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ORIGINAL ARTICLE

Synthesis and ammonolysis of nickel and cobalt tungstates and their characterisation

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Abstract The synthesis and characterization of NiW and CoW compounds are herein reported. The $NiWO_4$ and $CoWO_4$ samples, successfully synthesised by the hydrothermal method, were treated under NH_3 to obtain the metal nitride. The SEM micrographs show that this transformation is a topotactic process. Tungsten trioxide was also treated under NH_3 at similar operating conditions, and used as a reference. High nitrogen contents after ammonolysis were calculated, however, the percentages were below the theoretical values assuming the formation of pure NiWN, CoWN and WN. The XRD pattern indicates that WON is likely formed after ammonolysis of tungsten oxide whereas phase segregation was observed on the nickel and cobalt samples. Furthermore, the reactivity of the nitride samples as function of temperature was measured under argon and the results show that most of the nitrogen is removed from the cobalt and nickel samples whereas it was partially released from the tungsten specimen.

1. Introduction

Metal nitrides are of interest due to their electronic and magnetic properties, their hardness and their application as catalysts (Oyama, 1996; Alexander and Hargreaves, 2010). In terms of catalysis, much interest has centred upon the possibility of using certain metal nitrides as potential replacements for precious metal based catalysts, although caution should be exercised when drawing analogies with the activity of noble metals and nitrides should be recognized as interesting catalytic materials in their own right. Recently, attention has been focused upon the possibility of using certain interstitial metal nitrides as nitrogen transfer reagents wherein lattice nitrogen derived species could be directly transferred to organic target molecules potentially by-passing the requirement of ammonia as an intermediate reactant and indirectly utilizing N_2 as a reagent (Mckay et al., 2007, 2008; Hargreaves and Mckay, 2009; Cairns et al., 2010). Such processes would be very attractive

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since they could lead to a reduction in the requirement of ammonia which is produced industrially by a very intensive process. Some success in terms of the utilization of N_2 as a reactant for the preparation of organic nitrogen containing molecules has been achieved using organometallic Ti-containing systems (Mori, 2004). In terms of heterogeneous candidates, the reversible loss of lattice nitrogen from Co_3Mo_3N to yield the Co_6Mo_6N phase, which possesses the η-12 carbide structure which was previously unprecedented for nitrides has been accomplished by reduction using H_2 at elevated temperatures [8]. Restoration of the original η-6 carbide structure Co_3Mo_3N phase has been achieved using either an N_2/H_2 mixture or with N_2 alone. It is interesting to note that the lattice nitrogen in the isostructural Fe_3Mo_3N and the β-Mn structured Ni_2Mo_3N phases is apparently a lot less reactive than that in Co_3Mo_3N and analogous reduction processes have not so far been observed with these systems (Mckay et al.,2008; Hargreaves and Mckay, 2009; Hunter et al., 2010; Gregory et al., 2011). On this basis, it can be seen that ternary molybdenum nitrides present interesting behaviour in terms of their reduction characteristics which is dependent upon their composition. Accordingly, in order to gain improved understanding of the processes involved we have sought to extend our studies towards the elucidation of the behaviour of analogous ternary tungsten nitrides. The preparation and initial thermal stability screening of some such systems are presented within this manuscript.

2. Experimental

The synthesis of $NiWO_4$ and $CoWO_4$ was performed by a hydrothermal method. For this purpose, the required quantities of $Na_2WO_4{\cdot}2H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ (both obtained from Sigma–Aldrich) and $Ni(NO_3)_2{\cdot}2H_2O$ (obtained from J.T. Baker) were used as precursors. The tungsten salt was first dissolved in water under stirring and the second metal salt, previously dissolved in water, was poured into it, at room temperature. The slurry was then transferred to a Teflon lined reactor and kept at 110 °C for 15 h. The precipitated solid was then washed with deionised water and dried overnight at 110 °C and was then finally calcined at 500 °C for 5 h. WO_3 was obtained from Sigma–Aldrich and was used as supplied. For the synthesis of nitrided samples, about 0.8 g of $NiWO_4$, $CoWO_4$ or WO_3 was placed in a quartz reactor and treated under 94 ml/min of NH_3. The temperature was increased from ambient temperature to 358 °C at 5 °C/min, then at 0.5 °C/min to 448 °C and finally to 785 °C at 2 °C/min. At this final temperature a dwell time of 2.5 h was used. All samples were cooled down to ambient temperature under the NH_3 flow. The $CoWO_4$, $NiWO_4$ and WO_3 samples after ammonolysis were respectively labelled as CoWN, NiWN and WN. Finally the stability of the metal nitrides was determined by thermogravimetry. For this purpose about 0.03 g of the nitrided solid was placed in a crucible and heated from ambient temperature to 1000 °C at 5 °C/min. In addition 100 ml/min of argon was used as a carrier.

3. Characterization

X-ray diffraction (XRD) patterns of the powdered samples were acquired using a Siemens XRD 5000 diffractometer. The diffractometer was operated at 40 kV, 30 mA using Cu-Kα radiation (λ = 1.5406 Å). The step size used was 0.02° and patterns were recorded in the 2θ range from 5.0° to 85.0° using a counting rate of 1 s per step. Surface areas were determined using N_2 physisorption at 77 K applying the BET method and using a Micromeritics Gemini instrument. CHN analysis was performed using an Exeter Analytical CE-440 elemental analyser. SEM images were taken using a XL30 ESEM Philips microscope operating at 20 kV in order to study the morphological features. The elemental mapping images were acquired by using a JEOL JSM-6400 scanning electron microscope provided with a Bruker XFlash-4010 detector. The reactivity of the metal nitrides under argon was determined in a SDT Q 600 instrument supplied by TA Instruments.

4. Results and discussion

The XRD patters of the synthesised CoW and NiW oxides are presented in Fig. 1. The XRD pattern of the commercial WO_3 material, which is not presented, agrees well with the monoclinic WO_3 (JCPDS reference pattern 043-1035). The diffraction patterns presented in Fig. 1 match well with those expected. The pattern in red in Fig. 1, matches to $CoWO_4$ (JCPDS reference pattern 015-0867) with the strongest peak corresponding to the (1 1 1) reflection occurring at a d spacing of 2.916 Å. The pattern in black in Fig. 1, matches to $NiWO_4$ (JCPDS reference pattern 015-0755) and again the major peak is the (1 1 1) reflection at 2.889 Å. According to the JCPDS references, both the $CoWO_4$ and $NiWO_4$ phases are monoclinic and belong to the P2/a and P2/c space groups, respectively. Furthermore, the unit cell parameters for $CoWO_4$ are a = 4.947 Å, b = 5.682 Å, c = 4.669 Å and β = 90.000° whereas those for $NiWO_4$ are a = 4.600 Å, b = 5.665 Å, c = 4.912 Å and β = 90.000°. Both compounds are isostructural as is apparent from Fig. 1. Since a very good agreement between the patterns and the JCPDS database is observed, it can be concluded that the synthesis method favours the formation of $CoWO_4$ and $NiWO_4$.

The incorporation of nitrogen into the structure of the $CoWO_4$ and $NiWO_4$ during nitridation resulted in some physical and chemical changes as presented in Table 1. It can be observed that the metal oxide precursors exhibit low surface areas,

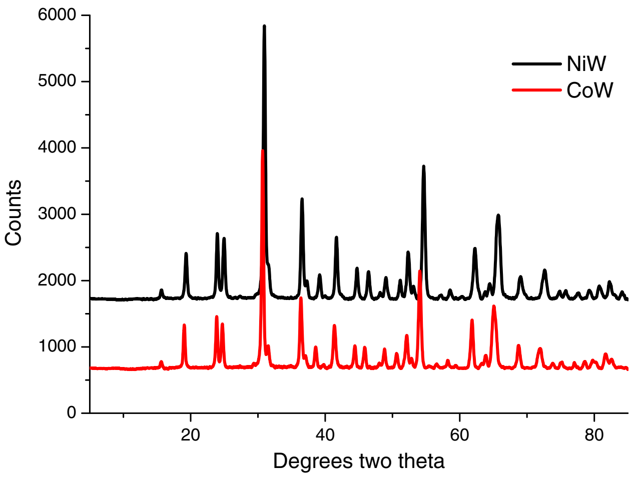

Figure 1 XRD patterns of the cobalt tungsten and nickel tungsten oxides.