Supporting Information

Activity Self-Optimization Steered by Dynamically Evolved Fe$^{3+}$@Fe$^{2+}$ Double-Center on Fe$_2$O$_3$ Catalyst for NH$_3$-SCR

Hai Yang Yuan$^{1,2}$, Ningning Sun$^1$, Jianfu Chen$^1$, Hua Gui Yang$^2$, P. Hu$^{1,3}$, Haifeng Wang$^1$*

$^1$ Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis and Center for Computational Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai, 200237, China.

$^2$ Key Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Engineering Research Center of Hierarchical Nanomaterials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China.

$^3$ School of Chemistry and Chemical Engineering, The Queen’s University of Belfast, Belfast BT9, UK.

* Email: hfwang@ecust.edu.cn
Figure S1. (a) Hexagonal unit cell of Fe$_2$O$_3$; (b) Rhombohedral primitive cell of Fe$_2$O$_3$ with an antiferromagnetic helical spin arrangement, where “↑” and “↓” stands represents the spin up and spin down, respectively.
**Note S1. NH₃ Dissociation**

NH₃ adsorbed on Fe site ([NH₃-Fe-Ol], $E_{ads} = -1.08$ eV) can not couple with the gaseous or adsorbed NO directly, forming the N-N bond owing to its bond saturation. Hence, the NH₃ dissociation is the fundament for the subsequent reactions. Here, two different lattice oxygen (O₁) were considered to assist the NH₃ dissociation, i.e., O₁ in [NH₃-Fe-Ol] or the adjacent [Fe-Ol] (donated as O₁₁ and O₁₂, Figure S2). The energy profile of O₁₁(or O₁₂)-assisted NH₃* dissociation on clean Fe₂O₃(001) is shown in Figure S2. Comparing the orange (O₁₁) and olive (O₁₂) lines in Figure S2, we can find that O₁₂ is more reactive to facilitate the breaking of the N-H bond in NH₃ to form NH₂* with a lower barrier of 0.74 eV compared with O₁₁ ($E_a = 0.86$ eV); in the optimized transition state (TS1, Figure 2a), the N-H bond is elongated to 1.643 Å, and the forming O₁-H bond is 1.075 Å. The further dissociations of NH₂* assisted by O₁₂ give a barrier of 0.90 eV and 0.62 eV for the process NH₂ + O₁₂ → NH + O₁₂H and NH + O₁₂ → N + O₁₂H, respectively, which is lower than the barriers of the NH₃ dissociation by O₁₁(TS2 vs. TS2' and TS3 vs. TS3'). The related transition states are shown in Figure S3. In general, O₁₂ exhibits a more reactivity to dissociate NH₃. Moreover, the further dissociation of NH₂ into NH or N has an evidently increased barrier, and gradually becomes more endothermic (Figure S2). Therefore, on Fe₂O₃, the deep dissociation of NH₃ would be restrained, the formation of NH₂ species could be more favored, which is the main intermediate to participate in the following NH₃-SCR.
**Figure S2.** Energy profiles of dissociation of NH$_3$ adsorbed on Fe$^{3+}$ site ([NH$_3$-Fe-O$_{1}$]) assisted by the lattice O$_1$ from its own [Fe-O$_1$] (O$_{1,1}$, the orange line) and adjacent [Fe-O$_1$] (O$_{1,2}$, the olive line). Inserted is the adsorption structures of NH$_3$. TS1~TS3 (or TS1’~TS3’) are the transition states of [NH$_3$-Fe-O$_1$] + O$_{1,2}$(or O$_{1,1}$) $\rightarrow$ [NH$_2$-Fe-O$_1$]+ O$_{1,2}$H(or O$_{1,1}$H), [NH$_2$-Fe-O$_1$] + O$_{1,2}$(or O$_{1,1}$) $\rightarrow$ [NH-Fe-O$_1$] + O$_{1,2}$H(or O$_{1,1}$H) and [NH-Fe-O$_1$] + O$_{1,2}$H(or O$_{1,1}$H) and [NH-Fe-O$_1$] + O$_{1,2}$(or O$_{1,1}$) $\rightarrow$ [N-Fe-O$_1$] + O$_{1,2}$H(or O$_{1,1}$H), which are shown in Figure S3, respectively.
Figure S3. Transition state structures for NH$_3$ dissociation, where TS1–TS3 and TS1’–TS3’ correspond transition states in Figure S2.
Note S2. NH$_2$NO Formation and Conversion

As the intermediate [NH$_2$-Fe-Oi] forms, it could react with NO into N$_2$ and H$_2$O. It is interestingly found that the NO in the gas phase can readily couple with NH$_2$ in [NH$_2$-Fe-Oi] into [NH$_2$NO-Fe-Oi] (the Eley-Rideal (E-R) mechanism), following an almost barrierless process in terms of total energy; even putting a NO molecule above NH$_2$* at a long distance of 3.225 Å (Figure S4), the NO gradually descends and bonds with NH$_2$ spontaneously upon a typical structural optimization, forming a monodentate NH$_2$NO configuration with the N-end in NH$_2$ group bonded with Fe site; such an adsorption configuration of NH$_2$NO further tends to transform into a thermodynamically more stable configuration with the N-end from NO anchored at Fe site (Figure S4). This whole process (NH$_2$* + NO(g) →NH$_2$N*O) is strongly exothermic ($\Delta H = -2.38$ eV).

The coupling between NH$_2$ and NO could be a radical-like reaction, thus resulting in a barrierless process.\(^1\)

The formed NH$_2$NO will converse into H$_2$O and N$_2$ easily, a thermodynamic and kinetic favorable pathway (a hydrogen push-pull mechanism, i.e., NH$_2$NO → NHNO → NHNOH → NNOH → N$_2$+OH) has been reported.\(^1\)-\(^3\) Firstly, NH$_2$NO dehydrogenates into NHNO assisted by Oi of the adjacent [Fe-Oi] with a low barrier of 0.10 eV ($\Delta H = -0.25$ eV). In the transition state (TS1, Figure S5), the N-H bond is elongated to 1.141 Å, and the O-H bond is shortened to 1.140 Å. Then, the H atom from the NH$_2$NO dehydrogenation transfers back and bonds with the O in NHNO, forming NHNOH with an energy barrier of 0.42 eV (TS2, Figure S5). NHNOH breaks its N-H bond with an energy barrier of 0.41 eV, leading to the formation of NNOH. The related transition state (TS3, Figure S5) shows that the N-H bond and O-H bond are 1.270 Å and 1.260 Å, respectively. For NNOH, its N-O bond is so weak, which can break easily upon simple optimization, leading to the formation of N$_2$ and a hydroxyl, and the similar result has also been found in our previous works.\(^1\),\(^2\) Finally, the formed hydroxyl overcomes a low barrier to capture a H from Oi to form a H$_2$O molecule ($E_a = 0.21$ eV, TS4, Figure S5), finishing the whole NH$_2$NO conversion process. Overall, as seen from the energy profile in Figure S5, it can be found that the whole NH$_2$NO
conversion into N₂ and H₂O is a strongly exothermic process and has low barriers, revealing the NH₂NO conversion being very easy.
Figure S4. Process of the gaseous NO attacking NH₂ on Fe site.
Figure S5. Energy profile and the transition states for the NH$_2$NO conversion by the hydrogen push-pull mechanism. TS1, TS2, TS3 and TS4 show the optimized transition states of the breaking of N-H bond in NH$_2$NO ([NH$_2$NO-Fe-O$_i$] + [Fe-O$_i$] → [NHNO-Fe-O$_i$]@[Fe-O$_i$H]), NHNO re-hydrogenation into NHNOH ([NHNO-Fe-O$_i$]@[Fe-O$_i$H] → [NHNOH-Fe-O$_i$] + [Fe-O$_i$]), the breaking of N-H bond in NHNOH ([NHNOH-Fe-O$_i$] + [Fe-O$_i$] → N$_2$ + [HO-Fe-O$_i$]@[Fe-O$_i$H]) and the hydrogenation of OH to form H$_2$O ([HO-Fe-O$_i$]@[Fe-O$_i$H] → [H$_2$O-Fe-O$_i$] + [Fe-O$_i$]), respectively.
**Note S3. H removal process**

Due to the former NH$_3$ dissociation and NH$_2$NO conversion, the lattice O$_l$ would be covered by H atoms (O$_l$H), thus the H removal pathways were studied. Initially, the adsorbed O$_2$ on Fe$^{3+}$ site was considered, while O$_2$ has a weak adsorption energy (only -0.35 eV); besides, O$_2$ adsorbed on Fe$^{3+}$ site difficultly dissociates into O atoms ($E_a = 2.85$ eV). These calculated results indicate that O$_2$ or O could have extremely low coverages on Fe$^{3+}$ sites, which would seriously limit the H removal process. Accordingly, we resorted the Mars-van Krevelen pathway (Scheme S1, see the detailed energy profile in Figure 1f), in which firstly two adjacent O$_l$H groups react with each other through a H transfer, generating a H$_2$O molecule and oxygen vacancy ([Fe-O$_v$]) with a low barrier of 0.30 eV (TS1, Figure S6). On O$_v$, O$_2$ adsorbs strongly ($E_{ads} = -2.27$ eV, see Figure S6), for which two possible channels were examined to remove H atoms, i.e. Path A and Path B.

In Path A, O$_2$ on O$_v$ ([Fe-O$_2$]) dissociates with a barrier of 0.70 eV (TS2, Figure S6), giving one O atom to Fe$^{3+}$ site ([O-Fe-O$_l$]); then, the formed [O-Fe-O$_l$] can capture two H atoms continuously to form a H$_2$O molecule easily with low energy barrier (Figure 1f). For Path B, [Fe-O$_2$] seizures a H atom, forming OOH on O$_v$ ([Fe-OOH]) with a barrier of 0.42 eV (TS5, Figure S6); subsequently, [Fe-OOH] prefers to break its O-O bond instead of capturing another H again to form H$_2$O (0.47 eV vs. 1.11 eV), and the related transition states are shown by TS6 and TS7 in Figure S7. By comparing the energy profile of the above H removal pathways for [Fe-O$_2$] in detail (Figure 1f), one can see that the Path A and Path B have similar effective barriers (0.70 eV vs. 0.71 eV), meaning energetically their both possible feasibility to remove H.
**Scheme S1.** Scheme for the possible pathways of H removal pathways on O₁ on Fe₂O₃(001).
Figure S6. Optimized transition states and important intermediates involved in the H removal process, which correspond to the energy states in Figure S6. In detail, TS1: the transition state of the intramolecular H migration between two [Fe-OlH], i.e., [Fe-OlH] + [Fe-OlH] → [Fe-OlH2] + [Fe-Ol]; TS2: the adsorption of O₂ on Ov; TS3: the transition state of the O₂ dissociation on Ov, i.e. [O₂-Fe-Ol] → [O-Fe-Ol]; TS4: the transition state of the O atom on Fe site capturing H atom, i.e., [O-Fe-Ol] + [Fe-OlH] → [HO-Fe-Ol] + [Fe-Ol]; TS5: the transition state of the hydroxyl on Fe site capturing H atom, i.e., [HO-Fe-Ol] + [Fe-OlH] → [H₂O-Fe-Ol] + [Fe-Ol]; TS6: the transition state of O₂ on Ov capturing H atom from the adjacent [Fe-OlH], i.e., [Fe-OlH] + [Fe-OlH] → [Fe-Ol] + [Fe-Ol] + H₂O respectively.
Note S4. Kinetic Details

According to the De Donder relation\(^4\), the net rate for elementary step \(i\) in terms of the forward rate constant, \(k_i\), the coverage of the reactant on active sites, \(\theta(j)\), and the reversibility, \(Z_i\), can be written as

\[
r_i = k_i \prod \theta(j)^{v_{ij}} (1 - Z_i)
\]

(Eqn-S1)

where \(Z_i = \prod \theta(j)^{v_{ij}}/K_{eq,i}\), which approaches zero as step \(i\) becomes irreversible and approach unity as step becomes in quasi-equilibrium. \(K_{eq,i}\) is the equilibrium constant of step \(i\), determined by the standard Gibbs free energy change of the reaction, \(K_{eq,i} = \exp(-\Delta G/RT)\). \(v_{ij}\) are the stoichiometric coefficients for the \(j\) reactants or products of step \(i\). \(Z_i\) can be solved by the following the steady state condition. In our micro-kinetic model, the condition that the sum of coverages of adsorbed species on [Fe-Ol] and [Fe-OlH] is equal to 1 was applied, and the H diffusion on Fe\(_2\)O\(_3\)(001) was considered. Then, the coverage of all species can be obtained, and the rate of the reaction can be calculated accordingly.

In order to distinguish the relative importance of each elementary step in the reaction mechanism, i.e. identifying which transition state really controls the net rate, the “degree of rate control” was used here,\(^5,6\) which provides an excellent quantitative tool for computing the sensitivity of each step in a reaction scheme. Suggested by Campbell et al., the “degree of rate control” \((\chi_{RC,i})\) for the step \(i\) can be defined in the term of the standard state Gibbs free energy of the transition state as

\[
\chi_{RC,i} = \frac{k_i}{r} \left( \frac{\partial r}{\partial k_i} \right)_{K_{eq,i}} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{K_{eq,i}} = \left( \frac{\partial \ln \left( \frac{\partial G^{TS}_{i} + \ln K_{ij}}{RT} \right)}{\partial G^{TS}_{i}} \right)_{K_{eq,i}}
\]

(Eqn-S2)

where the partial derivative is taken by holding the standard state Gibbs free energy of all other transition states for step \(j \neq i\) and all intermediate \(m\) constant, which is the same as holding the rate constants, \(k_j\) and the equilibrium constant, \(K_j\), constant \((j \neq i)\). Here, keeping \(K_{eq,i}\) constant means that \(k_{i+}\) and \(k_i\) must be changed together, whose ratio remains constant. Changing the Gibbs free energy of the transition state of step \(i\) while nothing else is changed can determine the influence of step \(i\) on the overall reaction rate in whole mechanism. The value of \(\chi_{RC,i}\) for step \(i\) is larger, the influence of this step \(i\)
on the overall reaction rate, \( r_i \), is bigger.

To study the importance of an intermediate’s stability (thermodynamics) in an overall complex mechanism, the degree of thermodynamic rate control \( X_{TRC,n} \) of intermediate \( n \) was defined. According to Campbell’s report, \(^6\) \( X_{TRC,n} \) could be written as:

\[
X_{TRC,n} = \frac{1}{r_i} \left( \frac{\partial r_i}{\partial \left( \frac{G^0_n}{RT} \right)} \right) = \left( \frac{\partial \ln r_i}{\partial \left( \frac{G^0_n}{RT} \right)} \right)
\]

(Eqn-S3)

in which the partial derivative is taken holding the standard-state Gibbs free-energy constant of all other intermediates \( m \neq n \) (\( G^0_{mn} \)) and Gibbs free energy of all transition states \( i \) constant (\( G^0_{nTS} \)). Here \( R \) is the universal gas constant and \( T \) is the absolute temperature. \( X_{TRC,n} \) is dimensionless, which describes the relative increase in the reaction rate per decrease the standard-state free energy for intermediate \( n \) when other species’ energies hold constant.

Here, we used the collision theory \(^7\) to estimate the barriers (\( E_a \)) of gas-phase molecule adsorption process, as well as the barrier of the gas-phase NO coupling with the surface NH\(_2^*\) species. Therefore, according to the transition state theory and collision theory, the reaction rate on a per site basis can be written as:

\[
r_i(T) = \frac{k_B T}{h} \exp \left( \frac{E_a}{k_B T} \right) \frac{P_i}{P} S(T) \frac{P A}{\sqrt{2 \pi k_B m_i T}}
\]

(Eqn-S4)

where \( k_B \), \( h \), \( T \), \( P_i \) and \( m_i \) are Boltzmann constant, Planck constant, reaction temperature, pressure and the mass of gas molecule, respectively. And, \( A \) is the area of the atom which is described as \( A = \pi r^2 \), in which \( r \) is the VDW radius of the atom. Here, we have assumed that the gas behaves ideally, and \( S(T) \), the sticking coefficient, is approximated as 1. Hence we could derive an equation about \( E_a \):

\[
E_a \approx -k_B T \ln \left( \frac{P_i A h}{k_B T \sqrt{2 \pi k_B m_i T}} \right)
\]

(Eqn-S5)

In our microkinetic simulation, the experimental condition for NH\(_3\)-SCR on Fe\(_2\)O\(_3\), \( P_{NH3} = 5.00 \times 10^{-4} \) atm, \( P_{NO} = 5.00 \times 10^{-4} \) atm, \( P_{O2} = 0.03 \) atm, \( P_{N2} = 0.8 \) atm and \( P_{H2O} = 0.05 \) atm.
Note S5. Kinetic analysis of NH3-SCR on the pristine Fe2O3 with only Fe3+ sites

To investigate the importance of each elementary step in the feasible NH3-SCR pathway on the pristine Fe2O3 catalyst with only Fe3+ site, the reversibility and degree of rate control \( (X_{RT,i}) \) of each elementary step was calculated. From Table S1, one can see that the coupling step of \( \text{NH}_2 \) and \( \text{NO} \) into \( \text{NH}_2\text{NO} \) (\( [\text{NH}_2\text{-Fe-O}] + \text{NO}(g) \rightleftharpoons [\text{NH}_2\text{NO-Fe-O}] \)) has a largest \( X_{RT} \) (about \( 6.65 \times 10^{-1} \)), and is extremely irreversible \( (Z_i = 4.17 \times 10^{-11}) \), indicating this step is the critical rate-limiting step. From its rate equation \( r_6 = \kappa^+ \theta([\text{NH}_2\text{-Fe-O}])*(P(\text{NO})/P^\theta) *(1-Z_i) \), it can see that except for \( \kappa^+ \), the coverage of \( \text{NH}_2, \theta([\text{NH}_2\text{-Fe-O}]) \), is a key factor influencing the reaction rate. However, \( \theta([\text{NH}_2\text{-Fe-O}]) \) is small, only \( 6.51 \times 10^{-12} \) (Table S2), which limits the NH3-SCR rate on the pristine Fe2O3 significantly. Besides, as shown by \( X_{RT,i} \) in Table S1, we can find that the adsorption of \( \text{O}_2 \) on the oxygen vacancy (Ov) has a relatively large \( X_{RT,i} \) of about \( 3.35 \times 10^{-1} \), meaning this step could be the second important step for NH3-SCR on the pristine Fe2O3. The difficult \( \text{O}_2 \) adsorption step could lead to the low coverage of \( \text{O}_2 \) on Ov (only \( 6.60 \times 10^{-16} \)), inhibiting the following H removal process to some extent. Therefore, increasing the \( \text{NH}_2 \) and \( \text{O}_2 \) coverages on Fe2O3 to contribute the \( \text{NH}_2\text{NO} \) formation and H removal processes could be effective methods to improve the catalytic activity of Fe2O3 for NH3-SCR.
**Table S1.** Kinetic data, $k^+ r_i Z_i$, for each elementary reaction step in NH$_3$-SCR over the pristine α-Fe$_2$O$_3$(001) at 600 K.

| Step / | Clean Fe$_2$O$_3$(110) |  |  |
|--------|----------------------|---|---|
| NH$_3$ adsorption/dissociation | | | |
| R1 NH$_3$(g) + [Fe-Ol] $\rightleftharpoons$ [NH$_3$-Fe-Ol] | $3.84 \times 10^{-8}$ | 1.00 | $3.32 \times 10^{-12}$ |
| R2 [NH$_3$-Fe-Ol] + [Fe-Ol] $\rightleftharpoons$ [NH$_3$-Fe-Ol]@[Fe-OH] | $3.84 \times 10^{-8}$ | 1.00 | $1.00 \times 10^{-11}$ |
| R3 [NH$_3$-Fe-Ol]@[Fe-OH] $\rightleftharpoons$ [NH$_3$-Fe-Ol] + [Fe-OH] | $3.84 \times 10^{-8}$ | 1.00 | $6.02 \times 10^{-8}$ |
| NH$_2$NO formation/conversion | | | |
| R4 [NH$_2$-Fe-Ol] + NO(g) $\rightleftharpoons$ [NH$_2$NO-Fe-Ol] | $3.84 \times 10^{-8}$ | 4.17$\times 10^{-11}$ | $6.65 \times 10^{-4}$ |
| R5 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightleftharpoons$ [NHNO-Fe-Ol]@[Fe-OH] | $3.84 \times 10^{-8}$ | 1.00 | $4.60 \times 10^{-15}$ |
| R6 [NHNO-Fe-Ol]@[Fe-OH] $\rightleftharpoons$ [NHNOH-Fe-Ol] + [Fe-Ol] | $3.84 \times 10^{-8}$ | 1.00 | $1.47 \times 10^{-14}$ |
| R7 [NHNOH-Fe-Ol] + [Fe-Ol] $\rightleftharpoons$ N$_2$(g) + [HO-Fe-Ol]@[Fe-OH] | $3.84 \times 10^{-8}$ | 2.83$\times 10^{-15}$ | $2.77 \times 10^{-11}$ |
| H removal | | | |
| R8 [HO-Fe-Ol] + [Fe-OH] $\rightleftharpoons$ [HO-Fe-Ol]@[Fe-OH] | $9.61 \times 10^{-9}$ | 1.00 | $1.46 \times 10^{-19}$ |
| R9 [HO-Fe-Ol]@[Fe-OH] $\rightleftharpoons$ [HO-Fe-Ol]@[Fe-OH] | $4.81 \times 10^{-4}$ | 1.00 | $4.42 \times 10^{-19}$ |
| R10 [H$_2$O-Fe-Ol] $\rightleftharpoons$ [Fe-O$_2$] + H$_2$O(g) | $4.81 \times 10^{-4}$ | 1.00 | $7.33 \times 10^{-12}$ |
| R11 [Fe-O$_2$] + [Fe-OH] $\rightleftharpoons$ [Fe-OH]@[Fe-OH] | $9.61 \times 10^{-9}$ | 1.00 | $1.12 \times 10^{-14}$ |
| R12 [Fe-OH]@[Fe-OH] $\rightleftharpoons$ [Fe-O$_2$] + [Fe-O$_2$] | $9.61 \times 10^{-9}$ | 1.00 | $4.02 \times 10^{-12}$ |
| R13 [Fe-O$_2$] $\rightleftharpoons$ H$_2$O(g) + [Fe-O] | $9.61 \times 10^{-9}$ | 1.00 | $1.84 \times 10^{-7}$ |
| R14 O$_2$(g) + [Fe-O$_2$] $\rightleftharpoons$ Fe$_2$O$_3$ | $9.61 \times 10^{-9}$ | 2.19$\times 10^{-8}$ | $3.35 \times 10^{-4}$ |
| R15 [Fe-O$_2$] $\rightleftharpoons$ [O-Fe-O] | $9.42 \times 10^{-9}$ | 4.87$\times 10^{-2}$ | $6.86 \times 10^{-9}$ |
| R16 [O-Fe-O] + [Fe-OH] $\rightleftharpoons$ [O-Fe-O]@[Fe-OH] | $9.42 \times 10^{-9}$ | 1.00 | $6.48 \times 10^{-14}$ |
| R17 [O-Fe-O]@[Fe-OH] $\rightleftharpoons$ [HO-Fe-O] + [Fe-O$_2$] | $9.42 \times 10^{-9}$ | 1.00 | $1.29 \times 10^{-19}$ |
| R18 [Fe-O$_2$] + [Fe-OH] $\rightleftharpoons$ [Fe-O$_2$]@[Fe-OH] | $1.92 \times 10^{-10}$ | 1.00 | $7.29 \times 10^{-16}$ |
| R19 [Fe-O$_2$]@[Fe-OH] $\rightleftharpoons$ [Fe-O$_2$] + [Fe-O] | $1.92 \times 10^{-10}$ | 1.00 | $4.31 \times 10^{-13}$ |
| R20 [Fe-OOH] + [Fe-O] $\rightleftharpoons$ [Fe-OOH]@[Fe-OH] | $1.92 \times 10^{-10}$ | 1.00 | $3.66 \times 10^{-29}$ |
| R21 [Fe-OOH]@[Fe-OH] $\rightleftharpoons$ H$_2$O(g) + [Fe-O] + [Fe-O] | $1.92 \times 10^{-10}$ | 5.94$\times 10^{-2}$ | $7.72 \times 10^{-20}$ |
| R22 [Fe-OOH] $\rightleftharpoons$ [HO-Fe-O] | $1.92 \times 10^{-10}$ | 4.89$\times 10^{-2}$ | $1.40 \times 10^{-10}$ |
Table S2. Coverage ($\theta(j)$) of some main reactants and intermediates at the steady state of NH$_3$-SCR on the pristine $\alpha$-Fe$_2$O$_3$(001) at 600 K.

| Species                        | $\theta(j)$       | Species                        | $\theta(j)$       |
|--------------------------------|-------------------|--------------------------------|-------------------|
| [Fe-Oi]                        | 9.82×10^{-1}      | [Fe-Oi]                        | 2.80×10^{-14}     |
| [NH$_3$-Fe-Oi]                 | 3.42×10^{-4}      | [Fe-Oi]                        | 6.00×10^{-16}     |
| [NH$_2$-Fe-Oi]                 | 6.51×10^{-12}     | [O-Fe-Oi]                      | 7.84×10^{-16}     |
| [NH$_3$-Fe-Oi]@[Fe-OiH]        | 1.71×10^{-9}      | [O-Fe-Oi]@[Fe-OiH]             | 8.01×10^{-13}     |
| [NH$_2$NO-Fe-Oi]               | 1.30×10^{-16}     | [H$_2$O-Fe-Oi]                 | 2.85×10^{-7}      |
| [NHNO-Fe-Oi]@[Fe-OiH]          | 1.61×10^{-14}     | [H$_2$O-Fe-Oi]@[Fe-OiH]        | 5.29×10^{-3}      |
| [NHNOH-Fe-Oi]                 | 8.69×10^{-18}     | [Fe-OiH]                       | 1.39×10^{-3}      |
| [Fe-OH]                       | 5.89×10^{-3}      | [Fe-OiH]@[Fe-OiH]              | 1.78×10^{-17}     |
| [Fe-OH]@[Fe-OiH]              | 2.12×10^{-8}      | [Fe-OOH]                      | 1.44×10^{-19}     |
| [Fe-H$_2$O]                   | 7.91×10^{-11}     | [Fe-OOH]@[Fe-OiH]             | 1.90×10^{-13}     |
Figure S7. Energy profile for the H removal pathway assisted by O$_2$ adsorbed on Fe$^{2+}$ site, and the related intermediates and transition states are shown in Figure S8.
Figure S8. (a) Adsorption structure of O$_2$ on Fe$^{2+}$ site; (b, c) Transition states of O$_2$ and OOH hydrogenation assisted by O$_2$ on Fe$^{2+}$ site ([O$_2$-Fe-OH]).
Note S6. Activity trend of NH$_3$-SCR on Fe$_2$O$_3$ as a function of reaction temperature

As shown in Figure 3b, starting from the low temperature, Fe$_2$O$_3$ catalyst has a poor catalytic activity for NH$_3$-SCR; almost all of Fe$^{3+}$([Fe-O$_{\text{j}}$]) sites on Fe$_2$O$_3$(001) are reduced to Fe$^{2+}$ ones ([Fe-O$_{\text{l}}$H]), that are the main active centers for NH$_3$-SCR ($\theta$(Fe$^{2+}$) = 1 ML, Figure 3c). On Fe$^{2+}$ sites, the mechanistic details of NH$_3$-SCR will change. NH$_3$ has a weaker adsorption compared with that on Fe$^{3+}$ sites ($E_{\text{ads}} = -1.18$ eV vs. $-0.57$ eV), and would have to adsorb on Fe$^{2+}$ sites, which thus yields the decreased overall reaction rate. Furthermore, comparing the related H removal process (Figure S9), one can see that on this reduced Fe$_2$O$_3$ catalyst surface with only Fe$^{2+}$ sites, O$_2$ adsorbed on Fe$^{2+}$ site becomes the dominant pathway to remove the H species from the NH$_3$ dissociation or NH$_2$NO conversion, but the MvK pathway was significantly limited, leading to the deactivation of H species on the lattice O$_{\text{i}}$. At this time, the H removal process is rate-limiting, illustrated by the degree of rate control ($X_{\text{RC}}$) analysis (Figure 3d). The larger $X_{\text{RC}}$ means the greater importance of elementary on the whole reaction. Hence, to improve the catalytic activity of Fe$_2$O$_3$ for NH$_3$-SCR at a low temperature, accelerating the H removal process (by activating the MvK pathway) could be an effective method; this essentially requires to activate the lattice oxygen, which could be achieved by introducing the more reducible metallic sites.

Driven by the increased temperature, the MvK pathway to remove H species on the catalyst surface is gradually promoted (Figure S9), reducing the H accumulation on O$_{\text{i}}$. Accordingly, the activity curve rises significantly with the increase of temperature. As temperature increases to middle-high one of about 590 K, the activity curve reaches the maximum point, implying the optimal catalytic activity at this time. It is noteworthy that this theoretical optimal temperature predicted is in agreement with the optimum experimental temperature range (~600 K) for NH$_3$-SCR on Fe$_2$O$_3$-based catalysts. From the coverage curves (Figure 3c), it can be found that as the temperature increases, $\theta$(Fe$^{2+}$) (or $\theta$(Fe$^{3+}$)) decreases (or increases) quickly, and around this optimal temperature (590 K), the ratio of $\theta$(Fe$^{3+}$) and $\theta$(Fe$^{2+}$) approaches about 1 : 1 at the steady state, demonstrating the existence of Fe$^{3+}$ and Fe$^{2+}$ double-centers on Fe$_2$O$_3$ catalyst in the
realistic NH3-SCR at this time. With the continuous increase of reaction temperature, the activity curve declines, implying the decreased NH3-SCR catalytic activity of Fe2O3 catalyst at high temperatures. From the degree of rate control ($X_{RC}$) analysis (Figure 3d), one can see that with the increase of temperature, the step changes to the NH2 and NO coupling step has the largest $X_{RC}$ after about 500 K, implying that the rate-determining step change to the NH2 and NO coupling process from the H removal process at low temperature. Thus, at the middle-high or high temperature, the activity of Fe2O3 catalyst is mainly limited by the NH2 and NO coupling step.

At high temperatures, Fe$^{3+}$ sites are the dominant active center, which is however not conductive for the NH2 and NO coupling, thus resulting in the decline of activity curve of NH3-SCR on Fe2O3. Furthermore, at a high temperature, NH3 has a very weak adsorption free energy due to the large entropy contribution, thus yielding extremely low NH2 coverage; at this time, the rate-determining step of NH2 coupling with NO is further limited, leading to the decreased NH3-SCR rate.
Figure S9. Variation of the Langmuir-Hinshelwood (red line) and Mars-van Krevelen (blue line) pathways used to remove H species on Fe₂O₃ catalyst at 590 K.
Table S3. The enthalpy ($\Delta H$) and enthalpy ($T\Delta S$) of each elementary step in NH$_3$-SCR process at 590 K.

| Step $i$ | Reduced Fe$_2$O$_3$(001) $\Delta H$/eV | $T\Delta S$/eV |
|----------|---------------------------------------|---------------|
| Fe$^{3+}$ site |                                        |               |
| NH$_3$ adsorption/ dissociation |                                        |               |
| Fe$^{3+}$ site |                                        |               |
| R1 NH$_3$(g) + [Fe-Ol] $\rightarrow$ [NH$_3$-Fe-Ol] | -1.18         | 1.17          |
| R2 [NH$_3$-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NH$_2$-Fe-Ol] + [Fe-OlH] | 0.63 | \            |
| R3 [NH$_2$-Fe-Ol] + [Fe-OlH] $\rightarrow$ [NH$_2$-Fe-Ol] + [Fe-Ol] | 0.56 | \            |
| Fe$^{2+}$ site |                                        |               |
| R4 NH$_3$(g) + [Fe-OlH] $\rightarrow$ [NH$_3$-Fe-OlH] | -0.57         | 1.17          |
| R5 [NH$_3$-Fe-OlH] + [Fe-Ol] $\rightarrow$ [NH$_2$-Fe-OlH] + [Fe-Ol] | 0.08 | \            |
| R6 [NH$_2$-Fe-OlH] + [Fe-Ol] $\rightarrow$ [NH$_2$-Fe-OlH] + [Fe-Ol] | -0.27 | \            |
| NH$_2$NO formation |                                        |               |
| Fe$^{3+}$ site |                                        |               |
| R8 [NH$_2$-Fe-Ol] + NO(g) $\rightarrow$ [NH$_2$NO-Fe-Ol] | -2.38         | 1.29          |
| NH$_2$NO conversion |                                        |               |
| Fe$^{3+}$ site |                                        |               |
| R9 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NHNO-Fe-Ol] + [Fe-OlH] | -0.25 | \            |
| R10 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NHNO-Fe-OlH] + [Fe-Ol] | -1.21 | -1.17         |
| R11 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NHNO-Fe-Ol] + [Fe-Ol] | 0.61 | \            |
| R12 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NHNO-Fe-Ol] + [Fe-Ol] | 0.22 | \            |
| H removal |                                        |               |
| MvK mechanism |                                        |               |
| R13 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NHNOH-Fe-Ol] + [Fe-Ol] | -0.39 | \            |
| R14 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NHNOH-Fe-Ol] + [Fe-Ol] | -2.29 | -1.17         |
| R15 [NH$_2$NO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [NHNOH-Fe-Ol] | 0.22 | \            |
| R16 [NHNOH-Fe-Ol] + [Fe-Ol] $\rightarrow$ N$_2$(g) + [HO-Fe-Ol] + [Fe-Ol] | -2.62 | -1.17         |
| R17 [NHNOH-Fe-Ol] + [Fe-Ol] $\rightarrow$ N$_2$(g) + [HO-Fe-OlH] + [Fe-Ol] | -2.62 | -1.17         |
| R18 [HO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [HO-Fe-Ol] + [Fe-Ol] | -0.78 | \            |
| R19 [HO-Fe-OlH] + [Fe-Ol] $\rightarrow$ [HO-Fe-OlH] + [Fe-Ol] | 0.37 | \            |
| R20 [HO-Fe-OlH] + [Fe-Ol] $\rightarrow$ [HO-Fe-OlH] + [Fe-Ol] | 0.07 | \            |
| R21 [HO-Fe-OlH] + [Fe-Ol] $\rightarrow$ [HO-Fe-OlH] + [Fe-Ol] | 0.40 | \            |
| R22 [HO-Fe-OlH] + [Fe-Ol] $\rightarrow$ [HO-Fe-OlH] + [Fe-Ol] | 0.22 | \            |
| R23 [H$_2$O-Fe-Ol] + [Fe-Ol] $\rightarrow$ [H$_2$O-Fe-Ol] + [Fe-Ol] | 0.99 | -1.15         |
| R24 [H$_2$O-Fe-Ol] + [Fe-Ol] $\rightarrow$ [H$_2$O-Fe-Ol] + [Fe-Ol] | 0.44 | -1.15         |
| R25 [Fe-OlH] + [Fe-Ol] $\rightarrow$ [Fe-OlH] + [Fe-Ol] | 0.37 | \            |
| R26 [Fe-OlH] + [Fe-Ol] $\rightarrow$ [Fe-OlH] + [Fe-Ol] | 0.29 | \            |
| R27 [Fe-OlH] + [Fe-OlH] $\rightarrow$ [Fe-OlH] + [Fe-Ol] | 1.74 | -1.15         |
| R28 O$_2$(g) + [Fe-Ol] $\rightarrow$ [Fe-Ol] | -2.17 | 1.25          |
| R29 [Fe-Ol] $\rightarrow$ [O-Fe-Ol] | -0.17 | \            |
| R30 [O-Fe-Ol] + [Fe-Ol] $\rightarrow$ [O-Fe-Ol] + [Fe-Ol] | -0.63 | \            |
| R31 [O-Fe-Ol] + [Fe-Ol] $\rightarrow$ [O-Fe-Ol] + [Fe-Ol] | -0.66 | \            |
| Reaction | Equation | ΔG (kJ/mol) |
|----------|----------|-------------|
| R32 | [HO-Fe-O₂] + [Fe-O₂H] → [HO-Fe-O₂@[Fe-O₂H]] | -0.78 |
| R33 | [Fe-O₂] + [Fe-O₂H] → [Fe-O₂@[Fe-O₂H]] | -0.09 |
| R34 | [Fe-O₂@[Fe-O₂H]] → [Fe-OOH] + [Fe-O₂] | 0.25 |
| R35 | [Fe-OOH] + [Fe-O₂H] → [Fe-OOH@[Fe-O₂H]] | 0.19 |
| R36 | [Fe-OOH@[Fe-O₂H]] → H₂O(g) + [Fe-O₂] + [Fe-O₂] | -1.52 -1.15 |
| R37 | [Fe-OOH] → [HO-Fe-O₂] | -1.62 |
| L-H mechanism | R38 | O₂(g) + [Fe-O₂H] → [O₂-Fe-O₂H] | -0.84 1.25 |
| by O₂ on Fe²⁺ | R39 | O₂-Fe-O₂H → [HOO-Fe-O₂] | 0.44 |
| site | R40 | [HOO-Fe-O₂] + [Fe-O₂H] → [HOO-Fe-O₂@[Fe-O₂H]] | -0.23 |
| | R41 | [HOO-Fe-O₂@[Fe-O₂H]] → H₂O(g) + [O-Fe-O₂] + [Fe-O₂] | -0.29 -1.15 |
Table S4. Kinetic data, $r_i$, $Z_i$ and $X_{RC,i}$ for each elementary reaction step in NH$_3$-SCR over the reduced α-Fe$_2$O$_3$(001) at 590 K.

| Step $i$ | Reduced Fe$_2$O$_3$(001) $r_i$/s$^{-1}$ | $Z_i$ | $X_{RC,i}$ |
|----------|--------------------------------------|------|------------|
| **NH$_3$** |                                      |      |            |
| Fe$^{3+}$ site adsorption | R1 NH$_3$(g) + [Fe-Ol] $\rightarrow$ [NH$_3$-Fe-Ol] | 3.46×10$^{-4}$ | 1.00 | 7.01×10$^{-5}$ |
| | R2 [NH$_3$-Fe$_2$O$_3$] + [Fe-Ol] $\rightarrow$ [NH$_3$-Fe$_2$O$_3$][Fe-Ol] | 3.46×10$^{-4}$ | 1.00 | 4.04×10$^{-7}$ |
| | R3 [NH$_3$-Fe$_2$O$_3$][Fe-Ol] $\rightarrow$ [NH$_3$-Fe$_2$O$_3$] + [Fe-Ol] | 9.18×10$^{-11}$ | 1.00 | 1.98×10$^{-16}$ |
| Fe$^{2+}$ site dissociation | R4 NH$_3$(g) + [Fe-OlH] $\rightarrow$ [NH$_3$-Fe-OlH] | 1.29×10$^{-5}$ | 1.00 | 9.38×10$^{-11}$ |
| | R5 [NH$_3$-Fe$_2$O$_3$][Fe-OlH] + [Fe-Ol] $\rightarrow$ [NH$_2$-Fe-OlH][Fe-OlH] | 1.29×10$^{-5}$ | 1.00 | 9.00×10$^{-8}$ |
| | R6 [NH$_2$-Fe-OlH][Fe-OlH] $\rightarrow$ [NH$_2$-Fe-OlH] + [Fe-OlH] | 3.46×10$^{-4}$ | 1.00 | 1.95×10$^{-6}$ |
| **NH$_2$NO** |                                      |      |            |
| Fe$^{3+}$ site formation | R7 [NH$_2$-Fe-OlH][Fe-OlH] $\rightarrow$ [NH$_2$-Fe-OlH] + [Fe-OlH] | 9.18×10$^{-11}$ | 1.31×10$^{4}$ | 1.93×10$^{-7}$ |
| | R8 [NH$_2$NO-Fe$_2$O$_3$] + NO(g) $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$] | 3.59×10$^{-4}$ | 2.29×10$^{-4}$ | 7.57×10$^{-7}$ |
| | R9 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] | 9.18×10$^{-11}$ | 1.00 | 1.52×10$^{-21}$ |
| | R10 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] + [Fe-Ol] $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] | 3.59×10$^{-4}$ | 5.80×10$^{-3}$ | 6.58×10$^{-5}$ |
| | R11 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$] + [Fe-Ol] | 3.59×10$^{-4}$ | 1.00 | 1.40×10$^{-8}$ |
| | R12 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$] + [Fe-Ol] | 1.29×10$^{-5}$ | 1.00 | 5.38×10$^{-10}$ |
| **NH$_2$NO** |                                      |      |            |
| Fe$^{2+}$ site conversion | R13 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] + [Fe-Ol] $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$] | 9.18×10$^{-11}$ | 1.00 | 1.47×10$^{-12}$ |
| | R14 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] + [Fe-Ol] $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$] | 5.07×10$^{-9}$ | 1.00 | 9.88×10$^{-11}$ |
| | R15 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] $\rightarrow$ [NH$_2$NO-Fe$_2$O$_3$] | 3.59×10$^{-4}$ | 9.88×10$^{-11}$ | 1.34×10$^{-9}$ |
| | R16 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] + [Fe-Ol] $\rightarrow$ N$_2$(g) + [HO-Fe-Ol][Fe-OlH] | 3.59×10$^{-4}$ | 1.06×10$^{-19}$ | 1.50×10$^{-4}$ |
| | R17 [NH$_2$NO-Fe$_2$O$_3$][Fe-Ol] + [Fe-Ol] $\rightarrow$ N$_2$(g) + [HO-Fe-Ol][Fe-OlH] | 5.07×10$^{-9}$ | 1.05×10$^{-19}$ | 2.13×10$^{-9}$ |
| **H removal** |                                      |      |            |
| MvK mechanism | R18 [HO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [HO-Fe-Ol][Fe-Ol] | 4.49×10$^{-5}$ | 1.00 | 3.98×10$^{-38}$ |
| | R19 [HO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [HO-Fe-Ol][Fe-Ol] | 4.49×10$^{-4}$ | 1.00 | 1.22×10$^{-13}$ |
| | R20 [HO-Fe-Ol][Fe-Ol] $\rightarrow$ [H$_2$O-Fe-Ol] + [Fe-Ol] | 4.49×10$^{-4}$ | 1.00 | 4.67×10$^{-15}$ |
| | R21 [HO-Fe-Ol][Fe-Ol] $\rightarrow$ [H$_2$O-Fe-Ol] + [Fe-Ol] | 4.49×10$^{-4}$ | 1.00 | 1.04×10$^{-9}$ |
| | R22 [HO-Fe-Ol] $\rightarrow$ [H$_2$O-Fe-Ol] | -4.49×10$^{-4}$ | 1.00 | 1.47×10$^{-12}$ |
| | R23 [H$_2$O-Fe-Ol] $\rightarrow$ [Fe-Ol] + H$_2$O(g) | 2.25×10$^{-9}$ | 1.00 | 5.95×10$^{-13}$ |
| | R24 [H$_2$O-Fe-Ol] $\rightarrow$ [Fe-Ol] + H$_2$O(g) | 4.49×10$^{-4}$ | 1.00 | 1.46×10$^{-10}$ |
| | R25 [HO-Fe-Ol] + [Fe-Ol] $\rightarrow$ [HO-Fe-Ol][Fe-Ol] | 7.79×10$^{-5}$ | 1.00 | 8.68×10$^{-15}$ |
| | R26 [HO-Fe-Ol][Fe-Ol] $\rightarrow$ [H$_2$O-Fe-Ol] + [Fe-Ol] | 7.79×10$^{-5}$ | 1.00 | 3.18×10$^{-12}$ |
| | R27 [H$_2$O-Fe-Ol] $\rightarrow$ [H$_2$O-Fe-Ol] | 7.79×10$^{-5}$ | 1.00 | 1.19×10$^{-7}$ |
| | R28 [O$_2$(g) + [Fe-Ol] $\rightarrow$ [Fe-Ol] | 7.79×10$^{-5}$ | 6.23×10$^{-4}$ | 2.11×10$^{-4}$ |
| | R29 [Fe-Ol] $\rightarrow$ [O-Fe-Ol] | 1.53×10$^{-5}$ | 1.87×10$^{-7}$ | 1.12×10$^{-10}$ |
| | R30 [O-Fe-Ol] + [Fe-Ol] $\rightarrow$ [O-Fe-Ol][Fe-Ol] | 2.72×10$^{-5}$ | 4.67×10$^{-4}$ | 2.04×10$^{-17}$ |
| | R31 [O-Fe-Ol][Fe-Ol] $\rightarrow$ [HO-Fe-Ol] + [Fe-Ol] | 2.72×10$^{-4}$ | 9.96×10$^{-4}$ | 1.80×10$^{-17}$ |
| Reaction | Reaction Equation | Forward Kinetic Constant | Backward Kinetic Constant | Activation Energy |
|----------|-------------------|--------------------------|---------------------------|------------------|
| R32     | \([\text{HO-Fe-Ol}] + [\text{Fe-OlH}] \rightarrow [\text{HO-Fe-Ol}]_@[_{\text{Fe-OlH}}]\) | \(4.49 \times 10^{-5}\) | 1.00 | 3.98 \times 10^{-18} |
| R33     | \([\text{Fe-O}_2] + [\text{Fe-OlH}] \rightarrow [\text{Fe-O}_2]_@[_{\text{Fe-OlH}}]\) | \(6.25 \times 10^{-5}\) | 1.00 | 4.08 \times 10^{-15} |
| R34     | \([\text{Fe-O}_2]_@[_{\text{Fe-OlH}}] \rightarrow [\text{Fe-OOH}] + [\text{Fe-Ol}]\) | \(6.25 \times 10^{-5}\) | 9.95 \times 10^{-3} | 2.73 \times 10^{-12} |
| R35     | \([\text{Fe-OOH}] + [\text{Fe-OlH}] \rightarrow [\text{Fe-OOH}]_@[_{\text{Fe-OlH}}]\) | \(2.40 \times 10^{-12}\) | 1.00 | -3.94 \times 10^{-23} |
| R36     | \([\text{Fe-OOH}]_@[_{\text{Fe-OlH}}] \rightarrow [\text{H}_2\text{O(g)}] + [\text{Fe-Ol}] + [\text{Fe-Ol}]\) | \(2.40 \times 10^{-12}\) | 1.06 \times 10^{-8} | 2.38 \times 10^{-17} |
| R37     | \([\text{Fe-OOH}] \rightarrow [\text{HO-Fe-Ol}]\) | \(6.25 \times 10^{-5}\) | 8.7 \times 10^{-10} | 4.55 \times 10^{-10} |
| R38     | \([\text{O}_2(g)] + [\text{Fe-OlH}] \rightarrow [\text{O}_2-\text{Fe-OlH}]\) | \(1.19 \times 10^{-5}\) | 1.00 | 2.33 \times 10^{-12} |
| R39     | \([\text{O}_2-\text{Fe-OlH}] \rightarrow [\text{HOO-Fe-Ol}]\) | \(1.19 \times 10^{-5}\) | 1.00 | 9.56 \times 10^{-11} |
| R40     | \([\text{HOO-Fe-Ol}] + [\text{Fe-OlH}] \rightarrow [\text{HOO-Fe-Ol}]_@[_{\text{Fe-OlH}}]\) | \(1.19 \times 10^{-5}\) | 1.00 | 9.22 \times 10^{-11} |
| R41     | \([\text{HOO-Fe-Ol}]_@[_{\text{Fe-OlH}}] \rightarrow [\text{H}_2\text{O(g)}] + [\text{O-Fe-Ol}] + [\text{Fe-Ol}]\) | \(8.64 \times 10^{-5}\) | 6.87 \times 10^{-24} | 3.21 \times 10^{-2} |
Table S5. The coverage ($\theta(j)$) of reactants and intermediates at the steady state of NH$_3$-SCR on the reduced $\alpha$-Fe$_2$O$_3$(001) at 590 K.

| Species                          | $\theta(j)$     | Species                          | $\theta(j)$     |
|----------------------------------|-----------------|----------------------------------|-----------------|
| [Fe-O]                           | $4.56 \times 10^{-1}$ | [HOO-Fe-O]@[Fe-OH]               | $1.48 \times 10^8$ |
| [NH$_3$-Fe-O]                    | $2.34 \times 10^{-4}$ | [Fe-OH]@[Fe-OH]                  | $1.54 \times 10^4$ |
| [NH$_3$-Fe-OH]                   | $1.49 \times 10^{-6}$ | [Fe-H$_2$O]                      | $1.13 \times 10^7$ |
| [NH$_2$-Fe-O]                    | $1.54 \times 10^{-14}$ | [Fe-O$_2$]                       | $2.25 \times 10^{-10}$ |
| [NH$_2$-Fe-OH]                   | $6.04 \times 10^{-8}$ | [Fe-O$_2$]                       | $1.19 \times 10^{-12}$ |
| [NH$_2$-Fe-O]@[Fe-OH]            | $4.42 \times 10^{-10}$ | [O-Fe-O$_2$]                     | $4.70 \times 10^{-18}$ |
| [NH$_2$-Fe-OH]@[Fe-OH]           | $1.41 \times 10^{-10}$ | [O-Fe-O]@[Fe-OH]                 | $7.87 \times 10^{-16}$ |
| [NHNO-Fe-O]                      | $3.20 \times 10^{-12}$ | [HO-Fe-O]                        | $7.42 \times 10^{-10}$ |
| [NHNO-Fe-OH]                     | $1.84 \times 10^{-15}$ | [HO-Fe-O$_2$]                    | $6.75 \times 10^{-2}$ |
| [NHNO-Fe-OH]@[Fe-OH]             | $1.56 \times 10^{-11}$ | [HO-Fe-O]@[Fe-OH]                | $1.16 \times 10^{-5}$ |
| [NHNO-Fe-O]@[Fe-OH]              | $1.99 \times 10^{-10}$ | [HO-Fe-O]@[Fe-O]                 | $2.20 \times 10^{-5}$ |
| [NHNO-Fe-OH]@[Fe-OH]             | $3.15 \times 10^{-13}$ | [H$_2$O-Fe-O]                    | $8.92 \times 10^{-4}$ |
| [NHNOH-Fe-O]                     | $2.04 \times 10^{-13}$ | [H$_2$O-Fe-O$_2$]                | $1.85 \times 10^{-6}$ |
| [NHNOH-Fe-OH]                    | $4.26 \times 10^{-14}$ | [Fe-O]@[Fe-OH]                   | $3.30 \times 10^{-12}$ |
| [Fe-OH]                          | $7.72 \times 10^{-1}$  | [Fe-OOH]                        | $5.27 \times 10^{-14}$ |
| [O$_2$-Fe-OH]                    | $4.08 \times 10^{-6}$  | [Fe-OOH]@[Fe-OH]                 | $3.10 \times 10^{-10}$ |
| [HOO-Fe-O]                       | $7.12 \times 10^{-10}$ |                                 |                 |
Figure S10. The energy profile for the complete NH$_3$-SCR process on Fe$_2$O$_3$(001).
Figure S11. Scheme for the NH$_3$ adsorption/dissociation and NH$_2$NO formation. $G_{\text{ads}}$(NH$_3$) is the adsorption free energy of NH$_3$ on Fe$^{3+}$ site ($G_{\text{ads}}$(NH$_3$) = $E_{\text{ads}}$(NH$_3$) - $T*S$), $E_{\text{ads}}$(NH$_3$) is the NH$_3$ adsorption energy from DFT calculations. $T$ is the reaction temperature, $S$ is the entropy of NH$_3$ molecule in the gaseous phase. $\Delta H_{\text{ads}}$(NH$_3$) is the enthalpy change of NH$_3$ dissociation on Fe$^{3+}$ sites. $\Delta G_d$(H) is the energy change of the stabilization NH$_2$ on Fe$^{2+}$ sites compared with that on Fe$^{3+}$ ones ([NH$_2$-Fe-O$_2$]@[Fe-O$_2$H]→[NH$_2$-Fe-O$_2$H]+[Fe-O$_2$]) of Fe$^{3+}@$Fe$^{2+}$ double-centers. $E_a$(NH$_2$NO) is the energy barrier of NH$_2$ coupling with NO from the collision theory. TS1 and TS2 are the transition states for the NH$_3$ dissociation on Fe$^{3+}$ sites and NH$_2$ coupling with NO, respectively.
Note S7. Discussion for Fe$_2$O$_3$ catalyst and MnO$_2$ catalyst

Fe$_2$O$_3$ and MnO$_2$-based oxides are both good basic materials for NH$_3$-SCR, which are however usually used at different reaction temperature. Fe$_2$O$_3$ is used at the middle-high temperature, and MnO$_2$ is used at the middle-low temperature. Essentially, the different reaction temperatures of Fe$_2$O$_3$ and MnO$_2$ catalysts are largely determined by the different reactivities of lattice oxygens on these two oxides. By calculating the vacancy formation energy ($E_{\text{vac}}$) of lattice oxygen of α-Fe$_2$O$_3$(001) and β-MnO$_2$(110), it can be found that $E_{\text{vac}}$ of MnO$_2$ is much lower than that of Fe$_2$O$_3$ (0.63 eV vs. 2.88 eV), implying the higher reactivity of lattice oxygen on MnO$_2$ catalyst.$^1$ The more reactive lattice oxygen means the easier NH$_3$ dissociation to form the key NH$_2$ intermediate which is usually one of the rate-limiting steps in NH$_3$-SCR. Thus, at low temperatures, MnO$_2$ could exhibit a more excellent activity for NH$_3$-SCR than Fe$_2$O$_3$. As temperature increases, the lattice oxygen on Fe$_2$O$_3$ could be activated for NH$_3$ dissociation and become catalytically active; however, at this time, due to the low $E_{\text{vac}}$ of MnO$_2$, its lattice oxygen is very easy to leach out and yields abundant oxygen vacancies on MnO$_2$, which are difficult to be supplied by O$_2$ for its low adsorption energy (-0.50 eV) and high entropy at high temperature (1.28 eV at 600 K),$^1$ thus MnO$_2$ could exhibit a poor activity for NH$_3$-SCR at high temperature. Therefore, MnO$_2$-based oxides are good basic materials for NH$_3$-SCR at low temperatures, and Fe$_2$O$_3$ prefers to work at a relatively high temperature.
Note S7. DFT-optimized coordinates of the surface model and the key reaction intermediates

Fe₂O₃(001) surface:

```
Fe    O
72    48
```

Selective dynamics

Direct

|                  |                  |                  |                  |                  |
|------------------|------------------|------------------|------------------|------------------|
| 0.19939000000000011 | 0.19041000000000000 | 0.0305800000000005 |
| 0.69939000000000011  | 0.19041000000000000 | 0.0305800000000005 |
| 0.3522899999999964  | 0.34355000000000005 | 0.0305800000000005 |
| 0.8522899999999964  | 0.34355000000000005 | 0.0305800000000005 |
| 0.04625000000000006  | 0.4964399999999998  | 0.0305800000000005 |
| 0.54625000000000006  | 0.4964399999999998  | 0.0305800000000005 |
| 0.19939000000000011  | 0.69041000000000000 | 0.0305800000000005 |
| 0.69939000000000011  | 0.69041000000000000 | 0.0305800000000005 |
| 0.3522899999999964  | 0.84355000000000005 | 0.0305800000000005 |
| 0.8522899999999964  | 0.84355000000000005 | 0.0305800000000005 |
| 0.04625000000000006  | 0.9964399999999998  | 0.0305800000000005 |
| 0.54625000000000006  | 0.9964399999999998  | 0.0305800000000005 |
| 0.21294999999999993 | 0.01012999999999666 | 0.1122099999999975 |
| 0.71294999999999993 | 0.01012999999999666 | 0.1122099999999975 |
| 0.36598000000000004 | 0.1631500000000017  | 0.1122099999999975 |
| 0.86598000000000004 | 0.1631500000000017  | 0.1122099999999975 |
| 0.0189999999999984  | 0.3571000000000026  | 0.1122099999999975 |
| 0.5189999999999984  | 0.3571000000000026  | 0.1122099999999975 |
| 0.21294999999999993 | 0.51012999999999666 | 0.1122099999999975 |
| 0.71294999999999993 | 0.51012999999999666 | 0.1122099999999975 |
| 0.36598000000000004 | 0.6631500000000017  | 0.1122099999999975 |
| 0.86598000000000004 | 0.6631500000000017  | 0.1122099999999975 |
| 0.0189999999999984  | 0.8571000000000026  | 0.1122099999999975 |
| 0.5189999999999984  | 0.8571000000000026  | 0.1122099999999975 |
| 0.03255999999999666 | 0.0238200000000006  | 0.1938400000000016 |
| 0.53255999999999666 | 0.0238200000000006  | 0.1938400000000016 |
| 0.1856999999999971  | 0.17670999999999999 | 0.1938400000000016 |
| 0.6856999999999971  | 0.17670999999999999 | 0.1938400000000016 |
| 0.3796999999999973  | 0.3298500000000004  | 0.1938400000000016 |
| 0.8796999999999973  | 0.3298500000000004  | 0.1938400000000016 |
| 0.03255999999999666 | 0.5238200000000006  | 0.1938400000000016 |
| 0.53255999999999666 | 0.5238200000000006  | 0.1938400000000016 |
``
|   |   |   |
|---|---|---|
| 0.3659800000000004 | 0.0101299999999966 | 0.0611900000000034 |
| 0.8659800000000004 | 0.0101299999999966 | 0.0611900000000034 |
| 0.3659800000000004 | 0.5101299999999966 | 0.0611900000000034 |
| 0.8659800000000004 | 0.5101299999999966 | 0.0611900000000034 |
| 0.1993099999999970 | 0.3434600000000003 | 0.0816099999999977 |
| 0.6993099999999970 | 0.3434600000000003 | 0.0816099999999977 |
| 0.1993099999999970 | 0.8434600000000003 | 0.0816099999999977 |
| 0.6993099999999970 | 0.8434600000000003 | 0.0816099999999977 |
| 0.0326400000000007 | 0.1768000000000001 | 0.1428099999999972 |
| 0.5326400000000007 | 0.1768000000000001 | 0.1428099999999972 |
| 0.5326400000000007 | 0.6768000000000001 | 0.1428099999999972 |
| 0.0326400000000007 | 0.6768000000000001 | 0.1428099999999972 |
| 0.3659800000000004 | 0.0101299999999966 | 0.1632299999999987 |
| 0.8659800000000004 | 0.0101299999999966 | 0.1632299999999987 |
| 0.3659800000000004 | 0.5101299999999966 | 0.1632299999999987 |
| 0.8659800000000004 | 0.5101299999999966 | 0.1632299999999987 |
| 0.1993099999999970 | 0.3434600000000003 | 0.2244200000000021 |
| 0.6993099999999970 | 0.3434600000000003 | 0.2244200000000021 |
| 0.1993099999999970 | 0.8434600000000003 | 0.2244200000000021 |
| 0.6993099999999970 | 0.8434600000000003 | 0.2244200000000021 |
| 0.5326398687449796 | 0.6771110302637311 | 0.2455602230019949 |
| 0.5327368000022688 | 0.171945540675901 | 0.2457905001337579 |
| 0.0327184108058560 | 0.1768276146685324 | 0.2457582052146776 |
| 0.0322923904984265 | 0.6770516400719728 | 0.2457955154219391 |
| 0.8660446358735356 | 0.0105181871350766 | 0.3041345794542565 |
| 0.3648897924941608 | 0.5127666648899520 | 0.304659959432759 |
| 0.3678692751077719 | 0.0093398802495944 | 0.304764694143652 |
| 0.8645378557860326 | 0.5097149208161156 | 0.3047070979900610 |
| 0.1990071582100086 | 0.3440629440589902 | 0.3257740277033747 |
| 0.700866626132606 | 0.8426410632907562 | 0.3271635485828241 |
| 0.198595959664208 | 0.8458279405932458 | 0.3271543940513055 |
| 0.6975616045966362 | 0.3436337003270751 | 0.3271588815669162 |
| 0.5346390574770652 | 0.1740657495178723 | 0.3906933934091228 |
| 0.0331864156813637 | 0.6801063864972861 | 0.3906705099549939 |
| 0.5323409948776359 | 0.6773650827136066 | 0.390242052243890 |
| 0.0289321496820278 | 0.1782949147159343 | 0.390433694998770 |
| 0.3666878306297718 | 0.5114758904227585 | 0.4071511281702058 |
| 0.8652488061877293 | 0.0112102537070697 | 0.4062115131505024 |
| 0.3664309312448779 | 0.0089736487280803 | 0.4072423228236630 |
| 0.8639010406256347 | 0.5119601516122785 | 0.407192579534128 |
| 0.1989517582294411 | 0.3443002405653104 | 0.4322691199623776 |
| 0.6992694510225377 | 0.8439358275928370 | 0.4504798547936915 |
| 0.1989472055411383 | 0.844476709980622 | 0.4504350961108372 |
| 0.6983602095215247 | 0.3440936799562166 | 0.4503572584348490 |
The reduced Fe$_2$O$_3$(001) surface:

|       | 1.0000000000000000 | 8.7636216999999995 | 5.0593000300000002 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 28.263938899999986 |
|-------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| H     | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 |
| O     | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 |
| Fe    | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 | 0.0000000000000000 |

Selectiv dynamics

Direct

|       | 0.479137513123925 | 0.301755540744587 | 0.468046681886626 | 0.699390000000001 | 0.1999410000000000 | 0.0305800000000005 |
|-------|------------------|-----------------|------------------|------------------|------------------|-----------------|
|       | 0.199390000000001 | 0.190410000000000 | 0.0305800000000005 |
|       | 0.352289999999996 | 0.343549999999993 | 0.0305800000000005 |
|       | 0.852289999999996 | 0.3435500000000005 | 0.0305800000000005 |
|       | 0.04625000000000006 | 0.496439999999998 | 0.0305800000000005 |
|       | 0.54625000000000006 | 0.496439999999992 | 0.0305800000000005 |
|       | 0.199939000000001 | 0.6904100000000000 | 0.0305800000000005 |
|       | 0.699390000000001 | 0.6904100000000000 | 0.0305800000000005 |
|       | 0.352289999999996 | 0.843549999999998 | 0.0305800000000005 |
|       | 0.852289999999996 | 0.8435500000000005 | 0.0305800000000005 |
|       | 0.04625000000000006 | 0.996439999999998 | 0.0305800000000005 |
|       | 0.54625000000000006 | 0.996439999999992 | 0.0305800000000005 |
|       | 0.212949999999996 | 0.163150000000001 | 0.0305800000000005 |
|       | 0.712949999999996 | 0.163149999999987 | 0.0305800000000005 |
|       | 0.365980000000001 | 0.357100000000002 | 0.0305800000000005 |
|       | 0.865980000000001 | 0.357100000000002 | 0.0305800000000005 |
|       | 0.018999999999984 | 0.357100000000002 | 0.0305800000000005 |
|       | 0.518999999999984 | 0.357100000000002 | 0.0305800000000005 |
|       | 0.212949999999996 | 0.510129999999996 | 0.0305800000000005 |
|       | 0.712949999999996 | 0.510129999999996 | 0.0305800000000005 |
|       | 0.365980000000001 | 0.663150000000001 | 0.0305800000000005 |
|       | 0.865980000000001 | 0.663149999999987 | 0.0305800000000005 |
|       | 0.018999999999984 | 0.857100000000002 | 0.0305800000000005 |
|       | 0.518999999999984 | 0.857100000000002 | 0.0305800000000005 |
|       | 0.185699999999971 | 0.176709999999999 | 0.0305800000000005 |
|       | 0.685699999999971 | 0.176709999999999 | 0.0305800000000005 |
|       | 0.379669999999973 | 0.329849999999993 | 0.0305800000000005 |
|       | 0.879669999999973 | 0.3298500000000004 | 0.0305800000000005 |
|       | 0.032559999999966 | 0.523820000000006 | 0.0305800000000005 |
|       | 0.532559999999966 | 0.523820000000006 | 0.0305800000000005 |
|       | 0.185699999999971 | 0.676709999999999 | 0.0305800000000005 |
|       | 0.685699999999971 | 0.676709999999999 | 0.0305800000000005 |
| 0.3796699999999973 | 0.8298500000000004 | 0.1938400000000016 |
|---------------------|--------------------|---------------------|
| 0.8796699999999973 | 0.8298499999999982 | 0.1938400000000016 |
| 0.1998459092591176 | 0.4982634318265298 | 0.2754569829368307 |
| 0.5459028689230223 | 0.8420399470133049 | 0.2752350025522361 |
| 0.7004393450931943 | 0.9976485453482056 | 0.2752931471723343 |
| 0.0448900046447704 | 0.8441232046940144 | 0.2754668152279507 |
| 0.3544812439938312 | 0.1878908467247999 | 0.2754818227046130 |
| 0.0441541664229999 | 0.3438647572898361 | 0.2756878195522361 |
| 0.8535183797038215 | 0.189277681739659 | 0.2755943759138049 |
| 0.3545050145738458 | 0.6892438613449414 | 0.275590340440206 |
| 0.6978472265126356 | 0.4982604276311946 | 0.2756603734355636 |
| 0.5439814674839525 | 0.3437901814967006 | 0.2760277916154479 |
| 0.855310809774557 | 0.6869507137597566 | 0.2762916370790194 |
| 0.1998112162315024 | 0.9986852386023888 | 0.276137349963854 |
| 0.5235804851156658 | 0.0069082428008542 | 0.3557023184395547 |
| 0.2083465234940436 | 0.6695001756508888 | 0.3570551659156109 |
| 0.8663922945535418 | 0.8545976509656858 | 0.357064037237909 |
| 0.7076913165062564 | 0.1675943677045382 | 0.3577685042393242 |
| 0.7114814143970136 | 0.6642964438134413 | 0.35751537314871 |
| 0.0206286545913485 | 0.0128250190787185 | 0.357460520460436 |
| 0.8650877220191166 | 0.3552861216215248 | 0.3572074193078052 |
| 0.3660885266800094 | 0.8556570377832813 | 0.3577734906126082 |
| 0.3658049994398596 | 0.3510154432614740 | 0.3585354554960674 |
| 0.5196272783826217 | 0.5103420909791225 | 0.3592552226796002 |
| 0.0313838359187599 | 0.5064838033115535 | 0.3598799855137713 |
| 0.2074002952384362 | 0.1721830692893604 | 0.3589873899825875 |
| 0.3785073521811455 | 0.1761866210161216 | 0.3469317424680617 |
| 0.521226997434404 | 0.3438430531534067 | 0.4453138156692162 |
| 0.1966519994985996 | 0.5219267038120492 | 0.4385191382699460 |
| 0.6900201694144315 | 0.0236810639391458 | 0.4374965395502031 |
| 0.874771441217482 | 0.6763523631771520 | 0.4379927092095013 |
| 0.0225836148097045 | 0.3391203318713707 | 0.4382514120350436 |
| 0.0271231829648642 | 0.8395298727723670 | 0.438205433057113 |
| 0.5290756949239181 | 0.8394797229466222 | 0.4380924784754399 |
| 0.3729995555684955 | 0.6784132837103556 | 0.4387264066555687 |
| 0.1924455228604600 | 0.021519590285027 | 0.4388528807439300 |
| 0.8772536533526747 | 0.1721633869292702 | 0.4387716960153725 |
| 0.6904977041093403 | 0.5254910469430456 | 0.4387962143323918 |
| 0.03264000000000007 | 0.1768000000000000 | 0.0000000000000000 |
| 0.53264000000000007 | 0.1768000000000000 | 0.0000000000000000 |
| 0.53264000000000007 | 0.6768000000000000 | 0.0000000000000000 |
| 0.03264000000000007 | 0.6767999999999930 | 0.0000000000000000 |
| 0.36598000000000004 | 0.0101299999999966 | 0.0611900000000034 |
| 0.86598000000000004 | 0.0101299999999985 | 0.0611900000000034 |
The NH₂ adsorption on Fe₂O₃(001) surface:

H    N    O    Fe
2     1    72    48

Selective dynamics

Direct

0.2060847051621001 0.4362725767729378 0.5520433018659482
0.1361066676991729 0.3189161216021094 0.5551625361754230
0.1903010435921473 0.358193322998885 0.5337113450304816
0.1993900000000013 0.1904099999999998 0.0305800000000005
0.6993900000000011 0.1904100000000000 0.0305800000000005
0.3522899999999965 0.3435500000000004 0.0305800000000005
0.8522899999999964 0.3435500000000004 0.0305800000000005
0.5462500000000007 0.4964399999999990 0.0305800000000005
0.0462500000000006 0.4964399999999990 0.0305800000000005
0.1993900000000013 0.6904099999999981 0.0305800000000005
0.6993900000000011 0.6904100000000000 0.0305800000000005
0.3522899999999965 0.8435499999999997 0.0305800000000005
0.8522899999999964 0.8435500000000005 0.0305800000000005
0.0462500000000006 0.9964399999999998 0.0305800000000005
0.5462500000000007 0.9964399999999998 0.0305800000000005
0.2129499999999993 0.0101299999999966 0.1122099999999975
0.7129499999999993 0.0101299999999966 0.1122099999999975
0.3659800000000017 0.1631500000000017 0.1122099999999975
0.8659800000000004 0.1631499999999965 0.1122099999999975
0.0189999999999984 0.3571000000000027 0.1122099999999975
0.5189999999999984 0.3571000000000027 0.1122099999999975
0.2129499999999993 0.5101299999999966 0.1122099999999975
0.7129499999999993 0.5101299999999966 0.1122099999999975
0.3659800000000004 0.6631500000000016 0.1122099999999975
0.8659800000000004 0.6631500000000016 0.1122099999999975
0.0189999999999984 0.8570999999999995 0.1122099999999975
0.5189999999999984 0.8570999999999995 0.1122099999999975
0.0325599999999966 0.0238200000000006 0.1938400000000016
0.5325599999999966 0.0238200000000006 0.1938400000000016
0.1856999999999971 0.1767099999999999 0.1938400000000016
0.6856999999999971 0.1767100000000000 0.1938400000000016
0.3796699999999973 0.3298499999999980 0.1938400000000016
0.8796699999999978 0.3298499999999999 0.1938400000000016
0.0325599999999966 0.5238200000000006 0.1938400000000016
0.5325599999999966 0.5238200000000006 0.1938400000000016
|                  |                  |                  |
|------------------|------------------|------------------|
| 0.3659800000000004 | 0.0101299999999966 | 0.0611900000000034 |
| 0.3659800000000004 | 0.0101299999999924 | 0.0611900000000034 |
| 0.3659800000000004 | 0.5101299999999966 | 0.0611900000000034 |
| 0.8659800000000004 | 0.0101299999999966 | 0.0611900000000034 |
| 0.8659800000000004 | 0.5101299999999966 | 0.0611900000000034 |
| 0.1993099999999970 | 0.3434600000000000 | 0.0816099999999977 |
| 0.6993099999999970 | 0.3434600000000000 | 0.0816099999999977 |
| 0.1993099999999970 | 0.8434600000000000 | 0.0816099999999977 |
| 0.6993099999999970 | 0.8434600000000000 | 0.0816099999999977 |
| 0.0326400000000007 | 0.1768000000000000 | 0.1428099999999972 |
| 0.5326400000000007 | 0.1767999999999999 | 0.1428099999999972 |
| 0.5326400000000007 | 0.6768000000000000 | 0.1428099999999972 |
| 0.0326400000000007 | 0.6767999999999963 | 0.1428099999999972 |
| 0.3659800000000004 | 0.0101299999999966 | 0.1632299999999987 |
| 0.8659800000000004 | 0.0101299999999966 | 0.1632299999999987 |
| 0.3659800000000004 | 0.5101299999999966 | 0.1632299999999987 |
| 0.8659800000000004 | 0.5101299999999966 | 0.1632299999999987 |
| 0.1993099999999970 | 0.3434600000000000 | 0.2244200000000021 |
| 0.6993099999999970 | 0.3434600000000000 | 0.2244200000000021 |
| 0.6993099999999970 | 0.8434600000000000 | 0.2244200000000021 |
| 0.0325828667692463 | 0.1768853257171459 | 0.2454798796585988 |
| 0.5317602946878264 | 0.1773503350583792 | 0.2454798796585988 |
| 0.5326436273836216 | 0.6761862479127945 | 0.2455221668324809 |
| 0.0329145667729763 | 0.6769471727562411 | 0.2454790091837848 |
| 0.3630026356486825 | 0.176853257171459 | 0.2451867015362620 |
| 0.3659286539970806 | 0.5097822968947983 | 0.3069250363249807 |
| 0.8642306480196291 | 0.142385493352845 | 0.3076971938833544 |
| 0.8695780914114325 | 0.5081859691947358 | 0.307693781781442 |
| 0.6988873994510159 | 0.8438543918136709 | 0.3241459087115988 |
| 0.6980906580263688 | 0.3459528082386525 | 0.3271677119835018 |
| 0.1971440103850112 | 0.8425504464533033 | 0.3271151551021775 |
| 0.201019482796481 | 0.3421674765845513 | 0.327527743909847 |
| 0.5296047690125256 | 0.1805621158345920 | 0.3957239960856443 |
| 0.0333922861579742 | 0.1782774539924313 | 0.3955395840048805 |
| 0.5286732045769121 | 0.6778581990495969 | 0.3955871419132233 |
| 0.036280059824570 | 0.6700390041916842 | 0.3962176378421775 |
| 0.3615777264186831 | 0.147818261230924 | 0.4081914977725459 |
| 0.3634036999977272 | 0.5086813862343056 | 0.4075915619103999 |
| 0.8713554910784342 | 0.5050907601453334 | 0.4087048802760163 |
| 0.8655902127907521 | 0.116533126651477 | 0.4080152790134864 |
| 0.698976254127545 | 0.8421150472559970 | 0.4262030728488356 |
| 0.19892078415378 | 0.842697484604480 | 0.4514016306834837 |
| 0.6985360754090125 | 0.3443050676958804 | 0.4518340358358520 |
| 0.1997157641660678 | 0.3429953336275922 | 0.465107401431223 |
The NH$_2$ adsorption on the reduced Fe$_2$O$_3$(001) surface:

|   | 1.000000000000000 | 8.76362169999995 | 0.000000000000000 | 10.119739680000000 | 0.000000000000000 | 28.26393889999986 |
|---|------------------|------------------|------------------|------------------|------------------|------------------|
| H | 3                | 1                | 72               | 48               |
| H | 0.4499745281960017 | 0.1303786861120031 | 0.4700010708699978 |
| N | 0.2065510762249971 | 0.4362634296820005 | 0.5539416359260017 |
| O | 0.1361385108619970 | 0.3201119243570005 | 0.5568707971969999 |
| Fe| 0.1955930768000016 | 0.3547412833500023 | 0.536067144870028 |
|   | 0.1939000000000011 | 0.1904100000000000 | 0.0305800000000005 |
|   | 0.6939000000000011 | 0.1904100000000000 | 0.0305800000000005 |
|   | 0.3522899999999964 | 0.3435500000000005 | 0.0305800000000005 |
|   | 0.8522899999999964 | 0.3435500000000005 | 0.0305800000000005 |
|   | 0.5462500000000006 | 0.4964399999999998 | 0.0305800000000005 |
|   | 0.0462500000000006 | 0.4964399999999998 | 0.0305800000000005 |
|   | 0.1939000000000011 | 0.6904100000000000 | 0.0305800000000005 |
|   | 0.6939000000000011 | 0.6904100000000000 | 0.0305800000000005 |
|   | 0.3522899999999964 | 0.8435500000000005 | 0.0305800000000005 |
|   | 0.8522899999999964 | 0.8435500000000005 | 0.0305800000000005 |
|   | 0.0462500000000006 | 0.9964399999999998 | 0.0305800000000005 |
|   | 0.5462500000000006 | 0.9964399999999998 | 0.0305800000000005 |
|   | 0.2129499999999993 | 0.0101299999999966 | 0.1122099999999975 |
|   | 0.7129499999999993 | 0.0101299999999966 | 0.1122099999999975 |
|   | 0.3659800000000004 | 0.1631500000000017 | 0.1122099999999975 |
|   | 0.8659800000000004 | 0.1631500000000017 | 0.1122099999999975 |
|   | 0.0189999999999984 | 0.3571000000000026 | 0.1122099999999975 |
|   | 0.5189999999999984 | 0.3571000000000026 | 0.1122099999999975 |
|   | 0.2129499999999993 | 0.5101299999999966 | 0.1122099999999975 |
|   | 0.7129499999999993 | 0.5101299999999966 | 0.1122099999999975 |
|   | 0.3659800000000004 | 0.6631500000000017 | 0.1122099999999975 |
|   | 0.8659800000000004 | 0.6631500000000017 | 0.1122099999999975 |
|   | 0.0189999999999984 | 0.8571000000000026 | 0.1122099999999975 |
|   | 0.5189999999999984 | 0.8571000000000026 | 0.1122099999999975 |
|   | 0.0325599999999966 | 0.0238200000000006 | 0.1938400000000016 |
|   | 0.5325599999999966 | 0.0238200000000006 | 0.1938400000000016 |
|   | 0.1856999999999971 | 0.1767099999999999 | 0.1938400000000016 |
|   | 0.6856999999999971 | 0.1767099999999999 | 0.1938400000000016 |
|   | 0.3796699999999973 | 0.3298500000000004 | 0.1938400000000016 |
|   | 0.8796699999999973 | 0.3298500000000004 | 0.1938400000000016 |
|   | 0.0325599999999966 | 0.5238200000000006 | 0.1938400000000016 |
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