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Short Communication

Au/Mo_2N as a new catalyst formulation for the hydrogenation of *p*-chloronitrobenzene in both liquid and gas phases

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ABSTRACT

The batch liquid phase hydrogenation of *p*-chloronitrobenzene over Mo_2N resulted in the sole formation of *p*-chloroaniline. 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/Mo_2N outperformed Au/Al_2O_3 as a benchmark. Under the same conditions, Pd/Mo_2N was *non*-selective, generating nitrobenzene and aniline *via* combined hydrodechlorination and hydrogenation. These results demonstrate the viability of Au/Mo_2N as a new catalyst formulation in selective substituted nitroarene hydrogenation.

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 $-NO_2$ with H_2 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 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] $-NO_2$ 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 H_2 [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 H_2 (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 Mo_2N 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 Mo_2N and Au/Mo_2N in both batch liquid and continuous gas phase operation. We have also compared the catalytic action of Au/Mo_2N with Au/Al_2O_3 (as benchmark [8]) to probe a possible support effect, *i.e.* Mo_2N *vs.* Al_2O_3.

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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/Mo_2N.

2. Experimental section

2.1. Catalyst preparation and characterisation

Mo_2N was prepared by heating MoO_3 (99.9995% w/w, Alfa Aesar) in 15 cm^3 min^{-1} ($GHSV = 1500$ h^{-1}) 15% v/v N_2/H_2 at 5 K min^{-1} to 933 K (18 h). Reduction/nitridation was quenched in Ar (65 cm^3 min^{-1}), the sample cooled to room temperature and passivated (in 1% v/v O_2/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 $HAuCl_4$ (300 cm^3, 3×10^{-4} M, Aldrich), aqueous urea (100 cm^3, 0.86 M) and Mo_2N 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 $AgNO_3$ test), dried in He (45 cm^3 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 Al_2O_3 (Puralox, Condea Vista Co.) was prepared by standard impregnation with $HAuCl_4$ as described previously [17], dried and stored as above.

Temperature programmed reduction (TPR) and H_2 chemisorption (at 290 K) measurements were conducted using the commercial CHEM-BET 3000 (Quantachrome) unit. Samples were activated in 17 cm^3 min^{-1} 5% v/v H_2/N_2 at 2 K min^{-1} to 493–673 ± 1 K (1 h), swept with 65 cm^3 min^{-1} N_2 (1.5 h) and cooled to room temperature. After TPR, the reduced samples were swept with a 65 cm^3 min^{-1} flow of N_2 for 1.5 h, cooled to room temperature and subjected to H_2 chemisorption using a pulse (10 μl) titration procedure. BET area was recorded in a 30% v/v N_2/He flow and pore volume determined at a relative N_2 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 Kα radiation) and identified against JCPDS-ICDD standards (Mo_2N (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 plasma-cleaner (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-Mo_2N or Al_2O_3 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 ($P_{H_2} = 11\ bar; T = 423\ K$) were carried out in a commercial batch stirred stainless steel reactor (100 cm^3 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 self-gassing 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 cm^3 min^{-1} H_2; $GHSV = 200$ h^{-1}) at 673 K, cooled to room temperature and transferred to the reactor in a flow of N_2. 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 (≤ 0.5 cm^3) 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 ($P_{H_2} = 1\ bar$; $T = 493\ K$) 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 (±1 K) were maintained by diluting the catalyst bed with ground glass (75 μm); 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, ≥99%) in ethanol (Sigma Aldrich, ≥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 $GHSV = 330$ min^{-1} with a catalyst mass to inlet p-CNB molar rate (W/F) in the range 8×10^3–8×10^4 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 ±7%.

3. Results and discussion

3.1. Catalyst characterization

The formation of Mo_2N was confirmed by XRD (see Fig. 1(AI)) where signals over the range $2\theta = 38°$–$81°$ 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-Mo_2N (112) plane. Moreover, nitrogen content (5.4% wt.), BET surface area (7 m^2 g^{-1}) and pore volume (0.02 cm^3 g^{-1}) are close to those quoted in the literature for molybdenum nitride [19]. The SEM micrograph of the *as*-prepared sample is presented in Fig. 1(A)III and shows an agglomeration of crystallites < 5 μm (see IIIa). As the starting MoO_3 is characterised by a platelet morphology [20], the reduction/nitridation process ($MoO_3 \rightarrow MoO_2 \rightarrow Mo \rightarrow Mo_2N$) resulted in a *non*-topotactic transformation where the precursor orthorhombic crystal structure was not maintained [21]. Temperature programmed reduction (TPR) of Mo_2N (Fig. 2, profile I) generated a single peak at $T_{max} = 637$ K that can be associated with hydrogen consumption for the removal of the passivation overlayer [22]. It has been proposed [23] that passivation of Mo_2N results in the formation of one or two chemisorbed oxygen monolayers. The incorporation of Au (0.25% w/w, see Table 1) with Mo_2N 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