



McAulay, K., Hargreaves, J.S.J., McFarlane, A., Price, D.J., Spencer, N.A., Bion, N., Can, B., Richard, M., Greer, H.F., and Zhou, W.Z.(2015) The influence of pre-treatment gas mixture upon the ammonia synthesis activity of Co-Re catalysts. *Catalysis Communications*, 68, pp. 53-57.

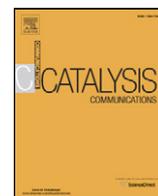
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Version: Published

<http://eprints.gla.ac.uk/104922/>

Deposited on: 16 April 2015



Short communication

The influence of pre-treatment gas mixture upon the ammonia synthesis activity of Co–Re catalysts



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ARTICLE INFO

Article history:

Received 21 February 2015

Received in revised form 30 March 2015

Accepted 10 April 2015

Available online 12 April 2015

Keywords:

Ammonia

Cobalt

Rhenium

Nitride

Hydrogen

ABSTRACT

CoRe₄ catalysts highly active for ammonia synthesis at ambient pressure and 400 °C can be prepared without an ammonolysis stage. Pre-treatments under 3:1 H₂:N₂ and 3:1 H₂:Ar atmospheres are shown to influence catalytic performance with the latter treatment leading to an induction period prior to development of activity upon switching to an ammonia synthesis feedstream. The difference in behaviour between the two pre-treatment atmospheres is manifested in temperature programmed nitrogen isotopic exchange experiments where H₂:Ar treated material is inactive and its H₂:N₂ treated counterpart is active.

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1. Introduction

Ammonia synthesis is a reaction of pivotal importance. Through the provision of synthetic fertilisers accomplished *via* the Haber Bosch Process, it can be directly credited with sustaining a large proportion of the world's population. The Haber Bosch Process involves the direct combination of pure N₂ and H₂ feedstreams *via* the use of promoted iron based catalysts [1]. It is operated at high pressure (ca. 100–300 atm) and moderate temperatures (ca. 400 °C) and in its entirety, including the production of the pure reactant streams, it is responsible for more than 1% of global energy demand. Whilst often viewed as a mature technology, the development of more active and/or poison tolerant catalysts could yield massive environmental and economic returns given the energy intensive nature of the process. Indeed, in principle, improvements made in catalyst activity could lead to a “win–win” situation since the moderately exothermic nature of the reaction between N₂ and H₂ means that the NH₃ synthesis equilibrium is favoured by a decrease in temperature.

It has been established that ruthenium based catalysts are effective alternatives to iron and they are of higher activity. To this end, Ru/C based catalysts are employed on an industrial scale resulting in a reduction in the severity of process operation. This is the basis of the KBR

Advanced Ammonia Process which is operated at lower pressure than in the Haber Bosch counterpart [2]. Investigations into Ru catalysed ammonia synthesis are on-going with very recent literature documenting very high activity for electride supported Ru catalysts [3]. Additional literature has reported that certain nitrides exhibit high activity, with Co₃Mo₃N based systems being particularly noteworthy [4–6], although high activity has also been documented for other systems such as Ni₂Mo₃N [4] which could offer advantages in terms of ease of nitridation [7]. Attention has also centred upon Re based catalysts, with bulk Re modified with Co (in the atomic ratio 4:1 Re:Co, hereafter referred to as CoRe₄) having been reported to be particularly active [8]. In the case of catalysts comprising of Re alone, a marked degree of deactivation with time on stream was evidenced which has been attributed to decomposition of the active nitride phase to a mixture of rhenium nitride and rhenium metal [8,9]. The high activity of CoRe₄ has been attributed to stabilisation of a nitride phase [8]. Further support for the formation of an active nitride in Re based systems is presented in a study of a caesium promoted rhenium catalyst supported on alumina where a pronounced influence of pre-treatment gas was reported with 3:1 H₂:N₂ leading to more active catalysts than H₂ alone [10]. In view of the difficulties encountered in characterising the rhenium nitride phases reported in the preceding study, coupled to the high activities of the systems and the importance of ammonia synthesis, we are undertaking an investigation of the CoRe₄ system. In this communication, we report

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our initial results upon the influence of the composition of the pre-treatment gas mixture.

2. Experimental

CoRe₄ samples were prepared by mixing 4 g of NH₄ReO₄ (Sigma Aldrich ≥99%) in 2 ml of distilled water with ca. 1 g Co(NO₃)₂·6H₂O (Sigma Aldrich ≥98%). The resultant mixture was dried in air at 125 °C for 12 h. The dry materials were then calcined in air at 700 °C (applying a 10 °C min⁻¹ ramp rate) for 3 h. Reaction studies were performed using ca. 0.3 g of material which was placed in a silica reactor tube held between silica wool plugs. Prior to reaction, samples were either activated *in situ* in the microreactor for 2 h at 600 °C under a 60 ml min⁻¹ flow rate of either 3:1 H₂:N₂ (BOC, H₂ 99.998%, N₂ 99.995%) or 3:1 H₂:Ar (BOC, H₂ 99.998%, Ar min. 99.99%). Following activation, reactions were undertaken applying the 3:1 H₂:N₂ feed gas flowing at 60 ml min⁻¹ at ambient pressure and a temperature of 400 °C. The vent gas was flowed through 200 ml of 0.00108 M H₂SO₄ solution and the rate of ammonia production was calculated from the decrease of conductivity monitored as a function of reaction time. Ammonia formation was also verified for selected reactions using a test employing Nessler's reagent.

Powder X-ray diffraction patterns were recorded using a Siemens D5000 diffractometer using Cu K_{α1} radiation. Samples were prepared by compaction into a sample holder and measurements were undertaken over the 5–85° 2θ range using a step size of 0.01° and a counting rate of 1 s per step. N analyses were undertaken using an Exeter Analytical CE-440 elemental analyser. Transmission electron microscopic (TEM) images were attained using a JEOL JEM-2011 electron microscope operating at an accelerating voltage of 200 kV. The TEM and high-resolution TEM (HRTEM) images were recorded using a Gatan 794 CCD camera.

N₂ isotopic exchange measurements were performed using the apparatus developed for oxygen isotopic exchange studies described previously [11,12]. A U-form reactor was placed in a closed recycle system which was connected on one side to a mass spectrometer (Pfeiffer Vacuum, QMS 200) for monitoring the gas phase composition and on the other side by a vacuum pump. The recycling pump placed in the system removes limitations due to gas-phase diffusion. Temperature programmed ¹⁵N₂/¹⁴N₂ homomolecular exchange (¹⁵N_{2(g)} + ¹⁴N_{2(g)} → 2¹⁴N¹⁵N_(g)) experiments were undertaken on 100 mg of CoRe₄ as described below. Samples were subjected to either a 3:1 H₂:N₂ or 3:1 H₂:Ar (80 ml min⁻¹) pre-treatment step at 600 °C for 1 h with a ramp rate of 10 °C min⁻¹ prior to cooling to 200 °C under the same gas mixture. Then, the system was purged using secondary vacuum at 200 °C for 1 h. 50 mbar of a mixture of ¹⁴N₂ and ¹⁵N₂ (98% + purity, supplied by Cambridge Isotope Laboratories, Inc.) was charged into the recycle system at 200 °C and the temperature was increased with a ramp rate of 2 °C min⁻¹ up to 600 °C. Another experiment of homomolecular exchange was undertaken with the addition of an activation step: After H₂:N₂ treatment, the catalyst was purged using N₂ flow (20 ml min⁻¹) at 600 °C for 30 min prior to cooling down to 200 °C under N₂. The masses 28, 29, 30 m/z were monitored as a function of time to follow the exchange and converted into ¹⁴N₂, ¹⁴N¹⁵N and ¹⁵N₂ partial pressures respectively. The m/z values of 2, 17 and 18 were also recorded to determine if H atoms remained at the surface of the nitride, thus yielding NH₃ or H₂ in the gas phase after decomposition. The absence of NO_x and O₂ was confirmed by monitoring the corresponding m/z values. The quantity of H₂ (mbar) was also estimated after the calibration step.

3. Results and discussion

Within the literature, active CoRe₄ catalysts have been prepared by pre-treatment of their precursors with NH₃ [8,9]. However, as discussed by Wise and Markel in relation to the binary molybdenum nitride system, ammonolysis is not practical on a large scale for the preparation

of nitrides from oxide precursors [13]. A number of issues such as heat transfer mean nitridation from reactant H₂:N₂ mixtures would be preferable. Accordingly, in this study, reduction has been undertaken using H₂:N₂ (3:1) with H₂:Ar (3:1) being employed for means of comparison to assess any potential role of possible nitride formation. For both resultant materials, the ambient pressure steady state ammonia synthesis activities at 400 °C are reported in Table 1. From the table it can be seen that ammonolysis is not a necessary step in the preparation of active catalysts and indeed the mass normalised rates determined exceed that of the material prepared by ammonolysis and run under comparable conditions as reported elsewhere (where rates of 600 μmol g⁻¹ h⁻¹ [8] and ca. 470 μmol g⁻¹ h⁻¹ [9] have been quoted). If thermodynamic equilibrium was attained under the reaction conditions, employed it would correspond to a mass normalised rate of ca. 2140 μmol g⁻¹ h⁻¹. Upon making comparisons with other systems reported to display high activity in the literature, rates of 652 μmol g⁻¹ h⁻¹ for Co₃Mo₃N [5], ca. 400 μmol g⁻¹ h⁻¹ for Ni₂Mo₃N [7] and 437 μmol g⁻¹ h⁻¹ for Re/MCM-41 [14] have been reported for conditions comparable to those applied in this study. In the case of Ru dispersed on electride, a rate of 3550 μmol g⁻¹ h⁻¹ has been reported at atmospheric pressure and 340 °C [3].

Comparing the data in Table 1, a degree of influence of pre-treatment gas can be seen. Interestingly, as apparent in Fig. 1, there is an induction period associated with the development of activity in the case of the H₂:Ar pre-treated material. This is in marked contrast to that treated under H₂:N₂ and could tentatively be associated with the formation of an active nitride phase as proposed by Kojima and Aika [8]. In terms of the reaction profile, it is of interest to note that beyond the induction period, during which the material is apparently inactive, the catalyst exhibits steady state performance. In view of the earlier reports wherein Re₃N showed a pronounced deactivation rate within the first 2 h on stream at ambient pressure and 350 °C [8], we have undertaken extended testing of a CoRe₄ catalyst prepared by pre-treatment with H₂:N₂ and have shown it to exhibit steady state activity throughout an entire 48 h testing period. When pre-treated with H₂:N₂, the CoRe₄ material exhibits a steady state ammonia synthesis rate of 576 ± 86 μmol g⁻¹ h⁻¹ at 350 °C.

To obtain a more complete understanding of the role of pre-treatment and fundamental aspects of nitrogen activation, temperature programmed homomolecular exchange of a ¹⁴N₂:¹⁵N₂ mixture has been conducted. This process can be indicative of some of the fundamental N₂ activation steps. As can be observed in Fig. 2, there are significant differences between the exchange profiles as a function of pre-treatment. In the case of the H₂:Ar pre-treated sample, the ¹⁴N₂-¹⁵N₂ homoexchange reaction does not occur within the temperature range applied. However, in the case of the H₂:N₂ pre-treated system, there seems to be release of a very low amount of hydrogen (the maximum pressure recorded at 550 °C is about 0.1 mbar) followed by development of N₂ homolytic exchange. This clearly indicates the importance of pre-treatment with the N₂ containing mixture in the generation of an active surface. In addition, it has been observed that application of the secondary vacuum step at 600 °C yields materials which do not desorb hydrogen and which are unreactive for N₂ exchange whereas replacing this step by a 30 min 600 °C N₂ pre-treatment step does result in exchange which once again may follow evolution of a very small amount of H₂. These observations may have interesting implications since it could be imagined that *in vacuo* at 600 °C H₂ loss and/or removal of surface nitride may occur. It

Table 1

Mass normalised steady state ammonia synthesis rates at 400 °C for CoRe₄ samples as a function of pre-treatment gas.

Pre-treatment atmosphere	Ammonia synthesis rate (μmol NH ₃ g ⁻¹ h ⁻¹)
N ₂ /H ₂	943 ± 44
Ar/H ₂	844 ± 41

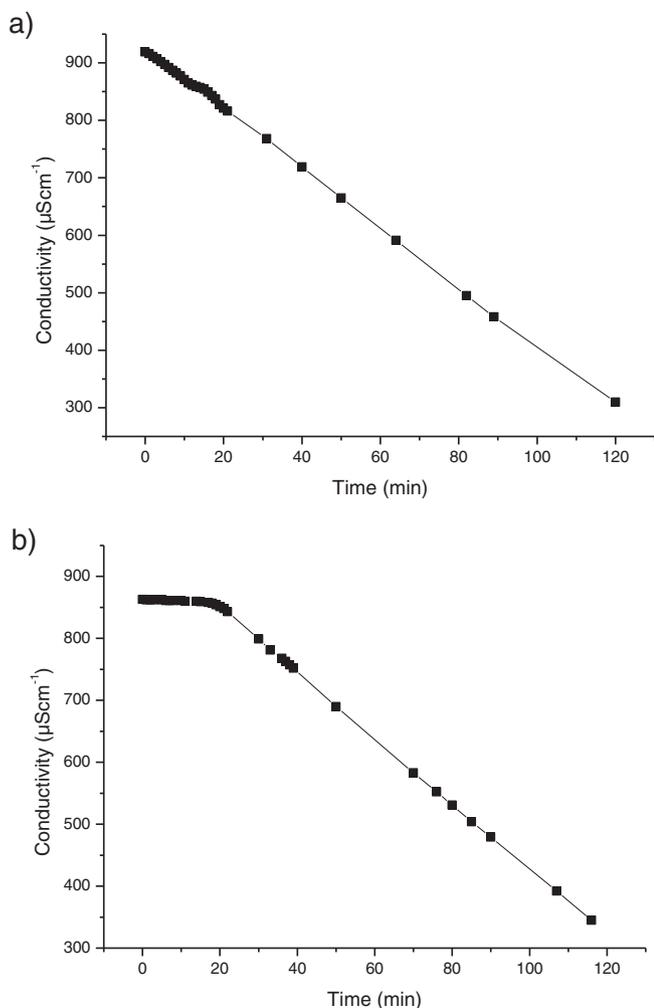


Fig. 1. Reaction conductivity profiles for 3:1 $\text{H}_2:\text{N}_2$ reaction at 400 °C (a) sample pre-treated with 3:1 $\text{H}_2:\text{N}_2$ for 2 h at 600 °C and (b) sample pre-treated with 3:1 $\text{H}_2:\text{Ar}$ for 2 h at 600 °C. The plots are truncated to demonstrate the initial period of activity illustrating the different effects of pre-treatment.

could also be the case that there are subtle changes in surface structure and/or composition which lead to the loss of N_2 activation ability and the application of *in-situ* XPS studies to probe these possibilities will be explored. In addition to activity for nitrogen activation, the evolution of H_2 suggests $\text{N}_2:\text{H}_2$ pre-treatment to lead to strong hydrogen adsorption.

In order to further elucidate the effect of the pre-treatment, a range of characterisation studies has been undertaken. Post-reaction powder X-ray diffraction patterns for materials activated under both $\text{H}_2:\text{Ar}$ and $\text{H}_2:\text{N}_2$, presented in Fig. 3, are consistent with the presence of rhenium, although it should be noted that the high backgrounds could disguise a significant degree of X-ray amorphous material. In addition, no cobalt containing phases are evident despite its relatively high concentration. This is contrary to the situation which pertains for the XRD patterns for CoRe_4 catalysts prepared by ammonolysis where a mixture of both Co and Re reflections is apparent [8,9]. Most interestingly, the background of the $\text{H}_2:\text{N}_2$ pre-treated material in the range ca 37.5–50° 2θ shows a possible broad feature distinctly different with respect to its $\text{H}_2:\text{Ar}$ pre-treated counterpart. Such a feature may be attributed to rhenium nitride, as reported elsewhere [10]. However, post-reaction nitrogen analyses undertaken by combustion upon both samples returned a nil result suggesting a very low (if any) content of N, which could still be consistent with the

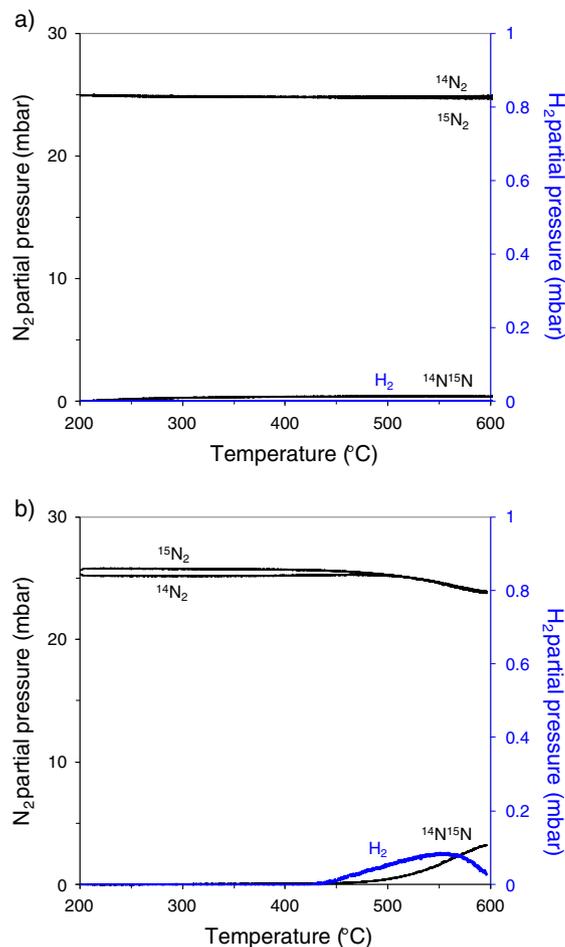


Fig. 2. Temperature programmed $^{14}\text{N}_2/^{15}\text{N}_2$ homomolecular exchange profiles for (a) CoRe_4 pre-treated with 3:1 $\text{H}_2:\text{Ar}$ at 600 °C for 1 h and application of a secondary vacuum at 200 °C for 1 h and (b) CoRe_4 pre-treated with 3:1 $\text{H}_2:\text{N}_2$ at 600 °C for 1 h and application of a secondary vacuum at 200 °C for 1 h.

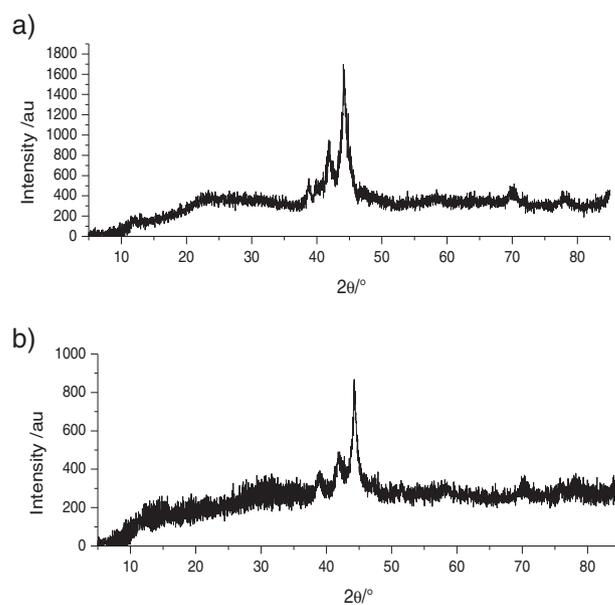


Fig. 3. Powder X-ray diffraction patterns of CoRe_4 samples following reaction with 3:1 $\text{H}_2:\text{N}_2$ at 400 °C and ambient pressure (a) sample pre-treated with 3:1 $\text{H}_2:\text{N}_2$ at 600 °C for 2 h and (b) sample pre-treated with 3:1 $\text{H}_2:\text{Ar}$ at 600 °C for 2 h.

presence of a surface and/or stable nitride phase in the case of the $\text{H}_2:\text{N}_2$ activated material.

TEM studies of both materials, both directly after the activation process and also after reaction, have been undertaken to determine potential differences in morphology and to provide a more detailed insight into any phases not apparent in the XRD studies. Representative micrographs are shown in Fig. 4. In these studies, a pronounced amorphous surface film, which is present to a lesser degree in the $\text{H}_2:\text{Ar}$ pre-treated system, was evident in the $\text{H}_2:\text{N}_2$ pre-treated material. From the image contrast pattern, which is different from that of amorphous carbon and also from the fact that double amorphous layers were sometimes observed, it is believed that this amorphous layer is likely formed due to surface reaction of the particles. Whilst this is a very apparent difference, a degree of caution has to be exercised as to its significance since, although it is clear that the materials behave differently upon pre-treatment, exposure to air has occurred prior to TEM measurement which could result in different degrees of surface oxidation. Overall, the $\text{H}_2:\text{Ar}$ pre-treated sample appears to be less ordered than its $\text{H}_2:\text{N}_2$ counterpart. The lattice spacings marked in Fig. 4(c) and (f) are consistent with the (101) plane of Re metal which is evident in the near surface region of samples prepared by both activation procedures, whilst

that evident in Fig. 4(i) could correspond to the (111) plane of Co_3O_4 . Co_3O_4 could either indicate incomplete reduction of the sample upon pre-treatment and subsequent reaction or could otherwise be formed by oxidation of reduced Co phase(s) upon the discharge of the catalyst from the reactor and/or its storage in air.

Taken together, a number of the above results provide tentative support for the significance of a nitride phase in relation to the activity of CoRe_4 ammonia synthesis catalyst, as detailed elsewhere [8], although such a phase is not directly evident from N analyses of active materials. However, indirect support for its formation is provided by the induction period evident upon the $\text{H}_2:\text{Ar}$ pre-treatment and the isotopic N_2 exchange behaviour, as well as from the background of the XRD pattern of the $\text{H}_2:\text{N}_2$ pre-treated catalyst. Alternatively, the different pre-treatment procedures may also exert effects by influencing the Co:Re surface ratio. Accordingly, it is our intention to address these aspects in comparative *in-situ* pre-treated depth profile XPS studies. It is also planned to undertake *in-situ* XRD/XAS measurements to provide a level of structural detail currently not possible in laboratory XRD investigations. The application of advanced techniques to more directly determine surface structure, also of potential significance, will be investigated. Despite the current uncertainties about the exact nature of the

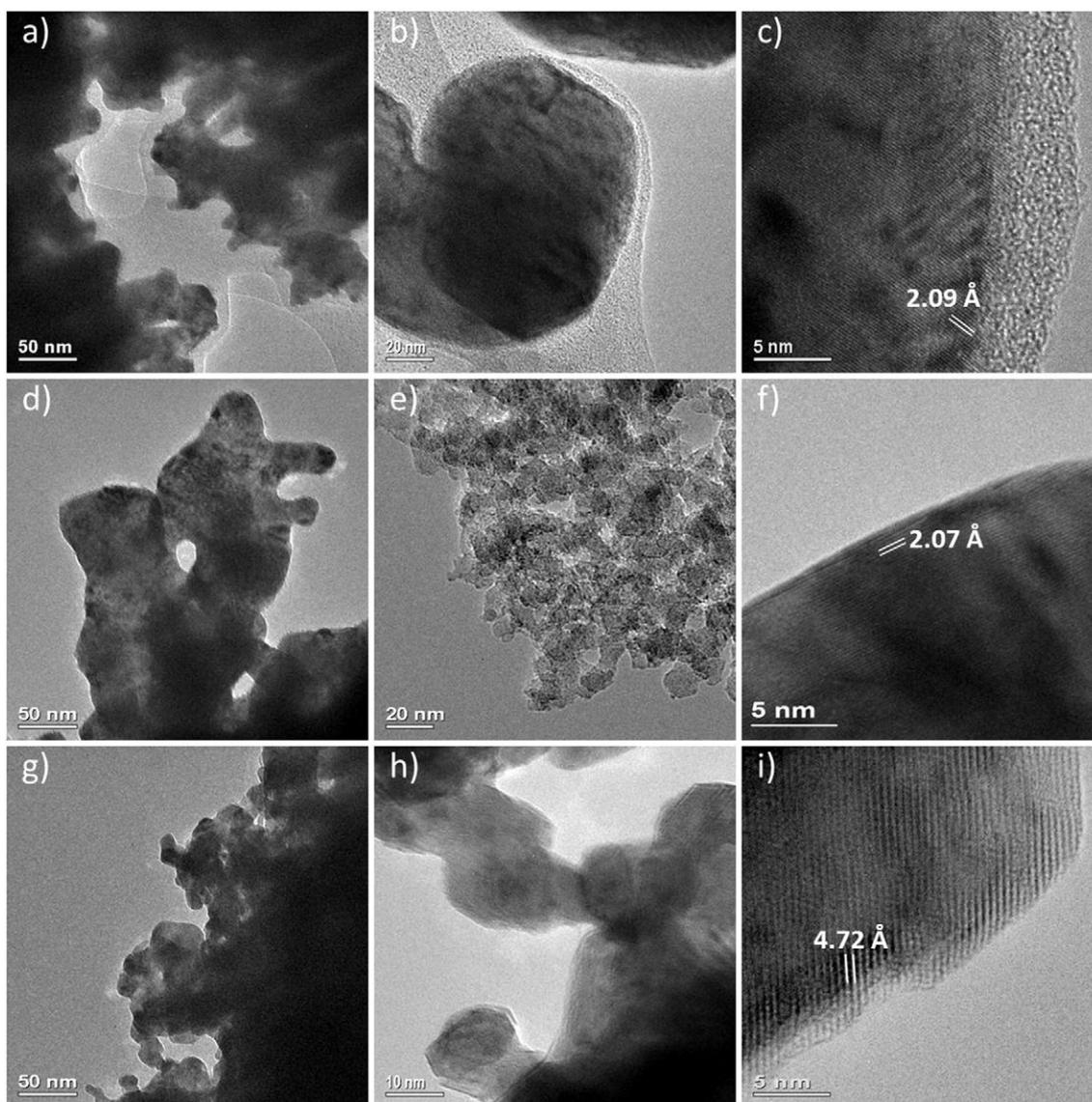


Fig. 4. TEM images of CoRe_4 samples (a)–(c) following pre-treatment with 3:1 $\text{H}_2:\text{N}_2$ at 600 °C for 2 h, (d)–(f) following pre-treatment with 3:1 $\text{H}_2:\text{Ar}$ at 600 °C for 2 h and (g)–(i) following pre-treatment with 3:1 $\text{H}_2:\text{N}_2$ at 600 °C for 2 h and reaction with 3:1 $\text{H}_2:\text{N}_2$ at 400 °C and ambient pressure.

active surface phase, from the results presented herein, it has been shown that ammonolysis is an unnecessary step for the preparation of CoRe₄ catalysts and also that such catalysts may be more active than non-promoted ternary nitride systems which have been the subject of some attention in the literature. These interesting findings indicate the system to be of further potential interest.

4. Conclusions

This study has demonstrated that it is not necessary to employ ammonolysis of precursors to yield highly active CoRe₄ ammonia synthesis catalysts. Employing H₂:N₂ (3:1) and H₂:Ar (3:1) pre-treatment leads to significant differences with the latter resulting in an induction period before catalytic activity develops at 400 °C once the feed is switched to H₂:N₂. Detailed combined XRD/XAS studies aimed at elucidating the structural consequences of the two activation procedures will be undertaken as will depth profiling XPS on samples pre-treated *in-situ*. The differences in activation procedure are mirrored in temperature programmed homomolecular N₂ isotopic exchange studies. In these studies H₂:Ar pre-treatment resulted in inactivity for exchange, whereas H₂:N₂ resulted in a material exhibiting N₂ exchange activity following desorption of hydrogen and providing that the secondary vacuum step was applied below 600 °C.

Acknowledgements

We would like to thank Mrs Kim Wilson, School of Chemistry, University of Glasgow for very kindly undertaking CHN analyses of materials. KMCA and JSJH would also like to thank the EPSRC and the School of Chemistry, University of Glasgow for the provision of a DTA Studentship to KMCA (through EP/K503058/1). ARMCF and JSJH gratefully acknowledge the EPSRC for funding through project EP/J018384/1.

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