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Nitrides, Hydrides and Carbides as Alternative Heterogeneous Catalysts for Ammonia Synthesis: A Brief Overview

Recent approaches to nitrogen activation

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There has been recent interest in the potential of nitrides, hydrides and carbides as novel heterogeneous catalysts for the production of ammonia in a sustainable manner on a local scale. It has been proposed that some of these materials can produce ammonia *via* Mars-van Krevelen based mechanistic pathways. Generally, for metal-based heterogeneous catalysts, dissociative nitrogen activation is believed to be the rate determining step in ammonia synthesis. However, associative pathways, which are more akin to enzymatic nitrogen activation, are being increasingly invoked in the literature. Such pathways may provide an opportunity for the development of novel catalysts that operate under milder reaction conditions. This brief overview provides a summary of some of the recent developments in relation to nitrides, carbides and hydrides as applied to ammonia synthesis.

Introduction

Driven by the desire to develop novel catalyst formulations which are applicable for localised, more sustainable routes, the area of heterogeneously catalysed ammonia synthesis has attracted much attention in the academic literature in recent times. One of the key incentives for this has been the idea that ammonia synthesis for the production of synthetic fertiliser can be conducted on, for example, a farm close to its point of application with the required hydrogen feedstream being derived from sustainable sources such as electrolysis of water accomplished using electricity produced using wind turbines or solar energy sources. Further drivers are the possible application of ammonia as a non-fossil based fuel and also as a means to indirectly store intermittent over-supply of sustainably derived electricity. In the literature, the energy intensive nature of the Haber-Bosch process, frequently quoted to be 1–2% of global energy demand, and its carbon dioxide footprint, stated to comprise 2.5% of fossil fuel based emissions, are statistics that are often quoted in justification for the search for new routes to ammonia production (1, 2). However, due recognition has to be given to the highly efficient nature of the Haber-Bosch process as currently operated. In relation to this, large scale synthesis of ammonia is highly optimised and it can be credited with the sustenance of *ca*. 40% of the global population. These considerations, coupled to the recently reported UK CO_2 supply chain shortage, related to a reduction in commercial fertiliser production (3), underline the importance of the highly integrated nature of the process.

In developing smaller localised sustainable ammonia synthesis units operating under milder reaction conditions, a step change in catalyst technology would be necessary requiring the development of catalysts being able to operate in the highly desirable lower temperature–lower pressure reaction regimes which have proved elusive for so long. Such catalysts should also be able to withstand a series of rapid start-up and shut-down procedures corresponding to the intermittent nature of sustainably derived electricity supply. A further consideration, not generally acknowledged nor widely explored, is the desirability of such new catalysts to withstand poisoning. In the following, we detail some of the approaches which have been described in the literature in recent years to bypassing the inherent limitations of the more conventional catalysts. While electrocatalysis and photocatalysis are increasingly explored in relation to nitrogen activation, we have concentrated on heterogeneous catalysis.

Nitrides

The paradoxical nature of scaling relationships in relation to conventional metal-based ammonia synthesis catalysts is widely acknowledged. This relates to the occurrence of a Sabatier volcano type relationship whereby catalysts of optimum activity possess intermediate nitrogen binding energies. In this way, the relative performance of metals known to be effective ammonia synthesis catalysts (such as iron, ruthenium and osmium) can be rationalised and the design of new active catalyst formulations can be undertaken by alloying metals of low nitrogen adsorption strength with those of high nitrogen adsorption strength (4). This rationale has been applied to explain the comparatively high performance of the Co_3Mo_3N ammonia synthesis catalyst (5, 6) on the basis of the combination of cobalt (low nitrogen adsorption enthalpy) with molybdenum (high nitrogen adsorption enthalpy) as expressed in the (111) surface plane (4). This explanation implies structure-sensitivity, which has not generally been explored with this material, and also considers the role of the lattice nitrogen to be induction of ordering such that the active surface crystallographic plane is exhibited (4).

An alternative viewpoint of the origin of the activity of this system is the potential occurrence of a Mars-van Krevelen mechanism. The Mars-van Krevelen mechanism, which is perhaps most frequently encountered in oxidation catalysis using metal oxide catalysts, involves the direct participation of reactive lattice species generating transient vacancies which are replenished to complete the catalytic cycle (7). For ammonia synthesised from metal nitrides, this would involve the synthesis of ammonia directly by hydrogenation of lattice nitrogen leading to vacancy sites where nitrogen is activated. To this end, direct hydrogenation of Co_3Mo_3N to produce ammonia occurs and can lead to the previously unprecedented Co_6Mo_6N phase (8). Co_3Mo_3N and Co_6Mo_6N are two line phases (with no intermediate stoichiometries being observed) with the transformation involving the loss of 50% of the lattice nitrogen upon reduction, with the residual lattice nitrogen relocating from the 16c to 8a crystallographic site (8). At ammonia synthesis temperature, using a hydrogen/nitrogen reaction feed, the rapid regeneration of Co_6Mo_6N to Co_3Mo_3N occurs. Such regeneration can also be accomplished by treatment with nitrogen alone (9) thereby opening the possibility of a chemical looping system for ammonia production (albeit with a very low gravimetric nitrogen content). Heterolytic isotopic exchange studies wherein $^{15}N_2$ is exchanged with the lattice nitrogen of Co_3Mo_3N (in which the nitrogen is predominantly ^{14}N reflecting normal isotopic abundance) demonstrate the lattice nitrogen to be highly exchangeable with 40% exchange occurring at 600ºC within 40 min (10). Computational modelling lends further support to the possibility of the participation of reactive lattice nitrogen for this system in ammonia synthesis with high concentrations of surface nitrogen vacancies being predicted at the temperatures applied (11). Recently, the possibility of an associative mechanistic pathway occurring has been demonstrated through modelling (12) and this proposal is consistent with the observation that Co_3Mo_3N is not effective for homomolecular $^{14}N_2/^{15}N_2$ exchange (which directly relates to the material's ability to dissociate nitrogen) at ammonia synthesis temperature despite being an active catalyst (10). Generally, for heterogeneously catalysed ammonia synthesis, dissociative pathways (wherein nitrogen is dissociated on the catalytic surface often in the rate determining step) are invoked and the occurrence of an associative pathway (in which hydrogenation of surface bound nitrogen occurs prior to its dissociation) is an exciting development since it potentially provides a premise for catalyst design and a link to enzymatic nitrogen fixation which operates, albeit comparatively very slowly, under ambient conditions.

The role of nitrogen vacancies as being of interest for the development of novel nitride-based catalysts has been exemplified in the recently reported nickel/lanthanum nitride catalyst (13). In this catalyst, which is reported to exhibit high activity and extended stability, it is proposed that the scaling limitation is circumvented *via* the occurrence of a dual site mechanism in which nitrogen activation occurs at the nitrogen vacancies of the lanthanum nitride with hydrogen dissociation being accomplished by the nickel component. This concept has been expanded to cerium nitride and yttrium nitride also, with cerium nitride being an effective catalyst in its own right in which both nitrogen activation and hydrogen activation can be accomplished on nitrogen vacancy sites (14). The application of dual sites to circumvent limiting scaling relations has also been applied to the development of catalysts based on the combination of metals or metal nitrides with lithium hydride in which activated N is believed to transfer to the lithium hydride component which is progressively hydrogenated to $LiNH_2$ and then ammonia, regenerating the lithium hydride component (15). In terms of this strategy, combination of various alkali and alkaline earth hydrides with manganese nitride has been undertaken with LiH-Mn_4N being particularly effective (16). Elsewhere, in a chemical looping based study, lithium-ion doping has been shown to significantly enhance lattice nitrogen lability in Mn_6N_{5+x} where computational modelling indicates that its presence reduces the nitrogen vacancy formation energy (17). Overall, it is arguable that the role of alkali metal doping and hydrogen activation have been less extensively studied for novel catalysts. For Co_3Mo_3N, low levels of Cs^+ ion doping have significant promotional effects but there are challenges in the preparation of the material related to phase stability issues (5).

Hydrides

High activities for ammonia synthesis have been reported for solid state hydrides and oxyhydrides in recent years. To this end, the performance of TiH_2 (18), $BaTiO_{2.5}H_{0.5}$ (18), $BaCeO_{3-x}H_yN_z$ (19), $VH_{0.39}$ (20) and $NbH_{0.6}$ (20) is documented within the literature. In a number of cases, hydrogen-based Mars-van Krevelen mechanisms have been invoked as the source of activity. The surfaces of some of these materials may possibly nitride in operation, as demonstrated by small shifts in lattice parameters and elemental analyses. In the case of $BaTiO_{2.5}H_{0.5}$, the formation of $BaTiO_{2.5}N_{0.2}H_{0.3}$ is documented although $BaTiO_{2.5}N_{0.3}$ when tested exhibited no activity, thereby emphasising the initial requirement for the hydride containing phase to be present. Lattice mobility is an important consideration in the Mars-van Krevelen mechanism wherein diffusion of species within the bulk of materials to their surfaces occurs. This consideration was applied to the development of the vanadium and niobium hydride based systems on the basis that their 'more open' body-centred crystal structures facilitate diffusion to a greater extent than the face-centred cubic based crystal structures based upon TiH_2 and the perovskite structure based $BaTiO_{2.5}H_{0.3}$ and $BaCe_{3-x}H_yN_z$ systems. This consideration, coupled with advantageous metal-nitrogen bond strengths, is invoked to explain the enhanced performance of these materials (20). This is an interesting design consideration from which novel catalyst compositions of apparent high activity have been developed from components which, in isolation, might not be expected to display good performance. Lanthanum oxyhydrides have been applied as supports for ruthenium where it is reported that catalytic performance relates to high surface hydride ion mobility leading to low work function electrons at hydride ion vacancies near the ruthenium interface enhancing nitrogen activation and reducing the effect of hydrogen poisoning on the ruthenium component (21). Surface hydride is proposed to be formed by the reaction of electrons at vacancies reacting with hydrogen adsorbed on the ruthenium component forming hydride ions which subsequently react with adsorbed nitrogen species releasing electrons back to the vacancy sites. It was also stated that the choice of oxyhydrides is important in reduction of the deleterious effect of nitridation. Ternary ruthenium hydrides have also very recently been reported as effective catalysts with Ba_2RuH_6/MgO outperforming the most active catalysts published to date (22). It is proposed that an associative pathway occurs for this system, which is stabilised by the $[RuH_6]$ centres, lattice hydrogen and alkaline earth metal cation. Experiments performed for Li_4RuH_6/MgO demonstrated the requirement for feeding both nitrogen and hydrogen for the generation of ammonia.

Carbides

In addition to interest in the role of nitrogen and hydrogen vacancies, activation of dinitrogen at dicarbide vacancies has been proposed to occur in relation to nickel-loaded rare earth dicarbides (23). In the case of Ni/CeC_2, the nickel component was reported to be important in promoting the formation of C_2 vacancies in cerium carbide by virtue of its enhanced hydrogen activation functionality. Furthermore, differences in nitrogen adsorption energy and configuration were noted in comparing Ni/CeN and Ni/CeC_2 although they were found to possess comparable ammonia synthesis activity under the testing conditions applied (23). In relation to the catalytic performance of carbides, earlier studies had shown β-Mo_2C to be an effective catalyst and more active than γ-Mo_2N, unlike the α-MoC_{1-x} phase which was not stable under reaction conditions (24). In a comparison between the performance of Co_3Mo_3N and Co_3Mo_3C, which had been carefully prepared so as to avoid any complicating effects of differing morphology, the carbide was shown to be less active requiring a higher reaction temperature and with activity developing after an initial lag period (25). Upon extended testing, gradual nitridation of the Co_3Mo_3C phase was observed to occur. Ammonia synthesis was related to the presence of nitrogen occupying the 16c crystallographic site although it was not possible to distinguish whether the presence of lattice nitrogen arose from the production of ammonia or was the cause of it (25). Co_6Mo_6C, which comprises carbon in the 8a lattice site, was found to be inactive under the conditions tested and the phase remained stable (25). This is contrary to the observations for Co_6Mo_6N referred to previously.

Concluding Remarks

In concluding this brief summary of some of the recent advances in relation to the development of ammonia synthesis catalysts, it is fair to say that there are very exciting and tantalising opportunities for the design of novel catalysts. The ability to synthesise more complex nitrides such as the quaternary phases $NiCoMo_3N$ (26) and $(NiM)_2Mo_3N$ (M = copper or iron) (27) provides the possibility to tune catalytic performance. Taking ternary metal nitrides as an example, in the comparison of the behaviour of Co_3Mo_3N, Fe_3Mo_3N, Ni_2Mo_3N and Co_2Mo_3N it can be observed that the role of composition and structure is complex (28) and computational modelling has a role to play in rationalising the origin of performance leading to the design of new catalysts. It is also noteworthy that the possibility of associative pathways is being invoked more widely. Such pathways are closer to enzymatic systems and, as such, may be related to the possibility of lower temperature catalytic routes. While surveying the literature uncovers many interesting and exciting advances in the area of alternative materials which can be extended to the further discovery of novel catalysts, the development of technology suitable for small scale sustainable ammonia synthesis has yet to be accomplished and remains an exciting and potentially highly rewarding challenge. In terms of application, consideration would need to be given to longevity of performance and also to poison tolerance as well as catalyst handling, storage and preparation. In relation to preparation, it is interesting to draw attention to the considerations of heat transfer in relation to the synthesis of active materials as has been discussed, for example, for binary molybdenum nitrides where nitridation of MoO_3 *via* ammonolysis and treatment with nitrogen/hydrogen mixtures has been compared (29, 30).

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