# Unlocking the Potential of Ruthenium Catalyst for Nitrogen Fixation with Subsurface Oxygen

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## Micro-kinetic simulation details

The elementary reaction steps involved in ammonia formation route are listed as follows:

$$N_2 + * = *N_2 \text{ (R1)}$$

$$H_2 + 2* = 2H* \text{ (R2)}$$

$$*N_2 + *H = *NNH + * \text{ (R3)}$$

$$*NNH + *H = *NHNH + * \text{ (R4)}$$

$$*NHNH + *H = *NHNH_2 + * \text{ (R5)}$$

$$*NHNH_2 + *H = *\ NH_2NH_2 + * \text{ (R6)}$$

$$*\ NH_2NH_2 + *H = *NH_2 + *NH_3 \text{ (R7)}$$

$$*NH_2 + *H = *NH_3 \text{ (R8)}$$

$$*NH_3 = NH_3 +* \text{ (R9)}$$

where * represents one reaction site.

Our kinetic model includes the following set of rate and equilibrium equations.

$$\theta_{*N2} = K_1 p_{N2} \theta_v \tag{1}$$

$$\theta_{*H} = \sqrt{K_2 P_{H2}}\, \theta_v \tag{2}$$

$$r_3 = \vec{k}_3 \theta_{*N2} \theta_{*H} - \overleftarrow{k}_3 \theta_{*NNH} \theta_v \tag{3}$$

$$r_4 = \vec{k}_4 \theta_{*NNH} \theta_{*H} - \overleftarrow{k}_4 \theta_{*NHNH} \theta_v \tag{4}$$

$$r_5 = \vec{k}_5 \theta_{*NHNH} \theta_{*H} - \overleftarrow{k}_5 \theta_{*NHNH2} \theta_v \tag{5}$$

$$r_6 = \vec{k}_6 \theta_{*NHNH2} \theta_{*H} - \overleftarrow{k}_6 \theta_{*NH2NH2} \theta_v \tag{6}$$

$$r_7 = \vec{k}_7 \theta_{*NH2NH2} \theta_{*H} - \overleftarrow{k}_7 \theta_{*NH3} \theta_{*NH2} \tag{7}$$

$$r_8 = \vec{k}_8 \theta_{*NH2} \theta_{*H} - \overleftarrow{k}_8 \theta_{*NH3} \theta_v \tag{8}$$

$$\theta_{*NH3} = p_{NH3} \theta_v / K_9 \tag{9}$$

$K_i$ are the adsorption or desorption equilibrium constants, $k_i$ are the rate constants assumed to be of the Arrhenius form, $\theta_{*M}$ is the coverage of the species *M, $\theta_v$denotes the free active sites. $p$ is the gas partial pressure, we assume that the ammonia conversion factor is 0.1.

For the $N_2$ adsorption and $NH_3$ desorption step, the reaction rate can be written as $k_i = A_i^{'} exp(-\frac{G_{a,i}}{k_B T})$, where $G_{a,i}$ denotes the activation free energy, and $A_i^{'}$ is an effective pre-exponential factor deduced by $A_i^{'} = x\frac{k_B T}{h}$, in this equation, $x$ is the effective coefficient, $k_B$is the Boltzmann constant, and $h$ is the Planck constant. Moreover, the equilibrium constant ($K_i$) can be expressed as $K_i = exp(-\frac{\Delta G_i}{k_B T})$, where $\Delta G_i$ is the free energy change of $N_2$ adsorption and $NH_3$ desorption step.

For the electrochemical step, such as R3-R8, when taking the electrode potential into consideration, the reaction rate can be written as $\vec{k}_i = A_i exp(-\frac{E_{a,i}}{k_B T}) exp(-\frac{e\beta_i(U - U_i)}{k_B T})$, where $E_{a,i}$ presents the activation barrier which can be calculated by CI-NEB method,

$U_i = -\frac{-\Delta G_i}{e}$, and $\beta_i$ denotes the symmetric factor taken as 0.50. In addition, the equilibrium constant ($K_i$) for electrochemical steps can be expressed as $K_i = exp(-\frac{eU + \Delta G_i}{k_B T})$. Therefore, the reverse rate constant can be obtained from the its rate constant and equilibrium constant, that is $\overleftarrow{k}_i = \frac{K_i}{\overrightarrow{k}_i}$.

Since only R3 is the rate limiting step (RLS), all the other elementary steps are in equilibrium, thus, $r_4 = r_5 = r_6 = r_7 = r_8 = 0$.

From the conservation law, the sum of coverage of all the reaction species equals to one:

$$\theta_{*N2} + \theta_{*H} + \theta_{*NNH} + \theta_{*NHNH} + \theta_{*NHNH2} + \theta_{*NH2NH2} + \theta_{*NH2} + \theta_{*NH3} + \theta_v = 1$$

(10)

Then, we can get the free active site $\theta_v$,

$$\theta_v = 1/(1 + K_1 p_{N2} + \sqrt{K_2 P_{H2}} + \overleftarrow{k}_4\overleftarrow{k}_5\overleftarrow{k}_6\overleftarrow{k}_7\overleftarrow{k}_8 p_{NH3}^2/(\overrightarrow{k}_4\overrightarrow{k}_5\overrightarrow{k}_6\overrightarrow{k}_7\overrightarrow{k}_8 K_9^2 (K_2 P_{H2})^{5/2}) + \overleftarrow{k}_5\overleftarrow{k}_6$$
$$/(\overrightarrow{k}_5\overrightarrow{k}_6\overrightarrow{k}_7\overrightarrow{k}_8 K_9^2 (K_2 P_{H2})^2) + \overleftarrow{k}_6\overleftarrow{k}_7\overleftarrow{k}_8 p_{NH3}^2/(\overrightarrow{k}_6\overrightarrow{k}_7\overrightarrow{k}_8 K_9^2 (K_2 P_{H2})^{3/2}) + \overleftarrow{k}_7\overleftarrow{k}_8 p_{NH3}^2/(\overrightarrow{k}_7 \overrightarrow{k}_8 K_9^2 K_2 P_{H2}) + \overleftarrow{k}_8 p_{NH3}/(\overrightarrow{k}_8 K_9 \sqrt{K_2 P_{H2}}) + p_{NH3}/K_9)$$

$$= 1/(1 + K_1 p_{N2} + \sqrt{K_2 P_{H2}} + p_{NH3}^2/(K_4 K_5 K_6 K_7 K_8 K_9^2 (K_2 P_{H2})^{\frac{5}{2}}) + p_{NH3}^2/(K_5 K_6 K_7 K_8 K_9^2 (K_2 P_{H2})^2) + p_{NH3}^2/(K_6 K_7 K_8 K_9^2 (K_2 P_{H2})^{\frac{3}{2}}) + p_{NH3}^2/(K_7 K_8 K_9^2 K_2 P_{H2}) + p_{NH3}/(K_8 K_9 \sqrt{K_2 P_{H2}}) + p_{NH3}/K_9)$$

(11)

Actually, when taking all the values into the equation 11 to calculate the free active site $\theta_v$, except for $K_1 p_{N2}, \sqrt{K_2 P_{H2}}, and\ p_{NH3}/K_9$, others are several orders of magnitude smaller, and can be omitted.

After getting the $\theta_v$, the reaction rate of the rate limiting step R3 can be expressed by the following equation:

$$r_3 = \vec{k}_3\theta_{*N2}\theta_{*H} - \overleftarrow{k}_3\theta_{*NNH}\theta_v = \vec{k}_3K_1p_{N2}\sqrt{K_2P_{H2}}\,\theta_v^2 - \overleftarrow{k}_3p_{NH3}^{\ 2}/(K_4K_5K_6K_7K_8K_9^2(K_2$$

(12)

Where, $\theta_v$ can obtained from equation 11. And the reverse reaction rate can be also omitted compared to the forward reaction rate. Then we can get the turnover frequency (TOF).

The current density of ammonia formation is calculated by $j_{NH3} = e\rho TOF.$ In the equation, $\rho$ denotes the surface density of active sites, which can be calculated by using surface active sites divided by surface area. $e$ is 1.602*10$^{-19}$ C. When considering the electrode potential.

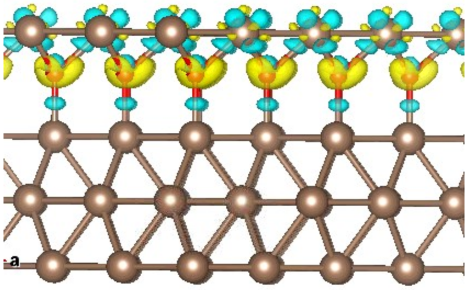

Figure S1. Charge density difference for Ru(0001) with ϴ=1.00 ML sub-oxygen dopants.

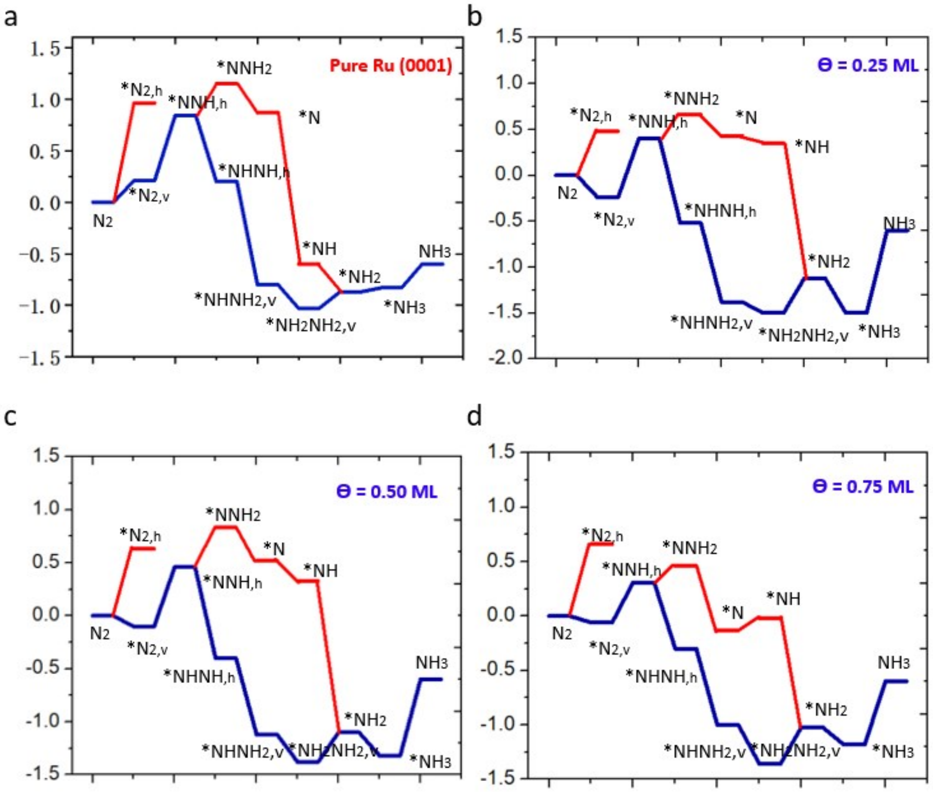

Figure S2. Calculated free energy change diagrams for pure Ru(0001), and Ru(0001) with different sub-oxygen coverages.

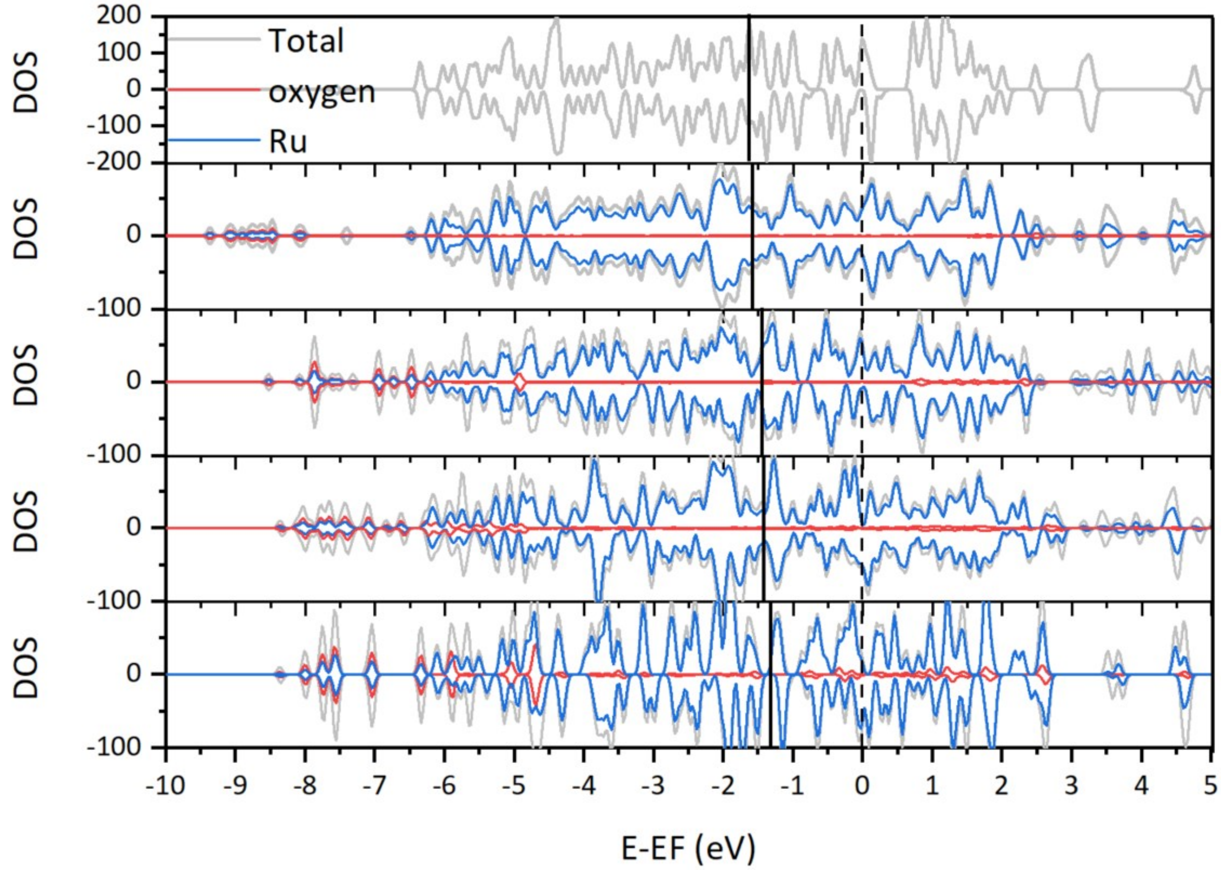

Figure S3. Calculated density of states (DOS) for Ru(0001), and Ru(0001) with 0.25 ML, 0.50 ML, 0.75 ML, and 1.00 ML suboxygen, the fermi level has been shifted to zero as shown in the black dashed line, and the black line indicates the d band center of five catalysts.

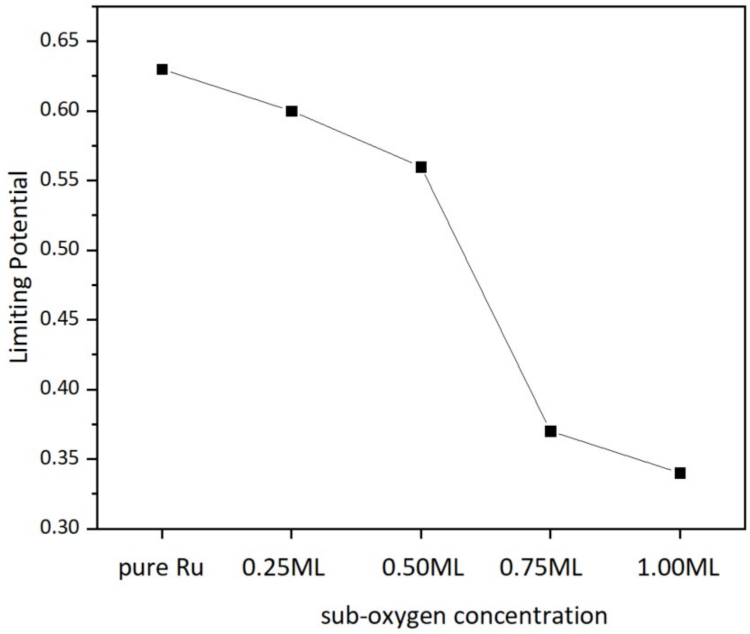

Figure S4. Calculated limiting potentials against sub-oxygen concentration in the subsurface of Ru(0001) catalysts.

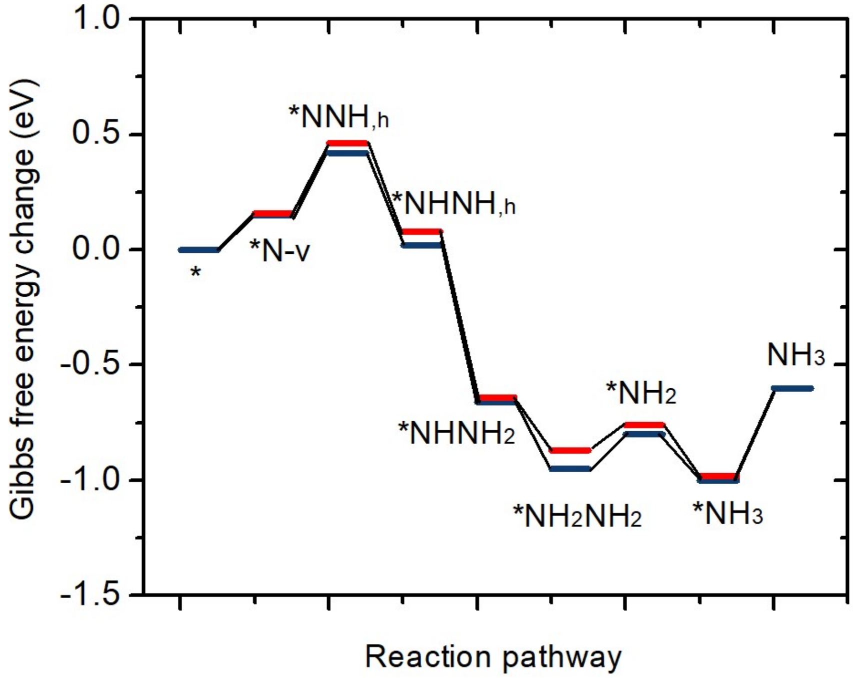

Figure S5. Calculated Gibbs free energy change diagram for N2 reduction on Ru(0001) with 1.00 ML suboxygen by using water (black line) and ethanol (red line) as the implicit solvent.

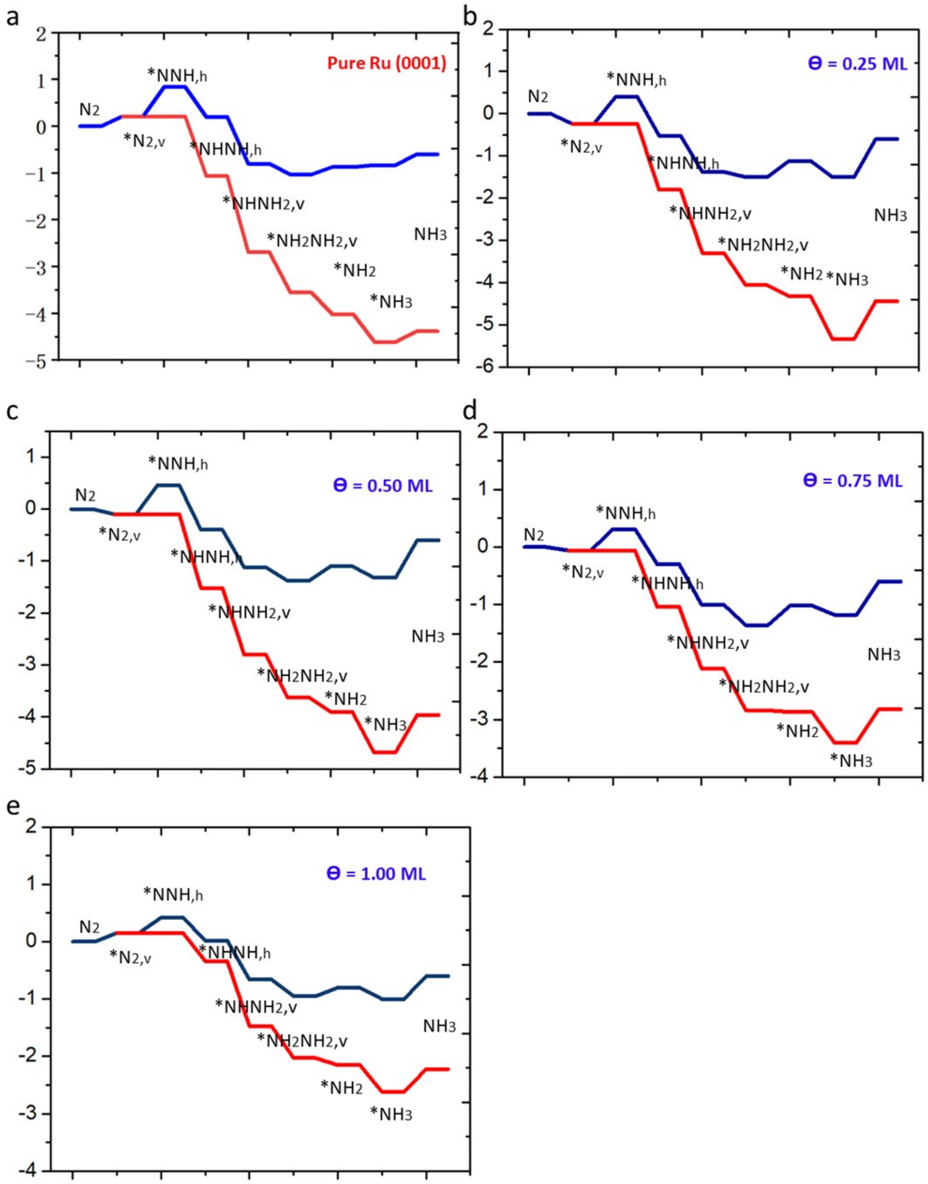

Figure S6. Gibbs free energy change diagrams for $N_2$ reduction on five catalysts with bias potential (U=limiting potential) and without electrochemical bias.

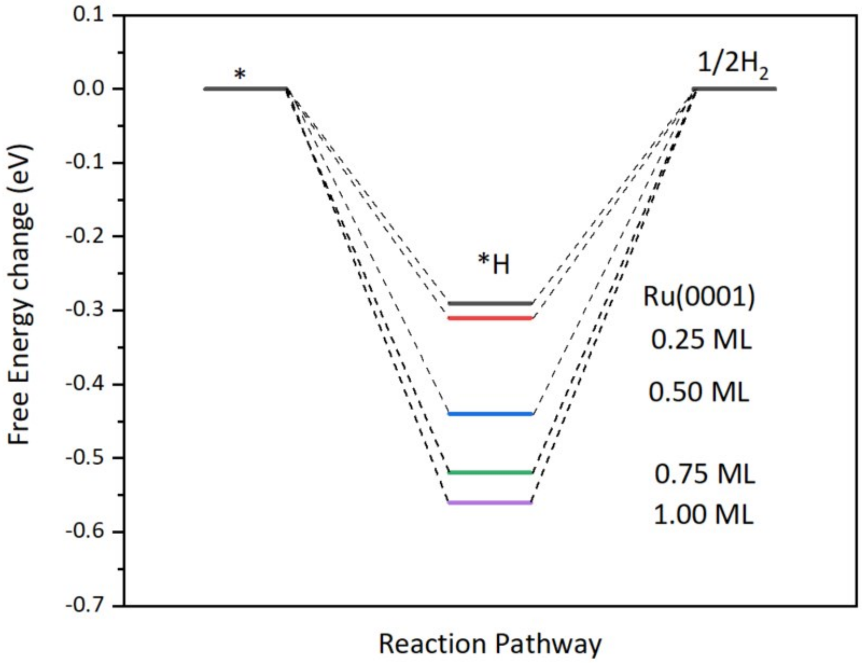

Figure S7. Calculated Gibbs free energy change diagram for HER process on pure Ru(0001) with and without suboxygen.