Supplementary Information

Tailoring Widely Used Ammonia Synthesis Catalysts for H and N Poisoning Resistance

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MATERIALS

Ru₃(CO)₁₂ was purchased from Tanaka Kikinzoku Industries Co. Fe₃(CO)₁₂, MgO, tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries Ltd. MgO was purchased from Kanto Chemical Co. All chemicals were used without further purification. All the solutions were prepared with deionized water.

MATERIAL SYNTHESIS

Ru-Fe/MgO, **Ru/MgO** and **Fe/MgO**: A series of MgO supported Ru-Fe nanoalloy catalysts (Ru-Fe/MgO) were prepared by hydrogen reduction of precipitates produced on MgO supports via thermal decomposition of impregnated carbonyl complexes of Ru and Fe ions. We firstly impregnated Ru₃(CO)₁₂ and Fe₃(CO)₁₂ on MgO in THF solvent. MgO (10 g) was dispersed in the 150 ml THF solution of Ru₃(CO)₁₂ and Fe₃(CO)₁₂. In the THF solution, 0.85 mmol of metal ions was included, which correspond to the number of Ru ions on 2.0wt% Ru/MgO. Alloy composition x in Ru_xFe_{100-x}/MgO was controlled by changing mixing ratio of starting complexes as shown in Table S1. The MgO mixture was stirred at 298 K under Ar flow for 4 hours and decomposed at 450°C under vacuum to remove the solvent. Finally, a Ru-Fe/MgO catalyst was prepared through hydrogen reduction of the impregnated MgO at 800°C for 5 hours. Both MgO supported Ru and Fe nanoparticles catalysts (Ru/MgO and Fe/MgO) were prepared in a similar way. Metal composition and loading amount were investigated by scanning electron microscopy combined with energy dispersive x-ray spectroscopy (SEM-EDS, JSM-IT100). Final compositions of the prepared catalysts were approximately proportional to the starting composition. Loading amounts of metal species on the catalysts were found to be in the range of 0.38-0.51atom%.

Catalyst name	Used amounts of	Used amounts of	Final composition	Metal loading
	Ru ₃ (CO) ₁₂ (mmol)	Fe ₃ (CO) ₁₂ (mmol)		(wt.%)
Ru/MgO	0.85		Ru	2.0
Ru ₉₀ Fe ₁₀ /MgO	0.76	0.09	Ru ₈₈ Fe ₁₂	2.4
Ru ₈₀ Fe ₂₀ /MgO	0.68	0.17	Ru ₈₀ Fe ₂₀	2.1
Ru ₇₀ Fe ₃₀ /MgO	0.59	0.26	Ru ₇₁ Fe ₂₉	1.6
Ru ₆₀ Fe ₄₀ /MgO	0.51	0.34	Ru ₅₈ Fe ₄₂	2.1
RuFe/MgO	0.42	0.43	$Ru_{49}Fe_{51}$	1.5
Ru ₄₀ Fe ₆₀ /MgO	0.34	0.51	Ru ₃₄ Fe ₆₆	1.5
Ru ₃₀ Fe ₇₀ /MgO	0.25	0.60	Ru ₂₉ Fe ₇₁	1.4
Fe/MgO		0.85	Fe	1.3

Table S1. Used amounts of $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$, compositions and metal loadings of catalysts.

CHRACTERIZATION OF CATALYSTS

X-ray diffraction (XRD): XRD patterns for the catalysts are conducted using a SmartLab X-ray diffractometer (Rigaku, Japan) equipped with

a Cu-Kα radiation source.



Fig. S1. XRD patterns of Ru-Fe/MgO with simulated XRD patters for Ru (red) and Fe metals (blue). The strong diffraction observed at 42.9 ° is 002 diffraction from MgO support.

Scanning transmission electron microscopy (STEM) and energy dispersible X-ray (EDX) mapping: STEM observations and STEM combined with EDS (STEM–EDS) analyses were carried out with a JEOL JEM-ARM 200F operated at 200 kV. STEM images represented that Ru-Fe nanoalloys are well dispersed on the MgO support.



Fig. S2. STEM images for (a)Ru90Fe10/MgO, (b)Ru80Fe20/MgO, (c)Ru70Fe30/MgO, (d)Ru60Fe40/MgO, (e)RuFe/MgO, (f)Ru40Fe60/MgO, (g)Ru30Fe70/MgO.

Catalyst	Average diameter (nm)		
Ru/MgO	6.2 ± 2.1		
Ru ₉₀ Fe ₁₀ /MgO	15 ± 6.0		
Ru ₈₀ Fe ₂₀ /MgO	23 ± 8.3		
Ru ₇₀ Fe ₃₀ /MgO	26 ± 13		
Ru ₆₀ Fe ₄₀ /MgO	19 ± 8.7		
Ru ₅₀ Fe ₅₀ /MgO	19 ± 5.7		
Ru ₄₀ Fe ₆₀ /MgO	24 ± 18		
Ru ₃₀ Fe ₇₀ /MgO	18 ± 6.4		
Fe/MgO	58 ± 9.2		

 Table S2. Average diameters of nanoparticle on the prepared MgO supported catalysts.



Fig. S3. (a) STEM image and (b) EDS line profile for RuFe/MgO. The profile was measured along the arrow shown in (a).

X-ray photoelectron spectroscopy: XPS charts were recorded on a XPS instrument (VersaProbell, ULVAC-PHI) with Al anode X-ray source. Before measurements, Ru/MgO, RuFe/MgO and Fe/MgO were reduced at 600 °C for 3 hours under H₂ gas flowing in the pretreatment chamber (VersaPrep, ULVAC-PHI) attached to the XPS which enabled to measure spectra for activated samples. Binding energies were corrected by referring a C 1s binding energy of the carbon atoms of the ligand in the specimens at 284.5 eV. The obtained XPS spectra were reproduced using a combination of Gaussian and Lorentzian functions.



Fig. S4. Ru 3d XPS spectra for (a)Ru/MgO and (b)RuFe/MgO and Fe 2p XPS spectra for (c)Fe/MgO and (d)RuFe/MgO.

CATALYTIC TEST CONCERNING NH₃ SYNTHESIS

The NH₃ synthesis rate on the catalyst was measured using a conventional flow system (BEL-REA, BEL Japan). Quartz wool was packed into a tubular Inconel reactor (i.d. = 7 mm), and 200 mg of the catalyst was loaded. Research-grade gas was supplied from high-pressure gas cylinders. The catalysts were reduced in pure H₂ and N₂ flow at 400 °C for 2 hour at 0.1 MPa and the pressure was then adjusted to 0.1, 0.5, or 1.0 MPa at 400 °C. An H₂/N₂ gas mixture with an H₂/N₂ molar ratio of 3 (gas hourly space velocity = 18,000 mL h⁻¹ g⁻¹) was then fed to the catalyst. The temperature of the catalyst was kept constant for 0.5 h to facilitate measurement of NH₃ synthesis rates. The NH₃ synthesis rate was determined from the rate of decrease of electron conductivity (CM-30R, DKK-TOA, Japan) of the dilute sulfuric acid solution that trapped the NH₃ produced under the experimental conditions. The catalyst was then heated in 50 °C increments to each measurement temperature (300, 350, 400, 450, 500, 550, and 600 °C).

As mentioned in the main text, catalytically active surface area (or the number of atoms) on Ru-Fe alloys cannot be experimentally determined because conditions for chemisorption of H₂ (or CO) molecules on Ru and Fe species are different. Thus, turn over frequency (TOF) normalizing with total surface area of nanoparticles (S_{total} , m⁻²) was obtained to compare catalytic performances of Ru/MgO and RuFe/MgO. Surface area (S, m²), volume (V, m³), weight of a particle (W, g) for a Ru or RuFe nanoparticle and total weight of the loaded metal (W_{total} , g) were calculated using composition, average atomic weight, average diameter determined from TEM images. Here, we assumed that lattice constants of Ru and RuFe nanoparticles are similar to that of bulk Ru because we did not observe considerably large shits in peak positions in XRD patterns of these nanoparticles from those of bulk Ru. Density of a nanoparticle (D, g cm⁻¹) was determined by considering density of bulk Ru (12.45 g cm⁻¹) and atomic weight of Ru, 101.07, and average atomic weight of RuFe (78.0 for Ru₄₉Fe₅₁). Total surface area of nanoparticles (S_{total}) and the number of nanoparticles (N_{total}) included in 0.2 g of a catalyst were calculated from S, V, W. TOF (NH₃ molecule m⁻² s⁻¹) on metal or alloy nanoparticles included in 0.2 g of a catalyst was calculated from S, V, W. TOF (NH₃ molecule m⁻² s⁻¹) = Effluent NH₃ mole fraction (vol%)/100×6.02×10²³×60(cm³)/22,400(cm³)/60(s)

 $N_{\text{total}} = W_{\text{total}} / W = W_{\text{total}} / (D \times V \times 1000000)$

eTOF (NH₃ molecule $m^{-2}s^{-1}$) = $R_{NH3}/S_{total} = R_{NH3}/(S \times n_{total})$



Fig. S5. Composition dependence of catalytic activities on Ru-Fe/MgO catalysts at 400 °C.

Catalyst	Drocouro	Data at 672K	Data at 672K	Deference
Catalyst	Pressure	Rale at 673K	Rale al 073K	Reference
	(MPa)	(µmol g _{catalyst} -1h-1)	(µmol g _{Ru} -1h-1)	
Ru/MgO	0.1	115	5,702	This work
Ru/MgO	0.5	108	5,326	This work
Ru/MgO	1.0	158	7,824	This work
RuFe/MgO	0.1	46	5,008	This work
RuFe/MgO	0.5	152	16,519	This work
RuFe/MgO	1.0	230	24,986	This work
Ru/MgO	0.1	2,017	25,213	Ref. [1]
(8wt%)		(653 K)	(653 K)	
Ru/MgO	1.1	1,920	24,000	Ref. [1]
(8wt%)		(653 K)	(653 K)	
Ru/MgO	0.1	379	18,950	Ref. [2]
(2wt%)				
Ru/Cs/MgO	0.1	418	20,900	Ref. [2]
(2wt%)				
Ru/Cs/MgO	1.0	12,117	201,950	Ref. [3]
(6wt%)				
Ru/C12A7:e ⁻	1.0	8,245	687,083	Ref. [3]
(1.2wt%)				

Table S3. Comparison of catalytic activities for NH₃ synthesis on Ru/MgO, RuFe/MgO and the reported catalysts.

COMPUTATIONAL MODEL AND METHODS

The Ru and RuFe surfaces are modeled with a four-layer slab with a vacuum gap of about 15Å in the z direction for separating two subsequent slabs. The atoms in the top two layers are allowed to relax, while the atoms on the bottom two layers are fixed at their ideal bulk positions for RuFe alloy. Throughout this calculation, the plane-wave-pseudopotential approach, together with the Perdew-Burke-Ernzerhof (PBE) [4] exchange-correlation functional, and Vanderbilt ultrasoft pseudopotentials [5] was utilized. The kinetic energy cut-offs of 544 ad 5440 eV were used for the smooth part of the electronic wavefuntions and augmented electron density, respectively. The Quantum-ESPRESSO code, PWSCF package [6], was used to perform the calculations. Brillouin zone integrations were performed using a Monkhorst-Pack [7] grid of 4× 4× 1 kpoints. All calculations are spin polarized. The structures were relaxed by using a Davidson iterative diagonalization algorithm until the magnitude of residual Hellman-Feynman force on each atom was less than 10⁻³ Ry/Bohr. The evaluation of the minimum energy reaction paths (MEPs) and Transition states (TSs) has been done using the climbing image nudged elastic-band (Cl-NEB) method [8-10]. In all electronic density of states (DOS) and projected density of states (PDOS) calculations, Monkhorst-Pack grid of 6× 6× 1 kpoints and a conventional Gaussian smearing of 0.1 eV was utilized. The adsorption energy of an adsorbate on the surface was calculated as, $\delta H_{ads} = E_{tot} - E_{bare} - E_{ad}$, where E_{tot} (E_{bare}) is the energy of the surface with (without) adsorbate and E_{ad} is the energy of the isolated adsorbate species calculated in the same supercell. Hence, a negative δH_{ads} indicates stable adsorption whereas a positive value indicates unstable adsorption.

Table S4: The calculated structural parameters and adsorption energies for NH ₃ synthesis reaction intermediates over Ru surface. The first,
second, third, and fourth column represents the adsorption site, the adsorption energy (δHads, in eV), the adsorbate height over the surface
(h, in Å), and the N-H bond length (BL, in eV), respectively.

Adsorbates	Most stable adsorption site	δH _{ads} , (eV)	h, (Å)	BL (N-N, N-H), (Å)
N ₂	Т	-0.665	2.023	1.125 (N-N)
Ν	Н	-5.568	1.091	-
Н	F	-2.925	1.051	-
NH	Н	-5.955	1.213	1.027 (N-H)
NH ₂	В	-2.876	1.657	1.024, 1.024 (N-H)
NH3	Т	-1.076	2.231	1.024,1.024,1.025 (N-H)

Table S5. The calculated structural parameters and adsorption energies for NH_3 synthesis reaction intermediates over RuFe surface. The first, second, third, and fourth column represents the adsorption site, the adsorption energy (δH_{ads} , in eV), the adsorbate height over the surface (h, in Å), and the N-H bond length (BL, in eV), respectively.

Adsorbates	Most stable adsorption site	δH _{ads} , (eV)	h, (Å)	BL (N-N, N-H), (Å)
N ₂	T-Ru	-0.837	2.012	1.127 (N-N)
N	H-Fe3Ru	-5.840	0.983	-
Н	F-Ru2Fe	-2.985	1.062	-
NH	F-Fe2Ru	-6.126	1.128	1.027 (N-H)
NH ₂	B-RuFe	-2.974	1.614	1.025, 1.025 (N-H)
NH ₃	T-Ru	-1.067	2.240	1.024,1.024,1.024 (N-H)

The work function of the surfaces considered here are obtained from the Fermi energy E_F as $\delta W = \phi - E_F$, where ϕ represents the vacuum

level calculated from the planar average of the electrostatic potential in the unit cell along the z-axis.



Fig. S6. The spin density $(\rho \uparrow - \rho \downarrow)$ of (a) Ru and (b) RuFe catalyst surfaces.



Fig. S7. Planar average of the electrostatic potential along the z-axis for the (a) Ru (0001) surface, (b) RuFe alloy surface, and (c) Fe(111) surface. Red line represents the Fermi level.



Fig. S8. The d-PDOS of Ru (red), RuFe (blue), and Fe (green) surfaces. The positive and negative values represent spin-up and spin down states, respectively. The d-band centers of spin up and spin down states of Ru, RuFe and Fe surfaces are represented vertical red, blue and green lines, respectively.



Fig. S9. The five-fold degenerate $t_{2g} (d_{xz}, d_{yz'}, d_{zx})$ and $e_g (d_{x^2-y^2} and d_{z^2})$ d-states of the RuFe alloy catalyst.



Fig. S10. Calculated adsorption energy for nitrogen on Ru, Ru-Fe, Fe catalyst surfaces.



Fig. S11. The top view of supercell representing the geometry for N/Fe(111). This geometry is reported to be the most stable for N adsorption on Fe(111) surface [11]. N and Fe atoms are highlighted in light blue and red, respectively.

We investigated the overall reaction energetics for NH_3 synthesis on both Ru and RuFe surfaces by analyzing the associative as well as dissociative mechanisms. The associative mechanism, where reaction proceeds via adsorption of N_2 on the surface with subsequent hydrogenation of the adsorbed N_2 atom, have the following elementary steps:

$$* + N_2 \rightleftharpoons * N_2,$$

$$* N_2 + * H \rightleftharpoons * N_2 H,$$

$$* N_2 H + * H \rightleftharpoons * N_2 H_2,$$

$$* N_2 H_2 + * H \rightleftharpoons * N_2 H_3,$$

$$* N_2 H_3 + * H \rightleftharpoons * N_2 H_4,$$

$$* N_2 H_4 + * H \rightleftharpoons * N H_2 + N H_3,$$

$$* N H_2 + N H_3 + * H \rightleftharpoons * N H_3 + N H_3,$$

$$* N H_3 \rightleftharpoons N H_3 + *,$$

The dissociative mechanism, where reaction proceeds via dissociation of N_2 on the surface with subsequent hydrogenation of the adsorbed N atoms, have the following elementary steps:

$$2 * + N_2 \rightleftharpoons 2 * N,$$

$$2 * N + * H \rightleftharpoons N + * NH,$$

$$* N + * NH + * H \rightleftharpoons 2 * NH,$$

$$2 * NH + * H \rightleftharpoons NH + * NH_2,$$

$$* NH + * NH_2 + * H \rightleftharpoons 2 * NH_2,$$

$$2 * NH_2 + * H \rightleftharpoons NH_2 + * NN_3,$$

$$* NH_2 + * NH_3 + * H \rightleftharpoons 2 * NH_3,$$

$$2 * NH_3 \rightleftharpoons NH_3 + NH_3 + *,$$

$$* NH_3 + NH_3 \rightleftharpoons 2NH_3 + 2 *$$

In the above equations "*" stands for an empty site on the surface.

As in associative mechanism (discussed in the main text), in dissociative mechanism as well two NH₃ molecules are formed with one N_2 and three H₂ molecules. The calculated energetics for dissociative mechanism for both Ru and RuFe surfaces are represented in Figure S12. In the first step the N₂ molecule dissociates, which is well known to be the rate-limiting step for ammonia synthesis on Ru surface [12]. In the next steps, the H atoms are added to the nitrogen atom one-by-one, and the most stable adsorption site and configuration are found for each number of hydrogen atoms. We obtained the minimum energy configurations of the N₂H₂, N₂H₃ and N₂H₄ by adsorbing 2, 3 and 4 hydrogens, respectively, at the most stable N_2 site [13]. After addition of three H atoms, the first NH_3 molecule desorbs from the surface and the formation of the second NH_3 molecule continues. It is clear from Figure S12 that NH_2 and NH are the first unstable intermediates on the Ru and RuFe surfaces, respectively, and the overall reaction is exothermic for both surfaces.



Fig. S12. Calculated energy diagrams showing energies of the intermediates of the NH₃ synthesis reaction on Ru and RuFe surfaces via dissociative mechanism. "*" stands for an empty site on the surface.

In order to further estimate the relative catalytic activity of Ru and RuFe surfaces for NH₃ synthesis through dissociative mechanism we performed CI-NEB calculations with 7 images for N₂ dissociation, which is considered as the rate limiting step. It was found that on both Ru and RuFe surfaces the N₂ molecule, which is standing perpendicular to the surface in the molecularly adsorbed state, is first rotated into a metastable, flat-lying molecular precursor. The reaction path was found to have similar TS for both the surfaces, where the N₂ molecule dissociates into two N atoms bonded to the surface atoms. Our calculations of activation energy barrier, E_a indicate that N≡N bond breaking from the initial state (IS) to the TS mainly contributes to the activation energy barrier of N₂ dissociation for both the surfaces. Figure S13 represents the preliminary results for MEP between IS and final state (FS) for N₂ dissociation on Ru and RuFe surfaces, respectively, along with the IS, TS, and FS geometries. The IS corresponds to the most stable geometry of the adsorbed N₂ molecule on the surface and the FS corresponds to dissociated N₂ molecule. The chosen TS configuration corresponds to the highest energy point along the MEP. The activation energy barrier, E_a is defined as E_a = E_{TS} - E_{IS2}, where E_{TS} is the energy of the TS and E_{IS} is the energy of IS. The activation energy barrier of about ~1.3 eV is obtained for Ru surface, whereas, clearly the N₂ dissociation barrier is lowered by ~1.0 eV/molecule on the RuFe alloy surface explaining the high activity of the alloy compared to pristine Ru surface as observed experimentally. Also, the reaction energy (defined as $\Delta E = E_{TS} - E_{TS}$, where E_{TS} is the energy of the TS and barrier is lowered by cherentally. Also, the reaction energy

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Fig. S13. The reaction barrier of single nitrogen molecule dissociation on pristine Ru and Ru-Fe surfaces from Climbing Image Nudged Elastic Band (CI-NEB) simulation. Ru, Fe and N atoms are highlighted in grey, red and light blue, respectively.

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