au-Pd/Mo ₂ C-10	0.84	14	1.96	34	437	1-7	4.3	2.1	$84.2 (340.8^{a})$	228.4
^{<i>a</i>} Pd $3d_{3/2}$.										

Table 1 Gold content (% w/w), Au/Pd and Mo/C ratios, BET surface area, temperature-related H₂ consumption maximum during TPR (T_{max}), metal particle size range and surface area-weighted mean diameter (d), H₂ chemisorption and XPS binding energies (BE) for Au 4f_{7/2}, Pd 3d_{3/2} and Mo 3d_{5/2}

cannot be attributed to metal particle size and must be due to additional chemisorption on the Mo₂C support (Table 1).

The electronic structure of the supported metal can have an impact on performance in the hydrogenation of nitroarenes^{28,52} as -NO₂ adsorption/activation is favoured on electron-deficient sites.^{28,53} Electronic character was probed by XPS analysis and the resultant spectra are presented in Fig. 5. The Au 4f binding energy (BE) showed a dependence on the support but was unaffected by Pd inclusion (Table 1) where the Au $4f_{7/2}$ BE for the Al₂O₃-supported samples (83.0 eV) was appreciably lower than that (84.2 eV) recorded for the carbide systems (Fig. 5(A)). Previous studies reported that such a shift of the Au $4f_{7/2}$ BE to lower energy can be related to reduced screening of core holes in an assembly of lowcoordinated surface Au atoms⁵⁴ or to a reduced coordination number of Au atoms associated with the degree of rounding of Au nanoparticles, which is dependent on metal-support interactions.55 The equivalent particle size obtained for Au/ Al₂O₃ and Au/Mo₂C suggests that such effects alone cannot account for the variation of Au 4f7/2 BE. Taking the reference BE for metallic Au as 84.0 eV,⁵⁶ the XPS results could also suggest electron transfer from support surface defects to nano-scale Au particles.57 Previous XPS studies of TiO2- and Al₂O₃-supported catalysts have indicated metal-support interactions that result in electron transfer from the oxide to the supported Au particles.⁵⁸ In contrast, the Au 4f_{7/2} BE recorded for the carbide systems coincides with that of the metallic reference, suggesting negligible electron transfer. Care must be taken regarding such interpretation as charging effects in XPS measurements can differ significantly between insulating (Al_2O_3) and highly conductive (Mo_2C) supports. We have observed a Pd 3d_{3/2} signal at 340.8 eV for Au-Pd/Mo₂C-10 (Table 1 and Fig. 5(B)), which is close to the BE reported for metallic Pd $3d_{3/2}$ (at 340.5 ± 0.1 eV).^{28,53} A similar response (Pd 3d_{3/2} at 340.9 eV) has been recorded for Pd-Mo₂C/graphitic carbon.⁵⁹ The second signal at 335.7 eV (Fig. 5(B)) can be attributed to Au $4d_{5/2}$ but it should be noted that Au $4d_{5/2}$ and Pd 3d_{5/2} XPS signals can overlap, as reported elsewhere.⁶⁰ The very low intensity of the XPS signal in the Pd 3d region in the case of Au-Pd/Al₂O₃-10 (not shown) precluded detection of a Pd 3d_{3/2} contribution. The XPS spectrum over the Mo 3d region (Fig. 5(C)) shows Mo 3d_{5/2} peaks at 228.4 and 231.6 eV consistent with a Mo₂C phase.^{59,61} In addition to the carbidic Mo contribution, Mo $3d_{5/2}$ signals at higher BE can be attributed to oxidised states of Mo arising from



Fig. 2 Temperature-programmed reduction (TPR) profiles of Au-Pd/ Al₂O₃-10 (I) and Au-Pd/Mo₂C-10 (II).



Fig. 3 XRD patterns of Au-Pd/Al₂O₃-10 (I) and Au-Pd/Mo₂C-10 (II). Peak assignments are based on JCPDS-ICDD reference standards: δ-Al₂O₃ (●, 16-394); β-Mo₂C (■, 11-0680); Au (▲, 04-0784).



Fig. 4 Representative TEM images (I) with associated particle size distribution (II) for Au-Pd/Al₂O₃-10 (A) and Au-Pd/Mo₂C-10 (B).

passivation, *i.e.* Mo(rv) (229.0 eV),⁶² Mo(v) (231.2 eV)⁶³ and Mo(vi) (232.4 eV).⁶⁴ Deconvolution of the C 1s profile (Fig. 5(D)) provides evidence of carbidic (283.4 eV)⁶⁵ and graphitic (284.6 eV) carbon⁵⁹ with contributions (at 286.3 and 288.6 eV) due to C–O (ref. 62) and C=O.⁶⁶

3.2 Catalytic response

This is the first reported application of a Mo₂C-supported bimetallic (Au-Pd) catalyst in (gas phase) hydrogenation where we examine nitroarene (nitrobenzene, p-chloronitrobenzene and p-nitrobenzonitrile) conversion, carrying Au/Al₂O₃ and Au-Pd/Al₂O₃ through as benchmarks. The target amine products are commercially important in the production of a diversity of agrochemicals, pharmaceuticals and fine chemicals.^{67,68} Initial conversion (representative time-on-stream plots shown in Fig. 6(A)) was used to obtain reaction rates (normalised with respect to molar Au loading) using the approach described previously.⁶⁹ Reduction of nitrobenzene generated aniline where Au/Mo₂C outperformed Au/Al₂O₃ and delivered a greater than three-fold higher rate (Fig. 6(B)). This can be ascribed, at least in part, to the greater amount of available surface hydrogen determined in pulse chemisorption measurements (Table 1) as H₂ activation is the rate-limiting step in hydrogenation over Au. In previous work,³² we established Au particle size effects in -NO₂ hydrogenation with an increase in intrinsic activity with decreasing particle size (from 10 to 3 nm). This should not be a contributory effect here given the equivalency of size distribution and mean. Alumina (without a metal additive) is inactive in hydrogenation, whereas Mo_2C alone can promote H_2 activation with $-NO_2$ reduction³⁴ and contribute directly to the higher reaction rate. Incorporation of Pd with Au resulted in increased H_2 chemisorption capacity and a consequent enhanced activity with the highest values recorded for Au/Pd = 10.

Chemoselectivity in amine production is particularly relevant in the hydrogenation of *p*-chloronitrobenzene⁷⁰ where a range of intermediates and by-products, notably nitrobenzene and aniline, have been reported for reaction over Pd and Ni catalysts in both liquid and gas phases.^{28,53,71,72} A simplified reaction pathway is presented in Fig. 7(A), where the target p-chloroaniline formed via -NO2 reduction (step I) can undergo hydrodechlorination to aniline (step II) or alternatively nitrobenzene is first generated by hydrodechlorination (step III) with subsequent hydrogenation to aniline (step IV). In previous studies, reaction over Pd/Al₂O₃ generated nitrobenzene and aniline,²⁸ whereas supported Au was fully selective to chloroaniline.^{25,27,28,34} The chemoselectivity achieved with Au catalysts can be attributed to the preferential adsorption of the reactants through the nitro group at the support (notably TiO₂) and metal/support interface, where the Au (metal) sites provide reactive dissociated H2.73,74 In this study, hydrogenation of p-chloronitrobenzene resulted in exclusive p-chloroaniline formation with 100% yield over Au-Pd/Mo₂C-10 and Au-Pd/Mo₂C-30, *i.e.* full selectivity to p-chloroaniline at 100% conversion of the inlet p-chloronitrobenzene feed.



Fig. 5 XPS spectra: (A) over the Au 4f region for $Au-Pd/Al_2O_3-10$ (I) and $Au-Pd/Mo_2C-10$ (II); (B) over the Au 4d and Pd 3d regions for $Au-Pd/Mo_2C-10$; (C) with peak deconvolution over the Mo 3d region for $Au-Pd/Mo_2C-10$; (D) with peak deconvolution over the C 1s region for $Au-Pd/Mo_2C-10$.

This result is of importance as we previously observed that the incorporation of Pd on Au/Al_2O_3 (Au/Pd = 8) favoured hydrodechlorination with formation of nitrobenzene.³ Performance must be influenced by catalyst synthesis where the colloidal method with PVA used here has been shown to generate surface isolated Pd atoms (Pd monomers) surrounded by Au atoms in bimetallic particles.¹⁸ This effect appears to extend to the carbide system. In contrast, preparation by deposition-precipitation results in segregated Pd sites that promote hydrodechlorination at low Au/Pd ratios.³ This is consistent with the observation of Gao et al.7 that enhanced selectivity/activity (in H2O2/vinyl acetate synthesis) was attributed to an "ensemble effect" resulting from dilution of surface Pd by Au which was dependent on Au content. The Mo₂C-supported catalysts again generated appreciably higher rates than the equivalent alumina-supported samples (Fig. 6(C)) with increased activity resulting from the inclusion of Pd.

Catalytic performance was further assessed in the gas phase hydrogenation of *p*-nitrobenzonitrile. The limited available literature^{67,75-77} refers to batch liquid phase reactions at elevated pressures (up to 6 MPa) where high selectivity to *p*-aminobenzonitrile has proved challenging. Koprivova and Cerveny⁷⁶ identified 15 possible intermediates and products that involve disproportionation, reduction, condensation,

hydrodenitrogenation and hydrodecarbonation reactions. A reaction pathway that includes the major reported products^{76,77} is presented in Fig. 7(B). Conversion of *p*-nitrobenzonitrile to the target *p*-aminobenzonitrile (step I) can be accompanied by further hydrogenation/hydration to *p*-aminobenzamide (step III) or hydrogenation to *p*-aminobenzylamine (step II)⁷⁶ with subsequent hydrogenolysis to p-aminotoluene (step IV).^{76,77} In recent work, we have established that oxide-supported Pd and Ni are nonselective, generating *p*-aminotoluene as a by-product.⁷⁸ Each catalyst in this study was fully selective to p-aminobenzonitrile with 100% yield over Au-Pd/Mo₂C-10 and Au-Pd/Mo₂C-30, exceeding the highest reported values for supported Au (96-97% over Au/TiO267 and Au/Fe2O375) operated in batch liquid phase at elevated pressure (25 bar H₂). Economies of scale favour continuous processes for high throughput.²⁵ Palladium again served as a promoter with higher rates recorded for the carbide catalysts (Fig. 6(D)). The only reported gas phase catalysis study dates back from the 1950s where Hata and Watanabe77 investigated the hydrogenation of various aromatic nitriles (including the three nitrobenzonitrile isomers) over a Ni-Cu catalyst at 523-573 K and reported aniline, toluidine and aminobenzonitrile as principal products (<32% yield). Our results represent a significant advance in the sustainable

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Fig. 6 (A) Variation of NB fractional conversion (x_i) over Au/Mo₂C (\blacksquare), of *p*-CNB over Au-Pd/Mo₂C-30 (\bullet) and of *p*-NBN over Au-Pd/Mo₂C-10 (\blacktriangle) with time-on-stream. Reaction rate (*r*) with the associated selectivity (S_i) to the target amines (aniline, *p*-chloroaniline and *p*-aminobenzonitrile) in the hydrogenation of (B) nitrobenzene, (C) *p*-chloronitrobenzene and (D) *p*-nitrobenzonitrile.



Fig. 7 Reaction pathways for (A) *p*-chloronitrobenzene and (B) *p*-nitrobenzonitrile hydrogenation.

production of a target amine where reaction exclusivity at full reactant conversion removes the requirement for energyintensive down-stream separation/purification unit operations.

4. Conclusions

We provide the first reported synthesis of Mo₂C-supported (Au-Pd) bimetallic catalysts used to promote the gas phase hydrogenation of nitroarenes (nitrobenzene, p-chloronitrobenzene and p-nitrobenzonitrile). The Mo₂C support was synthesised by temperature-programmed carburisation (of H_2MoO_4 in CH_4/H_2) and confirmed by XRD analysis. Bimetallic catalyst synthesis with Au and Pd colloids employed polyvinyl alcohol (PVA) as a stabiliser to avoid agglomeration and resulted in nano-scale (1-8 nm size range) supported metal particles with a mean size of 4-5 nm. The bimetallic catalysts exhibited increased H₂ chemisorption capacity with higher uptake on Au-Pd/ Mo₂C relative to Au-Pd/Al₂O₃. XPS analysis suggests electron donation from Al₂O₃ to Au, whereas the BE recorded for Au on Mo₂C (for both monometallic and Au-Pd bimetallic systems) was close to that of the metallic Au reference. All the catalysts were 100% selective in -NO₂ hydrogenation to the target amine. The Mo₂C-supported Au system exhibited a higher (greater than 3-fold) hydrogenation rate that was further enhanced by addition of Pd (Au/Pd from 30 to 10), which can be attributed to an increase in available surface reactive hydrogen. We achieved 100% amine yield over Au-Pd/Mo₂C-10 and Au-Pd/Mo₂C-30 in continuous operation. The results have established controlled preparation of well-dispersed Au-Pd on Mo₂C and application in the clean continuous production of high value amines.

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