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A comparison of the reactivity of lattice nitrogen in Co_3Mo_3N and Ni_2Mo_3N catalysts

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ABSTRACT

The influence of nitriding conditions upon the ammonia synthesis activities and structures of cobalt molybdenum and nickel molybdenum-based catalysts has been compared. Ammonolysis of cobalt molybdate is observed to produce a more active catalyst than H_2/N_2 pre-treatment. Post-reaction XRD analysis shows a pure Co_3Mo_3N phase in the former case and a mixed phase, containing some Co_3Mo_3N, in the latter. Both ammonolysis and N_2/H_2 pretreatment of nickel molybdate lead to a mixture of Ni_2Mo_3N and Ni, with the latter pretreatment leading to catalysts of higher activity. The reactivity of lattice nitrogen in η-6 carbide structure Co_3Mo_3N and the β-Mn structure Ni_2Mo_3N has been investigated. In both cases, lattice nitrogen is found to be reactive towards both H_2 and C_6H_6 and comparisons demonstrate Co_3Mo_3N to be the more reactive. For Co_3Mo_3N, reaction with benzene yields Co_3Mo_3C and graphite whereas a carbonitride and graphite is produced with Ni_2Mo_3N. In the case of reaction with H_2, the nickel molybdenum system reacts to form $Ni_2Mo_3N_{1-x}$, whereas comparable conditions with Co_3Mo_3N produce a novel Co_6Mo_6N phase.

1. Introduction

Spurred by the development of the ammonolysis procedure, in which high ammonia space velocities and controlled temperature ramp rates are applied to the preparation of high surface area nitrides typically from oxide precursors [1], there has been a resurgent effort in the catalytic activity of nitrides [2–4]. Catalytic attention has almost exclusively centred upon interstitial nitrides, and in particular molybdenum nitride, in which parallels between their catalytic behaviour and that for platinum group metals have been drawn. Amongst reactions studied to date have been ammonia synthesis [5,6], hydrazine decomposition [7,8], hydrodenitrogenation [2,4], NO reduction [9,10] and carbon monoxide hydrogenation [11]. Recently, Cs^+ doped Co_3Mo_3N has attracted interest in terms of its ammonia synthesis activity where claims have been made that it displays higher efficacy than the commercial iron-based catalyst [12–17]. Jacobsen and co-workers [18] have explained the high activity of this system in terms of a volcano relationship in which the combination of Co (with too low a nitrogen binding energy) and Mo (with too high a binding energy) produces an alloy with an optimum nitrogen binding energy not too dissimilar to that for Ru. In this proposal, lattice nitrogen has been reported to be inactive and its role has been ascribed to ensuring that the required ordering occurs resulting in the catalyst preferentially exposing the (1 1 1) surface termination plane in which both Co and Mo are present.

We have been interested in the possibility of applying metal nitrides as nitrogen transfer agents. It has been our aim to assess the reactivity of lattice nitrogen to determine if novel nitrogen transfer catalysis can be developed. This possibility has parallels in oxidation catalysis, where the well-known Mars-van Krevelen mechanism has been long established, and analogous processes have also been reported to occur in catalytic reactions involving sulfides [19] and carbides [20]. To this end, we have studied a series of binary and interstitial molybdenum nitrides in terms of the reactivity of their lattice nitrogen with hydrogen feedstreams in which comparisons can be drawn between ammonia synthesis rates in the presence and absence of co-fed gas-phase nitrogen. In the case of Co_3Mo_3N, which we have studied in greatest detail, we have demonstrated that at high temperature (i.e. 700 °C), it is possible to remove 50% of the lattice nitrogen, with that remaining relocating from the 16c to the 8a Wyckoff position, generating a novel η-12 carbide structure nitride, which was previously unknown [21]. This new phase has recently been confirmed in powder neutron diffraction studies. The original η-6 carbide structure Co_3Mo_3N phase can be rapidly restored by switching the feedstream from Ar/H_2 to N_2/H_2. In this way, it may prove possible to develop catalysts capable of directly transferring lattice nitrogen species from the lattice to an organic receptor molecule. To this end, it is interesting to note

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that Mori and co-workers have developed homogeneous titanium containing systems which they have shown capable of incorporating active nitrogen species, generated from gas-phase N_2 at low temperature, into a variety of organic molecules [23–27]. In terms of heterogeneous systems, Segal and Sebba have previously described the high efficacy of lattice nitrogen within uranium nitride during ammonia synthesis [28,29]. More recently in a TAP reactor study, Olea et al. [30] have proposed the occurrence of a double Mars-van Krevelen mechanism involving the transfer of both lattice oxygen and nitrogen during propane ammoxidation over VAlON catalysts. In addition, based on the dramatic onset of ammonia decomposition activity associated with the β- to β′-phase transition of zirconium oxynitride, Soerijanto et al. [31] suggested a mechanism in which part of the product nitrogen originates from the lattice in a catalytic cycle wherein its is subsequently replenished from gas-phase NH_3.

In this study, a comparison between the η-6 carbide structure Co_3Mo_3N and Ni_2Mo_3N, which possesses the β-Mn structure [32], has been made. We have investigated the role of preparation on ammonia synthesis efficacy, i.e. ammonolysis versus treatment with N_2/H_2, since the latter would be preferable in terms of large-scale application [33]. Comparison of the reactivity of lattice nitrogen species in the two systems has been made in terms of the ammonia synthesis activities with a Ar/H_2 feed and also the reactivity with C_6H_6 at high temperature.

2. Experimental

$CoMoO_4{\cdot}nH_2O$ precursor was prepared by adding aqueous solutions of $Co(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich, 98+%) to $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Alfa Aesar, 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 was washed twice with distilled water, once with ethanol and then dried overnight at 150 °C. The powder was calcined in air at 500 °C. When nitrided by ammonolysis, approximately 1 g of material was placed in a vertical quartz reactor into which a 94 ml min^{-1} 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} and then to 447 °C at 0.5 °C min^{-1}, then to 785 °C at 2.1 °C min^{-1} at which point it was held for 5 h. The nitrided material was cooled in flowing ammonia to ambient temperature then nitrogen was flushed through the system at 100 ml min^{-1}. To prevent bulk oxidation on exposure of the material to air, the material was passivated overnight using a mixture containing <0.1% O_2.

$NiMoO_4$ was prepared by dropwise addition of 400 ml (0.25 M) of an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich), to a 150 ml solution of $Na_2MoO_4{\cdot}(H_2O)_2$. A green precipitate was obtained after vacuum filtration and the precipitate was washed twice with distilled water, once with ethanol and dried overnight at 150 °C. The powder was then calcined at 700 °C for 6 h under a flow of nitrogen gas (5 ml min^{-1}). Where appropriate, the nickel molybdate was nitrided under a flow of NH_3, as described above for Co_3Mo_3N.

Reaction studies were performed using 0.4 g of material placed in a silica reactor tube and held centrally between two silica wool plugs within the heated zone of a tube furnace. All materials were pre-treated at 700 °C with 60 ml min^{-1} of 1/3 N_2/H_2 (BOC, H_2 99.998%, N_2 99.995%) for 2 h. Ammonia synthesis experiments were then performed at 400 °C using this gas mixture, following cooling under the reactant gas mixture. The vent gas from the reactor was flowed through 200 ml of a 0.00108 M sulfuric acid solution and the rate of ammonia formation was calculated by determined from the rate of change of conductivity with respect to time. H_2/Ar reactions were performed using a 1/3 Ar/H_2 mixture (BOC, H_2 99.998%, Ar min 99.99%) following the 700 °C pre-treatment and subsequent cooling to 400 °C under H_2/N_2.

Table 1
Ammonia synthesis activities of ternary nitrides prepared by ammonolysis and mixed oxides exposed to the reaction mixture (60 ml min^{-1} 1/3 N_2/H_2, 0.4 g catalyst)

Catalyst	Surface area (m^2 g^{-1})	NH_3 synthesis rate (μmol h^{-1} g^{-1})
Co_3Mo_3N	18	165
Ni_2Mo_3N	1	27
$CoMoO_4{\cdot}nH_2O$	13	135
$NiMoO_4$	3	46

Reactions with C_6H_6 were performed by bubbling 60 ml min^{-1} of 1/3 N_2/H_2 through a C_6H_6 (Sigma AnalR) saturator. This yielded a feedstream containing ca. 12% benzene by volume.

Powder diffraction analyses were performed using a Siemens D5000 instrument operating with Cu Kα radiation. A 2θ range between 5° and 85° was scanned using a counting rate of 1 s per step with a step size of 0.02°. Samples were prepared by compaction into a Si sample holder.

CHN analysis was performed using an Exeter Analytical CE-440 elemental analyser.

BET surface areas were determined from nitrogen physisorption isotherms measured at liquid nitrogen temperature using a Micromeritics Gemini instrument.

3. Results and discussion

As discussed by Wise and Markel [33], it is preferable to apply N_2/H_2 mixtures rather than NH_3 for nitridation on the large scale. Accordingly, we have compared the use of NH_3 and N_2/H_2 as nitriding agent for both Co_3Mo_3N and Ni_2Mo_3N. For nitridation with N_2/H_2, the oxide precursors were subjected to treatment with the stoichiometric 1/3 ammonia synthesis mixture at 700 °C for 2 h prior to reaction, as were the passivated materials prepared by ammonolysis. The steady state rates for ammonia synthesis at 400 °C are shown in Table 1. In all cases, the same mass of material (0.4 g) has been loaded into the reactor and the rates are normalised to this mass. It can be seen that the cobalt molybdenum containing catalyst is more active when nitrided with NH_3, although that producing using N_2/H_2, a far simpler technique, is almost as active. In the case of the nickel molybdenum catalyst, a more active catalyst is generated with N_2/H_2. Fig. 1 presents the powder diffraction pattern for the Co_3Mo_3N phase prepared by ammonolysis. Prior to reaction, it can be seen that the passivated catalyst contains

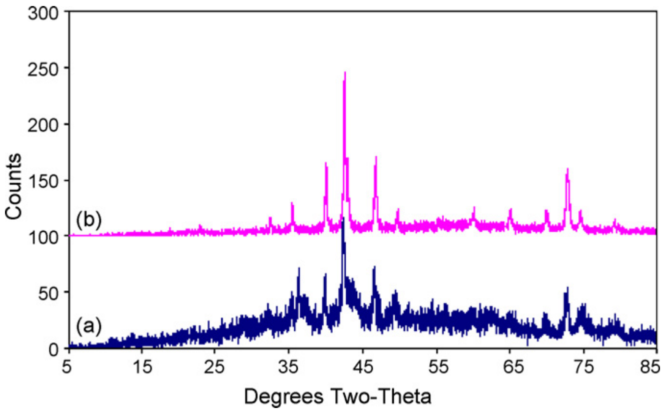

Fig. 1. Powder X-ray diffraction patterns of (a) pre-reaction and (b) post-reaction Co_3Mo_3N prepared by ammonolysis.