Supporting information

Elucidating the rate-determining step of ammonia decomposition on Ru-based catalysts using ab initio–grounded microkinetic modeling

Shekhar R Kulkarni[a,$], Natalia Realpe[a,$], Attada Yerrayya[a], Vijay Kumar Velisoju[a], Salvador Sayas[a], Natalia Morlanes[a], Jose Cerillo[a], Sai P. Katikaneni[b], Stephen N. Paglieri[b], Bandar Solami[b], Jorge Gascon[a], Pedro Castaño[a]*

[a] *KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

[b] *Carbon Management R&D Division, Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia 31311*

[$] These authors contributed equally

* Corresponding author: pedro.castano@kaust.edu.sa

Microkinetic modeling derivation

Based on the Quasi-equilibrium hypothesis, the macrokinetic model developed in this study relies on the following steps to obtain the species coverage:

i. Select a reaction mechanism
ii. Make a rate law for each step, which are assumed to be elementary
iii. Propose a rate-determining step (RDS)
iv. For the proposed RDS: k is small, while the remaining reactions are assumed to be in equilibrium, i.e., −r/k = 0 is valid for the rest.
v. Solve all the intermediate concentrations and write a site balance to solve θ^* by considering the expression: $\sum \theta_i^* = 1$.

Detailed derivations for the rate laws included in the main article are presented in this section.

For the six elementary reactions, R1–R6, the respective rate laws are formulated as follows:

$$r_1 = k_1 P_{NH_3}\theta^* - k_{1'}\theta^*_{NH_3} = k_1\left(P_{NH_3}\theta^* - \frac{\theta^*_{NH_3}}{K_1}\right) \quad \text{(a1)}$$

$$r_2 = k_2\theta^*_{NH_3}\theta^* - k_{2'}\theta^*_{NH_2}\theta^*_H = k_2\left(\theta^*_{NH_3}\theta^* - \frac{\theta^*_{NH_2}\theta^*_H}{K_2}\right) \quad \text{(a2)}$$

$$r_3 = k_3\theta^*_{NH_2}\theta^* - k_{3'}\theta^*_{NH}\theta^*_H = k_3\left(\theta^*_{NH_2}\theta^* - \frac{\theta^*_{NH}\theta^*_H}{K_3}\right) \quad \text{(a3)}$$

$$r_4 = k_4\theta^*_{NH}\theta^* - k_{4'}\theta^*_N\theta^*_H = k_4\left(\theta^*_{NH}\theta^* - \frac{\theta^*_N\theta^*_H}{K_4}\right) \quad \text{(a4)}$$

$$r_5 = k_5{\theta^*_N}^2 - k_{5'}P_{N_2}{\theta^*}^2 = k_5\left({\theta^*_N}^2 - \frac{P_{N_2}{\theta^*}^2}{K_5}\right) \quad \text{(a5)}$$

$$r_6 = k_6\theta_H^{*2} - k_{6}{'}P_{H_2}\theta^{*2} = k_6(\theta_H^{*2} - \frac{P_{H_2}\theta^{*2}}{K_6}) \quad \text{(a6)}$$

Step iii can be further applied for the NH_3 decomposition reaction where one of the three possible cases is assumed to be the RDS:

i. Case A: Dissociation of adsorbed NH_3 with N–H bond scission.
ii. Case B: Desorption of adsorbed N atoms.
iii. Case C: Dissociation of adsorbed NH with N–H bond scission.

These are the most commonly proposed RDSs for NH_3 decomposition via experimental and modeling studies in the literature. However, desorption of adsorbed N adatoms (Case B) is the most widely accepted option for the tested metal–support pairs.

Step 1: Select the reaction mechanism

Adsorption: $NH_3 + * \leftrightarrow NH_3^*$ (R1)

Surface reaction 1: $NH_3^* + * \leftrightarrow NH_2^* + H^*$ (R2)

Surface reaction 2: $NH_2^* + * \leftrightarrow NH^* + H^*$ (R3)

Surface reaction 3: $NH^* + * \leftrightarrow N^* + H^*$ (R4)

Desorption 1: $2N* \leftrightarrow N_2 + 2^*$ (R5)

Desorption 2: $2H* \leftrightarrow H_2 + 2^*$ (R6)

Step 2: Make the rate law for each step

$$r_1 = k_1P_{NH_3}\theta^* - k_{1}{'}\theta_{NH_3}^* = k_1(P_{NH_3}\theta^* - \frac{\theta_{NH_3}^*}{K_1}) \quad \text{(a1)}$$

$$r_2 = k_2\theta_{NH_3}^*\theta^* - k_{2}{'}\theta_{NH_2}^*\theta_H^* = k_2(\theta_{NH_3}^*\theta^* - \frac{\theta_{NH_2}^*\theta_H^*}{K_2}) \quad \text{(a2)}$$

$$r_3 = k_3\theta^*_{NH_2}\theta^* - k_{3'}\theta^*_{NH}\theta^*_H = k_3(\theta^*_{NH_2}\theta^* - \frac{\theta^*_{NH}\theta^*_H}{K_3}) \quad \text{(a3)}$$

$$r_4 = k_4\theta^*_{NH}\theta^* - k_{4'}\theta^*_N\theta^*_H = k_4(\theta^*_{NH}\theta^* - \frac{\theta^*_N\theta^*_H}{K_4}) \quad \text{(a4)}$$

$$r_5 = k_5\theta^{*2}_N - k_{5'}P_{N_2}\theta^{*2} = k_5(\theta^{*2}_N - \frac{P_{N_2}\theta^{*2}}{K_5}) \quad \text{(a5)}$$

$$r_6 = k_6\theta^{*2}_H - k_{6'}P_{H_2}\theta^{*2} = k_6(\theta^{*2}_H - \frac{P_{H_2}\theta^{*2}}{K_6}) \quad \text{(a6)}$$

Step 3: Propose the RDS

According to the literature, the most common RDS for NH_3 decomposition are

(a) Dissociation of adsorbed NH_3 with N–H bond scission
(b) Desorption of adsorbed N atoms
(c) Dissociation of adsorbed NH with N–H bond scission

To obtain the kinetic equations, one step is considered to be the RDS and the rest are assumed to be in equilibrium.

For RDS: k is small

For others: −r/k = 0

Case (a): Dissociation of adsorbed NH_3 with N–H bond scission is assumed as the RDS

Step 4: Solve intermediate concentrations

Since the surface reaction 1 is the RDS,

$$\frac{r_1}{k_1} = 0 => P_{NH_3}\theta^* - \frac{\theta^*_{NH_3}}{K_1} = 0 => \theta^*_{NH_3} = K_1 P_{NH_3}\theta^* \quad \text{(a7)}$$

$$\frac{r_3}{k_3} = 0 => \theta^*_{NH_2}\theta^* - \frac{\theta^*_{NH}\theta^*_H}{K_3} = 0 => \theta^*_{NH}\theta^*_H = K_3\theta^*_{NH_2}\theta^* \quad \text{(a8)}$$

$$\frac{r_4}{k_4} = 0 => \theta_{NH}^{*}\theta^{*} - \frac{\theta_N^{*}\theta_H^{*}}{K_4} = 0 => \theta_N^{*}\theta_H^{*} = K_4\theta_{NH}^{*}\theta^{*} \quad \text{(a9)}$$

$$\frac{r_5}{k_5} = 0 => \theta_N^{*2} - \frac{P_{N_2}\theta^{*2}}{K_5} = 0 => \theta_N^{*} = \sqrt{\frac{P_{N_2}}{K_5}}\theta^{*} \quad \text{(a10)}$$

$$\frac{r_6}{k_6} = 0 => \theta_H^{*2} - \frac{P_{H_2}\theta^{*2}}{K_6} = 0 => \theta_H^{*} = \sqrt{\frac{P_{H_2}}{K_6}}\theta^{*} \quad \text{(a11)}$$

By introducing the values of θ_N^{*} and θ_H^{*} from Eqs. a10 and a11 in Eq. a9,

$$\theta_{NH}^{*} = \frac{1}{K_4}\sqrt{\frac{P_{N_2}P_{H_2}}{K_5\ K_6}}\theta^{*} \quad \text{(a12)}$$

By introducing the values of θ_{NH}^{*} and θ_H^{*} from Eq. a12 and a11 in Eq. a8,

$$\theta_{NH_2}^{*} = \frac{P_{H_2}}{K_3K_4K_6}\sqrt{\frac{P_{N_2}}{K_5}}\theta^{*} \quad \text{(a13)}$$

Step 5: Write a site balance and solve θ^{*}

$$\theta^{*} + \theta_{NH_3}^{*} + \theta_{NH_2}^{*} + \theta_{NH}^{*} + \theta_N^{*} + \theta_H^{*} = 1$$
(a14)

By introducing the values of $\theta_{NH_3}^{*}, \theta_{NH_2}^{*}, \theta_{NH}^{*}, \theta_N^{*},$ and θ_H^{*} from Eqs. a7, a13, a12, a10, and a11 in Eq. a14 and taking θ^{*} common,

$$\theta^{*}\left(1 + K_1P_{NH_3} + \frac{P_{H_2}}{K_3K_4K_6}\sqrt{\frac{P_{N_2}}{K_5}} + \frac{1}{K_4}\sqrt{\frac{P_{N_2}P_{H_2}}{K_5\ K_6}} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right) = 1$$

Therefore,

$$\theta^{*} = \frac{1}{\left(1 + K_1P_{NH_3} + \frac{P_{H_2}}{K_3K_4K_6}\sqrt{\frac{P_{N_2}}{K_5}} + \frac{1}{K_4}\sqrt{\frac{P_{N_2}P_{H_2}}{K_5\ K_6}} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)}$$
(a15)

$$\theta^{*2} = \frac{1}{\left(1 + K_1 P_{NH_3} + \frac{P_{H_2}}{K_3 K_4 K_6}\sqrt{\frac{P_{N_2}}{K_5}} + \frac{1}{K_4}\sqrt{\frac{P_{N_2} P_{H_2}}{K_5\ K_6}} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$
(a16)

By introducing the values of $\theta^*_{NH_3}$, $\theta^*_{NH_2}$, and θ^*_H from Eqs. a7, a13, and a11 in Eq. a2,

$$r_2 = k_2 \left(K_1 P_{NH_3}\theta^{*2} - \frac{P_{H_2}}{K_2 K_3 K_4 K_6}\sqrt{\frac{P_{N_2}}{K_5}}\sqrt{\frac{P_{H_2}}{K_6}}\theta^{*2}\right) \tag{a17}$$

and substituting the value of θ^{*2}

$$r_2 = \frac{k_2 \left(K_1 P_{NH_3} - \frac{P_{H_2}{}^{3/2}}{K_2 K_3 K_4 K_6{}^{3/2}}\sqrt{\frac{P_{N_2}}{K_5}}\right)}{\left(1 + K_1 P_{NH_3} + \frac{P_{H_2}}{K_3 K_4 K_6}\sqrt{\frac{P_{N_2}}{K_5}} + \frac{1}{K_4}\sqrt{\frac{P_{N_2} P_{H_2}}{K_5\ K_6}} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$
(a18)

The slow step/RDSs are partially reversible, which means that the second term in the above equation is negligible; therefore,

$$r_2 = \frac{k_2\, K_1 P_{NH_3}}{\left(1 + K_1 P_{NH_3} + \frac{P_{H_2}}{K_3 K_4 K_6}\sqrt{\frac{P_{N_2}}{K_5}} + \frac{1}{K_4}\sqrt{\frac{P_{N_2} P_{H_2}}{K_5\ K_6}} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$
(a19)

Case (b): Desorption of adsorbed N atoms is assumed as the RDS

Starting from step 4 and solving the intermediate concentrations, since the desorption 1 is the RDS,

$$\frac{r_1}{k_1} = 0 \Rightarrow P_{NH_3}\theta^* - \frac{\theta^*_{NH_3}}{K_1} = 0 \Rightarrow \theta^*_{NH_3} = K_1 P_{NH_3}\theta^* \tag{b1}$$

$$\frac{r_2}{k_2} = 0 \Rightarrow \theta^*_{NH_3}\theta^* - \frac{\theta^*_{NH_2}\theta^*_H}{K_2} = 0 \Rightarrow \theta^*_{NH_2} = \frac{K_2 \theta^*_{NH_3}\theta^*}{\theta^*_H} \tag{b2}$$

$$\frac{r_3}{k_3} = 0 => \theta_{NH_2}^* \theta^* - \frac{\theta_{NH}^* \theta_H^*}{K_3} = 0 => \theta_{NH}^* \theta_H^* = K_3 \theta_{NH_2}^* \theta^* \tag{b3}$$

$$\frac{r_4}{k_4} = 0 => \theta_{NH}^* \theta^* - \frac{\theta_N^* \theta_H^*}{K_4} = 0 => \theta_N^* \theta_H^* = K_4 \theta_{NH}^* \theta^* \tag{b4}$$

$$\frac{r_6}{k_6} = 0 => \theta_H^{*2} - \frac{P_{H_2} \theta^{*2}}{K_6} = 0 => \theta_H^* = \sqrt{\frac{P_{H_2}}{K_6}} \theta^* \tag{b5}$$

By substituting the values of $\theta_{NH_3}^*$ and θ_H^* from Eq. b1 and b5 in Eq. b2,

$$\theta_{NH_2}^* = \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} \theta^* \tag{b6}$$

By substituting the values of $\theta_{NH_2}^*$ and θ_H^* from Eq. b6 and b5 in Eq. b3,

$$\theta_{NH}^* = \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} \theta^* \tag{b7}$$

By substituting the values of θ_{NH}^* and θ_H^* from Eq. b7 and b5 in Eq. b4,

$$\theta_N^* = \frac{K_1 K_2 K_3 K_4 K_6^{3/2}}{P_{H_2}^{3/2}} P_{NH_3} \theta^* \tag{b8}$$

Step 5: Write the site balance and solve for θ^*

$$\theta^* + \theta_{NH_3}^* + \theta_{NH_2}^* + \theta_{NH}^* + \theta_N^* + \theta_H^* = 1$$
(b9)

By introducing the values of $\theta_{NH_3}^*$, $\theta_{NH_2}^*$, θ_{NH}^*, θ_N^*, and θ_H^* from Eqs. b1, b6, b7, b8, and b5 in Eq. b9 and taking θ^* common,

$$\theta^* \left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \frac{K_1 K_2 K_3 K_4 K_6^{3/2}}{P_{H_2}^{3/2}} P_{NH_3} + \sqrt{\frac{P_{H_2}}{K_6}} \right) = 1$$

Therefore,

$$\theta^* = \frac{1}{\left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \frac{K_1 K_2 K_3 K_4 {K_6}^{3/2}}{{P_{H_2}}^{3/2}} P_{NH_3} + \sqrt{\frac{P_{H_2}}{K_6}}\right)}$$

(b10)

$$\theta^{*2} = \frac{1}{\left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \frac{K_1 K_2 K_3 K_4 {K_6}^{3/2}}{{P_{H_2}}^{3/2}} P_{NH_3} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$

(b11)

By substituting the values of θ_N^* from Eq. b8 in Eq. a5,

$$r_5 = k_5 \left(\left(\frac{K_1 K_2 K_3 K_4 {K_6}^{3/2}}{{P_{H_2}}^{3/2}} P_{NH_3}\right)^2 - \frac{P_{N_2}}{K_5} \right) \theta^{*2} \tag{b12}$$

and substituting θ^{*2} from Eq. b11 in Eq. b12,

$$r_5 = \frac{k_5 \left(\left(\frac{K_1 K_2 K_3 K_4 {K_6}^{3/2}}{{P_{H_2}}^{3/2}} P_{NH_3}\right)^2 - \frac{P_{N_2}}{K_5} \right)}{\left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \frac{K_1 K_2 K_3 K_4 {K_6}^{3/2}}{{P_{H_2}}^{3/2}} P_{NH_3} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$

(b13)

The slow step/RDSs are partially reversible, which means that the second term in the above equation is negligible; therefore,

$$r_5 = \frac{k_5 \left(K_1 K_2 K_3 K_4\right)^2 {K_6}^3 {P_{NH_3}}^2}{{P_{H_2}}^{3/2} \left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \frac{K_1 K_2 K_3 K_4 {K_6}^{3/2}}{{P_{H_2}}^{3/2}} P_{NH_3} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$

(b14)

Case (c): Dissociation of adsorbed NH with N–H bond scission is assumed as the RDS

Starting from step 4 and solving the intermediate concentrations, since the surface reaction 3 is the RDS,

$$\frac{r_1}{k_1} = 0 => P_{NH_3}\theta^* - \frac{\theta^*_{NH_3}}{K_1} = 0 => \theta^*_{NH_3} = K_1 P_{NH_3}\theta^* \tag{c1}$$

$$\frac{r_2}{k_2} = 0 => \theta^*_{NH_3}\theta^* - \frac{\theta^*_{NH_2}\theta^*_H}{K_2} = 0 => \theta^*_{NH_2} = \frac{K_2\theta^*_{NH_3}\theta^*}{\theta^*_H} \tag{c2}$$

$$\frac{r_3}{k_3} = 0 => \theta^*_{NH_2}\theta^* - \frac{\theta^*_{NH}\theta^*_H}{K_3} = 0 => \theta^*_{NH}\theta^*_H = K_3\theta^*_{NH_2}\theta^* \tag{c3}$$

$$\frac{r_5}{k_5} = 0 => \theta^{*2}_N - \frac{P_{N_2}\theta^{*2}}{K_5} = 0 => \theta^*_N = \sqrt{\frac{P_{N_2}}{K_5}}\theta^* \tag{c4}$$

$$\frac{r_6}{k_6} = 0 => \theta^{*2}_H - \frac{P_{H_2}\theta^{*2}}{K_6} = 0 => \theta^*_H = \sqrt{\frac{P_{H_2}}{K_6}}\theta^* \tag{c5}$$

By substituting the values of $\theta^*_{NH_3}$ and θ^*_H from Eq. b1 and b5 in Eq. b2,

$$\theta^*_{NH_2} = \frac{K_1K_2\sqrt{K_6}}{\sqrt{P_{H_2}}}P_{NH_3}\theta^* \tag{c6}$$

By substituting the values of $\theta^*_{NH_2}$ and θ^*_H from Eqs. b6 and b5 in Eq. b3,

$$\theta^*_{NH} = \frac{K_1K_2K_3K_6}{P_{H_2}}P_{NH_3}\theta^* \tag{c7}$$

Step 5: Write a site balance and solve θ^*

$$\theta^* + \theta^*_{NH_3} + \theta^*_{NH_2} + \theta^*_{NH} + \theta^*_N + \theta^*_H = 1$$
(c8)

By introducing the values of $\theta^*_{NH_3}$, $\theta^*_{NH_2}$, θ^*_{NH}, θ^*_N, and θ^*_H from Eqs. b1, b6, b7, b8, and b5 in Eq. b9 and taking θ^* common,

$$\theta^*\left(1 + K_1P_{NH_3} + \frac{K_1K_2\sqrt{K_6}}{\sqrt{P_{H_2}}}P_{NH_3} + \frac{K_1K_2K_3K_6}{P_{H_2}}P_{NH_3} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right) = 1$$

Therefore,

$$\theta^* = \frac{1}{\left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)}$$

(c9)

$$\theta^{*2} = \frac{1}{\left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$

(c10)

By substituting the values of $\theta^*_{NH}, \theta^*_{N},$ and θ^*_{H} from Eqs. c7, c4, and c5 in Eq. a4,

$$r_4 = k_4\left(\frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} - \sqrt{\frac{P_{N_2}}{K_5}}\sqrt{\frac{P_{H_2}}{K_6}}\frac{1}{K_4}\right)\theta^{*2} \quad \text{(c11)}$$

and substituting θ^{*2} in Eq. c11,

$$r_4 = \frac{k_4\left(\frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} - \sqrt{\frac{P_{N_2}}{K_5}}\sqrt{\frac{P_{H_2}}{K_6}}\frac{1}{K_4}\right)}{\left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2}$$

(c12)

The slow step/RDSs are partially reversible, which means that the second term in the above equation is negligible; therefore,

$$r_4 = \frac{k_4 K_1 K_2 K_3 K_6 \left(P_{NH_3}\right)}{P_{H_2}\left(1 + K_1 P_{NH_3} + \frac{K_1 K_2 \sqrt{K_6}}{\sqrt{P_{H_2}}} P_{NH_3} + \frac{K_1 K_2 K_3 K_6}{P_{H_2}} P_{NH_3} + \sqrt{\frac{P_{N_2}}{K_5}} + \sqrt{\frac{P_{H_2}}{K_6}}\right)^2} \quad \text{(c13)}$$

Supplementary tables

Table S1. Adsorption energies (eV) for different species present in the NH_3 decomposition process on pure Ru (111) and Ru–K/CaO surfaces

	Fe (110)	Co (111)	Ni (111)	Ni (100)	Cu (111)	Pd (111)	Ru (this work)	Ru/K(this work)
NH_3 (g) to NH_3 (s)	0				0	0	0.00	0
NH_3 (s) to NH_3 (g)	0.83	0.68	0.75		0.46	0.84	0.24	0.04
NH_3 to NH_2 + H	0.72	1.01	1.11	0.96	1.84	1.71	1.27	0.68
NH_2 + H to NH_3	1.34	1.15	1.39	1.21	1.1	1.22	1.44	2.08
NH_2 to NH + H	0.24	0.21	0.59	1.63	1.59	1.54	0.77	0.66
NH + H to NH_2	1.35	0.65	1.16	1.09	0.74	1.39	1.18	1.26
NH to N + H	1.16	1.06	1.11	0.89	2.19	1.7	1.17	0.92
N + H to NH	1.59	0.96	1.05	0.60	0.49	0.99	0.96	1.57
N_2 to N + N	1.19	1.24	1.37	1.68	3.45	2.83	1.42	0.71
N + N to N_2	2.85	1.86	1.86	1.66	0.2	0.76	1.82	1.24
H_2 to H + H					0.56		0.00	0.15
H + H to H_2					0.99		1.22	1.88

Table S2. Comparison of the best-fitted activation energy values for the Ru/CaO and Ru–K/CaO catalysts.

E	**Ru/CaO**				**Ru–K/CaO**			
(kJ mol^{-1})	**Case A**	**Case B**	**Case C**	**DFT**	**Case A**	**Case B**	**Case C**	**DFT**
E_2	159.76	98.47	88.19	121.92	140.26	72.37	108.33	65.28
E_3	36.33	77.43	10.04	73.92	60.13	63.27	14.20	63.36
E_4	82.31	67.33	89.91	112.32	95.49	103.94	40.42	88.32
E_5	315.39	119.11	186.54	174.72	124.58	130.40	152.54	119.04
E_6	202.33	112.64	113.25	117.12	200.23	211.20	129.62	180.48
E_{11}	35.31	21.09	65.04	23.04	7.81	3.19	69.53	3.84
E_{22}	31.32	124.89	118.02	138.24	197.36	172.60	92.12	199.68
E_{33}	255.82	104.91	20.28	113.28	121.36	133.72	26.74	120.96
E_{44}	71.15	123.47	88.87	92.16	126.42	100.66	126.66	150.72
E_{55}	147.17	110.63	122.52	136.32	61.33	63.00	67.88	68.16
E_{66}	0.00	0.00	65.69	0	13.92	11.33	79.45	14.4
	0.9909	0.9705	0.9966		0.9929	0.9573	0.6859	**R^2**
	0.0233	0.0204	0.0012		0.0154	0.081	0.2449	σ^2
	0.1527	0.1430	0.0359		0.1243	0.2850	0.4949	σ

Supplementary figures:

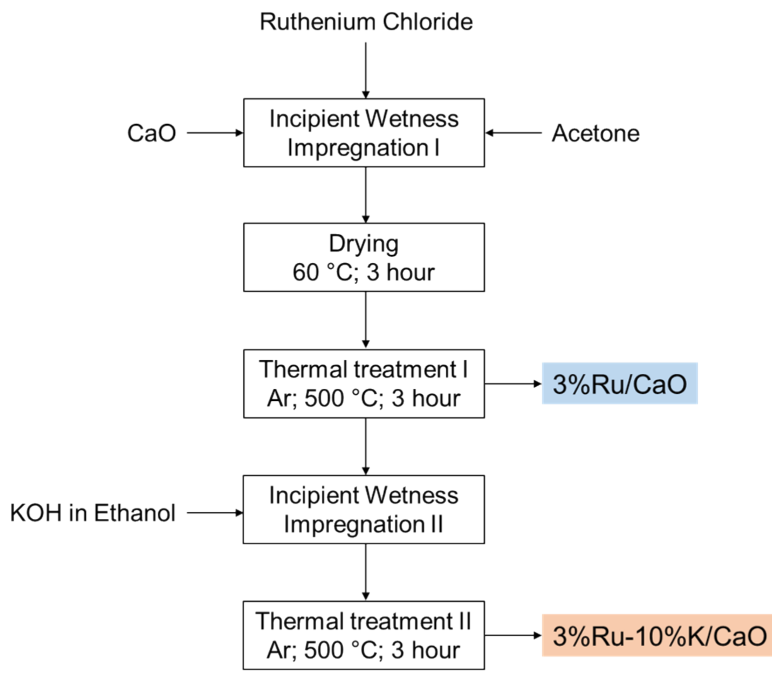

Figure S1. Catalyst synthesis protocols for the Ru/CaO and the Ru-K/CaO catalysts.

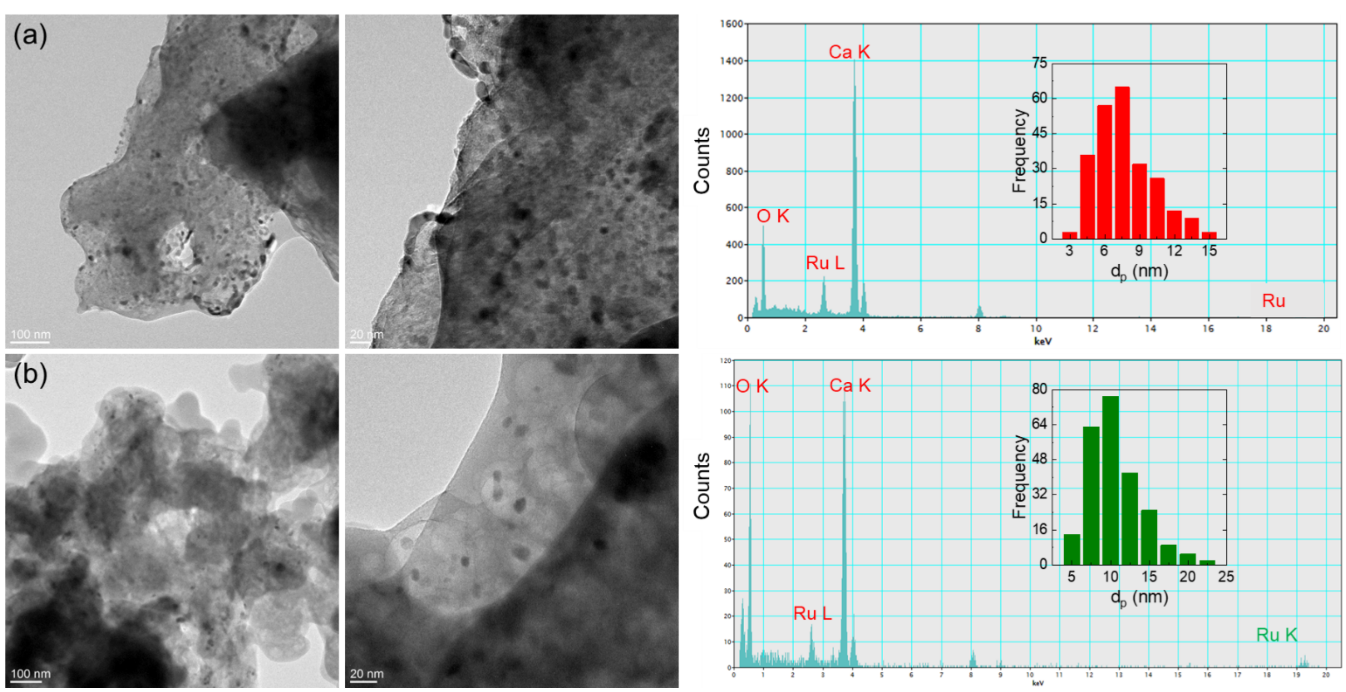

Figure S2. TEM images for the (a) Ru/CaO and the (b) Ru-K/CaO catalysts.

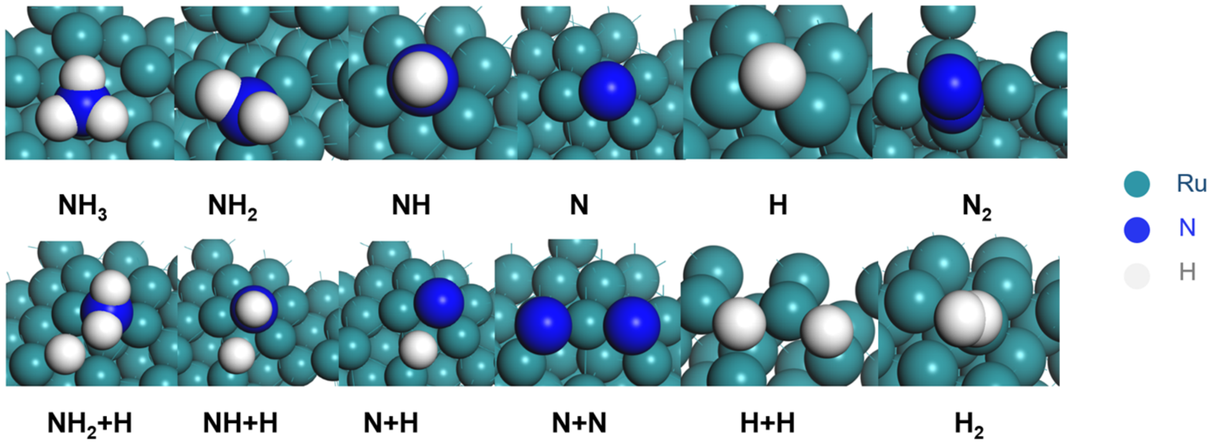

Figure S2. Optimized structures of various species involved in the NH_3 decomposition mechanism on the Ru (111) surface.

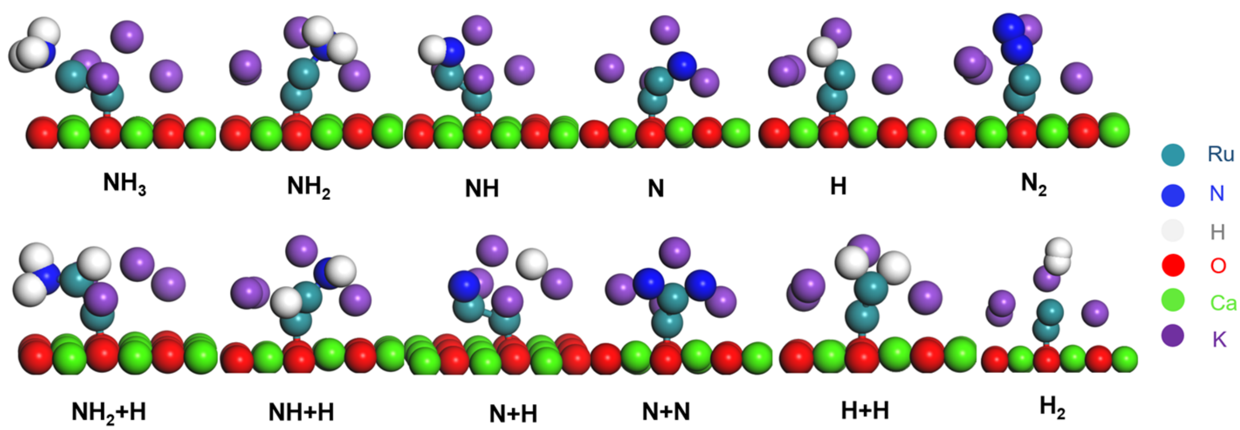

Figure S3. Optimized structures of various species involved in the NH_3 decomposition mechanism on the Ru-K/CaO catalyst.