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

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Abstract: A new complex ternary amide $Rb_2[Mn(NH_2)_4]$, 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. $Rb_2[Mn(NH_2)_4]$ can be facily synthesized by mechanochemical reaction at room temperature. It exhibits two temperature-dependent polymorphs i.e. low-temperature orthorhombic and high-temperature monoclinic structures. $Rb_2[Mn(NH_2)_4]$ decomposes to N_2 , H_2 , NH_3 , Mn_3N_2 , and $RbNH_2$ under inert atmosphere; whereas releases NH_3 at a temperature as low as 80 °C under H_2 atmosphere. Those unique behaviors enable $Rb_2[Mn(NH_2)_4]$ and its analogue $K_2[Mn(NH_2)_4]$ as excellent catalytic materials for ammonia decomposition and synthesis. Our 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 NH_3 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 discloses that manganese nitride synergistic with Rb/KH or Rb/K(NH₂)_xH_{1-x} are likely the active sites. The chemistry of $Rb_2/K_2[Mn(NH_2)_x]$ and Rb/K(NH₂)_xH_{1-x} with H_2/N_2 and NH_3 correlates closely with the catalytic performance.

Inorganic metal amides have attracted increasing attention as potential hydrogen storage materials^[1] and ammonia decomposition catalyst precursors.^[2] Among them, ternary alkali metal transition metal amides ($A[M(NH_2)_x]$, A=alkalis, M=transition metals) such as $A_2[Mn(NH_2)_4]$ ^[3] (A=Na, K),

$A_2[Zn(NH_2)_4]$ (A=K, Rb, Cs)^[3b, 4] are important intermediates for hydrogen storage^[5] and 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 ($P2_1/c$) $K_2[Zn(NH_2)_4]$ was synthesized by reaction of metallic Zn and KNH_2 at 450 °C and 249 MPa of NH_3 for more than 7 days (reaction 1).^[7]

Very recently, we have produced $K_2[Zn(NH_2)_4]$ and $K_2[Mn(NH_2)_4]$ by one-pot mechanochemical reaction at room temperature (RT) for the first time. After mixing them with LiH, they show excellent hydrogenation properties, e.g., both can absorb ca. 3 wt % of H_2 within 1 min under 50 bar of H_2 at 230 °C. Upon heating to 500 °C under vacuum, $K_2[Mn(NH_2)_4]$ -8LiH converts to an excellent electrode material $Li_7[MnN_4]$ and Mn_4N .^[5b] This shows a new route to synthesize TMNs. And TMNs can also be prepared upon heating ternary transition amides individually, e.g. the $Li_4[Zn(NH_2)_4](NH_2)_2$ turns into $LiNH_2/Li_2NH$ 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 using for 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, A is the promoter. Moreover, it is well known that in both ammonia decomposition 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 ($-NH_2$ or $-NH$) may be the abundant species with the presence of alkalis.^[10] In the structure of ternary transition metal amides, e.g., $K_2[Mn(NH_2)_4]$ and $Na_2[Mn(NH_2)_4]$, the $-NH_2$ moiety is coordinated with both alkalis and manganese cations,^[3a, 4a, 7] which is resemble to 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 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, i.e., $Rb_2[Mn(NH_2)_4]$, was successfully synthesized for the first time by ball milling rubidium and manganese in the molar ratio of 2:1. $Rb_2[Mn(NH_2)_4]$ exhibits two different crystalline structures depending on the application temperatures. The possibility of

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using $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ for catalytic ammonia decomposition and synthesis was investigated.

Figure 1. (a) In situ SR-PXD measurement of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ 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 (room temperature). (b) Low-temperature crystal structure (100) view of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ (56 °C) and (c) High-temperature crystal structure (010) view of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ (156 °C). The $[\text{Mn}(\text{NH}_2)_4]^{2-}$ tetrahedra are highlighted in blue. The solid red lines connecting the centers of $[\text{Mn}(\text{NH}_2)_4]^{2-}$ tetrahedra (i.e. Mn atoms) are visual aids and have no other significance. (d) Ar-TPR and (e) H_2 -TPR curves of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$, heated from 30 to 470 °C with a heating rate of 5 °C min⁻¹, under 50 ml min⁻¹ argon and hydrogen flows, respectively. (f) TG-DTA curves of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$, heated from 30 to 470 °C with a heating rate of 5 °C min⁻¹, under 50 ml min⁻¹ argon flow.

$\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ were prepared by ball milling Mn and Rb/K metals in a molar ratio of 1:2 at RT under 0.7 MPa of NH_3 for 12 h. The crystal structure as well as the thermal decomposition reaction path of the as-synthesized $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ were investigated via *in situ* SR-PXD under static vacuum (**Figure 1(a)**). 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 $a=7.2183(4)$ Å, $b=10.7474(6)$ Å, $c=18.3155(10)$ Å, and $V=1420.88(19)$ Å³ (low temperature phase: LT phase (**Figure 1(b)**). After heating to ca. 156 °C LT $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ converts to a high temperature phase (HT phase), which is assigned to a monoclinic structure (*P2₁/c*, No.14) with lattice parameters of: $a=7.8536(5)$ Å, $b=6.9449(5)$ Å, $c=13.8411(11)$ Å, $\beta=106.389(7)$, and $V=724.24(12)$ Å³ (**Figure 1(c)**). In both crystal structures Mn^{2+} are tetrahedrally coordinated by four NH_2^- , forming $[\text{Mn}(\text{NH}_2)_4]^{2-}$ 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**. About 4.57 wt % of cubic RbNH_2 is also detected along with $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ at temperatures below 210 °C (**Figure S2**). The detected phases are Mn_3N_2 and a Rb-based solid solution ($\text{Rb}(\text{NH}_2)_x\text{H}_{1-x}$) in the temperature range from 210 to 330 °C (**Figure 1(a)**). The $\text{Rb}(\text{NH}_2)_x\text{H}_{1-x}$ is most likely formed

(**Figure S3**) similar to the reaction of $x\text{KNH}_2-(1-x)\text{KH}$,^[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 RbNH_2 , metallic Rb and Mn_3N_2 .

Temperature-programmed-reaction (TPR) for the as-synthesized $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ was carried out under Ar and H_2 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)**). NH_3 , N_2 and H_2 co-exist in the first MS peak, however, only a slight trace of NH_3 can be detected in the second and the third MS signals, whilst the evolution of huge amounts of N_2 and H_2 are detected above 300 °C. In contrast to the Ar-TPR, H_2 -TPR (**Figure 1(e)**) shows NH_3 starts to form at ca. 80 °C and reaches its peak temperature at around 180 °C. Such a low onset temperature for NH_3 formation indicates the dissociation of H_2 as well as the hydrogenation of NH_x moiety to form NH_3 is an energy-favorable pathway. Since both reactions are involved in the transition metal-catalyzed ammonia synthesis process, H_2 -TPR result show a potential similar application of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ in catalysis. These unique distinct TPR properties under different gaseous

atmospheres suggest $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ could be a novel material for ammonia decomposition and synthesis.

Thermal decomposition events of the as-synthesized $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ was 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 1(a). 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 stupendous 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 1(a)), the Ar-TPR (Figure 1(d)), and the weight loss (Figure 1(f)), the process at 210 °C can be represented by **reaction (2)**. It can also be seen that the theoretical weight loss of the reaction 2 is 7.8%, which well matches the observed value well in Figure 1(f).

$6\text{Rb}_2[\text{Mn}(\text{NH}_2)_4] \rightarrow 12\text{RbNH}_2 + 2\text{Mn}_3\text{N}_2 + 6\text{NH}_3 + \text{N}_2 + 3\text{H}_2$ (2)
After the occurrence of reaction 2, RbNH_2 is likely to change to $\text{Rb}(\text{NH}_2)_{x\text{H}_{1-x}}$ as observed in Figure 1(a). Increasing the reaction temperatures, at ca. 330 °C $\text{Rb}(\text{NH}_2)_{x\text{H}_{1-x}}$ may decompose to some Rb-based species (Rb-N-H species) and release N_2 , H_2 and NH_3 . Following that, NH_3 is decomposed by the synergetic effect of Rb-based materials and Mn_3N_2 , which may be similar to the case of MnN - NaNH_2 and MnN - KNH_2 reported by Chang et al.^[12] It is possible that Mn_3N_2 may facilitate the NH_x coupling on Rb-based species to form N_2 , H_2 , Rb metal, $\text{Rb}(\text{NH}_2)_{x\text{H}_{1-x}}$ or RbH intermediates. The subsequently formed Rb metal or RbH can

react with the rest NH_3 to form RbNH_2 , which would then initiate another cycle of ammonia decomposition. In the following, the possible catalytic role of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ amide in NH_3 decomposition was tested.

Under the reaction conditions of NH_3 decomposition, the Rb metal or RbH intermediate species can further react with NH_3 to regenerate $\text{RbNH}_2/\text{Rb}(\text{NH}_2)_{x\text{H}_{1-x}}$. In order to investigate this phenomenon further, the NH_3 decomposition properties of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$, $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ as well as the reference MnN were studied (**Figure 2(a)**). $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ was chosen based on its similarities with $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ (**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 NH_3 decomposition and the product of NH_3 synthesis.^[13] The decomposition of NH_3 over $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ starts at around 350 °C, which is close to the main appearance temperature of N_2 and H_2 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 NH_3 decomposition properties. At this temperature, the NH_3 decomposition conversions of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ reach 68% and 48%, respectively. These NH_3 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 composites catalysts composed of MnN and $\text{NaNH}_2/\text{KNH}_2$.^[12] Both composites show much better catalytic performances than the neat MnN and $\text{NaNH}_2/\text{KNH}_2$. The Na(K)-Mn-amide/imide species have been proposed as intermediates during NH_3 decomposition reaction of MnN - NaNH_2/MnN - KNH_2 .^[12]

Figure 2. (a) NH_3 conversion of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$, $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ and MnN as a function of reaction temperature between 350 and 500 °C. Around 30 mg of each sample is measured at 5% NH_3 -Ar mixture gas with a flow rate of 30 ml min⁻¹. (b) NH_3 -synthesis rate of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$, $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$, MnN and Ru/MgO as a function of temperature from 200 to 400 °C; Inset is their NH_3 synthesis rate in the temperature range of 200 and 300 °C. Around 30 mg of each sample is measured under 10 bar of syngas ($\text{N}_2:\text{H}_2=1:3$) with a flow rate of 30 ml min⁻¹

According to the microscopic reversibility, a good ammonia decomposition catalyst is also possible good at its reverse reaction, i.e., ammonia synthesis. Considering the good performance of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ 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 NH_3 from syngas using $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ was investigated. During the heating process under a flow of syngas, large amount of ammonia was formed from the reaction of amides and H_2 (Figure 1(e) and Figure S4). To avoid such artifacts, $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ were heated under the syngas flow from RT to 250 °C for a certain time, until

the ammonia synthesis rate levels off (**Figure S6**). The temperature dependence of the NH_3 synthesis rate of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ are displayed in **Figure 2(b)**. The temperature dependence of the NH_3 synthesis rate using the catalysts MnN and Ru/MgO are also reported in Figure 2(b) for comparison. In the temperature range between 200 and 350 °C, the neat MnN does not show any NH_3 synthesis activity. However, under the same applied conditions both $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ show excellent catalytic activities on NH_3 synthesis rate, which are much better than that of the Ru/MgO catalyst. As shown in the inset of Figure 2(b), the synthesis of NH_3 with the use of $\text{Rb}_2[\text{Mn}(\text{NH}_2)_4]$ and $\text{K}_2[\text{Mn}(\text{NH}_2)_4]$ as catalysts precursors is

observed even at temperatures well below 200 °C, which is 50 °C lower than that of Ru/MgO catalyst. At 225 °C, the NH₃ synthesis rates of Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] are 223 and 198 μmol g⁻¹ h⁻¹, respectively. Ammonia synthesis activity increases with increasing temperature. At 350 °C (**Table 1**), the activities of Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] reached 3076 and 3313 μmol g⁻¹ h⁻¹, respectively. These values are more than 3 orders of magnitude higher than that of MnN and even twice higher than that of Ru/MgO.

Furthermore, after 15 h under 10 bar of syngas at 300 °C, the NH₃ synthesis rates are still about 1400 and 800 μmol 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] are 54 and 57 kJ mol⁻¹, respectively. The much higher *E_a* of Ru/MgO, i.e., 98 kJ mol⁻¹ (**Table 1**), than that of Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] could be due to their different reaction mechanisms compared to these ternary manganese systems.

Table 1. Ammonia synthesis activities of Rb₂[Mn(NH₂)₄], K₂[Mn(NH₂)₄], Ru/MgO, and MnN at 350 °C, and their *E_a* in the temperature range of 200–350 °C.

Name	Rb ₂ [Mn(NH ₂) ₄]	K ₂ [Mn(NH ₂) ₄]	Ru/MgO	MnN
Activities (μmol g ⁻¹ h ⁻¹)	3076	3313	1685	0
<i>E_a</i> (kJ mol ⁻¹)	54.4	57.3	98.4	-

Figure 3. In situ SR-PXD measurements of (a) Rb₂[Mn(NH₂)₄] and (b) K₂[Mn(NH₂)₄] under 10 bar of syngas (N₂-3H₂). The samples were 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 to be cooled down to RT.

To reveal the interactions of ternary manganese amides and syngas, thermal decompositions of Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] in a closed system under 10 bar of syngas were investigated via *in situ* SR-PXD (**Figure 3**). From reaction 2 and Figure 3(a), the thermal decomposition of Rb₂[Mn(NH₂)₄] could *in situ* generate RbNH₂, which subsequently reacts with H₂ to form RbH. The rubidium amide and hydride then react with each other to produce solid solution (reaction 3).

Different from the reaction under vacuum (Figure 1(a)), 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 atmosphere. 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 that performed under vacuum (**Figure S11**). Under vacuum the K(NH₂)_xH_{1-x} stabilizes 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 what are 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 Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)₄] in the flow system was plotted in **Figure S12**, where Mn₂N and Mn₄N are observed. Differently from the flow system, the only detected Mn-based phase is Mn₃N₂ in the *in situ* SR-PXD (Figures 1(a) and 3), which could be due to the relatively higher partial pressure of ammonia in the closed system coming from the decomposition of Rb₂[Mn(NH₂)₄]/K₂[Mn(NH₂)₄], which hinders the formation of the N-deficient nitride phases such as Mn₂N and Mn₄N.^[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 (**reaction 4-7**).^[15]

Based on the results obtained via TPR reactions (Figures 1(d) and (e)), *in situ* SR-PXD (Figures 1(a) and 3) and

NH₃ synthesis activity (Figure 2(b)), it is reasonable to deduce that Rb₂[Mn(NH₂)₄] and K₂[Mn(NH₂)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(NH₂)_xH_{1-x}/K(NH₂)_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.

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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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The first case of using $A_2[Mn(NH_2)_4]$ ($A=Rb$ and K) for low temperature NH_3 synthesis and decomposition.

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