

Molybdenum on solid support materials for catalytic hydrogenation of N₂-into-NH₃

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Abstract: Very stable *in-operando* and low-loaded atomic molybdenum on solid support materials have been prepared and tested to be catalytically active for N₂-into-NH₃ hydrogenation. Ammonia synthesis is reported at atmospheric pressure and 400°C with NH₃ rates of ca. 1.3·10³ μmol h⁻¹ g_{Mo}⁻¹ using a well-defined Mo-hydride grafted on silica (SiO₂₋₇₀₀). DFT modelling on the reaction mechanism suggests that N₂ spontaneously binds on monopodal [(≡Si-O-)MoH₃]. Based on calculations, the fourth hydrogenation step involving the release of the first NH₃ molecule represents the rate-limiting step of the whole reaction. The inclusion of cobalt co-catalyst and an alkali caesium additive impregnated on mesoporous SBA-15 support increases the formation of NH₃ with rates of ca. 3.5·10³ μmol h⁻¹ g_{Mo}⁻¹ under similar operating conditions and maximum yield of 29·10³ μmol h⁻¹ g_{Mo}⁻¹ when pressure is increased to 30 atm.

Ammonia (NH₃) synthesis is amongst the most globally important processes in the chemical industry due to the use of NH₃ as the source of most fertilisers.^[1] According to data provided by L. E. Apodaca,^[2] 2013 worldwide production of NH₃, with China, India, the Russian Federation, the United States and the European Union at the top of producers, reached 0.14 Gton. Since it is estimated that 3% of the global CO₂ emissions into the atmosphere are due to industrial, large-scale NH₃ synthesis,^[3] this supposes the release of approximately 1 billion tonnes of CO₂ residues per year.^[4] Against this background, the environmental impact of NH₃ synthesis certainly deserves special attention.

Although Nobel laureate Fritz Haber^[5] reported the use of osmium (also uranium) as the first industrial catalyst for NH₃ synthesis from air-source dinitrogen (N₂), the scarcity of this rare metal meant that the only alternative until the mid-80s of the last century was based on iron oxides^[6] materials. These provided stable activities during reaction and practically unlimited access

due to the low-cost and abundance of Fe ores. However, the very harsh operating conditions, with temperatures around 350–525°C and pressures varying between 10–30 MPa (100–300 atm) of Fe-based Haber–Bosch catalytic NH₃ synthesis,^[7] ask for the searching of new alternatives. To date, ruthenium^[8] has been profiled as the only realistic replacement. Although operating conditions can be decreased to 325–450°C and ≤10 MPa, methanation of the carbon material from the carriers in the Ru catalyst under ammonia synthesis conditions results, however, in a loss of active carbon carrier and the shortening of the lifetime of the catalyst. In addition to this and even though Ru is more economically accessible than other precious metals (such as gold or platinum), current market price has practically quadrupled with respect to one year ago (65 \$/ozt at 1st May '17, while 250 \$/ozt at 1st May '18).^[9]

In an attempt to design new strategies for N₂-into-NH₃ conversion, well-defined single-site heterogeneous catalysts^[10] deserve special attention since they have proven to be effective catalysts for several reactions such as olefin^[11] or *n*- and branched alkane metathesis,^[12] amongst other outstanding transformations. (Cycloisomerisation of alkynes, Ziegler–Natta polymerisation, imine metathesis or alkane hydrogenolysis, are some of many other examples).^[10] In 2007 we reported N₂ dissociation and hydrogenation on an isolated surface tantalum atom supported on silica, (SiO₂₋₇₀₀),^[13] a work that later inspired Li *et al.*^[14] and Eisenstein and co-workers^[15] in the elucidation of the mechanism through a DFT approach. They hypothesised that the formation of the [(≡SiO-)₂TaH-(NH₂)₂] species by hydrogenation of [(≡SiO-)₂TaH-(η²-N₂)] followed an associative mechanism that releases ca. 90 kcal mol⁻¹. Although these works helped to understand the chemistry of N₂ activation and hydrogenation by well-defined single-site Ta-hydrides on silica, NH₃ synthesis was not reported due to the high stability of the amidated Ta centre. Amongst the variety of alternatives, molybdenum might exhibit promising prospects for total conversion of N₂ into NH₃.^[16]

Herein, we present experimental evidence supported by theoretical mechanistic interpretations for catalytic NH₃ synthesis by single-site molybdenum hydride on silica, reporting, for the first time, the capabilities of these kinds of materials as N₂ fixation catalysts. Based on these findings, we also propose other molybdenum on solid support materials with higher rates of NH₃ production in the presence of a cobalt co-catalyst and an alkali caesium additive.

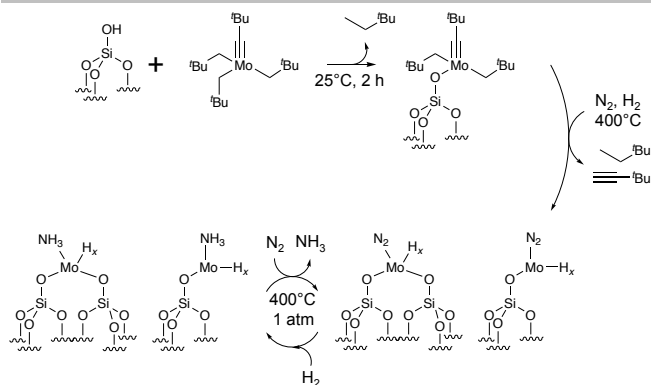
The so-called "Mo-neopentyl" on silica material (MoNp),^[17] corresponding to [(≡Si-O-)Mo(≡C-Bu)(Np)₂], was prepared by reaction of a solution of Mo(≡C-Bu)(Np)₃ in pentane with partially dehydroxylated silica at 700°C, Aerosil® SiO₂₋₇₀₀, during 2 h at room temperature conditions (see Scheme 1). After reaction, the resulting light brown solid was washed with pentane (3 × 20 mL) and dried under dynamic vacuum to get

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Scheme 1. Schematic experimental procedure for $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C-tBu})(\text{Np})_2]$ synthesis and proposed mechanism for N_2 -into- NH_3 conversion by chemical hydrogenation under 400°C and 1 atm operating conditions.

the light brown powder corresponding to the formula $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C-tBu})(\text{Np})_2]$.

Fourier-Transform Infrared (FTIR) spectroscopy analysis (see Fig. S4 in the Supporting Information, SI) on this material reveals the presence of several peaks associated to C–H stretching (2953 , 2900 , 2866 cm^{-1}) and bending (1465 , 1354 cm^{-1}) modes. Liquid-state ^1H NMR spectrum for Schrock $\text{Mo}(\equiv\text{C-tBu})(\text{Np})_3$ complex shows three peaks at 1.4 , 1.3 and 1.0 ppm corresponding to CH_2 and CH_3 protons in $\equiv\text{C-tBu}$ and neopentyl moieties. The further confirmation comes from ^{13}C NMR spectrum, revealing the most characteristic peak at 322 ppm (carbyne) along with other peaks in the region of 87 to 29 ppm for carbons of methylene and ^tBu (see Fig. S6). Solid-state CP/MAS ^1H NMR shows a broad peak centred at 1.5 ppm and a shoulder at 1.8 ppm, and ^{13}C NMR spectrum reveals three peaks at 89 , 32 and 29 ppm, being assigned by analogy with the ^{13}C spectrum of the parent $\text{Mo}(\equiv\text{C-tBu})(\text{Np})_3$ complex in solution.

The MoNp material, kept inside a glove box, was introduced into a stainless-steel cylinder reactor, which remained isolated from the glove box atmosphere, to subsequently place in the setup for the study of the reaction under dynamic conditions. After connecting to the gas lines and purging the tubes, a mixture of H_2 and N_2 (total flow-rate of 40 mL min^{-1} , 3:1 $\text{H}_2:\text{N}_2$ ratio) was introduced onto the catalyst bed (200 mg of catalyst). The reactor outlet was connected to a Mass-Vac Spectrometer for continuous monitoring of the NH_3 mass signal. As seen in Scheme 1, the MoNp material is indeed used as precursor, since under H_2 and N_2 atmosphere and 400°C , elimination of 2,2-dimethylbutane and 3,3-dimethylbut-1-yne groups occur to form the catalytically active Mo hydride (MoH_x) species. FTIR measurements (at 75 and 100°C) on this material indicate a peak at 1880 cm^{-1} corresponding to Mo–H stretching modes (see Fig. S5).

Fig. 1a indicates NH_3 production at different temperatures (400 – 550°C) in an experiment carried out during 6 days with temperature changes in intervals of 24 h and atmospheric pressure. NH_3 production rate remains practically constant when operating at a given temperature and this increases when temperature is higher. This reveals a high-stability of the catalytic performance of the MoH_x catalyst, which is also accompanied by a growing accumulated turnover number.

MoNp precursor material is constituted by 2 wt.% of Mo metal and it is assumed that, as always in surface organometallic chemistry (SOMC) methods of preparation, all

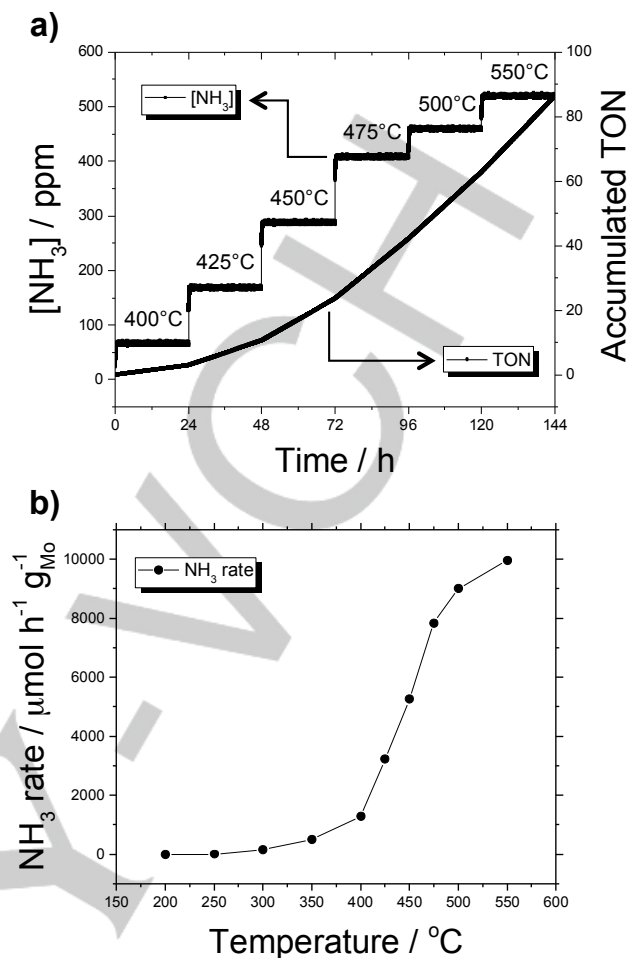


Figure 1. (a) NH_3 production, in ppm, at different temperatures and along 6 days of reaction (in intervals of 24 h) catalysed by 2 wt.% Mo of MoH_x catalyst from MoNp precursor and accumulated turnover number (TON, as the number of moles of product that a mole of catalyst produces in the timeframe of the experiment or before being deactivated); (b) NH_3 rate, in $\mu\text{mol h}^{-1}\text{ g}_{\text{Mo}}^{-1}$, at different temperatures (200 – 550°C) in intervals of 1 h. Note: 200 mg catalyst, total flow-rate of 40 mL min^{-1} , 3:1 $\text{H}_2:\text{N}_2$ ratio, $P = 1\text{ atm}$.

Mo centres act as active sites. Fig. 1b indicates no NH_3 production for temperatures below 300°C , and NH_3 rate of $1276\text{ }\mu\text{mol h}^{-1}\text{ g}_{\text{Mo}}^{-1}$ has been registered at 400°C and atmospheric pressure. Our values can be compared with previous experiments carried out by Ding and co-workers^[18] on supported molybdenum nitrides and carbides with NH_3 rates of 275 , 1124 , and $1195\text{ }\mu\text{mol h}^{-1}\text{ g}_{\text{Mo}}^{-1}$ for $\text{MoN}_x/\text{Al}_2\text{O}_3$, $\text{MoN}_x/\text{ZSM-5}$, and $\text{MoC}_x/\text{ZSM-5}$, respectively. (In their case: 2.17 wt.% Mo, 30 mL min^{-1} total flow-rate, and 400°C , 1 atm, 3:1 $\text{H}_2:\text{N}_2$ ratio operating conditions). A similar NH_3 rate ($1250\text{ }\mu\text{mol h}^{-1}\text{ g}^{-1}$) was recently reported by Hosono and co-workers at similar reaction conditions, despite employing a Co-based material of LaCoSi .^[19] The NH_3 production rate for our MoH_x catalyst derived from MoNp precursor increases to $9955\text{ }\mu\text{mol h}^{-1}\text{ g}_{\text{Mo}}^{-1}$ at the maximum temperature tested of 550°C .

In order to define a model for the elucidation of the mechanistic events taking place during reaction, it should be noticed that, at high temperatures, hydride transfers to neighbouring siloxane bridges occur.^[20] This might lead to the formation of supported bipodal metal hydride species (see Scheme 1). Together with the presence of Mo–H stretching

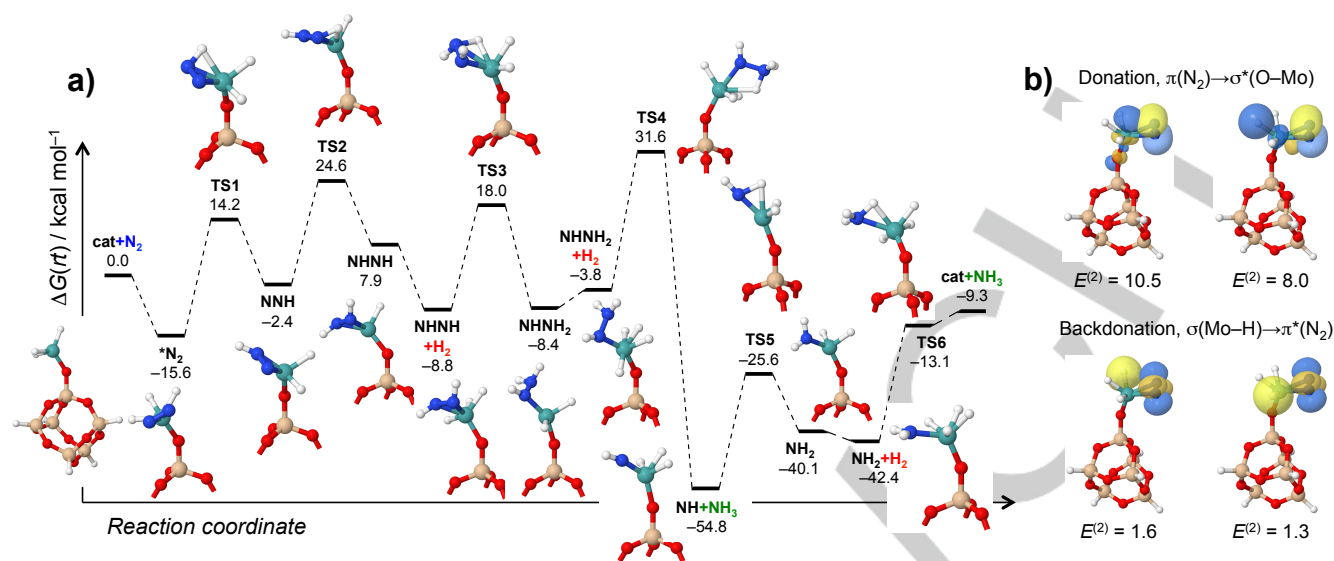


Figure 2. (a) Gibbs free energy profile (room temperature, in kcal mol⁻¹), for N₂-into-NH₃ reaction mechanism catalysed by monopodal [(≡Si-O)Mo^(IV)H₃]. Si₆O₁₀H₅ cluster has been used as silica model. Mo atom is assumed to switch between Mo^(IV) and Mo^(VI) oxidation states during the catalysis. Energy results are shown at the M06/TZVP//PBE/SVP(Si,O,H)/TZVP(Mo) computational level; (b) NBO interpretation, $E^{(2)}$ in kcal mol⁻¹, for donation-backdonation interaction scheme in chemisorbed N₂ on [(≡Si-O)Mo^(IV)H₃] (see Supporting Information for full computational details).

modes in the FTIR spectrum at Fig. S5, this makes us to hypothesise a set of [(≡Si-O)MoH_x] species as potential catalysts to carry out our DFT modelling (see SI for full computational details). In this regard, we contemplate both, the monopodal (Fig. 2) and bipodal (Figs. S8 and S9) scenarios.

For the specific case of monopodal Mo^(IV)-hydride on silica, e.g., [(≡Si-O)MoH₃] as catalytic species, N₂ gas is calculated to be spontaneously chemisorbed on the Mo centre, forming the [(≡Si-O)MoH₃-(η²-N₂)] species with binding Gibbs free energy at room temperature of -15.6 kcal mol⁻¹. An interpretation from the Natural Bond Orbital (NBO) perspective points towards the existence of charge transfer from the occupied π(N₂) orbital to the empty σ*(O-Mo) orbitals, displaying orbital interaction energies of 10.5 and 8.0 kcal mol⁻¹. Obeying a classical donation-backdonation scheme,^[21] synergic interactions from the occupied σ(Mo-H) orbital to the empty π*(N₂) are also seen, with $E^{(2)} = 1.6$ and 1.3 kcal mol⁻¹ (see Fig. 2b). As a result of this, a chemisorbed N₂ molecule experiences an elongation of the N≡N triple bond by 0.09 Å with respect to the isolated molecule in gas phase ($d_{NN} = 1.112$ Å), which activates it for the subsequent hydrogenation steps. This notorious elongation is accompanied by an important redshift in 650 cm⁻¹ of the N≡N stretching vibrational mode.

Based on calculations, we hypothesise that MoH_x on silica catalysing N₂-into-NH₃ conversion follows a non-distal associative mechanistic route^[22] that consists in successive hydrogenations steps. For the specific case of [(≡Si-O)MoH₃], the first hydrogenation step involves one H transfer from Mo in [(≡Si-O)MoH₃-(η²-N₂)] to N₂ in [(≡Si-O)MoH₂-(η²-N=NH)] followed by a second transfer to get [(≡Si-O)MoH-(η²-NHNH)]. These processes involve changes in the oxidation state of Mo, switching from (VI) to (IV) with the intermediacy of (V). Relative activation energies, $\Delta\Delta G_{act}$, for *N₂ state as reference, lie in 29.8 and 40.2 kcal mol⁻¹, in each case. At this stage, the Mo^(IV) centre is assumed to gain one H₂ molecule to follow-up with the reduction process. The further H transfer leads to [Mo]-NHNH₂,

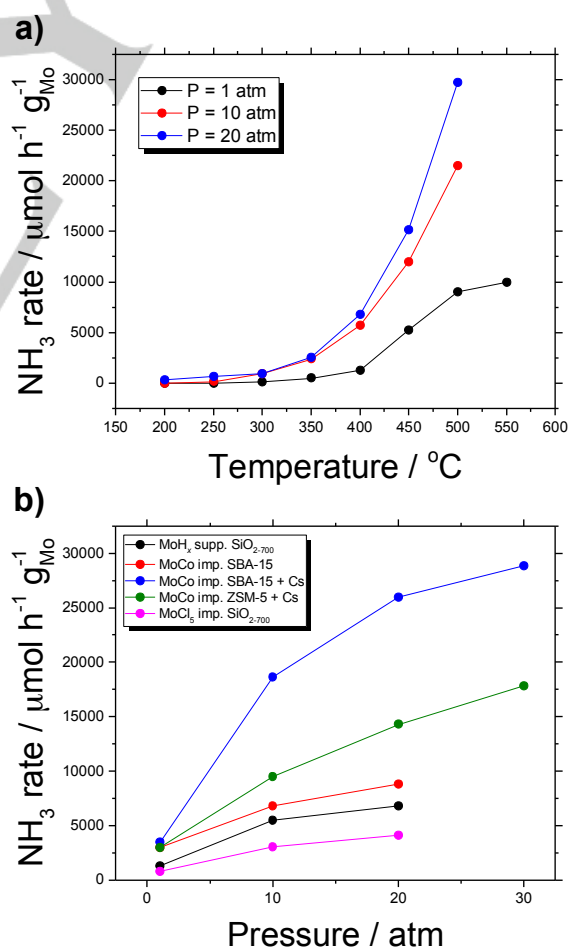


Figure 3. NH₃ rate, in μmol h⁻¹ g_{Mo}⁻¹: (a) at different temperatures (200-550°C) and pressures (1, 10, 20 atm) in intervals of 1 h, catalysed by 2 wt.% Mo of

MoH_x catalyst from MoNp precursor; (b) at different pressures (1–30 atm) and 400°C, catalysed by 2 wt.% MoCo, 1:1 Mo:Co molar ratio, on different supports and in presence of caesium additive. Note: 200 mg catalyst, total flow-rate of 40 mL min⁻¹, 3:1 H₂:N₂ ratio.

and after the gain of a second H₂ molecule, a [Mo]=NH intermediate state is produced with the release of the first NH₃ molecule. Relative activation energies for such steps reach 33.6 and 47.2 kcal mol⁻¹, respectively. The fact that the fourth H transfer from [Mo]-NHNH₂ to give [Mo]=NH (plus one NH₃ molecule released) represents the limiting step of the whole reaction is in contrast with what has been observed for the hydrogenation of N₂ on Ta-hydride supported on silica, but also with the general assumption that the rate-determining step is usually due to the first H transfer.^[23] Amination of the Mo active centre ([Mo]=NH state) entails an energy drop to -54.8 kcal mol⁻¹. The fifth H transfer leads to [Mo]-NH₂ with a relative barrier of 29.2 kcal mol⁻¹. Finally, the introduction of the third H₂ molecule and the subsequent NH₃ elimination with a barrier of 41.7 kcal mol⁻¹ balances the N₂ + 3H₂ → 2NH₃ chemical equation with a reaction energy of -9.3 kcal mol⁻¹ at the M06/TZVP//PBE/SVP(Si,O,H)/TZVP(Mo) computational level (see Supporting Information for full computational details). This is close to the experimental value of -7.8 kcal mol⁻¹ at standard conditions.

An exploration of the mechanism with the monopodal molybdenum *pentakis*-hydride, [(≡Si-O)Mo^(V)H₅], reveals a quite large reaction Gibbs free energy for the first H transfer, 43.8 kcal mol⁻¹, so this reaction path is clearly dismissed. Alternative explorations using bipodal [(≡Si-O)₂Mo^(IV)H₂] and [(≡Si-O)₂-Mo^(IV)H₄] species (see Figs. S8 and S9) reveal very similar energy profiles, with non-spontaneous N₂-sorption (7.1 and 1.2 kcal mol⁻¹), and limiting activation barriers of 47.9 and 45.1 kcal mol⁻¹, respectively, also due to the fourth H transfer, *i.e.*, analogous to TS4 at Fig. 2a.

The effect of pressure in NH₃ rate, Fig. 3a, was also tested for 2 wt.% Mo of MoH_x catalyst from MoNp precursor. In a range of temperatures between 200 and 550°C and different pressures of 1, 10, and 20 atm, an increase of NH₃ production was seen with the pressure, *e.g.*, NH₃ rates at 500°C have been measured experimentally as 9011, 21496, and 29696 μmol h⁻¹ g_{Mo}⁻¹, respectively.

In the search for increased NH₃ rate activities, a new set of catalysts were prepared and tested by incipient aqueous wetness impregnation of different structured supports. In order to prepare impregnated MoCo catalysts, mesoporous silica SBA-15 and lower-cost microporous zeolite ZSM-5 were used and mixed with ammonium heptamolybdate hydrate and cobalt nitrate hexahydrate, with 2 wt.% Mo loading and 1:1 Mo:Co molar ratio. Fig. 3b gathers NH₃ rates at different pressures and 400°C, comparing NH₃ production data by action of these different examined catalysts: i) 2 wt.% Mo of MoH_x catalyst from MoNp precursor supported on silica SiO₂₋₇₀₀ (black); ii) 2 wt.% Mo of MoCo catalyst impregnated on mesoporous silica SBA-15 (red); iii) in microporous zeolite ZSM-5 and in presence of caesium additive (green); and iv) in mesoporous silica SBA-15 and in presence of caesium additive (blue). These catalysts have been systematically tested at 1, 10, 20, and eventually 30 atm of pressure in intervals of 1 h. In addition, 2 wt.% Mo coming from MoCl₅ impregnated on silica SiO₂₋₇₀₀ (violet) has been also prepared and tested for comparison with our well-defined single site catalyst.

According to measurements, the inclusion of cobalt co-catalyst and the use of structured supports increases NH₃ rates. This production growth is especially relevant in the presence of alkali caesium additive, reaching 28356 μmol h⁻¹ g_{Mo}⁻¹ under 30 atm and 400°C operating conditions and using SBA-15 support. (Change of support to ZSM-5 and under the same operating conditions, drops NH₃ rate to 17850 μmol h⁻¹ g_{Mo}⁻¹). In addition, the very low NH₃ rate of impregnated MoCl₅ on silica catalyst confirms the fundamental role played by Co co-catalyst in the N₂ fixation performance. In this sense, we are currently working on bi-metallic well-defined systems with the aim to understand the chemistry of this type of materials.

In summary, a set of molybdenum on solid support materials have been prepared and tested as catalysts for N₂-into-NH₃ conversion *via* chemical hydrogenation. Single-atom Mo-hydrides derived from well-defined, monopodal Mo-neopentyl precursor, [(≡Si-O)Mo(≡C-Bu)(Np)₂], have demonstrated proactive behaviours for NH₃ synthesis at atmospheric pressure and temperatures above 300°C. This material, containing only 2 wt.% Mo, has proven very stable catalytic activities with growing accumulated turnover numbers during operation. The reaction mechanism for N₂-into-NH₃ conversion catalysed by monopodal [(≡Si-O)Mo^(IV)H₃] and bipodal [(≡Si-O)₂Mo^(IV)H₂] and [(≡Si-O)₂Mo^(IV)H₄] species has been studied *via* DFT tools, suggesting maximum relative activation barriers of ca. 45 kcal mol⁻¹. Inclusion of cobalt co-catalyst impregnated on mesoporous SBA-15 support plus alkali caesium additive increases NH₃ rates. Amongst all the studied materials, 2 wt.% Mo of MoCo catalyst (1:1 Mo:Co molar ratio) impregnated on mesoporous silica SBA-15 plus caesium additive have produced ca. 3.5, 19, 26, and 29·10³ μmol h⁻¹ g_{Mo}⁻¹ of NH₃ under 1, 10, 20, and 30 atm of pressure (at 400°C). Finally, we expect that this work would stimulate further interests in order to achieve greater progresses in this hot research topic.

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Keywords: N₂ fixation • NH₃ synthesis • Haber–Bosch alternative • molybdenum-based catalyst • *in-silico* design

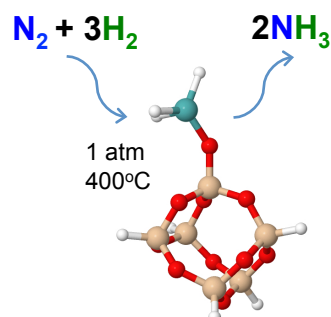
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Table of Contents

COMMUNICATION

N₂-into-NH₃ conversion is one of the most globally important processes in the chemical industry. In this work, we present a set of molybdenum on solid support materials catalysing N₂ fixation under atmospheric pressure accompanied by DFT analysis for an in-depth elucidation of the mechanistic events taking place during reaction

A procedure for catalytic N₂ fixation

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Molybdenum on solid support materials for catalytic hydrogenation of N₂-into-NH₃