

Gas Phase Hydrogenation of *m*-Dinitrobenzene over Alumina Supported Au and Au–Ni Alloy

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Abstract We report, for the first time, 100% selectivity in the continuous gas phase hydrogenation of *m*-dinitrobenzene to *m*-nitroaniline (*m*-NAN) over Au/Al₂O₃. The synthesis and application of an alumina supported Au–Ni alloy is also described where alloy formation is demonstrated by XRD, diffuse reflectance UV–Vis and HRTEM analyses. Under the same reaction conditions, Au/Al₂O₃ delivered a higher (by close to an order of magnitude) hydrogenation rate compared with the alloy. Au–Ni/Al₂O₃ promoted the formation of both *m*-NAN and *m*-phenylenediamine, i.e. partial and complete hydrogenation: the results are consistent with a stepwise reduction mechanism.

Keywords Selective hydrogenation · *m*-dinitrobenzene · Au/Al₂O₃ · Au–Ni/Al₂O₃ · Supported alloy

1 Introduction

Aromatic amino compounds are important chemicals, used as intermediates in the manufacture of a range of fine chemicals, e.g. pesticides, pigments and cosmetics [1]. Amino derivatives are typically synthesised via the reduction of the corresponding nitro-compound, either by Fe promoted reduction in acid media (Bechamp process) or transition metal promoted liquid phase hydrogenation [2]. The production of toxic by-products (ferric oxide sludge), in the former case, and the low associated target

product yields has shifted attention to the catalytic hydrogenation option as a cleaner alternative [3]. Conventional supported monometallic (e.g. Pt or Pd) catalysts can deliver high conversions but an exclusive selectivity in terms of nitro-group reduction has yet to be achieved [4]. The ineffectiveness of these systems is particularly marked in the synthesis of *m*-nitroaniline (*m*-NAN) from *m*-dinitrobenzene (*m*-DNB) where the formation of *m*-phenylenediamine (*m*-PDM) (i.e. reduction of both –NO₂ groups) is also promoted [5, 6]. The use of Au in the selective hydrogenation of nitroarenes is now gaining increasing attention with recent reports of batch liquid phase hydrogenation over Au supported on SiO₂ [7], TiO₂ [8], Fe₂O₃ [8] and ZrO₂ [9] but the requirement of high hydrogen pressures (3–4 MPa) [7, 8] and/or the formation of highly toxic compounds (azoxy-derivates) [8, 9] represent decided drawbacks. Structure sensitivity has been proposed [10] while a selective activation of the nitro-group via interaction with Au sites may have a critical role to play [11]. We have recently reported reaction exclusivity in terms of –NO₂ group reduction for the continuous gas phase hydrogenation of a series of nitrohaloarenes over supported Au [12, 13]. We have now focused our attention on the selective hydrogenation of *m*-DNB and report here our preliminary results.

A significant recent development in catalysis by Au has seen the use of Au based alloys, which have delivered distinct selectivity and activity responses [14, 15]. Hutchings et al. [16], studying the gas phase hydrogenation of O₂ to H₂O₂, recorded higher activity (by a factor of 2) over a supported Au–Pd alloy when compared with Au and Pd. Pârvulescu et al. [17], using silica supported Au, Pd and Au–Pd in the hydrogenation of cinnamaldehyde, demonstrated that the alloy outperformed the monometallic catalysts in terms of activity and selectivity with respect to

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cinnamyl alcohol. Fierro et al. [18], in the gas phase hydrogenation of naphthalene over silica supported Au and Pt–Au, ascribed the higher activity observed for the bimetallic catalysts to the formation of a Pt–Au alloy. There is, however, a dearth of literature dealing with the catalytic implications of Ni–Au combinations and a comprehensive search did not unearth any study dealing with the preparation and catalytic application of an alumina supported Au–Ni alloy. Nevertheless, we can flag related studies involving supported Au–Ni systems: (i) Molenbroek et al. [19] reported improved butane steam reforming stability for reaction over Au–Ni/SiO₂ relative to Ni/SiO₂ and ascribed this response to the formation of a Au–Ni surface alloy that served to limit coke deposition and prolong catalytic activity; (ii) Triantafyllopoulos and Neophytides [20] and Chin et al. [21] have noted that the addition of Au to Ni/YSZ and Ni/MgAl₂O₄ served to suppress carbon deposition during methane steam reforming; (iii) Yuan et al. [22] observed an enhanced hydrodechlorination activity over Au–Ni/SiO₂ and Au–Ni/TiO₂ that they associated with a surface Au–Ni synergism.

In this paper we provide the first report of the catalytic action of Au/Al₂O₃ in the gas phase hydrogenation of *m*-DNB, comparing activity/selectivity with that obtained using an Al₂O₃ supported Au–Ni alloy. We link catalyst performance to critical structural information.

2 Experimental

2.1 Catalyst Preparation and Activation

The Al₂O₃ support (Puralox) was obtained from Condea Vista Co. and used as received. A 1 mol % Au/Al₂O₃ sample was prepared by impregnation with HAuCl₄ (Aldrich, 0.0025 g cm^{−3}). The slurry was heated (ca. 2 K min^{−1}) to 353 K and maintained under agitation (600 rpm) with a constant He purge. The solid residue was dried in a flow of He at 383 K for 5 h. A Ni/Al₂O₃ (10 mol %) was prepared by impregnation where a 2-butanolic Ni(NO₃)₂ solution was added drop wise at 353 K to the substrate with constant agitation (600 rpm) and oven dried at 393 K for 12 h. The alumina supported Au–Ni precursor was prepared by activation of the Ni/Al₂O₃ catalyst in a stream of H₂ at 2 K min^{−1} to 723 ± 1 K, which was maintained for 2.5 h. The gas flow was switched to He and cooled to room temperature, at which point the sample was passivated in 1% v/v O₂/He. This treatment served to provide a protective oxide layer over the surface Ni that prevented bulk oxidation upon exposure to the atmosphere. The passivated sample was contacted with HAuCl₄, post-treatment as above. After preparation, the sample (sieved into a batch of 75 μm average diameter) was activated in

60 cm³ min^{−1} H₂ at 2 K min^{−1} to 603 ± 1 K, cooled to room temperature in a He flow and subsequently subjected to a temperature controlled treatment in 65 cm³ min^{−1} N₂ at 50 K min^{−1} to 1273 ± 1 K. The latter step was necessary to generate the supported alloy as the Au–Ni miscibility gap is such that bulk alloy formation is not possible at temperatures below 1083 K [23]. The Au/Al₂O₃ sample underwent the same annealing treatment to facilitate a direct comparison of catalytic performance with that of the alloy. The samples were then cooled in N₂ and passivated in 1% v/v O₂/He at room temperature for off-line analysis. Metal loading was determined (to within ±2%) by inductively coupled plasma-optical emission spectrometry (ICP-OES, Vista-PRO, Varian Inc.) from the diluted extract of aqua regia.

2.2 Catalyst Characterization

Temperature programmed reduction (TPR) and H₂ chemisorption were determined using the commercial CHEM-BET 3000 (Quantachrome) unit. The samples were loaded into a U-shaped Quartz cell (100 mm × 3.76 mm i.d.) and heated in 17 cm³ min^{−1} 5% v/v H₂/N₂ (Brooks mass flow controlled) to 603 ± 1 K (Au/Al₂O₃ and Au–Ni/Al₂O₃) or 723 ± 1 K (Ni/Al₂O₃) at 2 K min^{−1}. The effluent gas passed through a liquid N₂ trap and H₂ consumption was monitored by a thermal conductivity detector, with data acquisition/manipulation using the TPR WinTM software. The reduced samples were maintained at the final temperature until the signal returned to the baseline. After the reduction step, the catalysts were cooled in a He flow and subjected to the annealing step described above, with subsequent H₂ chemisorption (at room temperature) using a pulse (10 μl) titration procedure, as described elsewhere [24]. BET surface area analysis and total pore volume were performed using the commercial Micromeritics Flowsorb II 2300 unit. Prior to analysis, the samples were outgassed at 423 K for 1 h in 20 cm³ min^{−1} N₂. BET area was obtained in a 30% v/v N₂/He flow (20 cm³ min^{−1}) with at least three cycles of N₂ adsorption–desorption using the standard single-point BET method. Total pore volume was obtained at a relative N₂ pressure of $P/P_0 = 0.95$. The BET area and pore volume data were reproducible to within ±3% and the values quoted in this paper are the mean. Powder X-ray diffractograms were recorded on a Bruker/Siemens D500 incident X-ray diffractometer using Cu Kα radiation. The samples were scanned at 0.02° step^{−1} over 20° ≤ 2θ ≤ 90° (scan time = 5 s step^{−1}). Diffractograms were identified using the JCPDS-ICDD reference standards, i.e. γ-Al₂O₃ (10-0425), Au (4-0784) and Ni (45-1027), and Ref. [25] for the Au–Ni alloy. Metal particle size (d_{hkl}) was estimated using the Scherrer equation:

$$d_{\text{hkl}} = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (1)$$

where $K = 0.9$, λ is the incident radiation wavelength (1.54056 Å), β is the peak width at half the maximum intensity and θ represents the diffraction angle corresponding to the main plane associated with metallic Au ($2\theta = 38.1^\circ$) and Au–Ni alloy ($2\theta = 42.8^\circ$). Diffuse reflectance UV–Vis (DRS UV–Vis) measurements were conducted using a Perkin Elmer Lambda 35 UV–Vis Spectrometer with BaSO₄ powder as reference; absorption profiles were calculated from the reflectance data using the Kubelka–Munk function. Transmission electron microscopy analysis was conducted using a JEOL JEM 2011 HRTEM unit with a UTW energy dispersive X-ray detector (Oxford Instruments) operated at an accelerating voltage of 200 kV, employing Gatan DigitalMicrograph 3.4 for data acquisition/manipulation. The specimens were prepared by dispersion in acetone and deposited on a holey carbon/Cu grid (300 Mesh).

2.3 Catalysis Procedure

Reactions were carried out under atmospheric pressure, in situ immediately after activation, in a fixed bed vertical plug-flow glass reactor (l = 600 mm; i.d. = 15 mm) at 573 K. The catalytic reactor and operating conditions to ensure negligible heat/mass transport limitations have been fully described elsewhere [26]. Isothermal reaction conditions (± 1 K) were ensured by diluting the catalyst bed with ground glass (75 µm). The reaction temperature was continuously monitored by a thermocouple inserted in a thermowell within the catalyst bed. A butanolic solution of *m*-DNB was delivered to the reactor via a glass/teflon airtight syringe and teflon line using a microprocessor controlled infusion pump (Model 100 kd Scientific) at a fixed calibrated flow rate. A co-current flow of *m*-DNB and ultra pure H₂ (<1% v/v *m*-DNB/H₂) was maintained at $GHSV = 2 \times 10^4 \text{ h}^{-1}$ with a molar metal (n) to inlet molar –NO₂ feed rate (F) ratio that spanned the range 15–50 $\times 10^{-3}$ h; inlet *m*-DNB flow = 0.05–0.15 mmol h^{–1}. The H₂ content was up to 300 times in excess of the stoichiometric requirement, the flow rate of which was monitored using a Humonics (Model 520) digital flow-meter. In a series of blank tests, passage of *m*-DNB in a stream of H₂ through the empty reactor or over the support alone, i.e. in the absence of Au or Au–Ni, did not result in any detectable conversion. The reactor effluent was frozen in a liquid N₂ trap for subsequent analysis which was made using a Perkin-Elmer Auto System XL gas chromatograph equipped with a programmed split/splitless injector and a flame ionization detector, employing a DB-1 50 m $\times$ 0.20 mm i.d., 0.33 µm film thickness capillary column

(J&W Scientific). *m*-DNB (Aldrich, $\geq$ % purity) and the solvent (1-butanol: Riedel-de Haën) were used as supplied without further purification. The degree of nitro-group reduction (x_{NO_2}) is given by

$$x_{\text{NO}_2} = \frac{[-\text{NH}_2]_{\text{out}}}{[-\text{NO}_2]_{\text{in}}} = \frac{2 \times [m\text{-PDM}]_{\text{out}} + [m\text{-NAN}]_{\text{out}}}{2 \times [m\text{-DNB}]_{\text{in}}} \quad (2)$$

where $[m\text{-NAN}]$ and $[m\text{-PDM}]$ are, respectively, the concentrations of *m*-NAN and *m*-PDM and the subscripts *in* and *out* refer to the inlet and outlet streams. Catalyst activity is also quantified in terms of the fractional conversion of *m*-DNB ($x_{m\text{-DNB}}$)

$$x_{m\text{-DNB}} = \frac{[m\text{-DNB}]_{\text{in}} - [m\text{-DNB}]_{\text{out}}}{[m\text{-DNB}]_{\text{in}}} \quad (3)$$

while selectivity in terms of (say) *m*-NAN ($S_{m\text{-NAN}}$) is given by

$$S_{m\text{-NAN}} = \frac{[m\text{-NAN}]_{\text{out}}}{[m\text{-DNB}]_{\text{in}} - [m\text{-DNB}]_{\text{out}}} \quad (4)$$

Repeated reactions using different samples from the same batch of catalyst delivered conversion/selectivity data that were reproducibility to within $\pm 6\%$.

3 Result and Discussion

Characterisation measurements are presented in Table 1, which include the T_{max} values associated with the TPR of the catalyst precursors and critical values (H₂ uptake, BET

Table 1 Temperature programmed reduction (TPR) T_{max} values, H₂ uptake, BET surface areas, total pore volumes, metal particle size and DRS UV–Vis spectroscopic characteristics for Au/Al₂O₃ and Au–Ni/Al₂O₃ with associated pseudo-first order rate constants (k) and reaction products (+selectivities) obtained under conditions of equal activity ($x_{m\text{-DNB}} \sim 0.15$) in the reduction of *m*-DNB

	Au/Al ₂ O ₃	Au–Ni/Al ₂ O ₃
TPR T_{max} (K) ^a	434	446, 603
H ₂ uptake (µmol g _{catalyst} ^{–1})	0.1	0.2
BET area (m ² g ^{–1})	122	68
Pore Volume (10 ^{–3} cm ³ g ^{–1})	258	212
d_{hkl} (nm) ^b	37	23 ^c
DRS UV–Vis A_{max} (nm)	540	– ^d
k (10 ³ mmol _{–NO₂} mol _{metal} ^{–1} h ^{–1})	2.0	0.3
Product(s) (% selectivity)	<i>m</i> -NAN (100)	<i>m</i> -NAN (75) <i>m</i> -PDM (25)

^a T_{max} associated with the dominant TPR peak is given in bold

^b Based on XRD line broadening analysis: see Eq. 1

^c Based on XRD response at $2\theta = 42.8^\circ$

^d No distinguishable peak(s)

surface area, pore volume, average metal particle size and characteristic DRS UV–Vis absorbance peaks) associated with the activated catalysts. The catalytic properties of the two systems were evaluated using the gas phase hydrogenation of *m*-DNB as a model reaction. Conversion of *m*-DNB generated *m*-NAN (partial nitro-group reduction) and *m*-PDM (complete nitro-group reduction) as the sole products with no evidence of hydrodenitrogenation or aromatic ring reduction.

3.1 Au/Al₂O₃

3.1.1 Catalyst Characterization

The result of the TPR analysis for Au/Al₂O₃ is presented in Fig. 1 (profile I) where the appearance of a single positive peak ($T = 434$ K) can be attributed to the reduction of Au³⁺ to Au⁰, as proposed elsewhere [27]. Bus et al. [28], using time-resolved in situ XAS, have established the presence of Al₂O₃-supported oxidic or hydroxidic Au³⁺ species in the precursor that were reduced in H₂ at 440 K to yield metallic Au. Hydrogen uptake (Table 1) on the activated sample was low, consistent with the limited H₂ chemisorptive capacity of supported gold reported in the literature [10]. The X-ray diffraction pattern for Au/Al₂O₃ is given in Fig. 2 (profile Ia) with four broad peaks between 30° and 70°, corresponding to the (311), (222), (400) and (440) planes associated with cubic γ -Al₂O₃ (JCPDS-ICDD 10-0425). In addition, the peaks at $2\theta = 38.1^\circ$, 44.4° , 64.7° and 77.5° consistent with, respectively, the (111), (200),

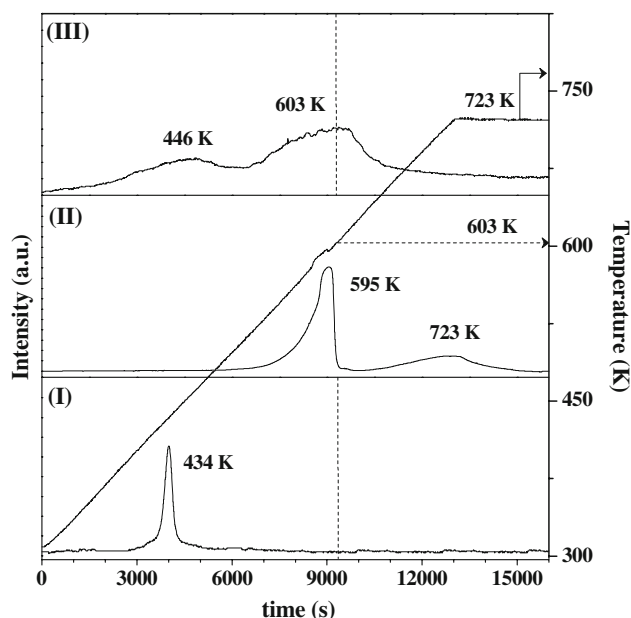


Fig. 1 TPR profiles for (I) Au/Al₂O₃, (II) Ni/Al₂O₃ and (III) Au–Ni/Al₂O₃. Dashed line represents final isothermal hold for Au/Al₂O₃ and Au–Ni/Al₂O₃

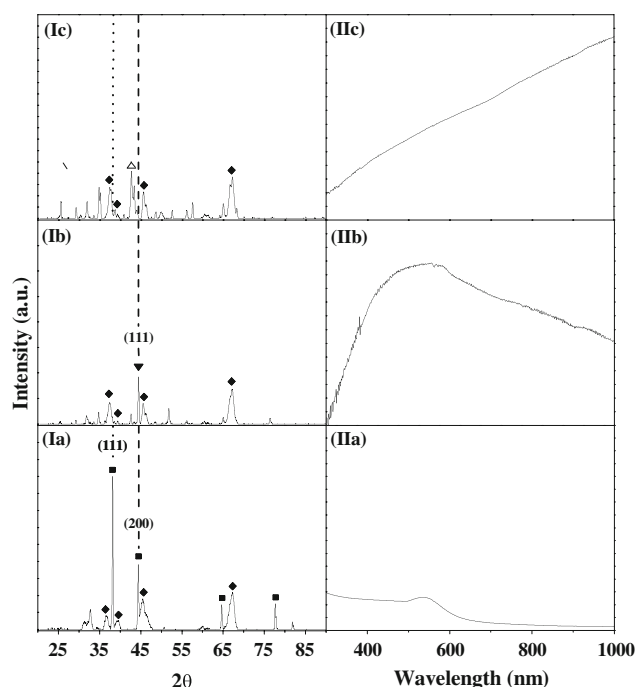


Fig. 2 (I) XRD patterns and (II) DRS UV–Vis spectra for (a) Au/Al₂O₃, (b) Ni/Al₂O₃ and (c) Au–Ni/Al₂O₃. Note: Dotted line identifies position of the (111)_{Au} peak and dashed line the position of the (200)_{Au} and (111)_{Ni} peaks. JCPDS-ICDD reference data: (◆) γ -Al₂O₃ (10-0425); (■) Au (4-0784), (▼) Ni (45-1027) and (Δ) Au–Ni alloy [25]

(220) and (311) planes of metallic Au (JCPDS-ICDD 4-0784). The DRS UV–Vis spectrum for Au/Al₂O₃ (Fig. 2, profile IIa) presents a maximum at 540 nm corresponding to metallic Au, where the weak signal intensity is due to the low Au loading in the sample. Gluhoi et al. [29] have ascribed a DRS UV–Vis band between 500–600 nm, for Au/Al₂O₃ prepared by deposition–precipitation, to the presence of Au⁰. Representative TEM images are presented in Fig. 3. In common with reported TEM analyses of impregnated Au/Al₂O₃ [12, 13, 30], the Au is present as discrete particles with a pseudo-spherical morphology. The Au particles present a wide size distribution (<5–200 nm). Selected area electron diffraction analysis confirmed that Au was present in the metallic form.

3.1.2 Catalyst Activity/selectivity

In the conversion of *m*-DNB, Au/Al₂O₃ delivered 100% selectivity to the partially reduced *m*-NAN. This product is a valuable raw material employed in the manufacture of several fine chemicals [1]. Reactant conversion, presented in Fig. 4(I) as the ratio of *m*-DNB in the exit ($(n)_{out}$) relative to that in the inlet ($(n)_{in}$) stream, exhibited essentially a temporal invariance. We have already established [12, 13] the applicability of a pseudo-first order kinetic treatment for nitroarene reduction over supported Au where

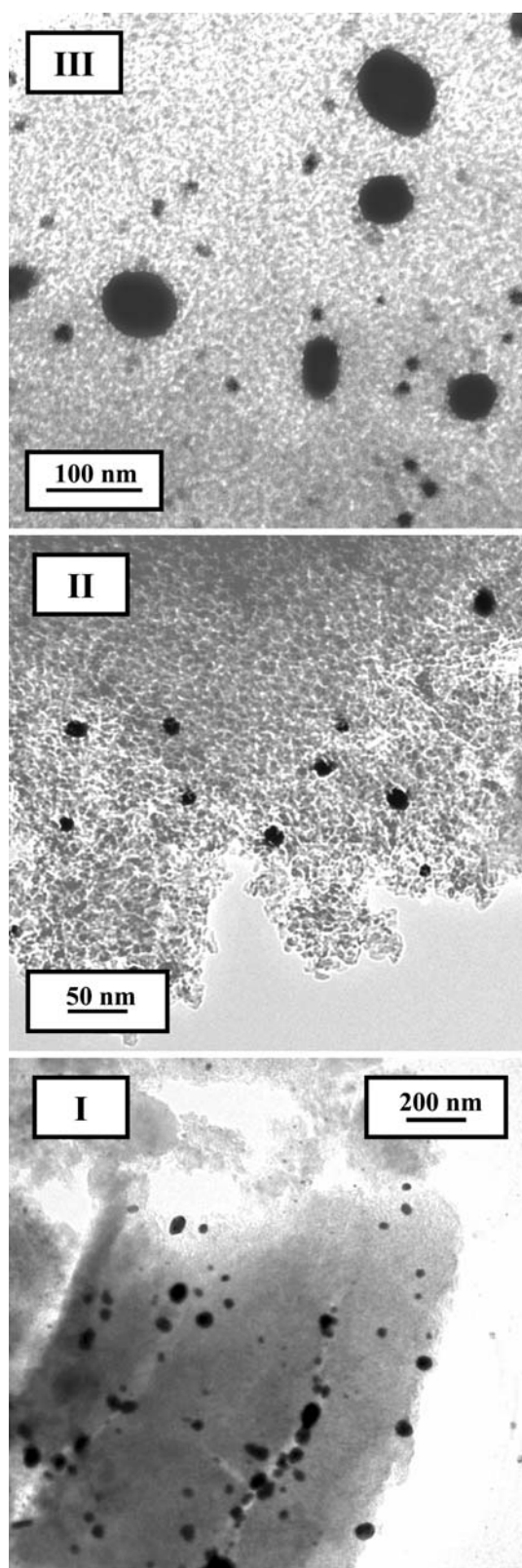


Fig. 3 Representative TEM images of Au/Al₂O₃; (I) low, (II) and (III) medium resolution

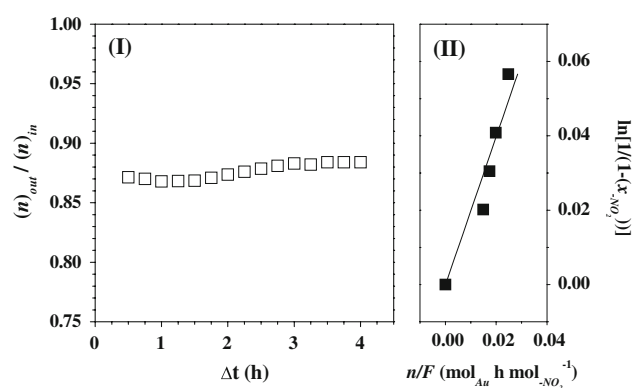


Fig. 4 (I) Ratio of *m*-DNB in the exit stream ($(n)_{out}$) relative to that in the inlet stream ($(n)_{in}$) for reaction ($-\text{NO}_2/\text{Au} = 40 \text{ mol}_{-\text{NO}_2} \text{ mol}_{\text{Au}}^{-1} \text{ h}^{-1}$) over Au/Al₂O₃; (II) Pseudo-first-order kinetic plot for the reduction of *m*-DNB

$$\ln \left[\frac{1}{(1 - (x_{-\text{NO}_2}))} \right] = k \left(\frac{n}{F} \right) \quad (5)$$

The parameter $(x_{-\text{NO}_2})$ represents hydrogenation activity and (n/F) has the physical meaning of contact time. The linear relationship between $\ln((1 - (x_{-\text{NO}_2}))^{-1})$ and n/F is shown in Fig. 4(II) and the resultant pseudo-first order rate constant (k) is given in Table 1. The available published data dealing with the selective hydrogenation of *m*-DNB are very limited and we could not find any report that has demonstrated the exclusive formation of *m*-NAN. It is, nevertheless, worth flagging work conducted at high hydrogen pressures (10–45 atm) in the gas phase over Pt/C under supercritical CO₂ ($P_{\text{CO}_2} = 150 \text{ atm}$) [31] and in the liquid phase using Pd/C [32] and polyvinylpyrrolidone stabilized Ru/Al₂O₃ [33] where *m*-NAN selectivities in excess of 80% have been recorded.

3.2 Au–Ni/Al₂O₃

3.2.1 Catalyst Characterization

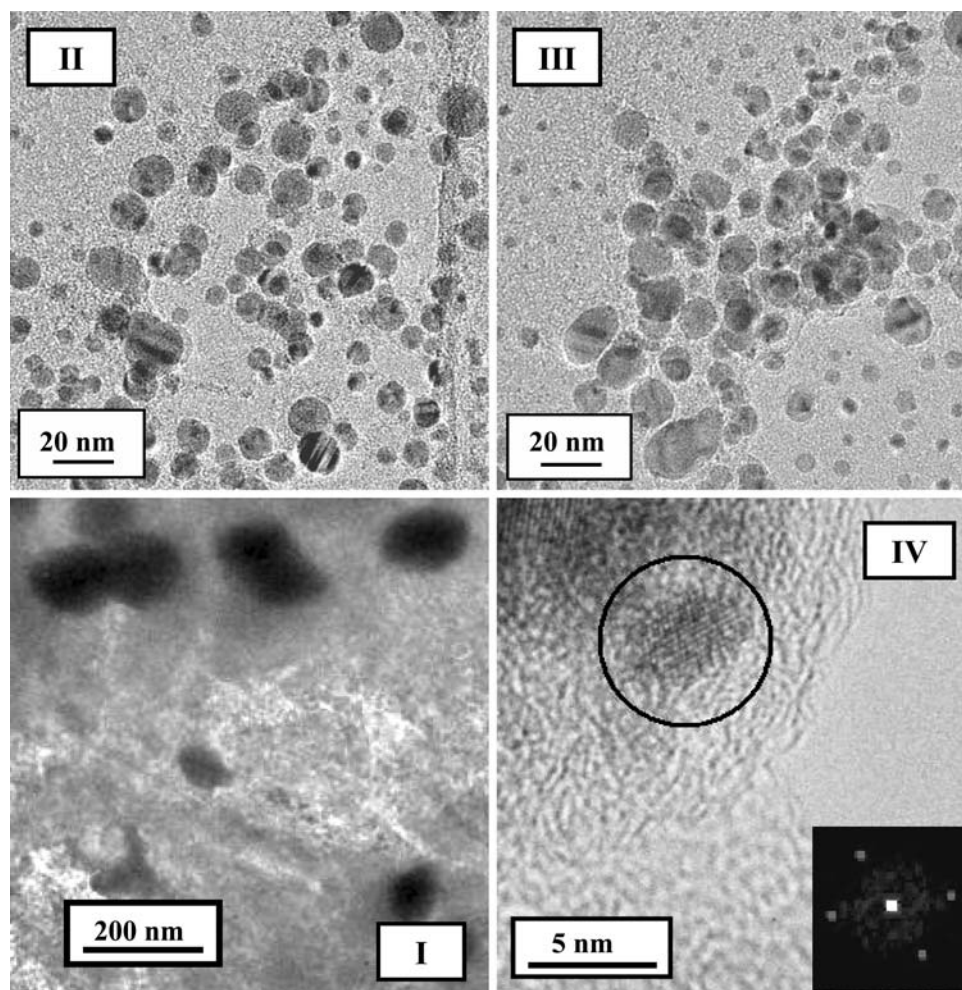
The TPR response (Fig. 1, profile II) for the Ni/Al₂O₃ precursor is characterised by two stages of reduction during the temperature ramp with peak maxima at 595 K and 723 K, corresponding to the sequential $\text{Ni}(\text{NO}_3)_2 \rightarrow \text{NiO} \rightarrow \text{Ni}^0$ steps [24]. TPR of Au–Ni/Al₂O₃ (see profile III), prepared by the reductive deposition of Au onto passivated Ni, was accompanied by a low intensity H₂ consumption response with two ill-defined peaks at 446 and 603 K. In this preparative route (direct redox method), Ni with a lower electrochemical potential serves to reduce the deposited Au precursor (HAuCl_4) and, consequently, undergoes oxidation [34]. In common with Au/Al₂O₃,

Au–Ni/Al₂O₃ also exhibited a low H₂ uptake (<1 $\mu\text{mol g}^{-1}$). BET area of both supported catalysts was significantly lower than that of the starting Al₂O₃ support (190 m² g^{−1}). This decrease in area was accompanied by a reduction in pore volume (Table 1), which can be attributed to a partial pore filling by the metal particles.

XRD analysis was undertaken to demonstrate Au–Ni alloy formation (see Fig. 2). The diffractogram generated for Ni/Al₂O₃ (profile Ib) is characterised by a peak at $2\theta = 44.5^\circ$ due to the (111) plane of metallic Ni (JCPDS-ICDD 45-1027). XRD analysis of the bimetallic sample (profile Ic) did not reveal any peaks due to the individual metals (Au or Ni) but a new metallic phase is in evidence, with a characteristic $2\theta = 42.8^\circ$, that is located between the peaks for (111)_{Au} ($2\theta = 38.1^\circ$) and (111)_{Ni} ($2\theta = 44.5^\circ$), the positions of which are illustrated in Fig. 2 by dotted and dashed vertical lines, respectively. This new phase can be attributed to the formation of a Au–Ni alloy. Indeed, this assertion is supported by the work of Togasaki et al. [25] who attributed an XRD peak at $2\theta = 42^\circ$ to amorphous

Au–Ni alloy (8–51% mol Au) prepared by the addition of KAu(CN)₂ to a Ni–W plating bath. Metal particle size was evaluated by the standard Scherrer line broadening approach (Table 1) where the metal particle size was smaller in the alloy compared with the monometallic sample. Au–Ni alloy formation is also supported by DRS UV–Vis analysis. The DRS UV–Vis response for Ni/Al₂O₃ shows a maximum (530–580 nm) that corresponds to metallic Ni [35]. In marked contrast, the spectrum recorded for Au–Ni/Al₂O₃ (profile IIc) did not generate any detectable peak/signal corresponding to metallic Au or Ni. Indeed, Mulvaney [36] established the formation of a Au–Ag alloy on the basis that the DRS UV–Vis spectrum did not exhibit the absorption bands for the component metals. Representative low (I), medium (II and III) and high (IV) resolution TEM images of Au–Ni/Al₂O₃ are presented in Fig. 5. The particles exhibit a predominantly pseudo-spherical morphology, with a wide size distribution (<5–200 nm), similar to that observed for Au/Al₂O₃. The diffractogram pattern for an isolated particle is shown in Fig. 5(IV) where the characteristic

Fig. 5 Representative TEM images of Au–Ni/Al₂O₃; (I) low, (II) and (III) medium and (IV) high resolution

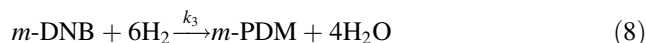
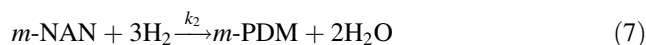
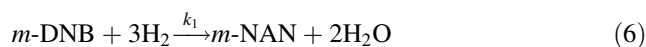


d-spacing is consistent with that obtained by XRD, confirming alloy formation.

3.2.2 Catalyst Activity/Selectivity

A pseudo-first order kinetic treatment of the data generated for Au–Ni/Al₂O₃ is presented in Fig. 6(I) and the associated rate constant value (*k*) is given in Table 1. The studies to date that have considered Au based alloy systems (Au–Pd [17, 37] and Au–Pt [18]) have resulted in an increased hydrogenation activity relative to the mono-metallic Au catalyst. In this study Au–Ni/Al₂O₃ delivered a significantly lower (by a factor of 7) rate compared with Au/Al₂O₃. We could not find any directly related study that has compared the hydrogenation performance of a supported Au–Ni alloy with that of the constituent metals. Chin et al. [21] employed MgAl₂O₄-supported Au–Ni alloy to promote CH₄ reforming and observed a decrease in catalytic activity that was ascribed to an occlusion of the Ni step and edge sites by Au. Vasil'kov et al. [38] have recently quoted an increased catalytic activity (up to two orders of magnitude) for the isomerization of allylbenzene over Au–Ni/SiO₂ as a consequence of a surface Au–Ni synergism (demonstrated by XPS). A series of experiments were conducted to probe the effect(s) of alloy formation on reaction selectivity. The results are presented in Fig. 6(II) where quite distinct selectivity responses are in evidence. While Au/Al₂O₃ delivered 100% selectivity to the partially

reduced *m*-NAN, Au–Ni/Al₂O₃ generated a mixture of partially and fully (*m*-PDM) reduced products with a shift in favour of the latter with increasing *m*-DNB conversion. We tentatively link the differences in the activity/selectivity responses presented in Fig. 6(II) for the two systems to differences in reactant adsorption/activation. Indeed, a distinct mechanism for the adsorption of nitroarenes on Au compared with Au–M (*M* = Pb, Tl) has been proposed elsewhere [39]. The hydrogenation of *m*-DNB can proceed via consecutive/parallel steps according to:



and

$$\frac{dN_{m\text{-DNB}}}{d(n/F_{m\text{-DNB}})} = -(k_1 + k_3) \times N_{m\text{-DNB}} \quad (9)$$

$$\frac{dN_{m\text{-NAN}}}{d(n/F_{m\text{-DNB}})} = k_1 \times N_{m\text{-DNB}} - k_2 \times N_{m\text{-NAN}} \quad (10)$$

$$\frac{dN_{m\text{-PDM}}}{d(n/F_{m\text{-DNB}})} = k_2 \times N_{m\text{-NAN}} + k_3 \times N_{m\text{-DNB}} \quad (11)$$

where *N_i* represents the molar fraction of the *i*th compound and *k_j* is the pseudo-first order rate constant of step *j*. Combination of Eqs. 9 and 10 gives

$$\frac{dN_{m\text{-NAN}}}{dN_{m\text{-DNB}}} = -L + M \times \left(\frac{N_{m\text{-NAN}}}{N_{m\text{-DNB}}} \right) \quad (12)$$

with

$$L = \frac{k_1}{k_1 + k_3} \quad \therefore \quad M = \frac{k_2}{k_1 + k_3} \quad (13)$$

which, by formal integration, results in:

$$N_{m\text{-NAN}} = \frac{L}{1 - M} \times (N_{m\text{-DNB}}^M - N_{m\text{-DNB}}) \quad (14)$$

The values of *L* and *M* determine the preferred reaction pathway; a stepwise –NO₂ group reduction mechanism (with *m*-NAN as intermediate) should result in a value for *L* close to unity (*k₃* ~ 0) and *M* > 1 (*k₂* > (*k₁* + *k₃*)). Indeed, the fit of our experimental results for Au–Ni/Al₂O₃ to Eq. 14 (see Fig. 6(III)) yields values of *L* = 1.1 and *M* = 5.0 that are consistent with a stepwise reaction network.

One unique aspect of this work has been the exclusive production of the partially reduced *m*-NAN product over Au/Al₂O₃, i.e. (*k₁* >> (*k₂* + *k₃*)). This level of exclusivity in a continuous process can serve as the basis for the development of a new sustainable route to a range of high value amino-compounds. Moreover, we have provided the

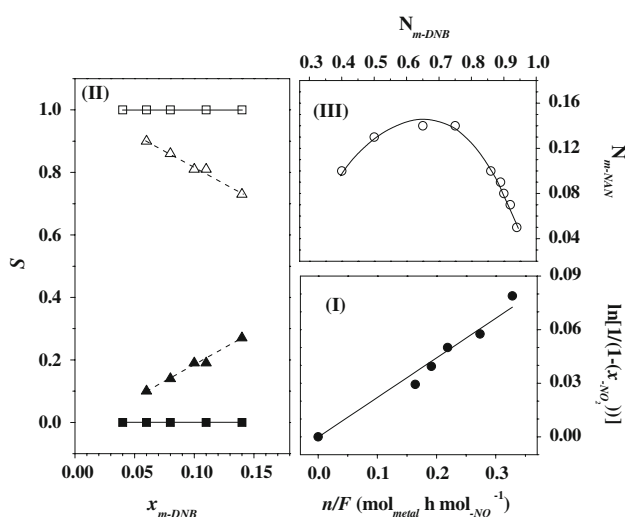


Fig. 6 (I) Pseudo-first-order kinetic plot for the reduction of *m*-DNB over Au–Ni/Al₂O₃; (II) Variation of *m*-PDM (solid symbols) and *m*-NAN (open symbols) selectivity (*S*) with *m*-DNB fractional conversion (*x_m-DNB*) for reaction over Au/Al₂O₃ (■/□, solid line) and Au–Ni/Al₂O₃ (▲/△, dashed line); (III) Dependence of *m*-NAN mole fraction (*N_m-NAN*) on *m*-DNB conversion for reaction over Au–Ni/Al₂O₃. Note: line represents fit to the parallel/consecutive model, see Eq. 14

first reported catalytic application of (alumina) supported Au–Ni alloy in a hydrogenation process. The requirement of a high treatment temperature to form the supported alloy [23] (see Sect. 2), which was also applied to Au/Al₂O₃ to facilitate a direct comparison of catalytic performance, has resulted in the formation of larger supported metal particles (see Table 1, Figs. 3 and 5). The dependence of activity and selectivity on particle size in Au catalytic systems is still unclear. It has been proposed that surface defects and smaller Au particle sizes (<10 nm) are required for significant hydrogenation activity [10]. Bailie et al. [40], studying the hydrogenation of but-2-enal over Au/ZnO, have suggested that a high selectivity to but-2-en-1-ol required larger Au particles (10–20 nm). Moreover, Hofmeister et al. [41] reported lower hydrogenation rates associated with Au particles <2 nm and ascribed this to quantum size effects that modified the electronic properties of the Au particles. Future work will focus on the role of particle size in selective hydrogenation with a consideration of alternative catalyst formulations, activation and reaction conditions with the goal of delivering enhanced reaction rates while retaining the product exclusivity that we report here.

4 Conclusions

The results presented in this report demonstrate that Au/Al₂O₃ exclusively promotes the partial reduction of *m*-DNB to *m*-NAN in gas phase continuous operation with no detectable catalyst deactivation (up to 4 h on-stream). We have provided, for the first time, evidence of catalytic hydrogenation activity associated with an alumina supported Au–Ni alloy. Alloy formation has been established by XRD (new reflection at $2\theta = 42.8^\circ$) and confirmed by TEM analyses. In addition, the DRS UV–Vis spectrum for Au–Ni/Al₂O₃ did not exhibit the absorption bands that characterised Au/Al₂O₃ and Ni/Al₂O₃. The supported alloy delivered a lower hydrogenation rate (by almost an order of magnitude) and promoted both partial and complete hydrogenation, following a stepwise reaction mechanism.

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