

Amides

Transition and Alkali Metal Complex Ternary Amides for Ammonia Synthesis and Decomposition

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Abstract: A new complex ternary amide, Rb₂[Mn(NH₂)₄], which simultaneously contains both transition and alkali metal catalytic sites, is developed. This is in line with the recently reported TM-LiH composite catalysts, which have been shown to effectively break the scaling relations and achieve ammonia synthesis under mild conditions. Rb₂[Mn(NH₂)₄] can be facilely synthesized by mechanochemical reaction at room temperature. It exhibits two temperature-dependent polymorphs, that is, a low-temperature orthorhombic and a high-temperature monoclinic structure. Rb₂[Mn(NH₂)₄] decomposes to N₂, H₂, NH₃, Mn₃N₂, and RbNH₂ under inert atmosphere; whereas it releases NH₃ at a temperature as low as 80 °C under H₂ atmosphere. Those unique behaviors enable $Rb_2[Mn(NH_2)_4]$, and its analogue K₂[Mn(NH₂)₄], to be excellent catalytic materials for ammonia decomposition and synthesis. Experimental results show both ammonia decomposition onset temperatures and conversion rates over $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ are similar to those of noble metal Ru-based catalysts. More importantly, these ternary amides exhibit superior capabilities in catalyzing NH₃ synthesis, which are more than 3 orders of magnitude higher than that of Mn nitride and twice of that of Ru/ MgO. The in situ SR-PXD measurement shows that manganese nitride, synergistic with Rb/KH or Rb/K(NH₂)_xH_{1-x}, are likely the active sites. The chemistry of Rb₂/K₂[Mn(NH₂)_x] and Rb/K(NH₂)_xH_{1-x} with H₂/N₂ and NH₃ correlates closely with the catalytic performance.

Inorganic metal amides have attracted increasing attention as potential hydrogen storage materials $^{\left[1\right] }$ and ammonia decom-

position catalyst precursors.^[2] Among them, ternary alkali metal transition metal amides $(A[M(NH_2)_X], A = alkali metal, M = transition metal)$ such as $A_2[Mn(NH_2)_4]^{[3]}(A = Na, K)$ and $A_2[Zn(NH_2)_4]$ (A = K, Rb, Cs)^[3b,4] are important intermediates for hydrogen storage^[5] and the synthesis of transition metal nitrides (TMNs).^[6] In general, transition metal amides are synthesized by ammonothermal reaction,^[6] and the formation process needs high pressures, high temperatures, and long reaction times. For instance, monoclinic ($P2_1/c$) K₂[Zn(NH₂)₄] was synthesized by reaction of metallic Zn and KNH₂ at 450 °C and 249 MPa of NH₃ for more than 7 days [Reaction 1, Eq. (1)].^[7]

$$2 \operatorname{KNH}_2 + \operatorname{Zn} + 2 \operatorname{NH}_3 \to \operatorname{K}_2[\operatorname{Zn}(\operatorname{NH}_2)_4] + \operatorname{H}_2 \tag{1}$$

Very recently, we have produced K₂[Zn(NH₂)₄] and K₂[Mn(NH₂)₄] by one-pot mechanochemical reaction at room temperature (RT) for the first time. After mixing them with LiH, they show excellent hydrogenation properties, for example, both can absorb about 3 wt.% of H₂ within 1 min under 50 bar of H₂ at 230 °C. Upon heating to 500 °C under vacuum, K₂[Mn(NH₂)₄]-8LiH converts to an excellent electrode material Li₇[MnN₄] and Mn₄N.^[5b] This shows a new route to synthesize TMNs. TMNs can also be prepared upon heating ternary transition amides individually, for example, the Li₄[Zn(NH₂)₄](NH₂)₂ turns into LiNH₂/Li₂NH and LiZnN upon heating.^[8]

Apart from the applications in hydrogen storage and producing transition metal nitrides, ternary transition metal amides may also be used in other areas such as ammonia synthesis and decomposition. Having both transition metals and alkalis, the ternary amides ($A[M(NH_2)_x]$) contain key elements of catalysts that are widely applied in catalytic ammonia synthesis and decomposition, where TM is the active metal and A is the promoter. Moreover, it is well known that in both ammonia de-

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composition and synthesis, NH_x (x = 0, 1, and 2) species are the key intermediates on the transition metal surfaces.^[9] And it also has been proposed that a surface metal amide or imide (-NH₂ or -NH) may be the abundant species with the presence of alkalis.^[10] In the structure of ternary transition metal amides, for example, K₂[Mn(NH₂)₄] and Na₂[Mn(NH₂)₄], the -NH₂ moiety is coordinated with both alkali and manganese cations, $^{\scriptscriptstyle [3a,4a,7]}$ which resembles the micro environment of NH_x adsorbed on transition metal surfaces. Meanwhile, structures of transition metal amides can also be stabilized by the addition of alkali metals. Having TM, A, N, and H, ternary amides genetically have linkage to the catalysis of ammonia decomposition and synthesis. However, to the best of our knowledge, such an application has not yet to be explored. Therefore, it would be interesting to investigate the role of the ternary transition metal amides in catalyzing ammonia decomposition, as well as the more important ammonia synthesis process.

In this work, a new ternary manganese amide, $Rb_2[Mn(NH_2)_4]$, was successfully synthesized for the first time

by ball milling rubidium and manganese in the molar ratio of 2:1 under an NH₃ atmosphere. Rb₂[Mn(NH₂)₄] exhibits two different crystalline structures depending on the application temperatures. The possibility of using Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] for catalytic ammonia decomposition and synthesis was investigated.

Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] were prepared by ball milling Mn and Rb/K metals in a molar ratio of 1:2 at RT under 0.7 MPa of NH₃ for 12 h. The crystal structure, as well as the thermal decomposition reaction path of the as-synthesized Rb₂[Mn(NH₂)₄] were investigated through in situ synchrotron radiation PXD (SR-PXD) under static vacuum (Figure 1a). From the diffraction patterns, the crystal structure of the starting material can be solved using an orthorhombic cell (space group *Pbca*, No.61) with lattice parameters of *a*=7.2183(4), *b*= 10.7474(6), *c*=18.3155(10) Å, and *V*=1420.88(19) Å³ (low temperature phase: LT-phase (Figure 1 b). After heating to about 156 °C LT-Rb₂[Mn(NH₂)₄] converts to a high temperature phase (HT-phase), which is assigned to a monoclinic structure (*P*2₁/*c*,



Figure 1. a) In situ SR-PXD measurement of $Rb_2[Mn(NH_2)_4]$ under static vacuum. The sample was heated from RT to 420 °C with a heating rate of 10 °C min⁻¹ and then it was kept at 420 °C for 10 min before cooling down to RT. b) Low-temperature crystal structure (100) view of $Rb_2[Mn(NH_2)_4]$ (56 °C) and c) high-temperature crystal structure (010) view of $Rb_2[Mn(NH_2)_4]$ (156 °C). The $[Mn(NH_2)_4]^{2-}$ tetrahedra are highlighted in blue. The solid red lines connecting the centers of $[Mn(NH_2)_4]^{2-}$ tetrahedra (i.e. Mn atoms) are visual aids and have no other significance. d) Ar-TPR, and e) H₂-TPR curves of $Rb_2[Mn(NH_2)_4]$, heated from 30 to 470 °C with a heating rate of 5 °Cmin⁻¹, under 50 mLmin⁻¹ argon and hydrogen flows, respectively. f) TG-DTA curves of $Rb_2[Mn(NH_2)_4]$, heated from 30 to 470 °C with a heating rate of 5 °Cmin⁻¹, under 50 mLmin⁻¹ argon flow.

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No.14) with lattice parameters of: a = 7.8536(5), b = 6.9449(5), c = 13.8411(11) Å, $\beta = 106.389(7)^{\circ}$, and V = 724.24(12) Å³ (Figure 1 c). In both crystal structures Mn^{2+} is tetrahedrally coordinated by four NH_2^{-} , forming $[Mn(NH_2)_4]^{2-}$ complex anions. These complex anions then arrange in different anion arrays in LT and HT phases and Rb⁺ cations are located in the cavities between these complex anions. Corresponding Rietveld fits are shown in Figure S1 and S2 in Supporting Information. About 4.57 wt.% of cubic RbNH₂ is also detected along with Rb₂[Mn(NH₂)₄] at temperatures below 210°C (Figure S2). The detected phases are Mn₃N₂ and a Rb-based solid solution $(Rb(NH_2)_xH_{1-x})$ in the temperature range from 210 to 330 °C (Figure 1 a). The $Rb(NH_2)_xH_{1-x}$ is most likely formed (Figure S3) similarly to the reaction of xKNH₂-(1-x)KH,^[11] the detailed results will be given in a separate paper. The formation of amide-hydride solid solution may play a role in catalyzing ammonia synthesis, which will be discussed later. After cooling down to 45 °C, the final products are cubic RbNH₂, metallic Rb, and Mn₃N₂.

Temperature-programmed-reaction (TPR) for the as-synthesized Rb₂[Mn(NH₂)₄] was carried out under Ar and H₂ flows; the released gaseous products were recorded by a mass spectrometry (MS) (Figure 1 d and e). Three MS events are observed at around 210, 330, and 440 °C in Ar-TPR (Figure 1 d). NH₃, N₂, and H₂ co-exist in the first MS peak, however, only a slight trace of NH₃ can be detected in the second and the third MS signals, whilst the evolution of huge amounts of N₂ and H₂ are detected above 300 °C. In contrast to the Ar-TRR, H₂-TPR (Figure 1e) shows that NH_3 starts to form at about $80^{\circ}C$ and reaches its peak temperature at around 180 °C. Such a low onset temperature for NH₃ formation indicates that the dissociation of H₂, as well as the hydrogenation of NH_x moieties, to form NH_3 is an energy-favorable pathway. Since both reactions are involved in the transition metal-catalyzed ammonia synthesis process, H₂-TPR result show a potentially similar application of Rb₂[Mn(NH₂)₄] in catalysis. These unique distinct TPR properties under different gaseous atmospheres suggest Rb₂[Mn(NH₂)₄] cold be a novel material for ammonia decomposition and synthesis.

Thermal decomposition events of the as-synthesized Rb₂[Mn(NH₂)₄] were also investigated by TG-DTA measurement under argon flow (Figure 1 f). The first endothermic peak at 153 °C in TG-DTA correlates well with the LT-HT phase transition temperature (156°C) shown in Figure 1a. The second endothermic signal occurs at 203 °C, at the same time, a mass loss of about 7.8% is detected from the TG curve; no further mass losses are detected until the temperature reaches the third endothermic event at 330 °C. The fourth endothermic event happens around 440°C with a larges mass loss. The second, third, and fourth endothermic signals in the DTA measurement correspond to those Ar-TPR events at around 210, 330, and 440 °C in Figure 1 d. Combination of the in situ SR-PXD (Figure 1a), the Ar-TPR (Figure 1d), and the weight loss (Figure 1 f), the process at 210 °C can be represented by Reaction 2 [Eq. (2)]. It can also be seen that the theoretical weight loss of the reaction is 7.8%, which matches well with the observed value in Figure 1 f.

$$6 \text{ Rb}_2[\text{Mn}(\text{NH}_2)_4] \rightarrow 12 \text{ Rb}\text{NH}_2 + 2 \text{ Mn}_3\text{N}_2 + 6 \text{ NH}_3 + \text{N}_2 + 3 \text{ H}_2 \tag{2}$$

After the occurrence of the reaction 2, RbNH₂ is likely to change to Rb(NH₂)_xH_{1-x} as observed in Figure 1 a. Increasing the reaction temperatures, at about 330 °C Rb(NH₂)_xH_{1-x} may decompose to some Rb-based species (Rb-N-H species) and release N₂, H₂, and NH₃. Following that, NH₃ is decomposed by the synergetic effect of Rb-based materials and Mn₃N₂, which may be similar to the case of MnN–NaNH₂ and MnN–KNH₂ reported by Chang et al.^[12] It is possible that Mn₃N₂ may facilitate the NH_x coupling on Rb-based species to form N₂, H₂, Rb metal, Rb(NH₂)_xH_{1-x}, or RbH intermediates. The subsequently formed Rb metal or RbH can react with the remaining NH₃ to form RbNH₂, which would then initiate another cycle of ammonia decomposition. In the following, the possible catalytic role of Rb₂[Mn(NH₂)₄] amide in NH₃ decomposition was tested.

Under the reaction conditions of NH₃ decomposition, the Rb metal or RbH intermediate species can further react with NH₃ to regenerate $RbNH_2/Rb(NH_2)_xH_{1-x}$. In order to investigate this phenomenon further, the NH3 decomposition properties of Rb₂[Mn(NH₂)₄], K₂[Mn(NH₂)₄], as well as the reference MnN, were studied (Figure 2a). K₂[Mn(NH₂)₄] was chosen based on its similarities with Rb₂[Mn(NH₂)₄] (Figures S4 and S5). MnN is selected as a reference catalyst because it is stable under a certain concentration of ammonia, which is the precursor for NH₃ decomposition and the product of NH₃ synthesis.^[13] The decomposition of NH₃ over Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] starts at around 350 °C, which is close to the main appearance temperature of N₂ and H₂ in the Ar-TPR spectra (Figure 1 d). This ammonia decomposition temperature is similar to those of the noble metal catalysts for ammonia decomposition.^[13] At 500 °C, both amide systems show good NH₃ decomposition properties. At this temperature, the NH₃ decomposition conversions of $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ reach 68% and 48%, respectively. These NH₃ decomposition conversions are much higher than that of MnN (15%) and similar to that of Ru/MgO catalyst^[13] under the same reaction conditions. Similar phenomena were found in the previous results using composite catalysts composed of MnN and NaNH₂/KNH₂.^[12] Both composites show much better catalytic performances than the neat MnN and NaNH₂/KNH₂. The Na(K)-Mn-amide/imide species have been proposed as intermediates during NH₃ decomposition reaction of MnN–NaNH₂/MnN–KNH₂.^[12]

According to the microscopic reversibility, a good ammonia decomposition catalyst is also possibly good at its reverse reaction, that is, ammonia synthesis. Considering the good performance of $Rb_2[Mn(NH_2)_4]$ in ammonia decomposition, as well as the facile hydrogenation property (Figure 1 e), it is interesting to study its function in ammonia synthesis. In the following, the synthesis of NH₃ from syngas using $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ was investigated. During the heating process under a flow of syngas, a large amount of ammonia was formed from the reaction of amides and H₂ (Figure 1 e and Figure S4). To avoid such artifacts, $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ were heated under the syngas flow from RT to 250 °C for a cer-

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Figure 2. a) NH₃ conversion of Rb₂[Mn(NH₂)₄], K₂[Mn(NH₂)₄], and MnN as a function of reaction temperature between 350 and 500 °C. Around 30 mg of each sample is measured in 5 % NH₃-Ar mixture gas with a flow rate of 30 mL min⁻¹. b) NH₃-synthesis rate of Rb₂[Mn(NH₂)₄], K₂[Mn(NH₂)₄], MnN, and Ru/MgO as a function of temperature from 200 to 400 °C; Inset is their NH₃ synthesis rate in the temperature range of 200–300 °C. Around 30 mg of each sample is measured under 10 bar of syngas (N₂:H₂=1:3) with a flow rate of 30 mL min⁻¹.

tain time, until the ammonia synthesis rate leveled off (Figure S6). The temperature dependence of the NH₃ synthesis rate of $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ are displayed in Figure 2b. The temperature dependence of the NH₃ synthesis rate using the catalysts MnN and Ru/MgO are also reported in Figure 2b for comparison. In the temperature range between 200 and 350 °C, the neat MnN does not show any NH₃ synthesis activity. However, under the same applied conditions both Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] show excellent catalytic activities on NH₃ synthesis rate, which are much better than that of the Ru/MgO catalyst. As shown in the inset of Figure 2b, the synthesis of NH_3 with the use of $Rb_2[Mn(NH_2)_4]$ and K₂[Mn(NH₂)₄] as catalysts precursors is observed even at temperatures well below 200°C, which is 50°C lower than that of the Ru/MgO catalyst. At 225 $^\circ\text{C},$ the NH_3 synthesis rates of $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ are 223 and 198 μ molg⁻¹h⁻¹, respectively. Ammonia synthesis activity increases with increasing temperature. At 350 °C (Table 1), the activities of and $Rb_2[Mn(NH_2)_4]$ $K_2[Mn(NH_2)_4]$ reached 3076 and 3313 μ mol g⁻¹ h⁻¹, respectively. These values are more than 3 orders of magnitude higher than that of MnN and even twice as high as that of Ru/MgO.

Table 1. Ammonia synthesis activities of Rb ₂ [Mn(NH ₂) ₄], K ₂ [Mn(NH ₂) ₄], Ru/
MgO, and MnN at 350 $^{\circ}$ C, and their E_{a} in the temperature range of 200–
350 °C.

Compound	Rb ₂ [Mn(NH ₂) ₄]	K ₂ [Mn(NH ₂) ₄]	Ru/MgO	MnN
activities [μ mol g ⁻¹ h ⁻¹]	3076	3313	1685	0
E_a [kJ mol ⁻¹]	54.4	57.3	98.4	-

Furthermore, after 15 h under 10 bar of syngas at 300 °C, the NH₃ synthesis rates are still about 1400 and 800 μ mol g⁻¹ h⁻¹ for Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄], respectively. Therefore, Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] appear to preserve their catalytic activities (Figure S7). Figure S8 shows that the apparent activation energies (*E*_a) of NH₃ synthesis for Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] are 54 and 57 kJ mol⁻¹, respectively. The *E*_a of Ru/MgO is 98 kJ mol⁻¹ (Table 1), which is about two times higher than that of Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄; this could be due to the different reaction mechanisms compared to these ternary manganese systems.

To reveal the interactions of ternary manganese amides and syngas, thermal decompositions of $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ in a closed system under 10 bar of syngas were investigated through in situ SR-PXD (Figure 3). From Reaction 2 and Figure 3 a, the thermal decomposition of $Rb_2[Mn(NH_2)_4]$ could generate $RbNH_2$ in situ, which subsequently reacts with H_2 to form RbH. The rubidium amide and hydride then react with each other to produce solid solution [Reaction 3, Eq. (3)].

$$x \operatorname{RbNH}_2 + (1-x) \operatorname{RbH} \to \operatorname{Rb}(\operatorname{NH}_2)_x \operatorname{H}_{1-x}$$
(3)

Different from the reaction under vacuum (Figure 1a), Rb(NH₂)_xH_{1-x} co-exists only with HT-Rb₂[Mn(NH₂)₄] below 250 °C under syngas. The decomposition temperature of HT-Rb₂[Mn(NH₂)₄] is shifted to 250 °C, which is 40 °C higher than that observed under vacuum. The Rietveld refinements of the SR-PXD patterns acquired for Rb₂[Mn(NH₂)₄] in syngas under different temperatures are reported in Figures S9 and S10. Figure 3 b shows the decomposition process of K₂[Mn(NH₂)₄] under 10 bar of syngas. The presence of K(NH₂)_xH_{1-x} can be detected below 220 °C, which is different from the study under vacuum (Figure S11), Under vacuum the K(NH₂)_xH_{1-x} is stable up to around 400 °C. Under syngas atmosphere, at temperatures higher than 250 °C the in situ SR-PXD results (Figure 3) do not show diffraction peaks of Rb(NH₂)_xH_{1-x}/K(NH₂)_xH_{1-x}; probably because these phases are in a molten state.

Under the flow of 10 bar syngas, the reaction intermediates could be different from those observed in the closed system, because of the different gas phase chemical potential. The PXD of the products obtained after the NH₃ synthesis experiment using $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ in the flow system were plotted in Figure S12, where Mn_2N and Mn_4N are observed. Differently from the flow system, the only detected Mn-based phase in the in situ SR-PXD is Mn_3N_2 (Figure 1 a and Figure 3), which could be due to the relatively higher partial pressure of ammonia in the closed system coming from the decomposition of $Rb_2[Mn(NH_2)_4]/K_2[Mn(NH_2)_4]$, which hinders

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Figure 3. In situ SR-PXD measurements of: a) Rb₂[Mn(NH₂)₄], and b) K₂[Mn(NH₂)₄] under 10 bar of syngas (N₂:H₂=1:3). The samples were heated from RT to 420 °C with a heating rate of 10 °Cmin⁻¹ and were then kept at 420 °C for 10 min before cooling down to RT.

the formation of the N-deficient nitride phases such as Mn_2N and $Mn_4N.^{[14]}$

It should be highlighted that TM(N)s–LiH composites has recently been reported for ammonia synthesis by our coauthors, Chen et al.^[15] TM(N)s–LiH composites show high catalytic activities in the temperature range of 150–327 °C. The improved catalytic properties of the TM(N)s–LiH composites has been proposed to be related to the introduction of a second active center (i.e., LiH) beside that of TM(N)s surfaces, which breaks the intrinsic scaling relations on transition metal surfaces. The second active center LiH can effectively pull N_{ad} away from the TM(N) surface, and perform the hydrogenation of N_{ad} outside of transition metal surface. The production of NH₃ in the TM(N)s–LiH composites can be divided into 3 different steps [Reactions 4–7, Eqs. (4)–(7)]:^[15]

$$N_2 \rightarrow N_{ad}$$
 (4)

 $\text{LiH} + \text{N}_{\text{ad}} \rightarrow [\text{LiNH}] \tag{5}$

$$[\mathsf{LiNH}] + \mathsf{H}_2 \to \mathsf{NH}_3 + \mathsf{LiH} \tag{6}$$

Overall reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ (7)

Based on the results obtained through TPR reactions (Figure 1 d and e), in situ SR-PXD (Figure 1 a and Figure 3) and NH_3

synthesis activity (Figure 2 b), it is reasonable to deduce that $Rb_2[Mn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ may follow a similar reaction mechanism as the LiH–Mn composite. That is, Mn nitride is responsible for N₂ dissociation to generate the adsorbed N atoms, and RbH/KH or $Rb(NH_2)_xH_{1-x}/K(NH_2)_xH_{1-x}$ pulls the N_{ad} away to form NH_x species, which is then followed by hydrogenation to release NH₃.

The observed amide-hydride solid solutions in the in situ SR-PXD measurements indicate they may be thermodynamically stable under a certain condition. Under this reaction condition of ammonia synthesis, although the amide-hydride crystalline phase was not observed, it is still possible that an amorphous layer of solid solutions exists on the interface of Mn nitride and hydride. The RbNH₂ or KNH₂ formed after N transfer may migrate away to form relatively more stable amide-hydride species, or it could also be reacted with manganese nitride to product amorphous Rb₂/K₂[Mn(NH₂)_x] under the ammonia atmosphere. This process may be important for catalytic ammonia synthesis, because the migration of RbNH₂ or KNH₂ may lead to clean hydride sites on the interface for further N transfer reactions. To verify this, a detailed characterization using in situ FTIR or Raman as well as theoretical calculations may be beneficial, which would be our following works.

In summary, Rb₂[Mn(NH₂)₄] has been successfully synthesized by mechanochemical reaction under mild conditions for the first time. Rb₂[Mn(NH₂)₄] possesses two distinct crystalline phases depending on the application temperatures. The crystal structures of both phases were successfully solved using combined SR-PXD and first-principles calculations. The determined crystal structures confirm the coexistence of the TM and the alkali metal active centers, which was previously reported to be critical for ammonia production catalysis. Both Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] show excellent NH₃ decomposition and synthesis activities, especially at low temperatures. In the temperature range of 250 to 350°C, the NH₃ synthesis rates of Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] under syngas atmosphere are more than 3 orders of magnitude higher than the reference MnN catalyst, and are even higher than that reported for the noble metal catalysts. To the best of our knowledge, this is the first reported case of using only amide for ammonia synthesis. The key factor contributed to this unexpected behavior is most likely the continuous variation of hydride-amide on the surface of manganese nitrides under syngas atmosphere, which shed lights on promoting nitrides for heterogeneous catalysis by compositing nitrides and alkali hydrides/ amides. In addition, the application of ternary transition amide is extended to heterogeneous catalysis for the first time.

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Conflict of interest

The authors declare no conflict of interest.

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