



Review

A comparison of the activities of various supported catalysts for ammonia synthesis

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ABSTRACT

The present study presents an empirical screening study of the catalytic performance of a variety of supported materials for ammonia synthesis at 400 and 500 °C. Amongst the materials tested, those derived from Ru/Al₂O₃ exhibited the best performance. Supported Os and CoRe catalysts also demonstrated comparatively high activities indicating them to be potentially worthy of further investigation.

1. Introduction

The development of the Haber Bosch Process was undoubtedly a major achievement of the 20th Century. Through provision of a route to access synthetic fertiliser, it can be credited with sustaining 40% of the global population. It has been estimated that it is responsible for 2% of the global commercial energy requirement [1]. This figure takes into account the production of reactants for which the hydrogen required is generally prepared via fossil based feedstocks. As a whole the process, which currently runs on a production scale of ca 174 million tonnes per annum, accounts for 670 million tonnes of CO₂ emissions per year equating to around 2.5% of worldwide fossil fuel based CO₂ emissions [1]. It is therefore a very important major process for which a number of superlatives apply. On the industrial scale, ammonia synthesis is conducted at high pressure (> 100 atmospheres) and moderate temperatures, ca. 400 °C. The catalysts employed are either based upon iron or ruthenium. Although thermodynamically ammonia synthesis is favoured by lowering reaction temperature, the conditions employed are dictated by the requirement for acceptable process kinetics. In current commercial application, the process is highly integrated and very efficient. However, with the increasing availability of renewable electricity it is becoming more and more practical to produce the hydrogen required for localised ammonia synthesis via, for example, electrolysis. The possibility for localised sustainable “green” ammonia synthesis which could, for example, be conducted on farmland for provision of on-demand fertiliser is a strong driver for the discovery of more active catalysts which can be applied more easily under such conditions. There is also increasing interest in the application of ammonia as a fuel or

hydrogen carrier. There are a number of alternative directions currently being investigated in terms of sustainable ammonia production and these include electrocatalytic approaches [2,3], photocatalytic ammonia synthesis [4,5] and chemical looping routes [6,7].

In terms of investigation of catalysts for ammonia synthesis, it is generally the case that individual studies in the literature tend to focus in detail on small subsets of related materials and it is often difficult to benchmark such materials against different material classes reported by other groups due to issues such as differences in experimental procedure. This is a driver for the present manuscript in which we present an empirical overview of the performance of a wide range of supported catalysts which have been selected on the basis of their expected activity. Relevant considerations which have been documented in the literature are highlighted presenting a structured overview of some of the previous literature in relation to the materials screened. Further investigation would involve performance evaluation under conditions of greater relevance to application, such as operation at higher pressure and inclusion of ammonia in the feedstream. The conditions which have been selected correspond to those reported in a number of studies and which we have applied in our previously published studies to discern structure-composition and activity relationships which might otherwise be obscured by operation at higher reaction pressure and/or the inclusion of a low level of ammonia in the reactant feed. Accordingly, the study is intended to be a starting point for further development of active catalytic materials and the systems we have screened have neither been optimised nor characterised in great detail. The data reported suggest potential directions for further investigation where further detailed systematic investigation may, for example, provide the basis for

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computationally aided design [8].

2. Experimental section

The materials screened within this study were prepared as follows.

5% Ru/Al₂O₃ was used as commercially obtained (Sigma Aldrich, Ru 5 wt. % on alumina, powder, reduced, dry). The material was pre-treated at 500 °C under 60 mL/min of 3:1 H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%).

5% Ru/Al₂O₃ + 1% KOH - approximately 1 g of Ru/Al₂O₃ (Sigma Aldrich, Ru 5 wt. % on alumina, powder, reduced, dry) was impregnated by dropwise addition of an aqueous solution of 1 wt percent KOH (Sigma Aldrich, reagent grade, 90%, flakes). The material was then dried in air overnight at 110 °C and was pretreated at 500 °C under 60 mL/min of 3:1 H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%).

5% Os₃(CO)₁₂/SiO₂ and 5% Os₃(CO)₁₂/γ-Al₂O₃ - triosmium dodecacarbonyl (Os₃(CO)₁₂, Sigma Aldrich, 98%) was supported onto silica (amorphous, precipitated, Sigma Aldrich) or alumina (γ-alumina, Condea Chemie, alumina extrudates) using the method outlined by Collier et al. [9]. The support was impregnated with a solution of Os₃(CO)₁₂ in dichloromethane. The volume of dichloromethane required was determined by point of wetness for each support. The material was then dried at 40 °C to remove the dichloromethane to produce a yellow powder. The material was prepared to achieve a 5% loading by weight of osmium. The material was pretreated at 500 °C under 60 mL/min of 3:1 H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%).

5% Os₃(CO)₁₂/SiO₂ + 1% KOH - approximately 1 g of 5% Os₃(CO)₁₂/SiO₂ was impregnated by dropwise addition of an aqueous solution of 1 wt percent of KOH (Sigma Aldrich, reagent grade, 90%, flakes). The material was then dried in air overnight at 90 °C. The material was pretreated at 500 °C under 60 mL/min of 3:1 H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%).

5% Os₃(CO)₁₂/SiO₂ dehydroxylated - silica (amorphous, precipitated, Sigma Aldrich) was dried following the method detailed by Collier et al. [9]. The support was dried at 500 °C for 16 h under a flow of nitrogen at 60 mL/min. The ramp rate for heating was 10 °C/min. After 16 h, the material was cooled under nitrogen. Triosmium dodecacarbonyl (Os₃(CO)₁₂, Sigma Aldrich, 98%) was then supported onto the dried silica. The support was impregnated with a solution of Os₃(CO)₁₂ in dichloromethane. The volume of dichloromethane required was determined from the point of incipient wetness for silica. The material was then dried at 40 °C to remove the dichloromethane to produce a yellow powder. The material was pretreated at 500 °C under 60 mL/min of 3:1 H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%).

10% CoRe supported on silica, alumina and zirconia - 5 g of silica (amorphous, precipitated, Sigma Aldrich), alumina (α-alumina, Fisher Chemicals, aluminium oxide-calcined) or zirconia (monoclinic zirconium (IV) oxide, Sigma Aldrich, powder, < 5 μm, 99% metal basis) were impregnated simultaneously with an aqueous solution of ammonium perrhenate (NH₄ReO₄, Sigma Aldrich, assay, form, powder or crystals, ≥ 99%, 0.55 g) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, Sigma Aldrich, ACS reagent, ≥ 98%, 0.60 g). The material was stirred for 1 h at room temperature. The material was then dried at 125 °C overnight. Following this, the material was calcined in air at 700 °C (applying a 10 °C/min ramp rate) for 3 h. Prior to reaction, 0.5 g of the sample was pre-treated for 2 h at 600 °C under a 60 mL/min flow rate of 3:1 H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%). The material was prepared to give a 10 wt% of CoRe on support with a 1:1 wt ratio of cobalt to rhenium.

5% Re/SiO₂ - 5 g of silica (amorphous, precipitated, Sigma Aldrich) was impregnated simultaneously with an aqueous solution of ammonium perrhenate (NH₄ReO₄, Sigma Aldrich, assay, form, powder or crystals, ≥ 99%, 0.55 g). The material was stirred for 1 h at room temperature. The material was then dried at 125 °C overnight. Following this, the material was calcined in air at 700 °C (applying a 10 °C/min ramp rate) for 3 h. Prior to reaction, 0.5 g of the sample was

pre-treated for 2 h at 600 °C under a 60 mL/min flow rate of 3:1 H₂/N₂ (BOC, H₂ 99.998%, N₂ 99.995%). The material was prepared to target a loading of 5 percent by weight of rhenium.

10% CoRe/MgO - 5 g of magnesium oxide (Sigma Aldrich, 325 mesh 99%+ metals basis) was impregnated simultaneously with aqueous solutions of precursors (5 wt.% loading of Co and 5 wt.% loading of Re), then stirred for 60 min at room temperature. The material was then dried at 125 °C for 12 h and then calcined in air at 700 °C using a ramp rate of 10 °C/min for 3 h. 0.5 g of this material was placed in a quartz glass reactor tube and charged to the reactor, it then underwent pre-treatment by flowing gas mixture of 60 mL/min N₂:H₂ (BOC, H₂ 99.998%, N₂ 99.995%) (1:3) at 600 °C for 2 h using a ramp rate of 10 °C/min.

5% Ni₂Mo₃N/SiO₂ - 5 g of silica (amorphous, precipitated, Sigma Aldrich) was impregnated simultaneously with aqueous solutions of precursors (2 wt.% loading of Ni and 3 wt.% loading of Mo) and stirred for 60 min at room temperature. The material was then dried at 150 °C overnight. 0.6 g of this material was then calcined in 5 mL/min flowing N₂ at 700 °C using a ramp rate of 10 °C/min for 6 h. 0.4 g of this material was placed in a quartz glass reactor tube and charged to the reactor, it then underwent pre-treatment by flowing gas mixture of 60 mL/min N₂:H₂ (BOC, H₂ 99.998%, N₂ 99.995%) (1:3) at 700 °C for 2 h using a ramp rate of 10 °C/min.

10% Co/SiO₂ - 5 g of silica (amorphous, precipitated, Sigma Aldrich) was impregnated with an aqueous solution of precursor (10 wt.% loading for Co) and stirred for 10 min at room temperature. The material was then dried at 110 °C overnight and then calcined in air at 600 °C using a ramp rate of 10 °C/min for 4 h. 0.5 g of this material was placed in a quartz glass reactor tube and charged to the reactor, it then underwent pre-treatment by flowing gas mixture of 60 mL/min N₂:H₂ (BOC, H₂ 99.998%, N₂ 99.995%) (1:3) at 600 °C for 3 h using a ramp rate of 10 °C/min.

10% Co/α-Al₂O₃ - 5 g of α-alumina (α-Al₂O₃, Fisher Chemicals, aluminium oxide-calcined) was impregnated with an aqueous solution of precursor (10 wt.% loading for Co) and stirred for 10 min at room temperature. The material was then dried at 110 °C overnight and then calcined in air at 600 °C using a ramp rate of 10 °C/min for 4 h. 0.5 g of this material was placed in a quartz glass reactor tube and charged to the reactor, it then underwent pre-treatment by flowing gas mixture of 60 mL/min N₂:H₂ (BOC, H₂ 99.998%, N₂ 99.995%) (1:3) at 600 °C for 3 h using a ramp rate of 10 °C/min.

10% Mo₂N_{0.78}/SiO₂ - 5 g of silica (amorphous, precipitated, Sigma Aldrich) was impregnated with an aqueous solution of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Sigma-Aldrich (Germany) Puriss p.a., ACS reagent ≥ 99.0% (T)) corresponding to 10 wt.% loading for MoO₃ and stirred for 10 min at room temperature. The material was then dried at 110 °C overnight and then calcined in air at 450 °C for 2 h using a ramp rate of 10 °C/min. 0.5 g of this material was placed in a quartz glass reactor tube and charged to the reactor, it then underwent pre-treatment by flowing gas mixture of 60 mL/min N₂:H₂ (BOC, H₂ 99.998%, N₂ 99.995%) (1:3) at 700 °C for 2 h using a ramp rate of 5 °C/min.

10% MoPOMSi/α-Al₂O₃ and MoPOM/α-Al₂O₃ - 5 g of α-alumina (α-Al₂O₃, Fisher Chemicals, aluminium oxide-calcined) was impregnated with an aqueous solution of precursor (either phosphomolybdic acid (H + PMo12O₄₀, Sigma-Aldrich USA) or 12-molybdosilicic acid (H₄Mo₁₂O₄₀Si, Strem Chemicals USA) corresponding to 10 wt.% loading for MoO₃) and stirred for 10 min at room temperature. The material was then dried at 110 °C overnight and then calcined in air at 450 °C for 2 h using a ramp rate of 10 °C/min. 0.5 g of this material was placed in a quartz glass reactor tube and charged to the reactor, it then underwent pre-treatment by flowing gas mixture of 60 mL/min N₂:H₂ (BOC, H₂ 99.998%, N₂ 99.995%) (1:3) at 700 °C for 2 h using a ramp rate of 5 °C/min. In relation to terminology, “POMSi” refers to the material prepared using the 12-molybdosilicic acid precursor and “POM” refers to that derived from phosphomolybdic acid. The

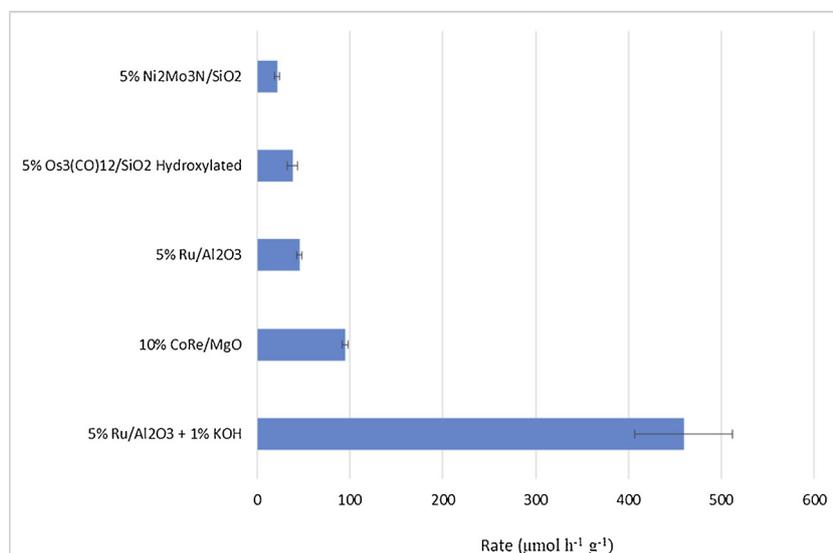


Fig. 1. The ammonia synthesis activity of supported materials at 400 °C (60 mL/min 3:1 H₂:N₂).

corresponding silica and zirconia analogues were prepared analogously using silica (amorphous precipitated, Sigma Aldrich) and monoclinic zirconia (Sigma–Aldrich (United Kingdom) zirconium (IV) oxide, powder, < 5 μm , 99% metal basis) respectively as supports. The same sample abbreviation indicating the precursor is used as for the case of α -Al₂O₃.

Catalytic activity was evaluated using a fixed bed microreactor operating at ambient pressure. 0.3 – 0.5 g of material was loaded into a quartz reactor tube, held between quartz wool plugs and heated using a Carbolite furnace. Brooks mass flow controllers were used to deliver 60 mL/min of 75 vol % H₂/N₂ (BOC, 99.98%) reactant gas through the reactor bed at the specified reaction temperatures. Ammonia production was determined by observing the decrease in conductivity of 200 mL of a 0.0018 M solution of H₂SO₄ which the exit stream of gas flowed through. The rates reported in the present study correspond to steady state reaction conducted over a minimum period of 8 h.

3. Results and discussion

Fig. 1 presents the mass normalised rates for ammonia synthesis determined at 400 °C for various materials. All materials were screened under this reaction condition but only a few were found to exhibit activity. It is notable that the K⁺ promoted Ru/Al₂O₃ presents the highest activity at 400 °C, with a pronounced enhancement due to K⁺ doping being evident. This is consistent with the literature in which Ru is considered to be a close to optimum catalyst [10] and which can be further promoted by the addition of alkali metals [11]. Such promoters, which include K⁺, are believed to function via donating electron density to the Ru surface, an effect which can be seen indirectly in the infrared spectra of adsorbed N₂ molecules [11]. Ru is also known to be a strongly structure sensitive catalyst for the reaction with activity being related to the B₅ step site which gives a pronounced particle size dependence [12], although it has been argued that mixed particle size distribution is most effective with larger particles activating mobile hydrogen species which migrate to small Ru particles promoting NH_x hydrogenation in the case of Ru/Al₂O₃ catalysts [13]. Modification of the support is also known to be of importance in the case of Ru catalysts with MgO [14], BN [15] and electrides [16] being reported to enhance performance. In the current study, we have applied a commercial Ru/Al₂O₃ reference as a benchmark and as such the material is not optimised. Whilst Ru, which forms the basis of the commercial KAAP catalyst [17], has attracted a lot of interest in the literature due to its high activity the Co-Re material which possesses the next highest activity at

400 °C in our study has been seldom studied. In fact, to our knowledge, this is the first report of the performance of MgO supported Co-Re. Previous reports of performance have focussed upon bulk CoRe₄ systems [18,19]. Active materials were originally prepared by ammonolysis and the suggestion had been made that the presence of Co stabilised an active rhenium nitride phase [18]. Subsequent studies have shown that catalysts of enhanced activity can be prepared by replacement of the ammonolysis step by 3:1 H₂:N₂ pre-treatment [19]. When the 3:1 H₂:N₂ pretreatment mixture is replaced by 3:1 Ar:H₂ activity develops following a short induction period [19]. Rhenium nitride has been reported to be an active catalyst which decomposes to yield lower activity rhenium metal during the course of reaction [18,20]. *In-situ* XAS based studies of bulk CoRe catalysts prepared via the H₂:N₂ and Ar:H₂ pretreatment steps shows that the active state of the catalyst is a complex mixture of bimetallic and monometallic species with no definitive evidence for a nitride phase being present [21]. In that study activity development was related to Co-Re mixing. In the context of the current study, attention is drawn to a previous report centring upon the activity of Al₂O₃ supported rhenium in which promoted with Cs⁺ is related to the removal of hydrogen inhibition [20]. Indirectly, this may suggest that application of a basic support may enhance performance and this was the basis for the selection of the MgO support. As a benchmark, we have previously reported an ammonia rate of 943 \pm 44 $\mu\text{mol h}^{-1} \text{g}^{-1}$ at 400 °C for bulk CoRe pretreated with N₂:H₂ and run in the same reactor system [19].

The fourth most active catalyst under our conditions was formed from SiO₂ supported Os₃(CO)₁₂. We were interested in inclusion of Os containing systems as historically Os had been identified as an active catalyst. In addition, Os can be found in the same group of the periodic table as Fe and Ru, the two elements on which different commercial ammonia synthesis catalysts are based. Indeed, the activity for ammonia synthesis is found to increase from Fe to Ru and, with Os lying below Ru, it was of interest to further compare Ru and Os despite obvious limitations such as the nature of the precursor *etc.* Concerns with the application of Os relate to potential toxicity arising from the formation of OsO₄ and, historically, element scarcity. To the authors' knowledge, there have not been very many studies which have reported the performance of Os based systems. One such study, reported a cyclical approach to ammonia synthesis which involved separate pulse sequences of N₂ and H₂ as a means to obtain high yield at reduced reaction pressure [22]. More recently, a DFT based investigation has been published in which a similar N₂ activation barrier over Ru and Os nanoparticles was reported [23] with Ru being the better catalyst due

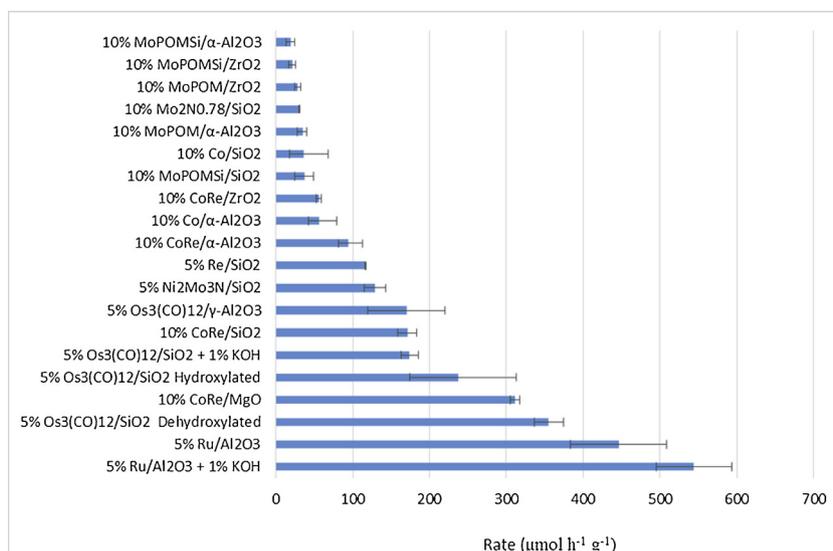


Fig. 2. The ammonia synthesis activity of supported materials at 500 °C (60 mL/min 3:1 H₂:N₂).

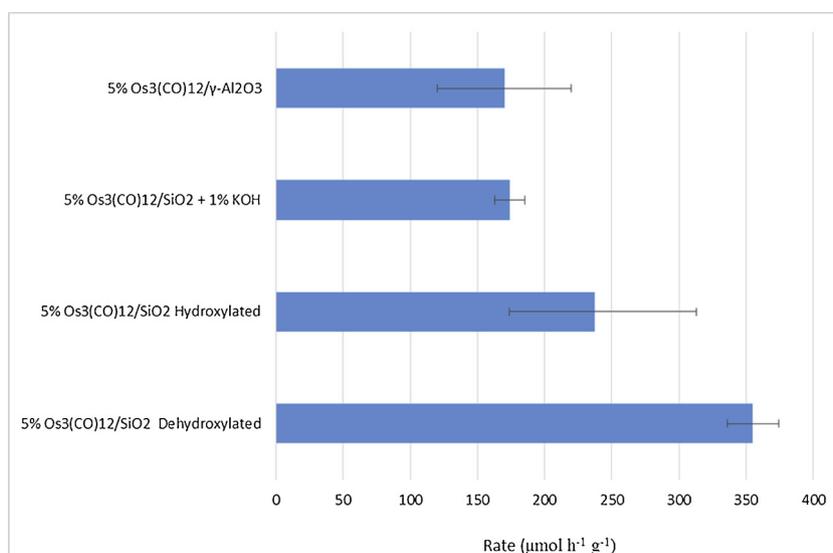


Fig. 3. The ammonia synthesis activity of supported Os based materials at 500 °C (60 mL/min 3:1 H₂:N₂).

to satisfying the requirements of activation energy, surface vacancy sites and number of step sites for particles of 2–4 nm diameter. In the present study, the continuous feed ammonia synthesis activity of the supported Os based system is interesting and can be directly compared to the 78.5 ± 0.5 μmol h⁻¹ g⁻¹ which we have measured at 400 °C on bulk osmium powder. Whilst there could be some loss of osmium through volatilisation, decomposition of the supported cluster via an intermediate hydride might occur [24]. The decomposition of supported osmium carbonyl clusters with respect to retention of nuclearity has been controversial [25–27] especially since the Os–Os and Os–CO bond strengths are similar. Collier et al. have argued that the cluster structure may be retained in their study which employed extensively dehydroxylated supports [10]. Hence, we have compared hydroxylated and dehydroxylated SiO₂ supports (see Figs. 2 and Fig 3) in the current study and observe a relatively small enhancement of rate on the dehydroxylated system at 500 °C with the hydroxylated SiO₂ supported system apparently being more active at 400 °C. Further investigation would be required to draw firm conclusions concerning the nature of the active phases. However, this preliminary screening exercise suggests that such further studies to both elucidate structure sensitivity and potentially optimise this catalytic system might be useful avenues of

further exploration. If nuclearity could be preserved by judicious choice of preparation route, the application of osmium carbonyl precursors provides a potential route to control ensemble size since a wide range of osmium carbonyl cluster sizes are documented [28]. In addition, the potential application of mixed metal osmium cluster precursors provides a potential route to systematic tuning of the activity of dispersed metal particles.

The fifth material to display measureable activity at 400 °C under the reaction conditions employed has been labelled as Ni₂Mo₃N/SiO₂, although we have not established the definite formation of the ternary nitride phase. This phase was targeted in view of the reported high catalytic activity of ternary nitrides [29–33]. Bulk Co₃Mo₃N, particularly when promoted with low levels of Cs⁺, has been widely recognised to be a very active catalyst for ammonia synthesis which has been variously ascribed to the result of a scaling relationship relating to N₂ adsorption enthalpy whereby the combination of Co and Mo yields an enhanced activity material comparable to the performance of Ru [10], or a N-based Mars-van Krevelen mechanism [34,35] possibly involving an associative mechanism [36]. In this case, Ni₂Mo₃N was targeted rather than Co₃Mo₃N due to the fact that it can be more easily prepared without an ammonolysis step (ammonolysis was not

employed at all in the present study due to concerns of NH_3 retention on the various supports and its subsequent release complicating reaction rate analyses) just employing the 3:1 H_2 : N_2 reaction mixture alone [37]. In addition, by application of a Pechini based route, it has been shown that $\text{Ni}_2\text{Mo}_3\text{N}$ with comparable performance to $\text{Co}_3\text{Mo}_3\text{N}$ can be prepared [38]. With this in mind, the activity of the supported material is not surprising although additional studies would be necessary to establish its nature.

Fig. 2 presents the mass normalised rates for ammonia synthesis determined at 500 °C for various materials. It is apparent that a wider range of materials exhibit activity at this temperature than at 400 °C, although the ammonia synthesis reaction is less thermodynamically favourable with increasing temperature (the thermodynamically limited yields are 0.44% and 0.129% at 1 atmosphere pressure and 400 °C and 500 °C respectively). Once again, it can be seen that the Ru based systems are the most active. However, the extent of K^+ promotion is lost with respect to the lower temperature. This may correspond to loss of K^+ as the reaction temperature is increased due to enhanced mobility, but this would have to be established by elemental analysis. Cs^+ is acknowledged to be a better promoter than K^+ [11] but we did not explore this as in other studies on different systems we have found it to be highly mobile and easily lost from the catalytic phase at elevated reaction temperature. It can also be seen that the $\text{Os}_3(\text{CO})_{12}$ derived catalysts are prominent amongst the higher activity materials (for reference the activity of bulk osmium powder was measured to be $282 \mu\text{mol h}^{-1} \text{g}^{-1}$ at 500 °C in the same reactor set up). An additional observation to be made in the present study is that there is no evidence of promotion by K^+ for the Os system. As discussed earlier, it is also possible that there are some support effects amongst these materials (Fig. 3), although when the error bars in relation to activity data are taken into account, the effect seems relatively small overall. This general observation is in marked contrast to the CoRe systems. In order to facilitate comparison, they are presented in Fig. 4 where a pronounced dependence of activity upon the support identity can be seen. MgO is found to be the best support of those investigated for this system and the origin in this observation may relate to its basic nature as discussed previously. Silica is found to be reasonably good as a support whereas $\alpha\text{-Al}_2\text{O}_3$ and particularly ZrO_2 are found to be much less effective with Re/SiO_2 exhibiting higher performance. The origin of these differences is not yet apparent and could relate to particle dispersion and/or mixing effects. In view of the relative performance of the CoRe systems it appears that they are worthy of further attention. To date, as for Os based catalysts, they have not been the subject of extensive investigation. As

stated previously, an ammonia synthesis rate of $943 \pm 44 \mu\text{mol h}^{-1} \text{g}^{-1}$ at 400 °C has been reported for the bulk material [19]. This material is known to possess very low surface area ($< 1 \text{ m}^2 \text{g}^{-1}$) and so on a surface area normalised basis CoRe is a comparatively highly active which warrants further investigation into supported CoRe systems. Unlike the case for the 400 °C tests, at 500 °C the supported Co systems are active. Co is fairly frequently found to be a component of active materials with CoRe being investigated in the present study, and being found to be comparatively active, and the activity of $\text{Co}_3\text{Mo}_3\text{N}$ being referred to. Within the literature, LaCoSi has been reported to be an effective catalyst [39]. Indeed when a comparison was made between CoMo/CeO₂, which is believed to form the supported active $\text{Co}_3\text{Mo}_3\text{N}$ phase, and Co/CeO₂ at 400 °C and 0.9 MPa, the Co/CeO₂ is initially observed to be significantly more active ($4 \text{ mmol h}^{-1} \text{g}^{-1}$ versus $< 3 \text{ mmol h}^{-1} \text{g}^{-1}$) although with time on stream the CoMo system maintains performance and the Co system significantly deactivates over the first 100 h on stream to ca. $2 \text{ mmol h}^{-1} \text{g}^{-1}$ [40]. The application of Co/CeO₂ has been discussed in terms of low-pressure ammonia synthesis and issues relating to deactivation via sintering of Co nanoparticles has been detailed in the literature very recently [41]. Incorporation of dopamine into the synthesis procedure and the associated removal of the resultant carbon layers has been reported to enhance the activity of a Co/CeO₂ catalyst from $3.81 \text{ mmol h}^{-1} \text{g}^{-1}$ to $19.12 \text{ mmol h}^{-1} \text{g}^{-1}$ at 425 °C and 1 MPa with stability being maintained for at least 50 h on stream [41]. This enhancement has been attributed to smaller resultant Co crystallite size, enhanced metal-support interaction and lowered N_2 activation energy. In the present study, the pH of the impregnating solution is 3 which is anticipated to be significantly below the point of zero charge of the supports [42]. This will result in a net surface charge and, given that the impregnating solution comprises $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, it can be anticipated that the Co dispersion would be poor leaving room for potential further optimisation.

The final sub-set of materials to compare, relate to those comprising molybdenum. Molybdenum oxide precursors are known to nitride under 3:1 H_2 : N_2 under the pretreatment conditions employed within this study [43]. MoO_3 can be nitrated to produce the $\beta\text{-Mo}_2\text{N}_{0.78}$ phase which, as reported elsewhere is active for NH_3 synthesis (a rate of $35 \mu\text{mol h}^{-1} \text{g}^{-1}$ at 400 °C and ambient pressure using a 3:1 H_2 : N_2 reaction mixture has been reported [43]). $\gamma\text{-Mo}_2\text{N}$ prepared by ammonolysis of the same precursor reportedly exhibits a very similar activity which is insensitive to morphology (the pseudomorphic nature of ammonolysis can be used to good effect here with MoO_3 precursors of different morphology) [43], although structure sensitivity for ammonia

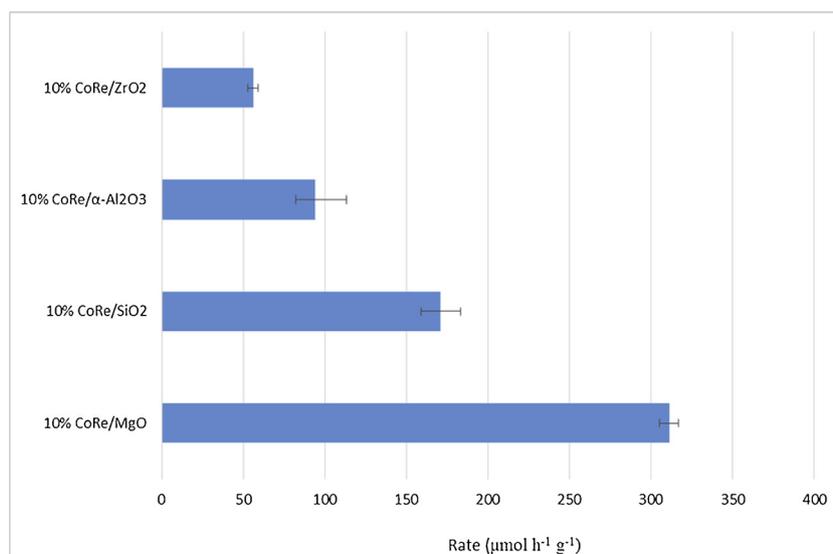


Fig. 4. The ammonia synthesis activity of supported CoRe materials at 500 °C (60 mL/min 3:1 H_2 : N_2).

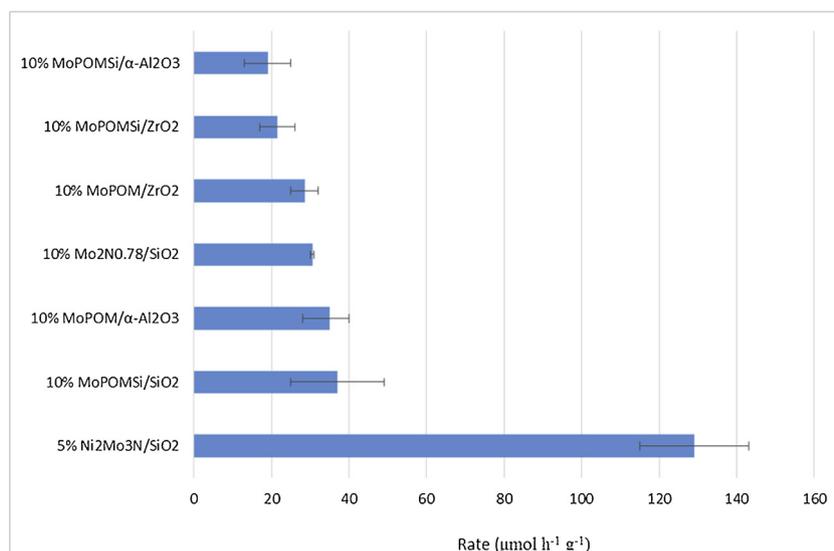


Fig. 5. The ammonia synthesis activity of supported Mo containing materials at 500 °C (60 mL/min 3:1 H₂:N₂).

synthesis at ambient pressure and 400 °C has been reported for Mo₂N where site time yield ratios of 40:25:1 have been reported for 63, 13 and 3 nm diameter particles respectively [44]. In the present study polyoxometallates have been explored as potential precursors to highly dispersed MoN_x phases for which controlled dopant levels (as achieved by the heteroatom) and size and composition could be achieved. Our initial studies have concentrated upon employing phosphomolybdic acid and silicomolybdic acid as Keggin structured precursors containing controlled levels of P and Si “dopant” respectively. As can be seen in Fig. 5, there is very limited influence of both MoN_x precursor and also dopant (in terms of the latter point, the activities are comparable to that of the Mo₂N_{0.78}/SiO₂ sample, which employs ammonium heptamolybdate as precursor). The composition Mo₂N_{0.78} has not been directly verified and is assumed based upon the anticipated binary molybdenum nitride phase which would result from the nitridation conditions employed within the current study [43]. The significant promotional effect of the inclusion of Ni, and suggested formation of the supported ternary nitride, is readily apparent in this figure as was discussed previously. In this context, it is important to establish that supported Ni is not expected to exhibit ammonia synthesis activity. In terms of benchmarking, the ammonia production rate measured with Co₃Mo₃N under comparable reaction conditions applying the same reactor is 489 ± 17 μmol h⁻¹ g⁻¹ [45].

4. Conclusion

In this manuscript, we have undertaken an empirical screening of a wide range of supported ammonia synthesis catalysts. The systems selected have been based on the known previous activity of component phases. Whilst, as might have been expected in terms of the literature, the Ru based systems we have studied were observed to exhibit the highest activity, there are a number of other potentially interesting observations. The activity of osmium based systems seems worthy of further investigation, perhaps employing carbonyl cluster precursors to control ensemble size and composition associated with preparation methods developed to retain cluster nuclearity. Supported CoRe systems, which demonstrate pronounced dependence upon the identity of the support, are also interesting candidates for further investigation, as are supported ternary nitrides.

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