Synthesis, characterisation and hydrogenation performance of ternary nitride catalysts

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ABSTRACT

Synthesis of phase pure Co_3Mo_3N and Fe_3Mo_3N by temperature programmed ammonolysis has been established by XRD and elemental analysis. The ternary nitrides are characterised by a η-6 structure and low surface area ($4–9\,m^2\,g^{-1}$). Pseudomorphic transformation of cobalt molybdate prepared using cobalt nitrate generated rod-shaped crystals while the use of iron chloride resulted in Fe_3Mo_3N aggregates with irregular morphology and wide size distribution. XPS measurements have revealed surface N enrichment relative to the bulk where the passivated samples show a range of oxidation states; Co_3Mo_3N exhibited Mo^{2+} and Co^{n+} ($0 \leq n \leq 3$) whereas Fe_3Mo_3N was characterised by higher oxidation states (Fe^{3+} and Mo^{3+}). Temperature programmed reduction (TPR) to 823 K served to remove the passivation layer where subsequent H_2 chemisorption and temperature programmed desorption (TPD) has demonstrated greater uptake on Fe_3Mo_3N relative to Co_3Mo_3N, resulting in a higher nitrobenzene hydrogenation rate (to aniline). Fe_3Mo_3N promoted selective reduction of $-NO_2$ in p-chloronitrobenzene to generate p-chloroaniline as sole product whereas Co_3Mo_3N favoured C-Cl scission with the formation of nitrobenzene (in addition to p-chloroaniline). Hydrodechlorination properties were further established for Co_3Mo_3N in the conversion of chlorobenzene (to benzene) under conditions where Fe_3Mo_3N was inactive. A temporal deactivation of both nitrides is associated with Cl poisoning of Co_3Mo_3N and structural changes to Fe_3Mo_3N.

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1. Introduction

It is established that nitrides of early transition metals (Groups IV–VI) exhibit interesting catalytic properties [1–4]. This has been attributed to hybridisation of the nitrogen p- and metal d-orbitals, resulting in an electronic structure with a Fermi energy close to that of Group VIII metals [1]. Studies to date have focused on binary nitrides such as W_2N [5], TiN [6], VN [7] and Mo_2N [4]. Ternary nitride systems are divided into two groups, i.e. metallic and covalent/ionic. The former represents catalytically active systems in which metal–metal interactions are dominant and N atoms are interstitial within the metal array. The catalytic properties of ternary Mo nitrides have been investigated to a limited extent, largely due to difficulties in synthesising

a pure phase that circumvents concomitant formation of Mo_2N and the second metal [8]. As Co_3Mo_3N has been identified as effective in hydrotreatment, the synthesis and catalytic application of intermetallic ternary Mo-nitride systems is receiving renewed attention [9,10]. The catalytic action of Co-Mo, Fe-Mo and Ni-Mo nitrides has been studied in NH_3 synthesis [10–14], pyridine [15,16] and quinoline [17] hydrodenitrogenation (HDN), thiophene [8,18–20] and dibenzothiophene [17,21] hydrodesulfurisation (HDS) and NO reduction [22,23]. The incorporation of a second metal has resulted in higher activity relative to the binary system (Mo_2N) [8,9,11–13,18,20,23]. In NH_3 synthesis [11–13], the increased activity has been correlated with energetics of N_2 adsorption/activation, which is a function of the second metal and follows the order $Co_3Mo_3N > Fe_3Mo_3N > Ni_2Mo_3N > Mo_2N$. In pyridine HDN, Chu et al. [15] proposed that H_2 is activated on the second metal and migrates to Mo sites, leading to HDN activity/selectivity that is distinct from the binary nitride.

Co_3Mo_3N and Fe_3Mo_3N are characterised by a face centred cubic (fcc) arrangement of the metal (Co and Mo or Fe and Mo) atoms

with the lattice nitrogen occupying octahedral interstitial sites [24,25]. These nitrides are typically synthesised by temperature programmed nitridation of a bimetallic oxide precursor, obtained from a combination of metal nitrate (or chloride) with ammonium heptamolybdate (or sodium molybdate) [8,14,23–26]. The precursors (*e.g.* $CoMoO_4 \cdot nH_2O$ and $FeMoO_4$) can be nitrided in a flow of NH_3 with temperature ramping to 873–1073 K [25,27]. The effects of precursor [13,28,29], nitridation (gas composition and final temperature) [30] and activation conditions [26,29] on nitride structure have been the subject of studies directed at optimising synthesis. While ternary Mo nitrides have shown activity in hydrogen mediated reactions (HDN, NO reduction and NH_3 synthesis) [28], there has been no reported application in hydrogenation. We can, however, flag studies that have established Mo_2N catalytic action in the hydrogenation of crotonaldehyde [31], ethyne [32] and nitroarenes [33,34]. Taking the latter, selective hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline is commercially important in the manufacture of polymers, dyes and agrochemicals [35]. Reaction over conventional metal (Pt [36] and Pd [37]) catalysts generates by-products resulting from hydrodeamination (chlorobenzene) and hydrodechlorination (nitrobenzene) with subsequent hydrogenation (aniline), as shown in Fig. 1. Work has focused on batch liquid phase operation [38] but we have demonstrated that reaction over Mo_2N in continuous gas phase delivers *p*-chloroaniline as the sole product [39]. Reactant adsorption/activation can be influenced by the degree of nitridation and (nitrogen deficient) Mo nitride site density [40,41], Mo oxidation state [42] and crystallographic phase (β- vs. γ-Mo_2N) [43]. The goal of this study is to probe the catalytic hydrogenation properties of bimetallic nitrides, taking Co_3Mo_3N and Fe_3Mo_3N as *iso*-structural stable ternary systems, employing *p*-chloronitrobenzene → *p*-chloroaniline as a model reaction.

2. Experimental

2.1. Catalyst preparation

In the synthesis of Co_3Mo_3N, the molybdate precursor was prepared by combining aqueous solutions of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma–Aldrich, >98%) and ammonium heptamolybdate ((NH_4)$6Mo_7O_{24} \cdot 4H_2O$, Sigma–Aldrich, 81–83% as MoO_3) and heating to 353 K for 3 h. In the case of Fe_3Mo_3N, the molybdate precursor was synthesised by drop-wise addition of $400 \, cm^3$ 0.25 M $FeCl_2 \cdot 4H_2O$ (Sigma–Aldrich, >99%) to 0.66 M $Na_2MoO_4 \cdot 2H_2O$ (Sigma–Aldrich, >99%). After vacuum filtration, the precipitate was washed twice with distilled water, once with ethanol and dried overnight at 393 K. The powders were calcined in air (Co-Mo) or N_2 (Fe-Mo) for 5 h at 773 K. The $CoMoO_4 \cdot nH_2O$ or $FeMoO_4$ obtained was loaded into a vertical quartz reactor (*i.d.* 10.5 mm) for nitridation by ammonolysis. A $94 \, cm^3 \, min^{-1}$ flow of NH_3 (BOC, 99.98%) was introduced to the reactor with temperature ramping over three stages using a temperature ramp rate procedure based on that adopted in previous studies [26] and optimised to generate high quality phase pure materials in our reactor, *i.e.* from ambient to 630 K (at $5.6 \, K \, min^{-1}$), then to 720 K (at $0.5 \, K \, min^{-1}$) and finally to 1058 K (at $2.1 \, K \, min^{-1}$), which was maintained for 5 h. The nitrided sample was cooled to ambient temperature in flowing NH_3, followed by a purge in N_2 to remove any residual NH_3. In order to prevent pyrolysis on exposure to air, the material was passivated in $100 \, cm^3 \, min^{-1}$ O_2/N_2 (v/v $O_2 < 0.1\%$) overnight.

2.2. Catalyst characterisation

The nitrogen content of Co_3Mo_3N and Fe_3Mo_3N was determined using an Exeter CE-440 Elemental Analyser after sample

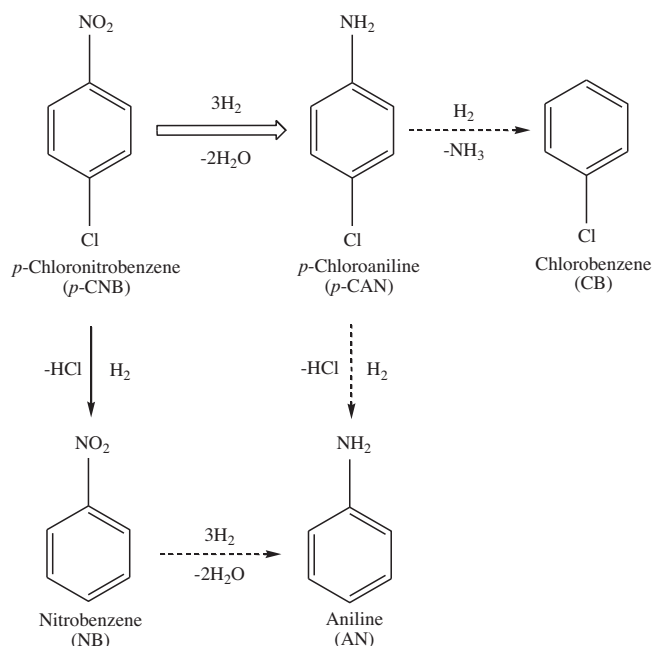**Fig. 1.** Reaction pathways for the hydrogenation of *p*-chloronitrobenzene to the target *p*-chloroaniline (*p*-CAN, ⇨), the observed by-product (nitrobenzene (NB), →) and reaction products (chlorobenzene (CB) and aniline (AN), ⋯➔) reported in the literature.

combustion at *ca.* 1873 K. Temperature programmed reduction (TPR), H_2 chemisorption and temperature programmed desorption (TPD) measurements were performed using the commercial CHEM-BET 3000 (Quantachrome) unit. The passivated samples were loaded into a U-shaped Quartz cell (10 cm × 3.76 mm *i.d.*) and heated in $17 \, cm^3 \, min^{-1}$ (Brooks mass flow controlled) 5% (v/v) H_2/N_2 at $2 \, K \, min^{-1}$ to 823 K. The effluent gas passed through a liquid N_2 trap and changes in H_2 consumption were monitored by TCD with data acquisition/manipulation using the TPR Win™ software. The final temperature was maintained (in a constant flow of H_2/N_2) until return of the signal to baseline, samples were swept with $65 \, cm^3 \, min^{-1}$ N_2 for 1.5 h and cooled to ambient temperature. The nitrides were then subjected to H_2 chemisorption using a pulse (10 μl) titration procedure, followed by H_2-TPD in N_2 ($65 \, cm^3 \, min^{-1}$) at $50 \, K \, min^{-1}$ to 973 K with an isothermal hold until the signal returned to the baseline. Nitrogen adsorption–desorption isotherms were obtained at 77 K using the commercial Micromeritics Gemini 2390 automated unit. Specific surface areas were calculated from the isotherms using the standard BET method. Average pore size and cumulative pore volume were obtained from BJH analysis of the desorption isotherms; samples were outgassed at 423 K in N_2 for 1 h prior to analysis.

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 the range $15° \leq 2\theta \leq 85°$. Diffractograms were identified using the JCPDS-ICDD reference standards for Co_3Mo_3N (89-7953) and Fe_3Mo_3N (89-7952). Crystal size (d_{hkl}) was estimated using the Scherrer equation, assuming negligible contribution from strain and instrumental broadening to reflection widths

$$d_{hkl} = \frac{K \times \lambda}{\beta \times \cos\theta} \qquad (1)$$

where $K = 0.9$ radians, λ is the incident radiation wavelength (1.5056 Å), β is the peak width at half the maximum intensity