Towards nitrogen transfer catalysis: reactive lattice nitrogen in cobalt molybdenum nitride

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Lattice nitrogen within the catalyst Co_3Mo_3N is both reactive and likely highly mobile, enabling potential novel nitrogen transfer pathways; evidence suggests that loss and subsequent regain of lattice nitrogen in the system reversibly cycles through the previously unknown nitride, Co_6Mo_6N.

In recent years, interest has centred around the application of metal nitrides in terms of their hardness, electronic and magnetic properties and their use as heterogeneous catalysts.[1] In the latter case, there has been a resurgent interest ever since Volpe and Boudart demonstrated that high surface area metal nitrides are accessible *via* ammonolysis of metal oxide precursors.[2] To date, the primary focus in metal nitrides and oxynitrides as catalysts has been directed towards their similar activity patterns with respect to platinum group metals and their application as base catalysts respectively.[3,4]

Recently, we have commenced an investigation into the possibility of applying metal nitrides as nitrogen transfer catalysts, in which the nitrides could be viewed as "reservoirs" of activated nitrogen. This approach has its origins based upon the Mars–van Krevelen mechanism frequently encountered in oxidation reactions catalysed by oxide catalysts.[5] In this mechanism, oxidation occurs *via* the transfer of lattice oxygen to the substrate, generating the oxidised product and a transient oxygen lattice vacancy within the oxide catalyst which is subsequently replenished by gas-phase oxygen containing species. This general type of mechanism, which may even be operative in non-reducible oxides,[6] has also been observed for sulfur transfer reactions involving sulfide catalysts[7] and with carbon in molybdenum carbide catalysts during methane partial oxidation.[8] To date, very limited attention has been directed towards nitrogen analogues of the Mars–van Krevelen mechanism, since nitrides are generally perceived as being inert. However, very recently, direct transfer of lattice nitrogen species from a VAlON catalyst for propane ammoxidation has been reported.[9] As a starting point in our investigation, we have examined the reactivity of lattice nitrogen species in Co_3Mo_3N. This system, which possesses the η-6 carbide structure based upon Co_3Mo_3C,[10] has been selected on the basis of recent independent reports of its remarkable activity for ammonia synthesis, particularly when doped with Cs^+.[11,12]

The approach we have taken to elucidate the reactivity of lattice nitrogen in Co_3Mo_3N is to make comparisons of the ammonia synthesis activity using stoichiometric N_2/H_2 mixtures (1 : 3 by volume) with Ar/H_2 mixtures (1 : 3 by volume) (Table 1). Initial activity comparisons have been made at 400 °C, the normal temperature for ammonia synthesis. Increased reaction temperature was used subsequently to differentiate between lattice nitrogen species of varying reactivity. Ammonia production was quantified by the decrease in conductivity of a 200 ml 0.00108 mol L^{-1} standard H_2SO_4 solution. In Fig. 1, comparative activity data is presented for different 0.4 g portions of the same Co_3Mo_3N batch synthesised by ammonolysis.‡ Comparing between the different feed compositions, it is apparent that for a N_2/H_2 stream, steady state rates of NH_3 synthesis activity are attained. However, for a Ar/H_2 feed, a degree of ammonia production is observed which, by contrast, diminishes relatively quickly. This NH_3 dimunition is consistent with the consumption of nitrogen species which are *not replenished.* At the lower temperatures employed, ammonia production may occur *via* the hydrogenation of sorbed NH_x species which are generated by the synthesis and pre-treatment procedure. However, CHN analysis (Table 1) demonstrates unequivocally that nitrogen is lost from the bulk samples. Analysis for the analogous reaction performed with N_2/H_2 under the same temperature programming regime, yields nitrogen contents which are as expected for stoichiometric Co_3Mo_3N within experimental error (ideally 2.93%). By stark contrast, the sample reacted under Ar/H_2 presents a dramatically reduced content, corresponding to the loss of very close to half (46%) of the N content of stoichiometric Co_3Mo_3N. It is notable that ammonia production only accounts for 19% of the lost nitrogen in the case for the Ar/H_2 sample which we believe is a consequence of the

Table 1 Nitrogen content (from CHN analysis) and cubic lattice parameters (from PXD) for Co_3Mo_3N samples

Sample and testing conditions	*a*/Å	N (wt%)
Co_3Mo_3N (N_2/H_2) after 4.5 h on stream at 400 °C (**1**)	11.032(1)	2.8(3)
Co_3Mo_3N (Ar/H_2) after 4.5 h on stream at 400 °C (**2**)	11.004(8)	2.5(3)
Co_3Mo_3N (N_2/H_2) reacted using the temperature profile shown in Fig. 1(b), with a maximum testing temperature of 700 °C (**3**)	11.016(2)	2.7(3)
Co_3Mo_3N (Ar/H_2) reacted using the temperature profile shown in Fig. 1(b), with a maximum testing temperature of 700 °C (**4**)	10.879(1)	1.5(3)
Sample (**4**) re-treated with N_2/H_2 at 700 °C (**5**)	11.025(4)	2.8(3)

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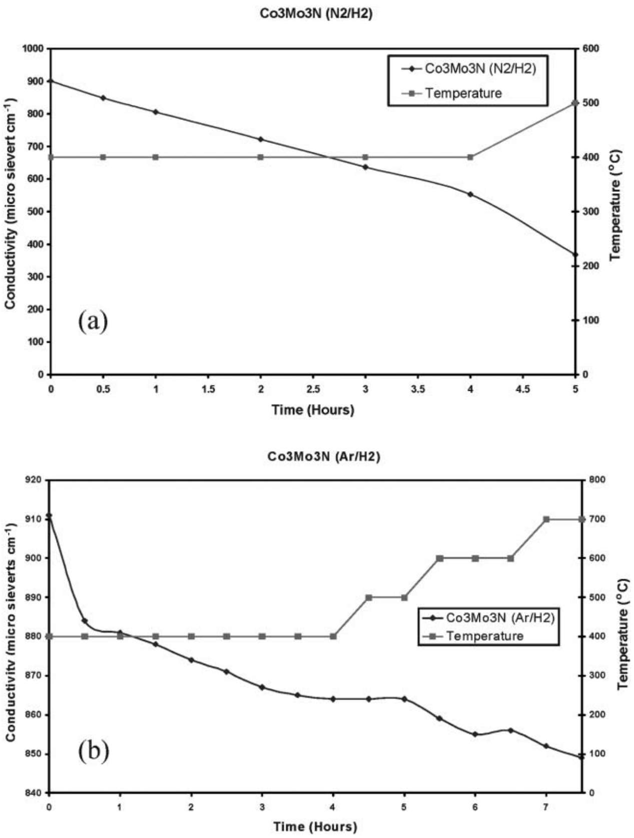

Fig. 1 Conductivity data for NH_3 synthesis over Co_3Mo_3N using (a) N_2/H_2 (**1**) and (b) Ar/H_2 (**4**). Initial data points (0 h) are recorded following stabilisation at 400 °C for 30 min on stream. For (a), only initial data is shown for 5.5 h on stream, corresponding to an NH_3 synthesis rate of 158 μmol g^{-1} h^{-1} at 400 °C and 369 μmol g^{-1} h^{-1} at 500 °C.

thermodynamics of the ammonia synthesis/decomposition reaction at 700 °C, where N_2 formation is favoured over NH_3 formation.

Strong evidence for the loss of bulk nitrogen species in (**4**) is observed from powder X-ray diffraction (PXD) data. Comparison with (**3**) shows a considerable shift of Bragg reflections to higher 2θ for (**4**) indicative of a significant reduction in the cubic cell volume (Fig. 2). The use of internal standards, NaCl (Fisher, 99.5%), confirmed that the peak shifts were intrinsic and non-systematic and initial indexing yielded unit cell parameters of $a = 11.016(2)$ Å, $V = 1336.8(4)$ Å^3 and $a = 10.879(1)$ Å, $V = 1287.53(11)$ Å^3 for (**3**) and (**4**), respectively. (*Cf.* earlier studies of stoichiometric Co_3Mo_3N where $a = 11.0270(4)$ Å and $V = 1340.8(1)$ Å^3.)[10a] Nitrogen analysis (Table 1) yields a stoichiometry close to Co_6Mo_6N for (**4**) and that there are substantial stoichiometric and structural changes after treatment from (**3**) to (**4**) is reinforced by preliminary Rietveld refinements against PXD data. The refined structure of (**3**) bears close resemblance to the literature models of Co_3Mo_3N[10] but data for (**4**) could not be fit so convincingly to the η-carbide structure of Co_3Mo_3N. The best fit for (**4**) (with lowest indices and esds) was obtained for the so-called η-12 carbide structure adopted by Co_6Mo_6C (also cubic space group $Fd\bar{3}m$)[13] but unprecedented in nitrides. Whether the ordered N-deficient η-12 structure or a non-stoichiometric η-6 variant is formed for (**4**) is only likely to be resolved incontrovertibly from forthcoming neutron experiments, but treatment under H_2/Ar clearly removes a substantial amount of the lattice nitrogen and consequently has profound effects on the eta carbide structure. More comprehensive structural studies as a function of temperature and H_2 partial pressure, along with those of the magnetic properties of the nitride phases are in progress.

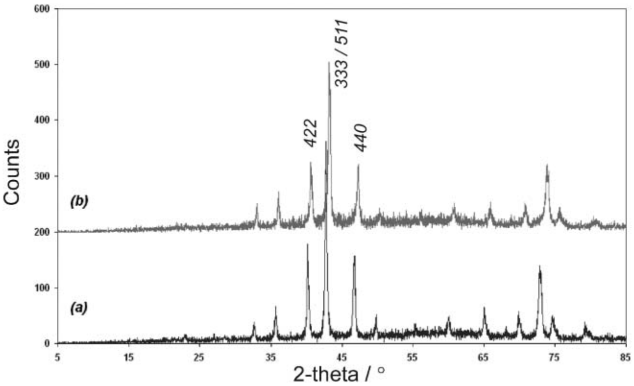

Fig. 2 PXD patterns for (a) sample (**3**) and (b) sample (**4**); higher temperature H_2/N_2 and H_2/Ar treated Co_3Mo_3N samples, respectively. The clear shift of reflections to higher 2θ and the change in relative intensities of the four major reflections for (**4**) over (**3**) are evident.

From additional experiments which we have performed, it is clear that the presence of H_2 is essential to obtain the nitrogen deficient nitride. These imply that the hydrogenation of nitrogen species is a key requirement for N loss from the Co_3Mo_3N lattice and suggests NH_x and/or NH_3 species to be of importance in the process. Whilst the predominant form of lost N may be as N_2, the possible transient formation of NH_3 or NH_x species allows the possibility of their entrapment by reacting species. Direct N transfer from lattice to substrate is thus possible and a new pathway to a host of nitrogen transfer reactions becomes attainable. However, to function as a nitrogen transfer catalyst, it must be possible to replenish the depleted lattice nitrogen in the nitride. In a series of Ar/H_2 and N_2/H_2 switching experiments, we have shown, crucially, that this is indeed possible. Co_3Mo_3N is restored from (**4**) by switching back from Ar/H_2 to N_2/H_2 at 700 °C (yielding (**5**); Table 1). Hence, importantly, the process of N-loss/replenishment is fully reversible and the Co–Mo–N catalyst can be readily regenerated. What is also clear from the combination of testing and switching experiments is that the interstitial nitrogen is remarkably mobile. The implications of this mobility in terms of, redox and transport properties (both ionic and electronic), in addition to the obvious potential impact on catalysis, could be enormous.

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Notes and references

‡ Co_3Mo_3N is prepared by nitriding a cobalt molybdate hydrate ($CoMoO_4 \cdot nH_2O$) precursor, which was prepared by adding aqueous solutions of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich, 98+%) to ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Alfa Aeser, JM 81–83% as MoO_3) and heating the mixed solution to approximately 80 °C. A

purple precipitate was obtained after vacuum filtration and the precipitate washed twice with distilled water and once with ethanol and then dried overnight at 150 °C. The powder was calcined in air at 500 °C. Typical experimental conditions used for nitriding are outlined below.

Approximately 1 g of material was held in a vertical quartz reactor into which a 94 ml $\min^{-1}$ flow of NH_3 (BOC, 99.98%) was introduced. The furnace was programmed to heat the material in three stages. The temperature was increased from ambient to 357 °C at a rate of 5.6 °C $\min^{-1}$ (60.1 min), then to 447 °C at 0.5 °C $\min^{-1}$ (180 min), then to 785 °C at 2.1 °C $\min^{-1}$ (160.9 min) and the furnace was held at this temperature for 5 h. The nitrided material was then cooled in flowing ammonia to ambient temperature and on reaching this temperature, nitrogen was flushed through the system at 100 ml $\min^{-1}$. To prevent potential bulk oxidation on exposure of the nitrided material to air, the material was passivated using a gas mixture containing $<0.1\%$ O_2.

Reaction studies were performed using 0.4 g of material placed in a silica reactor tube and held centrally between silica wool plugs within the heated zone of a furnace. The catalysts were pre-treated at 700 °C with the reactant gas (H_2/N_2 in a ratio of 3 : 1, respectively) at 60 ml $\min^{-1}$ for 2 h and then cooled to a reaction temperature, 400 °C, in the flowing gas. On reaching the reaction temperature the vent gas from the reactor was flowed through a sulfuric acid solution (0.00108 mol L^{-1}, 200 ml at ambient temperature) and the ammonia yield was calculated by detecting the conductivity decrease of protons in the sulfuric acid solution with respect to time. The initial activity data point was taken after 30 min at this temperature.

PXD measurements were performed on a Siemens D5000 instrument using Cu Kα radiation in Bragg–Brentano geometry. Scan times of 1 h were used for indexing and 12 h for Rietveld refinement. All scans were performed with step sizes of 0.02° 2θ. Rietveld refinements against PXD data for samples (**3**) and (**4**) treated under N_2/H_2 and Ar/H_2 (as per Fig. 1(b)) were performed using GSAS and EXPGUI packages.[14,15]

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