A Study of $^{15}\text{N}/^{14}\text{N}$ Isotopic Exchange over Cobalt Molybdenum Nitrides

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ABSTRACT: The $^{14}\text{N}/^{15}\text{N}$ isotopic exchange pathways over Co$_3$Mo$_3$N, a material of interest as an ammonia synthesis catalyst and for the development of nitrogen transfer reactions, have been investigated. Both the homomolecular and heterolytic exchange processes have been studied, and it has been shown that lattice nitrogen species are exchangeable. The exchange behavior was found to be a strong function of pretreatment with ca. 25% of lattice N atoms being exchanged after 40 min at 600 °C after N$_2$ pretreatment at 700 °C compared to only 6% following similar Ar pretreatment. This observation, for which the potential contribution of adsorbed N species can be discounted, is significant in terms of the application of this material. In the case of the Co$_6$Mo$_6$N phase, regeneration to Co$_3$Mo$_3$N under $^{15}\text{N}_2$ at 600 °C occurs concurrently with $^{14}\text{N}^{15}\text{N}$ formation. These observations demonstrate the reactivity of nitrogen in the Co−Mo−N system to be a strong function of pretreatment and worthy of further consideration.

KEYWORDS: nitrogen, isotopic exchange, cobalt molybdenum nitride, ammonia synthesis, heterogeneous catalysis

1. INTRODUCTION

Metal nitrides continue to attract attention as alternative catalysts. Among them, Co$_3$Mo$_3$N has been demonstrated to possess high activity for ammonia synthesis, particularly when promoted with low levels of Cs. Studies of Co$_3$Mo$_3$N have also been undertaken with the aim of determining the possibility of developing novel nitrogen transfer pathways, wherein the “lattice” N can be used as an activated form of nitrogen with the potential to undergo reaction with suitable target molecules. This could lead to interesting developments in the identification of new transformation pathways. As part of these studies, the formation of Co$_6$Mo$_6$N, a previously unreported nitride with the η-12 carbide structure, has been documented to occur when undertaking reduction with a 3:1 H$_2$:Ar feed at elevated temperature. The transformation is shown to occur between Co$_3$Mo$_3$N and Co$_6$Mo$_6$N line phases with no intermediate stoichiometries apparently being evident. The presence of hydrogen has been demonstrated to be essential in order for the transformation to occur, despite the observation that the nitrogen which is eliminated from the structure predominantly, but not exclusively, forms N$_2$. The regeneration of Co$_6$Mo$_6$N from the reduced Co$_3$Mo$_3$N phase has been observed to be rapid when applying a 3:1 H$_2$:N$_2$ feed and is also possible with pure N$_2$, albeit requiring higher temperatures and longer regeneration times. In the present communication, we extend the previous studies of this system by applying a series of temperature programmed nitrogen isotopic exchange (TPNIE) and isothermal nitrogen isotopic exchange (INIE) experiments. The isotopic exchange technique is well established for reactions of oxygen isotopes with metal oxide and metal oxide supported systems. In such studies, two general reaction types have been investigated:

(i) homomolecular exchange in which a mixture of labeled oxygen molecules, typically $^{18}\text{O}_2$ and $^{16}\text{O}_2$, is scrambled over a surface, and

(ii) heterolytic exchange in which a labeled molecule, typically $^{18}\text{O}_2$, is scrambled with the “lattice” oxygen species of the catalyst (generally $^{16}\text{O}$ species as dictated by the relative abundance of the various oxygen isotopes).

Historically, examples of nitrogen isotopic exchange can be found in the literature, where examples of gas-phase equilibration of $^{14}\text{N}_2/^{15}\text{N}_2$ mixtures have been reported on catalytic systems of interest for ammonia synthesis, most notably those based upon Fe, Ru, and Os. The results of such studies send a cautionary note in terms of their direct applicability as probes of ammonia synthesis activity in which N$_2$ activation is generally rate limiting. With the latter point in mind, it may be anticipated that the relative N$_2$ exchange rate could be directly related to NH$_3$ synthesis activity. However, in
some systems the simultaneous presence of H₂ in the gas phase is observed to enhance the isotopic scrambling rate, whereas in others it is observed to suppress it. Examples of each type of behavior can be found in closely related systems. For example, in the case of Ru, hydrogen enhances equilibration rate whereas in the case of potassium promoted systems it retards it.²⁹

Despite the limitations of N₂ exchange as a method to evaluate ammonia synthesis reaction activity, it is nevertheless a suitable and direct probe reaction with which to monitor the reactivity of "lattice" nitrogen species. Accordingly, we have undertaken studies involving both homomolecular and heterolytic nitrogen exchange pathways, with the aim of characterizing the reactivity of nitrogen (both gas-phase and "lattice") in terms of the cobalt molybdenum nitride system. To our knowledge, this is the first time that such studies have been reported for Co₃Mo₃N.

2. EXPERIMENTAL SECTION

2.1. Materials. The procedure applied for the preparation of Co₃Mo₃N has been documented in detail elsewhere.₁¹,₁₃,₁₄ In summary, a hydrated cobalt molybdate precursor was prepared and subjected to ammonolysis applying a carefully controlled temperature ramp rate. The sample was then cooled to ambient temperature under ammonia prior to being subjected to a passivation procedure enacted to facilitate removal from the preparation apparatus. The resultant sample was subsequently reactivated in a flow of 3:1 H₂:N₂ for 2 h at 700 °C to yield the crystalline Co₃Mo₃N phase. The purity of the phase was evaluated by powder X-ray diffraction (XRD) with a PANalytical Empyrean instrument, using Cu Kα radiation (λ = 0.154 nm) as the X-ray source. Data were collected in the range 5° ≤ 2θ ≤ 85° (step time = 1 s; step size = 0.017° 2θ). The surface area was determined by applying the Brunauer–Emmett–Teller (BET) method to the nitrogen physisorption isotherm obtained at −196 °C, in a Micromeritics equipment TRISTAR 3000 analyser. The nitride sample (0.3 g) was first heated up to 250 °C for 2 h under vacuum and degassed at 250 °C for 2 h prior to analysis.

2.2. Nitrogen Isotopic Exchange. Nitrogen isotopic exchange experiments were performed in a setup already described in oxygen isotopic exchange studies.₁⁶,₂² 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 the monitoring of 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. TPNIE and INIE experiments were undertaken on 200 mg of Co₃Mo₃N. The Co₃Mo₃N sample was additionally subjected to a 3:1 H₂:N₂ activation step at 700 °C for 1 h prior to cooling to either 400 °C for TPNIE or to various desired temperatures (see Results and Discussion) for INIE, at which point the system was purged (using vacuum and/or argon flow) and the isotopic mixture charged. Other protocols have also been used and will be described later in the text. The study of homolytic exchange (also called equilibration reaction) was performed using a mixture of ¹⁴N₂ and ¹⁵N₂ (98% + purity, supplied by Cambridge Isotope Laboratories, Inc.) whereas, for the study of the heterolytic exchange, the equimolar mixture was replaced by ¹⁵N₂ alone. A ramp rate of the temperature was 2 °C/min was used for TPNIE experiments. The masses 28, 29, and 30 m/z were monitored as a function of time to follow the exchange. 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 presence of NO and O₂ was also checked by monitoring the corresponding m/z values. The method by which the atomic fraction of ¹⁵N in the gas phase (αₑ) and the number of atoms exchanged (Nₑ) can be calculated is described in previous references.₁⁶,₁₇ Typically:

\[
\alpha_e = \frac{P_{30} + \frac{1}{2}P_{29}}{P_{30} + P_{29} + P_{28}}
\]

where P₃₀, P₂₉, and P₂₈ are the partial pressures of ¹⁵N₂, ¹⁴N¹⁵N, and ¹⁴N₂ respectively;

\[
N_e = N_\alpha (1 - \alpha_e)
\]

for heterolytic exchange where Nₑ is the number of ¹⁵N atoms in the gas phase at the beginning of the reaction. Finally the number of exchangeable atoms can be calculated when equilibrium between the gas phase and the solid is reached by using:

\[
N_i = \frac{N_e}{\alpha^*} = N_i \left[ 1 - \frac{1}{\alpha^*} \right]
\]

where αᵢ is the value of αₑ at equilibrium.

3. RESULTS AND DISCUSSION

3.1. Homomolecular versus Heterolytic Exchange over the Co₃Mo₃N Phase. Figure 1 shows the XRD pattern of the sample after treatment under a 3:1 H₂:N₂ flow at 700 °C for 2 h. In agreement with previous studies in which such a treatment was applied,¹⁴ the diffractogram matches to a pure Co₃Mo₃N phase (hereafter abbreviated as the 331 phase).

This material, which has a very low BET surface area (less than 5 m²/g) was subjected to nitrogen isotopic exchange. Taken together with the powder X-ray diffraction pattern in Figure 1 in which there is no evidence of any great degree of disorder, it is reasonable to suppose that the majority of nitrogen species are located within the bulk. In the first set of experiments, we studied the capacity of the 331 phase to activate the dinitrogen molecule via homomolecular exchange by using the TPNIE and INIE techniques. The results of the TPNIE experiment are shown in Figure 2a, in which it can be seen that there is a decrease in the partial pressure of ¹⁵N₂ as a function of increasing temperature during which the partial pressures of both ¹⁴N¹⁵N and ¹⁴N₂ increase. Closer inspection of the profile (Figure 2b) demonstrates the formation of ¹⁴N¹⁵N starts to become evident at ca. 450 °C.
In order to ascertain whether, at this temperature, formation occurs by homomolecular exchange \(14N_2(g) + 15N_2(g) \rightleftharpoons 2 14N15N(g)\) or heterolytic exchange \(15N_2(g) + 14N(s) \rightarrow 14N15N(g) + 15N(s)\), INIE of the \(14N_2/15N_2\) mixture was undertaken at 450 °C and the gas-phase \(15N\) concentration was quantified as a function of reaction time. The results are presented in Figure 3, where it can be seen that there is a progressive diminution of the partial pressure of \(15N_2\) during which the partial pressure of \(14N15N\) increases while the partial pressure of \(14N_2\) is constant. Finally the progressive reduction of the \(15N\) gas-phase atomic fraction as the reaction proceeds is indicative of the heterolytic pathway in which \(14N\) is supplied by the 331 phase. Pure equilibration is not detected for the 331 phase, suggesting that the material is not able to adsorb the dinitrogen molecule dissociatively.

The capacity of the 331 phase for exchange was then studied by performing TPNIE analysis between 450 and 700 °C introducing only \(15N_2\) (66.7 mbar) into the reactor cell at the beginning of the experiment. Figures 4a and 4b illustrate the evolution of the gas-phase \(15N\) atomic fraction (abbreviated hereafter as \(\alpha_g\)) and the progressive accumulation of exchanged \(N\) atoms (abbreviated hereafter as \(N_e\)) as a function of time, which corresponds to an increase of temperature. At the end of the experiment, after 30 min at 700 °C, the values of \(\alpha_g\) and \(N_e\) remain almost the same, which indicates that a gas/solid equilibrium is reached. At this stage, the value of \(N_e\) normalized per gram of solid \((49.5 \times 10^{19} N\) atoms\) corresponds to 40% of the lattice nitrogen atoms in the 331 phase. The value \(\alpha_g\) achieved at the equilibrium \((\alpha_g = 0.50)\) permits the calculation of the number of exchangeable atoms in the solid as explained in ref 16. It indicates that 80% of the nitrogen atoms in the 331 phase lattice are exchangeable. It is worth noting that all of these values are subject to some uncertainties since we observed a small increase of pressure as a function of increasing temperature, which was partly due to the presence of \(H_2\). One potential source of \(H_2\) is from \(NH_2\) surface species known to be present in nitrides prepared by ammonolysis and/or pretreated with \(N_2/H_2\).14,23,24

When a similar TPNIE experiment as above was performed in which \(Ar\) was substituted for \(15N_2\), we noticed a steady increase of the \(m/z = 2\) and 28 intensities (typically amounting to 3.5 mbar of \(H_2\) and 5 mbar of \(N_2\) respectively at 700 °C) as...
the temperature increased. In experiments reported elsewhere it has been shown that the production of NH$_3$ by Ar/H$_2$ treatment of a Co$_3$Mo$_3$N sample purposefully treated so as to eliminate the contribution of NH$_x$ species is much less than that of a comparable sample containing NH$_x$. Powder neutron diffraction experiments show no evidence of bulk hydride phases in this system, although there is the possibility of surface hydride phases. Here we demonstrate that part of the residual NH$_x$ species, which are not decomposed when the sample undergoes degassing at 450 °C.

3.2. Effect of the Nature of the Gas Purge. In order to assess the importance of NH$_x$ species in the present study, a high temperature (700 °C, 30 min) Ar purge of the sample pretreated with 3:1 H$_2$:N$_2$ flow was undertaken. The sample was then cooled under Ar at 600 °C and degassed under a secondary vacuum (less than 10$^{-5}$ mbar). The Co$_3$Mo$_3$N phase should be stable in the bulk under these conditions (even if very little reduction was observed to occur during the previous temperature-programmed experiment under Ar noted above). However, it could be anticipated that desorption or decomposition of residual NH$_x$ occurs at the surface of the nitride. INIE of $^{15}$N$_2$ was undertaken at 600 °C (Figure S5) demonstrating that the heterolytic exchange process occurs to a limited extent. This suggests that the behavior apparent in Figures 2 and 4 predominantly arises from exchange with or via surface NH$_x$ groups. We simultaneously observed a slight decrease of the total pressure in the system, confirming that a low level of reduction occurs due to the Ar purge and secondary vacuum degassing treatment. In order to generate NH$_x$ species, which would have been removed under Ar at 700 °C, we introduced a low partial pressure of H$_2$ (2.3 mbar) during the exchange process at 600 °C. The presence of H$_2$ did not induce any change in the evolution of the isotopomer nitrogen curves, meaning that surface NH$_x$ species, if produced under these conditions, do not play the role of an intermediate in the exchange mechanism (Figure S1 in the Supporting Information).

When an Ar purge is replaced by an He purge treatment, the result is worse since no exchange is observed. On the contrary, the behavior of the material totally changes when an Ar purge at 700 °C is replaced by a $^{14}$N$_2$ purge step. The results of the subsequent $^{15}$N$_2$ INIE experiment are presented in Figure 6a, in which it can be seen that there is a drastic diminution of the partial pressure of $^{15}$N$_2$. Simultaneously the partial pressures of $^{14}$N$^{15}$N and to lesser extent of $^{14}$N$_2$ increase. To ascertain that surface NH$_x$ species have been effectively removed after the N$_2$ purge, we successively purged the material at 700 °C with Ar and N$_2$ respectively for periods of 30 min each. The INIE curves taken at 600 °C after the introduction of $^{15}$N$_2$ (Figure 6b) demonstrate that the heterolytic exchange, which is still very important, does not arise from the exchange of NH$_x$ but results from the reactivity of lattice nitrogen. It also implies that the nature of the gas utilized for the purge considerably influences the reactivity of the lattice nitrogen. It is worth noting that, to be active in exchange reactions, the material has to be treated under N$_2$ at 700 °C since the same purge at 600 °C of a sample previously purged under He at 700 °C does not improve the reactivity of the nitrogen atoms toward exchange.

Another experiment (Figure S2 in the Supporting Information) demonstrated that the addition of a low pressure of H$_2$ to the $^{15}$N$_2$ stream does not modify the exchange process. Finally a temperature-programmed desorption experiment (Figure S3 in the Supporting Information) was performed on a Co$_3$Mo$_3$N sample treated with an N$_2$ purge at 700 °C and degassed at 600 °C prior to being cooled down to 400 °C. A pressure of 50 mbar of Ar was charged in the system, and the temperature was increased up to 700 °C. We observed a slight increase of the $m$/
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The extent of this activity is highly dependent on the pretreatment. This behavior could be attributed to the participation of the lattice nitrogen atoms in a catalytic cycle via a Mars–van Krevelen mechanism. At the beginning of the INIE experiments, a small decrease of the pressure in the system is observed, meaning that a small degree of reduction of the 331 phase would occur during the pretreatment (even under a nitrogen purge). It is therefore relevant to study the behavior of the reduced Co₆Mo₆N phase in exchange.

3.3. Behavior of the Co₆Mo₆N Phase. It is of interest to draw comparisons between the behavior of Co₃Mo₃N (331 phase) with that of Co₆Mo₆N. Accordingly, a sample of Co₆Mo₆N (hereafter denoted as the 661 phase) was prepared by reduction of the 331 phase with 3:1 H₂:Ar at 700 °C. The 331 phase is known to reduce to the 661 phase under these conditions. Following reduction, the system was purged with Ar at 700 °C to remove residual NH₃ groups and then, following evacuation under secondary vacuum, 50 mbar of N₂ was admitted. It can be anticipated that such a pretreatment should preserve the 661 phase at the beginning of the INIE experiment. The results of the subsequent INIE experiment are shown in Figure 7, in which it can be seen that there is a rapid loss of N₂ which is offset by the production of N₂ and N₂. In parallel, a strong loss of the pressure in the system is observed to occur as the reaction proceeds. This strong loss, explained by the regeneration of the 331 phase from the reduced 661 phase as already reported in a previous study, is quantified and reported in Table 1 (right column); 33.3 mbar of N₂ was consumed by the material after 20 min. This corresponds to 40% of the number of N atoms that compose the 331 phase, meaning that almost all of the sample was in the reduced form. The N₂ atomic fraction obtained at 40 min (%): ratio between the number of N atoms from the gas phase that exchanged with the solid and the number of N atoms in the material (considering the 331 phase).

Table 1. Comparison of the Activity to Exchange for Co–Mo–N Materials in INIE Reactions Using Different Pretreatments

| Pretreatment | H₂:N₂ (3:1) 700 °C/Ar 700 °C (30 min) | H₂:N₂ (3:1) 700 °C/N₂ 700 °C (30 min) | H₂:N₂ (3:1) 700 °C/Ar 700 °C (30 min) | H₂:N₂ (3:1) 700 °C/Ar 700 °C (30 min) |
|--------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Temp of exchange (°C) | 600 | 600 | 600 | 700 |
| 15N pressure introduced (mbar) | 55.6 | 55.1 | 55.0 | 53.0 |
| Total pressure at 40 min (mbar) | 51.4 | 48.5 | 52.3 | 19.7 |
| α₁ at 40 min (%) | 90.5 | 53.8 | 62.7 | 84.5 |
| 15N exchanged at 40 min (%) | 1.45 | 4.58 | 3.55 | 5.75 |
| 15N exchanged/N_total331 at 40 min (%) | 11 | 36 | 28 | 46 |
| 15N exchanged/N_total331 at 40 min (%) | 6 | 28 | 25 | 6 |

aα₁ at 40 min (%), 15N atomic fraction at 40 min calculated as explained in the Experimental Section. b15N exchanged at 40 min: number of 15N atoms that disappeared from the gas phase calculated from the α₁ value at 40 min and normalized per gram of Co₆Mo₆N material. c15N exchanged/N_total331 at 40 min (%): ratio between the number of 15N atoms that disappear from the gas phase and the number of N atoms present in the material (considering the 331 phase). d15N exchanged/N_total331 at 40 min (%): ratio between the number of 15N atoms from the gas phase that exchanged with the solid and the number of N atoms in the material (considering the 331 phase).

z = 28 intensity above 550 °C (typically amounting to 1 mbar of N₂ at 700 °C).

A quantification of the amount of nitrogen atoms exchanged depending on the pretreatment procedure of the material is presented in Table 1. After 40 min of reaction, the atomic fraction, α₁, of gas-phase 15N was 90.5% when the 331 phase was purged under an Ar flow and 53.8% when N₂ was used as the purge gas. The combination of the α₁ value with the comparison between the initial pressure of 15N₂ introduced and the total pressure measured at 40 min allows the calculation of the number of 15N atoms that are no longer present in the gas phase. This number amounts to 1.45 × 10²⁰ atoms, corresponding to 11% of the number of N atoms present in the 331 phase when Ar is the purge gas versus 4.58 × 10²⁰ atoms corresponding to 33% of the number of N atoms present in the 331 phase when Ar is replaced by N₂ as the purge gas. The decrease between the initial pressure and the pressure at 40 min could be tentatively explained by a regeneration of the 331 phase from the 331 phase that was partially reduced during the pretreatment, meaning that almost all of the sample was in the reduced form. The 15N atomic fraction obtained at 40 min (%): ratio between the number of 15N atoms that are no longer present in the gas phase and the number of N atoms in the material (considering the 331 phase). Such a value obtained at 700 °C shows that the Co₃Mo₃Nc a n

ACS Catal.

dx.doi.org/10.1021/cs400336z | ACS Catal. 2013, 3, 1719–1725

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when the solid was preactivated under H2/N2: (i) the end of the heterolytic exchange reaction (indicated by the plateaus in the curves of the distribution of the respective nitrogen isotopomers) is concomitant with the end of the regeneration (indicated by the plateau observed in the curve of the total pressure); (ii) the production of 14N2 remains almost null during the reaction, meaning that only simple heterolytic exchange occurs. We suggest that the 661 phase is able to activate the gas-phase dinitrogen by dissociation of the molecule into the “vacancies” of the reduced phase. Then exchange and regeneration simultaneously take place to generate a Co3Mo3N material, which is homogenously composed of 14N and 15N atoms. The exchange process is then stopped, meaning that a gas/solid equilibrium is reached.

The results reported in Figures 6 and 7 suggest that the N2 purge was able to create (or to preserve) preferential sites for the dissociative chemisorption of the 15N2 molecules, which is the limiting step of the exchange process.

In the ammonia synthesis reaction, the presence of an H2 reducing agent in large excess in the reactant flow would be crucial for the generation of “lacunary” sites or to generate preferential sites allowing the activation of dinitrogen. Thus, our study seems to demonstrate the possible existence of the Mars–van Krevelen mechanism with participation of bulk nitrogen atoms. It brings new elements with respect to the classical model described for the ammonia synthesis in industrial catalysts based on Ru and Fe.25 We should take into account that the standard temperature for NH3 synthesis is around 400 °C and the effects observed with isotopic exchange are in the range of 600 °C. Nevertheless we observed during the TPNIE experiment that exchange occurred before 450 °C (Figure 2) and the reactivity temperature could also be influenced by the unusual conditions of the isotopic exchange (low total pressure).

4. CONCLUSION

Nitrogen isotopic exchange was applied for the first time to the cobalt molybdenum nitride system with the aim of characterizing the reactivity of nitrogen (both gas-phase and “lattice”). Pure homomolecular exchange in which a mixture of 14N2 and 15N2 molecules is scrambled over a surface did not occur, indicating the low ability of the cobalt molybdenum nitride system for N2 dissociation. The heterolytic exchange in which the 15N2 is scrambled with the lattice nitrogen atoms was observed from 450 °C during the TPNIE experiment when the Co3Mo3N was subjected to 3:1 H2:N2 pretreatment until 700 °C followed by a degassing at 400 °C. Such a pretreatment did not permit us to exclude the participation of the surface adsorbed –N (or NHx) species in the exchange mechanism. Further purging (with Ar or 14N2) of the sample pretreated with 3:1 H2:N2 flow was undertaken with the aim to obtain a –N or NHx free surface for the exchange. At 700 °C, treatment of the 331 phase with an argon purge strongly inhibited the ability of the solid to exchange with the gas phase contrary to a nitrogen purge, although both types of purge resulted in the absence of surface adsorbed species. The behavior of the 661 phase was also checked by treating the solid with a 3:1 H2:Ar flow at 700 °C followed by an Ar purge at the same temperature. It confirmed that the process of N-loss/replenishment is fully reversible, as described in previous work using in situ XRD, and that the Co3Mo3N catalyst can be readily regenerated with N2 alone. The 661 phase was shown to be active in the exchange at 600 °C with a strong initial rate of exchange (comparable to the one observed for the 331 phase when the solid was purged with N2 flow) but to a lower extent in terms of number of exchanged atoms. The different exchange behavior in all these experiments was tentatively explained by a difference in the gas-phase dinitrogen activation that would require the presence of preferential sites such as vacancies in the nitride. The reactivity of the lattice nitrogen atoms with gas phase nitrogen was demonstrated, raising the idea of the possible occurrence of the Mars–van Krevelen mechanism in the ammonia synthesis reaction over this family of catalysts.

ASSOCIATED CONTENT

Supporting Information

Complementary INIE experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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J.S.J.H. and D.H.G. would like to acknowledge the School of Chemistry, University of Glasgow, and the EPSRC for the award of a DTA studentship to S.M.H.

REFERENCES

(1) Furimsky, E. Appl. Catal. A: Gen. 2003, 240, 1–28.
(2) Nagai, M. Appl. Catal. A: Gen. 2007, 322, 178–190.
(3) Hargreaves, J. S. J.; Mckay, D. Catalysis; Spivey, J. J., Dooley, K. M., Eds.; RSC: London, 2006; Vol. 19, p 84.
(4) Alexander, A.-M.; Hargreaves, J. S. J. Chem. Soc. Rev. 2010, 39, 4388–4401.
(5) Hargreaves, J. S. J. Coord. Chem. Rev. 2013, 257, 2015–2031.
(6) Jacobsen, C. J. H. Chem. Commun. 2000, 1057–1058.
(7) Kojima, R.; Aika, K.-I. Appl. Catal. A: Gen. 2001, 215, 149–160.
(8) Kojima, R.; Aika, K.-I. Appl. Catal. A: Gen. 2001, 218, 121–128.
(9) Kojima, R.; Aika, K.-I. Appl. Catal. A: Gen. 2001, 219, 157–170.
(10) Boisen, A.; Dahl, S.; Jacobsen, C. J. H. J. Catal. 2002, 208, 180–186.
(11) Mckay, D.; Gregory, D. H.; Hargreaves, J. S. J.; Hunter, S. M.; Sun, X.-L. Chem. Commun. 2007, 30513053.
(12) Mckay, D.; Hargreaves, J. S. J.; Rico, L.; Rivera, J. L.; Sun, X.-L. J. Solid State Chem. 2008, 181, 325–333.
(13) Hargreaves, J. S. J.; Mckay, D. J. Mol. Catal. A: Chem. 2009, 305, 125–129.
(14) Hunter, S. M.; Mckay, D.; Smith, R. I.; Hargreaves, J. S. J.; Gregory, D. H. Chem. Mater. 2010, 22, 2898–2907.
(15) Gregory, D. H.; Hargreaves, J. S. J.; Hunter, S. M. Catal. Lett. 2011, 141, 22–26.
(16) Martin, D.; Duprez, D. J. Phys. Chem. 1996, 100, 9429–9438.
(17) Duprez, D. In Isotopes in Heterogeneous Catalysis; Hargreaves, J. S. J., Jackson, S. D., Webb, G., Eds.; Imperial College Press: London, 2006; Chapter 6, p 133.
(18) Joris, G. G.; Taylor, H. S. J. Chem. Phys. 1939, 7, 893–898.
(19) Urabe, K.; Aika, K.-I.; Ozaki, A. J. Catal. 1976, 42, 197–204.
(20) Ogata, Y.; Aika, K.-I.; Onishi, T. J. Catal. 1988, 112, 469–477.
(21) Guyer, W. R. F.; Joris, G. G.; Taylor, H. S. J. Chem. Phys. 1941, 9, 287–294.
(22) Ojala, S.; Bion, N.; Rijo Gomes, S.; Keiski, R. L.; Duprez, D. ChemCatChem 2010, 2, 527–533.
(23) Wei, Z. B.; Xin, Q.; Grange, P.; Delmon, B. J. Catal. 1997, 168, 176–182.
(24) Hada, K.; Nagai, M.; Omi, S. J. Phys. Chem. B 2000, 104, 2090–2098.
(25) Jacobsen, C. J. H.; Dahl, S.; Clausen, B. S.; Bahn, S.; Logadottir, A.; Norskov, J. K. J. Am. Chem. Soc. 2001, 123, 8404–8405.