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Au/Mo₂N as a new catalyst formulation for the hydrogenation of *p*-chloronitrobenzene in both liquid and gas phases

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1. Introduction

Catalysis has a crucial role to play in sustainable chemical manufacture where chemoselectivity, the ability to react one functional group while preserving other (often more reactive) functionalities, is a major challenge [1]. Indeed, the appreciable waste resulting from the conversion of nitroarenes, the focus of this study, led Sheldon [2] to introduce the concept of the E(nvironmental) Factor (kg waste/kg product), which highlighted the severe environmental impact associated with the production of substituted amines as high value chemical commodities [3]. Taking the hydrogenation of chloronitrobenzenes as an example, nitroso- and hydroxylamine-intermediates can undergo side reactions to generate toxic (dichloroazoxybenzene, dichloroazobenzene and dichlorohydrazobenzene) by-products [3]. Moreover, C-Cl bond scission results in the formation of nitrobenzene (NB) and aniline (AN) as principal products [4]. A critical advancement in cleaner amine synthesis in batch operation using oxide supported Au catalysts has resulted from the work of Corma et al. [5], who demonstrated a preferential activation of - NO2 with H2 dissociation at low coordination Au sites by in situ IR spectroscopy and theoretical calculations. A recent brainstorming exercise involving the American Chemical Society (ACS), Green Chemistry Institute (GCI) and global pharmaceutical

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ABSTRACT

The batch liquid phase hydrogenation of *p*-chloronitrobenzene over Mo₂N resulted in the sole formation of *p*-chloroniline. Incorporation of Au nanoparticles (mean size = 8 nm) enhanced hydrogen uptake with a four-fold increase in rate, retention of ultraselectivity with stability over repeated reaction cycles. Reaction exclusivity to *p*-chloroaniline extended to continuous gas phase operation where Au/Mo₂N outperformed Au/Al₂O₃ as a benchmark. Under the same conditions, Pd/Mo₂N was *non*-selective, generating nitrobenzene and aniline *via* combined hydrodechlorination and hydrogenation. These results demonstrate the viability of Au/Mo₂N as a new catalyst formulation in selective substituted nitroarene hydrogenation.

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corporations (the ACS GCI Pharmaceutical Roundtable) has highlighted the switch from batch to continuous processing as crucial for the sustainable manufacture of fine chemicals [6]. Adopting this imperative, we have established in previous work [4,7,8] – NO₂ hydrogenation chemoselectivity over Au in gas phase continuous operation. Studies to date have shown low hydrogenation activity for Au that can be ascribed to a restricted activation/dissociation of H₂ [9], which is dependent on Au particle size [10]. Given that hydrogen activation can be a limiting factor, we have explored the use of a support for Au that can chemisorb H₂ (increasing surface concentration) as a possible route to higher hydrogenation rates.

Mo nitrides exhibit a significant hydrogen uptake capacity, which has been attributed to a contraction of the *d*-band and modification of electron density as a result of the interstitial incorporation of N in the Mo metal lattice [11]. The use of Mo nitrides in hydrogen mediated reactions has been considered to some extent with evidence of catalytic activity for gas phase NO reduction [12] and the hydrogenation of CO [13] and ethyne [14]. As Mo₂N can chemisorb hydrogen and Au is selective for nitro-group reduction, we propose in this study the combination of Au with Mo nitride as a new catalyst formulation directed at elevating hydrogenation rate while maintaining chemoselectivity. Taking *p*-chloronitrobenzene (*p*-CNB) as a test reactant, we have examined the catalytic action of Mo₂N and Au/Mo₂N in both batch liquid and continuous gas phase operation. We have also compared the catalytic action of Au/Mo₂N with Au/Al₂O₃ (as benchmark [8]) to probe a possible support effect, *i.e.* Mo₂N vs. Al₂O₃.



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Moreover, as Pd has shown enhanced activity in $-NO_2$ reduction [15], we have also examined the catalytic performance of Pd/Mo₂N.

2. Experimental section

2.1. Catalyst preparation and characterisation

Mo₂N was prepared by heating MoO₃ (99.9995% w/w, Alfa Aesar) in $15 \text{ cm}^3 \text{ min}^{-1}$ (GHSV = 1500 h⁻¹) $15\% \text{ v/v} \text{ N}_2/\text{H}_2$ at 5 K min⁻¹ to 933 K (18 h). Reduction/nitridation was quenched in Ar (65 $\text{cm}^3 \text{min}^{-1}$), the sample cooled to room temperature and passivated (in 1% v/v O₂/He) for off-line analysis. Nitride passivation post-synthesis served to provide a superficial oxide film and was required to avoid sample autothermal oxidation upon contact with air [16]. A suspension of HAuCl₄ (300 cm³, 3×10^{-4} M, Aldrich), aqueous urea (100 cm³, 0.86 M) and Mo₂N was mixed (at 300 rpm) and heated (1 K min⁻¹) to 353 K (2.5 h). The solid was filtered and washed with distilled water until the wash water was Cl-free (based on the AgNO₃ test), dried in He ($45 \text{ cm}^3 \text{ min}^{-1}$) at 383 K for 3 h, sieved into a batch of 75 µm average particle diameter and stored at 277 K under He in the dark. Pd/Mo_2N (2.5×10⁻⁴ M $Pd(NO_3)_2$, Aldrich) was synthesised following the same protocol. For comparison purposes, Au supported on Al₂O₃ (Puralox, Condea Vista Co.) was prepared by standard impregnation with HAuCl₄ as described previously [17], dried and stored as above.

Temperature programmed reduction (TPR) and H₂ chemisorption (at 290 K) measurements were conducted using the commercial CHEM-BET 3000 (Quantachrome) unit. Samples were activated in 17 cm³ min⁻¹ 5% v/v H₂/N₂ at 2 K min⁻¹ to 493-673 \pm 1 K (1 h), swept with 65 $\mbox{cm}^3\,\mbox{min}^{-1}\,\mbox{N}_2$ (1.5 h) and cooled to room temperature. After TPR, the reduced samples were swept with a $65 \text{ cm}^3 \text{ min}^{-1}$ flow of N₂ for 1.5 h, cooled to room temperature and subjected to H_2 chemisorption using a pulse (10 μ l) titration procedure. BET area was recorded in a 30% v/v N₂/He flow and pore volume determined at a relative N2 pressure of 0.95 using a Micromeritics Flowsorb II 2300 unit. Powder X-ray diffractograms were recorded on a Bruker/Siemens D500 incident X-ray diffractometer (Cu K α radiation) and identified against JCPDS-ICDD standards (Mo₂N (25-1368); Au (04-0784)). Analysis by scanning electron microscopy (SEM) was conducted on a Philips FEI XL30-SFEG operated at an accelerating voltage of 10-20 kV. The samples for analysis were subjected to a hydrocarbon decontamination treatment using a plasmacleaner (EVACTRON). Analysis of nitrogen content was performed using an Exeter CE-440 Elemental Analyser after sample combustion at *ca.* 1873 K. The Au and Pd content (supported on β -Mo₂N or Al₂O₃ and in solution during reaction) was determined by atomic absorption spectrometry (Shimadzu AA-6650 spectrometer) using an air-acetylene flame. High resolution transmission electron microscopy (HRTEM) employed a JEOL JEM 2011 unit operated at an accelerating voltage of 200 kV using Gatan DigitalMicrograph 3.4 for data treatment. The specimens were prepared by dispersion in acetone and deposited on a holey carbon/Cu grid (300 mesh). The mean metal (Au or Pd) particle size is given as surface area-weighted mean (d) [7] where over 200 individual metal particles were counted for each catalyst.

2.2. Catalysis procedures

Liquid phase reactions ($P_{H_2} = 11 \text{ bar}$; T = 423 K) were carried out in a commercial batch stirred stainless steel reactor (100 cm³ autoclave, Büchi AG, Uster, Switzerland). Operation under negligible mass transfer resistance was established using the Madon and Boudart approach [18]. A stainless steel 6-blade disc turbine impeller equipped with a selfgassing hollow shaft provided effective agitation at a stirring speed of 1800 rpm. A recirculator (HAAKE B-N3) was used to stabilize the reaction temperature at $T = 423 \pm 1$ K. The initial catalyst/p-CNB ratio spanned the range 320–1078 g mol⁻¹. Hydrogenation performance was assessed over three reaction cycles. In the first cycle, the catalyst was activated *ex-situ* in a quartz tube $(60 \text{ cm}^3 \text{ min}^{-1} \text{ H}_2; GHSV = 200 \text{ h}^{-1})$ at 673 K, cooled to room temperature and transferred to the reactor in a flow of N₂. Hydrogen consumption during reaction was monitored on-line with a press flow gas controller (BPC-6002, Büchi, Switzerland). In a series of blank tests, reactions carried out in the absence of catalyst did not result in any measurable conversion. A *non*-invasive liquid sampling system *via* a syringe with in-line filters allowed a controlled removal of aliquots (\leq 0.5 cm³) from the reactor. After reaction, the catalyst was filtered, reactivated as above and subjected to a second and a third reaction cycle.

Gas phase *p*-CNB hydrogenation was carried out ($P_{H_2} = 1 \text{ bar}$; T = 493 K) in a fixed bed vertical glass reactor (i.d. = 15 mm), operated under conditions of negligible heat/mass transport limitations. A layer of borosilicate glass beads served as preheating zone, ensuring that the organic reactant was vaporised and reached reaction temperature before contacting the catalyst. Isothermal conditions $(\pm 1 \text{ K})$ were maintained by diluting the catalyst bed with ground glass $(75 \,\mu\text{m})$; the ground glass was mixed thoroughly with catalyst before insertion in the reactor. The reaction temperature was continuously monitored using a thermocouple inserted in a thermowell within the catalyst bed. *p*-CNB (Sigma-Aldrich, \geq 99%) in ethanol (Sigma Aldrich, \geq 99.8%) was delivered at a fixed calibrated flow rate *via* a glass/Teflon air-tight syringe and Teflon line using a microprocessor controlled infusion pump (Model 100 kd Scientific). A co-current flow of *p*-CNB and ultra pure H_2 (<1% v/v organic in H_2) was maintained at $GHSV = 330 \text{ min}^{-1}$ with a catalyst mass to inlet *p*-CNB molar rate (*W*/*F*) in the range $8 \times 10^3 - 8 \times 10^4$ g mol⁻¹ min. Product composition was determined using a Perkin-Elmer Auto System XL chromatograph equipped with a programmed split/splitless injector and a flame ionization detector, employing a DB-1 capillary column. Repeated reactions with the same batch of catalyst delivered conversion/selectivity values that were reproducibility to within \pm 7%.

3. Results and discussion

3.1. Catalyst characterization

The formation of Mo₂N was confirmed by XRD (see Fig. 1(AI)) where signals over the range $2\theta = 38^{\circ} - 81^{\circ}$ can be assigned to the eight principal planes of β -nitride (JCPDS-ICDD 25–1368). The representative TEM image in Fig. 1(AII) coupled with diffraction analysis (IIa) establishes a spacing of 0.24 nm between the planes in the atomic lattice that is characteristic of the β -Mo₂N (112) plane. Moreover, nitrogen content (5.4% wt.), BET surface area $(7 \text{ m}^2 \text{ g}^{-1})$ and pore volume $(0.02 \text{ cm}^3 \text{ g}^{-1})$ are close to those quoted in the literature for molybdenum nitride [19]. The SEM micrograph of the asprepared sample is presented in Fig. 1(A)III and shows an agglomeration of crystallites < 5 µm (see IIIa). As the starting MoO₃ is characterised by a platelet morphology [20], the reduction/nitridation process $(MoO_3 \rightarrow MoO_2 \rightarrow Mo \rightarrow Mo_2N)$ resulted in a nontopotactic transformation where the precursor orthorhombic crystal structure was not maintained [21]. Temperature programmed reduction (TPR) of Mo₂N (Fig. 2, profile I) generated a single peak at $T_{\rm max} = 637$ K that can be associated with hydrogen consumption for the removal of the passivation overlayer [22]. It has been proposed [23] that passivation of Mo₂N results in the formation of one or two chemisorbed oxygen monolayers. The incorporation of Au (0.25% w/ w, see Table 1) with Mo₂N induced a shift in the main hydrogen consumption peak (by 34 K) to a lower temperature, demonstrating a more facile removal of the passivating oxygen due to the presence of Au (Fig. 2, profile II). Although we could not find any directly comparable TPR analysis in the open literature, our results are in line with the work of Wang et al. [24] who recorded a decrease in the reduction temperature (up to 150 K) of the passivation layer due to the inclusion of Ni. Chemisorption measurements have revealed a measurable



Fig. 1. (A) Mo₂N: XRD pattern (I, including peak assignments based on JCPDS-ICDD 25-1368), representative TEM image (II) with diffractogram pattern (IIa) and SEM micrograph (III) with higher magnification image (IIIa) illustrating crystal morphology. (B) Au/Mo₂N: representative medium (I) and high (II) resolution TEM images and metal particle size distribution (III). *Note:* diffractogram pattern of isolated Au particle (IIa) and intensity profile revealing distance between planes of the atomic lattice in the 12 nm segment marked on the nitride support (IIb).

increase in hydrogen uptake due to the inclusion of Au (Table 1), a result that suggests the presence of well dispersed Au nanoparticles (<10 nm) where dissociative adsorption can occur at low coordination sites, notably at steps, edges and corners [10]. The TEM image provided in Fig. 1(B)I serves to illustrate the nature of Au dispersion and morphology. The diffractogram pattern for an isolated Au particle (Fig. 1(B)IIa) confirms the presence of metallic Au with associated *d*-spacings = 0.20/0.23 nm consistent with the (200) and (111) planes of Au⁰ (JCPDS-ICDD 04–0784). The intensity profile across the support shown in Fig. 1(B)IIb delivered an average *d*-spacing = 0.24 nm, consistent with β -Mo₂N. The Au particles exhibit a *pseudo*-spherical morphology and a size distribution in the 2–14 nm range, as illustrated in the histogram given in Fig. 1(B)III, with a mean particle size of (*d* =) 8 nm (Table 1). It should be noted that there is an appreciable component of Au particles with

diameters \leq 10 nm, *i.e.* the proposed critical Au size range for catalytic activity in hydrogen mediated reactions [25].

As the aim of this work is to explore the possibility of an enhanced selective hydrogenation rate over Mo nitride supported Au, we have taken Au/Al₂O₃ as a benchmark catalysts that has exhibited ultraselectivity in $-NO_2$ group reduction [4]. We have established previously [17] that the reference Au/Al₂O₃ shows the same mean Au particle size (8 nm) as Au/Mo₂N. Given that nitroarene hydrogenation rate over supported Au is sensitive to dispersion [7], an explicit comparison of performance in terms of a support effect necessitates equivalence in terms of Au size. The synthesised Au/Mo₂N demonstrated an appreciably higher (by a factor of 8) level of hydrogen chemisorption relative to Au/Al₂O₃ (mmol mol_{Au}⁻¹, see Table 1), which must be due to a contribution from both Au and Mo₂N components. As both samples exhibit the same mean Au size, differences in



Fig. 2. TPR profiles for (I) Mo_2N and (II) Au/Mo_2N .

uptake can be attributed to the Au/support interface where electronic interactions have been proposed to impact on hydrogen chemisorption capacity [26]. Since the catalytic action of Pd in $-NO_2$ reduction is well established [27], we have also considered reaction over Pd/ Mo_2N in order to evaluate the effect of incorporating a different metal with Mo_2N . Pd/ Mo_2N presented a uniform distribution of Pd nanoparticles (size range = 1–7 nm, mean = 2 nm) and exhibited increased H₂ chemisorption (see Table 1) compared with the supported Au systems, as has been noted elsewhere [4].

3.2. Catalysis results

Table 1

3.2.1. Batch liquid phase operation

We achieved 100% selectivity to the target *p*-chloroaniline (*p*-CAN) for reaction over Mo₂N in batch liquid phase operation at 100% conversion of *p*-CNB. There was no detectable hydrogenolytic activity to produce chlorobenzene, NB, AN or benzene. This is an important finding in the light of previous studies where C-Cl scission accompanied high CNB conversion in liquid phase reaction. Indeed, dechlorination in the hydrogenation of chloroarenes has been a feature of reactions over supported Pt, Rh, Ru, Ni and Cu [28,29] catalysts. Reaction kinetics exhibited pseudo-first order behaviour (correlation coefficient, $r^2 > 0.98$; see Fig. 3(AI)) and catalytic activity can be quantified in terms of the initial rate of *p*-CNB consumption $(157 \,\mu\text{mol g}^{-1} \,\text{min}^{-1})$. Incorporation of Au with Mo₂N served to increase hydrogenation rate (by a factor of 4) with p-CAN again as the sole product (Fig. 3(A)II). Furthermore, 100% selectivity to p-CAN was retained at extended reaction times (up to 27 h, not shown). Catalyst stability was considered and the feasibility of reuse can be assessed from the entries in Fig. 3(B). The reaction rate generated using Au/Mo₂N after three consecutive runs was equivalent to that obtained in the first reaction cycle (632 vs. 639 μ mol g⁻¹ min⁻¹) and reaction exclusivity to p-CAN was maintained in each cycle. Moreover, there was no evidence of Au leaching during reaction. This is an important consideration that has been emphasised by Arens and Sheldon [30]: supported metal catalysts must be resistant to metal leaching into solution under operation conditions in order to have a real synthetic utility. While this feature has not been examined in any great detail for supported Au systems, there is evidence of

Hydrogen chemisorption, metal (Au or Pd) loading and particle size range and mean value (d).

Mo ₂ N	Au/Mo ₂ N	Au/Al ₂ O ₃	Pd/Mo ₂ N
2	0.25	1	0.22
-	0.23	1	0.52
0.29	0.42	0.21	0.51
-	32	4	-
-	2-14	1–20	1-7
-	8	8	2
	Mo ₂ N - 0.29 - -	Mo ₂ N Au/Mo ₂ N - 0.25 0.29 0.42 - 32 - 2-14 - 8	Mo ₂ N Au/Mo ₂ N Au/Al ₂ O ₃ - 0.25 1 0.29 0.42 0.21 - 32 4 - 2-14 1-20 - 8 8

significant Au leaching from TiO_2 and Al_2O_3 for reactions in liquid phase [31].

3.2.2. Continuous gas phase operation

Following on from the recommendations of the ACS GCI Pharmaceutical Roundtable [6], the potential of the Au/Mo₂N catalyst formulation was further tested in gas phase continuous operation. It must be stressed from the very outset that nitroarene hydrogenations to date have focused on batch liquid phase processing and this study represents the first instance where the feasibility of both operational modes is demonstrated. 100% selectivity to p-CAN extended to gas phase operation with increased p-CAN production over Au/Mo₂N relative to Mo₂N as a function of time on-stream (see Fig. 4(AI)). The improved catalytic performance resulting from the combination of Au with Mo₂N is further demonstrated in the pseudo-first order kinetic plots presented in Fig. 4(AII). This response then holds in both liquid and gas phase reactions and can be linked to the increased hydrogen uptake on Au/Mo₂N (Table 1). Variations in hydrogen surface concentration are known to influence the catalytic response where a concomitant increase in activity and surface hydrogen for molybdenum nitrides has also been reported elsewhere [32]. Zhang et al. [33], studying the hydrogenation of cyclohexene and the hydrodesulphurisation of thiophene over Mo₂N, associated the higher activity with the incorporation of Zr to an increase in weakly bound hydrogen.

A major finding in this work is the appreciably greater activity exhibited by Au/Mo₂N relative to Au/Al₂O₃ (at a common mean Au particle size), which is demonstrated in Fig. 4(B). We take this as a demonstration of a surface cooperative effect involving Au and Mo₂N that results in a concomitant enhanced hydrogen uptake (Table 1) and catalytic efficiency. This effect can be tentatively attributed to electronic interactions at the Au/support interface. Blaser et al. [3] concluded that reaction at the gold-support interface can contribute to overall hydrogenation rate acceleration. Shimizu et al. [34] studied the effect of the carrier for supported Ag catalysts in nitroarene reduction and reported a synergy between Ag and Al₂O₃ that governed the rate-limiting H_2 dissociation to generate a H^+/H^- pair at the metal/support interface. The hydrogenation rate can also be influenced by differences in *p*-CNB/surface interaction (-NO₂ activation) where the Au-Mo₂N interface may play a critical role. Corma and co-workers [35] have differentiated between - NO₂ group adsorption on the support and Au-support interface in terms of reactant activation, notably for Au/TiO₂. We have indirectly probed this effect by examining the catalytic action of Pd/Mo₂N where a higher p-CNB hydrogenation rate (Fig. 4(B)) relative to Au/Mo₂N was recorded. These results are consistent with published literature where increased hydrogen uptake/activity over supported Pd (relative to Au) has been reported [4]. In marked contrast to Au/Mo₂N and Au/ Al₂O₃, at a common *p*-CNB conversion Pd/Mo₂N promoted the formation of NB and AN as products of hydrodechlorination and hydrogenation (Fig. 4(B)). Interaction with Pd/Mo₂N serves to activate the C-Cl bond, which is then susceptible to hydrogenolytic cleavage. This catalytic response is consistent with the literature where hydrodechlorination has been shown to predominate in the hydrotreatment of chloronitrobenzenes over Pd/Al₂O₃ [4]. Use of Pd/Mo₂N in practical (industrial) application would require the incorporation of downstream separation units in order to extract the target *p*-CAN. This is circumvented in the case of Au/Mo₂N, which delivered the best performance in this study. Process efficiency can be further improved by operating multiple passes through the catalyst bed where the ultra-selectivity imposed by Au/Mo2N can deliver complete conversion of the inlet *p*-CNB to *p*-CAN.

The results presented in this study provide the first evidence of the combined catalytic action of Au and Mo_2N that serves to elevate surface hydrogen, resulting in an increased hydrogenation rate of *p*-CNB to the target *p*-CAN in both liquid and gas phase operations. Future work will focus on structural modification of molybdenum



Fig. 3. Catalytic response in batch liquid phase operation: (A) temporal variation of *p*-CNB (solid symbols) and *p*-CAN (open symbols) concentration (per g of catalyst, C_i/W) for reaction over (I) Mo₂N (\blacktriangle , \triangle) and (II) Au/Mo₂N (\blacksquare , \square); (B) temporal variation of *p*-CNB (\blacksquare) and *p*-CAN (\square) concentration (per g of catalyst, C_i/W) for reaction over Au/Mo₂N in three consecutive reactions (I–III); reaction conditions: $P_{H_2} = 11$ bar, T = 423 K.



Fig. 4. Catalytic response in continuous gas phase operation: (AI) time on-stream *p*-CAN production over Mo₂N (\blacktriangle) and Au/Mo₂N (\blacksquare); (AII) fractional initial conversion of *p*-CNB (X_0) as a function of *W/F* over Mo₂N (\bigstar) and Au/Mo₂N (\blacksquare) where the lines represent fit to pseudo-first order kinetics; (B) specific activity with selectivity to *p*-CAN (open bars), AN (hatched bars) and NB (solid bars) under conditions of equal fractional *p*-CNB conversion (X_0 ~0.2) over Au/Mo₂N, Au/Al₂O₃ and Pd/Mo₂N; reaction conditions: $P_{H_0} = 1$ bar, T = 493 K.

nitride (*e.g.* crystallographic phase and/or surface area) and control over Au particle size to increase activity while retaining selectivity. Catalytic applications will consider hydrogenation of polyfunctional nitroarenes where chemoselectivity is extremely challenging.

4. Conclusions

Au/Mo₂N as a new catalyst formulation promotes the (batch) liquid and (continuous) gas phase hydrogenation of *p*-CNB with 100% selectivity to *p*-CAN where the yield was maintained in repeated reaction cycles. Incorporation of Au with Mo₂N served to increase H₂ uptake with a four-fold higher hydrogenation rate relative to Mo₂N. Moreover, Au/Mo₂N outperformed a benchmark Au/Al₂O₃ catalyst that exhibited an equivalent mean Au particle size. Under the same reaction conditions, Pd/Mo₂N was *non*-selective and promoted a combined hydrodechlorination/hydrogenation to give NB and AN. We demonstrate here, for the first time, the viability of Au/Mo₂N in the selective reduction of nitroarenes with versatility in gas and liquid phase operations.

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