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-nitrobenzotrinitrobenzene, 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.

1. Introduction

The use of bimetallic catalysts is attracting increased research interest due to their enhanced activity, selectivity and resistance to poisoning in comparison with the corresponding mono-metallic systems. This has been exploited in commercial applications, notably Pd–Zn in hydrogen production, Pd–Au in vinyl acetate synthesis, Cu–Zn in methanol production and Fe–Cr in the water gas shift reaction. This study focuses on Au–Pd formulations, which to date have been used in the synthesis of hydrogen peroxide, NO₂ decomposition, hydrodesulphurisation (of thiophene and dibenzothiophene), hydrodechlorination (of trichloroethene), oxidation (of glycerol, CO, benzyl alcohol, cinnamyl alcohol, 2-octan-1-ol and n-octanol) and hydrogenation (of 1,3-butadiene, benzyaldehyde, naphthalene and toluene). Improved performance relative to monometallic Pd and Au catalysts has been attributed to ensemble, ligand or geometric effects. Prior studies have established chemoselectivity for supported Au in targeted –NO₂ reduction of functionalised nitrocompounds. Reaction exclusivity is important in minimising waste and addressing the sustainability gap in non-selective processes using standard (Pd, 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. 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. We have explored the use of Mo₂C as a support that can adsorb H₂ and increase surface concentration, leading to higher hydrogenation rates.
We have now examined the viability of \( \text{Mo}_2\text{C} \)-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 (incipient\(^{19}\) and wet\(^{15,17}\)) and (co)-deposition\(^{1,3,10,16,17,36,37}\). 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.\(^7\) 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 (\( \text{Fe}_2\text{O}_3, \text{TiO}_2, \text{ZrO}_2 \)) and \( \text{Al}_2\text{O}_3 \) have been used as Au–Pd supports with the predominance of \( \text{Al}_2\text{O}_3 \)\(^{3,13,17,19,20,37}\) and \( \text{SiO}_2 \)\(^{13,20,21,36,39}\) as carriers. In this study, we report the first preparation of Au–Pd/Mo\(_2\text{C} \) (Au/Pd > 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/Mo\(_2\text{C} \) in the hydrogenation of nitroarenes (nitrobenzene, \( \text{p}-\text{chloronitrobenzene} \) and \( \text{p}-\text{nitrobenzonitrile} \)) where Au–Pd/Al\(_2\text{O}_3 \) prepared using the same method served as a benchmark.

2. Experimental

2.1 Chemicals

Gold(m) chloride hydrate (HAuCl\(_4\cdot \text{xH}_2\text{O} \), 99.999%), palladium tetraamine dinitrate (Pd(NH\(_3\))\(_4\)(NO\(_3\))\(_2\)\), 99.99%) and polyvinyl alcohol (PVA, 87–89%) were obtained from Aldrich, while molybdic acid (\( \text{H}_2\text{MoO}_4 \), 99%) and NaBH\(_4 \) (>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, \( \text{p}-\text{chloronitrobenzene} \) and \( \text{p}-\text{nitrobenzonitrile} \), Aldrich (≥98%)) and solvent (1-butanol, Riedel-de Haen, 99.8%) were used as-received without further purification.

2.2 Catalyst preparation

\( \beta-\text{Mo}_2\text{C} \) was synthesised \( \text{via} \) temperature-programmed carboxylation of \( \text{H}_2\text{MoO}_4 \) (2 g) in 20% v/v CH\(_4\) in H\(_2\) (340 cm\(^3\) min\(^{-1}\)) at 1 K min\(^{-1}\) to 973 K, maintained for 1 h and decreased to ambient temperature under H\(_2\) with sample passivation in 1% v/v O\(_2\)/He (30 cm\(^3\) min\(^{-1}\)) for 1 h. The passivation step was necessary to circumvent autocatalytic oxidation upon contact with air.\(^{33}\) 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 Al\(_2\text{O}_3 \). Gold was incorporated using an Au sol that was deposited on Mo\(_2\text{C} \) (or Al\(_2\text{O}_3 \)) with a nominal loading of 1% w/w as reported previously.\(^{18}\) Aqueous solutions of HAuCl\(_4\) (6 cm\(^3\), 2.5 × 10\(^{-2}\) M) and PVA (1.5 cm\(^3\), 2.3 × 10\(^{-6}\) M; Au/PVA = 50) were added to 200 cm\(^3\) distilled water with vigorous agitation for 3 min, then a freshly prepared solution of NaBH\(_4\) (4.5 cm\(^3\), 0.1 M) was added (NaBH\(_4\)/Au = 3) with a resultant colour change from light yellow to red, indicating reduction of Au\(^+\) to Au\(^0\). The sol was acidified to pH = 2 with H\(_2\)SO\(_4\) (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/Mo\(_2\text{C} \) (or Au/Al\(_2\text{O}_3 \)) was suspended in 200 cm\(^3\) distilled water to which a known amount of PVA solution (2.3 × 10\(^{-6}\) M; Pd/PVA = 80) was added under vigorous stirring with subsequent addition of Pd(NH\(_3\))\(_4\)(NO\(_3\))\(_2\) (4.7 × 10\(^{-3}\) M; nominal Au/Pd = 10 or 30). Hydrogen (50 cm\(^3\) 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 cm\(^3\) min\(^{-1}\) N\(_2\) to 773 K for 1 h to remove the stabilising agents, cooled to ambient temperature and subjected to thermal reduction in 100 cm\(^3\) min\(^{-1}\) H\(_2\) 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/Mo\(_2\text{C} \) (or Al\(_2\text{O}_3 \))–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 \( \text{H}_2 \) chemisorption were measured using a commercial CHEM-BET 3000 (Quantachrome) unit. The passivated samples were loaded into a U-shaped Quartz cell (10 cm × 6932 mm i.d.) and heated in 17 cm\(^3\) 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 N\(_2\) trap and \( \text{H}_2 \) consumption was monitored by TCD with data acquisition/manipulation using the TPR Win\(^{TM}\) software. The samples were swept with 65 cm\(^3\) min\(^{-1}\) N\(_2\) for 1.5 h, cooled to ambient temperature and subjected to \( \text{H}_2 \) chemisorption using a pulse (10 μl) titration procedure. BET surface area was determined (post-TPR) in 30% v/v N\(_2\)/He using pure N\(_2\) (99.9%) as an internal standard. At least three cycles of \( \text{N}_2 \) adsorption–desorption in the flow mode were conducted to determine the total surface area using the standard single point method. BET area and \( \text{H}_2 \) 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 Kα radiation. The samples were scanned at 0.02° per step over the range 20° ≤ 2θ ≤ 85° and the diffractograms were identified using JCPDS-ICDD reference standards, i.e. Au (Card No. 04-0784), Pd (05-0681), β-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 area-weighted average (\(d\)) according to

\[
d = \frac{\sum n_i d_i^2}{\sum n_i} \tag{1}
\]

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 Kα (\(hν = 1486.6\) 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 vapourised 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 μm). 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 H₂ (400 ≤ H₂/nitroarene ≤ 2500) was maintained at GHSV = 2 × 10⁴ h⁻¹ with an inlet nitroarene flow (\(F\)) in the range 0.06–0.38 mmol h⁻¹; the molar Au (\(n_{Au}\)) to Fe (i.e. \(n_{Au}/F\)) spanned the range 2 × 10⁻³–6 × 10⁻³ h⁻¹. 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

\[
x_i = \frac{[p\text{-nitrobenzonitrile}]_{in} - [p\text{-nitrobenzonitrile}]_{out}}{[p\text{-nitrobenzonitrile}]_{in}} \times 100 \tag{2}
\]

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

\[
S_i(\%) = \frac{[p\text{-aminobenzonitrile}]_{in} - [p\text{-nitrobenzonitrile}]_{out}}{[p\text{-nitrobenzonitrile}]_{in}} \times 100 \tag{3}
\]

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 N₂ (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/Mo₂C-10 in N₂ 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.16

The temperature-programmed reduction (TPR) profiles of Au–Pd/Al₂O₃-10 and Au–Pd/Mo₂C-10 are presented in Fig. 2.
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 nanoparticle 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 gold–palladium catalysts (e.g. hydrogenation¹⁸ and oxidation¹¹). 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 alumina-supported catalysts are applicable to the Mo₂C systems.

Gold particle size is important in hydrogenation applications¹⁶ where particles <5 nm are intrinsically more active in the gas phase hydrogenation of p-chloronitrobenzene and m-dinitrobenzene⁵² 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.
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 nitroarenes28,52 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 4f7/2 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 4f7/2 BE to lower energy can be related to additional chemisorption on the Mo2C support (Table 1).

Table 1 Gold content (% w/w), Au/Pd and Mo/C ratios, BET surface area, temperature-related H2 consumption maximum during TPR (Tmax), metal particle size range and surface area-weighted mean diameter (d), H2 chemisorption and XPS binding energies (BE) for Au 4f7/2, Pd 3d3/2 and Mo 3d5/2.

| Catalyst | Au (w/w%) | Molar ratio | BET area (m2 g−1) | Tmax (K) | Particle size (nm) | H2 chemisorption (μmol g−1) | BE XPS (eV) |
|----------|-----------|-------------|-----------------|---------|--------------------|---------------------------|-------------|
| Au/Al2O3 | 0.94      | —           | 104             | —       | 1–8                | 5.4                       | 0.4         |
| Au-Pd/Al2O3-30 | 0.97      | 27          | 100             | —       | 1–8                | 4.6                       | 0.7         |
| Au-Pd/Al2O3-10 | 0.95      | 9           | 101             | —       | 1–7                | 4.5                       | 1.2         |
| Au/Mo2C  | —         | —           | 1.95            | 57      | 1–7                | —                         | 0.4         |
| Au/Al2O3 | 0.81      | —           | 1.95            | 42      | 1–7                | 4.3                       | 1.0         |
| Au-Pd/Al2O3-30 | 0.87      | 32          | 2.00            | 38      | 1–7                | 4.2                       | 1.5         |
| Au-Pd/Al2O3-10 | 0.84      | 14          | 1.96            | 34      | 1–7                | 4.3                       | 2.1         |

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

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 4f7/2 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 (Al2O3) and highly conductive (Mo2C) supports. We have observed a Pd 3d3/2 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 3d3/2 (at 340.5 ± 0.1 eV).28,53 A similar response (Pd 3d3/2 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 4d5/2 but it should be noted that Au 4d5/2 and Pd 3d5/2 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 3d3/2 contribution. The XPS spectrum over the Mo 3d region (Fig. 5(C)) shows Mo 3d5/2 peaks at 228.4 and 231.6 eV consistent with a Mo2C phase.59,61 In addition to the carbidic Mo contribution, Mo 3d3/2 signals at higher BE can be attributed to oxidised states of Mo arising from

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: α-Al2O3 (●, 16-394); β-Mo2C (■, 11-0680); Au (▲, 04-0784).
passivation, i.e. Mo(IV) (229.0 eV), Mo(V) (231.2 eV), and Mo(VI) (232.4 eV). Deconvolution of the C 1s profile (Fig. 5(D)) provides evidence of carbidic (283.4 eV) and graphitic (284.6 eV) carbon with contributions (at 286.3 and 288.6 eV) due to C–O and C=O.

3.2 Catalytic response

This is the first reported application of a Mo2C-supported bi-metallic (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. 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. Reduction of nitrobenzene generated aniline where Au/Mo2C outperformed 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. Chemoselectivity in amine production is particularly relevant in the hydrogenation of p-chloronitrobenzene 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. A simplified reaction pathway is presented in Fig. 7(A), where the target p-chloroaniline formed via reduction of nitrobenzene to aniline (step I) or alternatively nitrobenzene is first generated by hydrodechlorination (step II) with subsequent hydrogenation to aniline (step IV). In previous studies, reaction over Pd/Al2O3 generated nitrobenzene and aniline, whereas supported Au was fully selective to chloroaniline. 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. 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.
This result is of importance as we previously observed that the incorporation of Pd on Au/Al₂O₃ (Au/Pd = 8) favoured hydrodechlorination with formation of nitrobenzene. 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. 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. This is consistent with the observation of Gao et al. 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 refers to batch liquid phase reactions at elevated pressures (up to 6 MPa) where high selectivity to p-aminobenzamide has proved challenging. Koprivova and Cerveny identified 15 possible intermediates and products that involve disproportionation, reduction, condensation, hydrodenitrogenation and hydrodecarbonation reactions. A reaction pathway that includes the major reported products 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) with subsequent hydrogenolysis to p-aminotoluene (step IV). 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/TiO₂ and Au/Fe₂O₃) operated in batch liquid phase at elevated pressure (25 bar H₂). Economies of scale favour continuous processes for high throughput. 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 Watanabe 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
Fig. 6 (A) Variation of NB fractional conversion ($\chi_i$) over Au/Mo$_2$C (■), of p-CN over Au–Pd/Mo$_2$C-30 (●) and of p-NBN over Au–Pd/Mo$_2$C-10 (▲) 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 energy-intensive down-stream separation/purification unit operations.

4. Conclusions

We provide the first reported synthesis of Mo$_2$C-supported (Au-Pd) bimetallic catalysts used to promote the gas phase hydrogenation of nitroarenes (nitrobenzene, p-chloronitrobenzene and p-nitrobenzonitrile). The Mo$_2$C support was synthesised by temperature-programmed carburisation (of H$_2$MoO$_4$ 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 H$_2$ chemisorption capacity with higher uptake on Au–Pd/Mo$_2$C relative to Au–Pd/Al$_2$O$_3$. XPS analysis suggests electron donation from Al$_2$O$_3$ to Au, whereas the BE recorded for Au on Mo$_2$C (for both monometallic and Au–Pd bimetallic systems) was close to that of the metallic Au reference. All the catalysts were 100% selective in –NO$_2$ hydrogenation to the target amine. The Mo$_2$C-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/Mo$_2$C-10 and Au–Pd/Mo$_2$C-30 in continuous operation. The results have established controlled preparation of well-dispersed Au–Pd on Mo$_2$C and application in the clean continuous production of high value amines.

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