Supporting Information

Removal of Hydrogen Poisoning by Electrostatically Polar MgO Support for Low Pressure NH₃ Synthesis at High Rate over Ru Catalyst

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Experimental Procedures

1. Materials

Chemicals, reagents, and gases used for synthesis were: Ruthenium dodecacarbonyl (Sigma-Aldrich); CsNO_3 (reagent grade, Sigma-Aldrich); $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (reagent grade, Alfa Aesar); Vulcan carbon ® XC72R GP-3921 (Cabot); Benzoic acid (reagent grade, Sigma-Aldrich); Sodium hydroxide (reagent grade, Sigma-Aldrich); Tetrahydrofuran (anhydrous, $\geq 99.9\%$, inhibitor-free, Sigma-Aldrich); Magnesium oxide (reagent grade, Sigma-Aldrich); Ethanol (puriss. p.a., absolute $\geq 99.8\%$ (GC), Sigma-Aldrich); Acetone (99.9%, Sigma-Aldrich). H_2 (99.99%, BOC); N_2 (99.99%, BOC); Argon (99.99%, BOC); 5% H_2 in Ar (5% H_2 , 95% Ar, BOC). Previous study showed that trace amount of O_2 , CO_2 or H_2O poses significant inhibition to the catalytic activity¹. The purities of H_2 and N_2 were further improved from their supply cylinders with oxygen, carbon dioxide and moisture (HP and 5 Å molecular sieve) traps prior to their use for ammonia synthesis.

2. Synthesis

MgO preparation

a) MgO(100) support

MgO(100) (The MgO with preferential exposed (100) surface) was prepared using the traditional thermal decomposition method where the precursor $\text{Mg}(\text{NO}_3)_2$ was calcined directly at 500 °C for 5 hours ².

b) MgO(110) support

MgO(110) was prepared by the calcination under vacuum method. Typically, commercial MgO (500 mg) was boiled in deionised water for 5 hours. The raw product was then collected by filtration and was subsequently dried at 120 °C for 12 hours. The product was calcined under vacuum at 500 °C for 6 hours ².

c) MgO(111) support

MgO(111) was synthesized using the hydrothermal method with the aid of benzoic acid as surfactant. Typically, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (2 g) and benzoic acid (0.12 g) was dissolved in 60ml deionised water at room temperature. The mixture was stirred for 10 minutes. 2M NaOH (20 ml) was then added drop wise into the solution, forming a white precipitate. The slurry was subsequently transferred to a 100ml autoclave and gradually heated to 180 °C and maintained at this temperature for 24 hours. The $\text{Mg}(\text{OH})_2$ precursor was obtained after filtration followed by washing with water and drying at 80 °C under vacuum overnight. MgO(111) nanosheets were obtained after calcination in compressed air at 500 °C for 6 hours ³.

Activated carbon (AC) preparation

Vulcan carbon was pre-treated at 850 °C at a ramp rate of 5 °C/min and maintained for 24 hours under 5% H_2 in Ar.

Cs-Ru modified MgO and AC preparation

Typically, $\text{Ru}_3(\text{CO})_{12}$ was dispersed in THF for 2 hours under sonication. The mixture was then transferred to the MgO or activated carbon (AC) and allowed to sonicate at ambient

temperature for 8 hours where the solvent is subsequently removed by rotary evaporation. The obtained powder was dried in a 70 °C oven for 12 hours under vacuum. After that the powder is transferred to a temperature-programmed furnace and heated to 350 °C for 6 hours under Ar stream to remove the CO ligand from the Ru precursor. Cs(NO₃)₂ was then dissolved in water and loaded to the Ru/MgO (or AC) by the incipient wetness impregnation method (Cs:Ru molar ratio = 1:1). The obtained slurry was dried in a 70 °C oven which was then reduced under 5% H₂ in Ar at 350 °C for 6 hours.

3. Methods

Catalytic test - NH₃ synthesis production rate measurements

NH₃ synthesis production rate (activity) was evaluated on a quartz-lined stainless steel fixed bed micro-reactor under a continuous flow of syngas (N₂:H₂ = 1:3). Typically, 100 mg of catalysts was sandwiched between 2 layers of quartz wool in a steel tube (diameter 10 mm) which was then fitted to the reactor. Prior to each measurement the catalyst was pre-activated at 400 °C for 4 hours under syngas (N₂:H₂ = 1:3) flow (60 mL min⁻¹ at stp). After the pre-reduction procedure, the catalytic test was conducted under various temperature (350-400 °C) and pressure (1-10 bar). The products were analysed in situ by a connected gas chromatography (GC) equipped with two TCD detectors and one FID detector. Simultaneously, the exit gas was also purged into a 1M sulfuric acid trap. The ammonia yield can thus be determined by the titration of the trap after reaction. Kinetic data such as energy barrier (E_a) and rate order were generally collected at the rates at least more than 80% difference from that of the equilibrium conversion rates under our temperature and pressure range at a short residence time.

NH₃ production rate calculation:

- 1.) Volume of NH₃ produced per minute (mL min⁻¹) = NH₃ yield (%) * Flow of N₂ (mL min⁻¹) * 2
- 2.) No. of moles of NH₃ produced per minute (mol min⁻¹) = V_{NH₃} (mL min⁻¹) * (10⁻⁶) * 101,325 (Pa) ÷ 8.31 (J mol⁻¹K⁻¹) ÷ (25+273) (K)

Activity expressed in per gram catalyst per hour basis (mol g⁻¹ h⁻¹)

$$= n_{\text{NH}_3} \div m_{\text{catalyst}} (\text{g}) * 60$$

Activity expressed in per mol of metal used per hour basis (mol metal_{mol}⁻¹ h⁻¹)

$$= n_{\text{NH}_3} \div (m_{\text{catalyst}} (\text{g}) * W_{\text{metal}} (\%) \div \text{molar mass}_{\text{metal}}) * 60$$

Note: W_{metal} obtained from ICP-MS.

N₂, H₂ and NH₃ Kinetic studies

The investigation of the N₂ and H₂ reaction order was according to the methods reported in literature in a tubular reactor tube⁴. All the conversions are set below 20% at 370°C for 100mg catalyst at 60 mL min⁻¹ with the stoichiometric mass balance in N and H. The reactor is therefore in a differential mode under kinetic controlled regime, which is far from the equilibrium. The reaction order of N₂ was measured at a constant total pressure (10 bar) and H₂ pressure (5 bar) while changing N₂ and Ar partial pressure. The flow of H₂ is fixed at 30 mL min⁻¹ and the flow of N₂ is 15, 20, 25, 30 mL min⁻¹, respectively with the flow of Ar 15, 10, 5, 0 mL min⁻¹ respectively. The reaction order of H₂ was measured at a constant total pressure (10 bar) and N₂ pressure (1.7 bar) while changing H₂ and Ar partial pressure. The flow of N₂ is fixed at 10 mL min⁻¹ and the flow of H₂ is 20, 30, 35, 40 mL min⁻¹, respectively with the flow of Ar 30, 20, 15, 10 mL min⁻¹.

¹ respectively. The reaction order of NH₃ was measured with a fixed ratio of N₂:H₂=1:3 with total flows at 60, 80, 100, 120 mL min⁻¹.

TMPO-adsorbed MgO preparation.

100 mg of the MgO sample was placed in a home-made glass tube, activated at 298 K for 2 h under vacuum (10⁻¹ Pa), mixed with a CH₂Cl₂ solution containing 0.1M TMPO under nitrogen, treated by ultrasound for 1 h (for equilibrium), and then the solvent was evacuated under vacuum. Finally, the sample tube was sealed for storage and transferred to Bruker 4 mm ZrO₂ rotor with a Kel-F endcap in a glove box under nitrogen atmosphere before NMR spectroscopy measurement.

¹H and ³¹P NMR measurement.

The Solid state magic angle spinning (MAS) NMR experiments were carried out using a Bruker Avance III 400WB spectrometer at room temperature for both ¹H and ³¹P nucleus. Particularly, the high power decoupling (HPDEC) was thus used for the quantitative ³¹P analysis. Considering the long relaxation time of ³¹P nuclei in NMR experiment, we used 30° pulse with the width of 1.20 μs, 15 s delay time. The radiofrequency for decoupling was 59 kHz. The spectral width was 400 ppm, from 200 to -200 ppm. The number of scanning was 800. The ³¹P chemical shifts were reported relative to 85% aqueous solution of H₃PO₄, with NH₄H₂PO₄ as a secondary standard (0.81 ppm). It is noted that the NMR combined with selected probing molecules, such as TMP or TMPO to characterise surface acidity/basicity of solid facets have been recently reviewed (reference 21 in the main text). Particularly, the high surface polarity of polar surfaces such as ZnO (0002) and CeO₂(100) can induce the significant ³¹P chemical shifts of the molecule. This is for the first time to use TMPO to probe the polar MgO(111) and the pronounced chemical shift in line with other polar surfaces can be experimentally observed.

FTIR measurement.

The Fourier-Transform Infra-Red (FTIR) experiments were carried out using a Thermo Scientific Nicolet 6700 spectrometer equipped with CaF₂ windows at 200 °C. Spectra were obtained by collecting 32 scans with a resolution of 4 cm⁻¹ and are presented in absorbance unit. Powder of freshly prepared samples were pressed into pellets and loaded onto the sample holder. The sample was then flushed with He for 30 minutes to clean the surface under 200 °C. After collecting background spectra, N₂ gas was passed through the sample holder for 15 minutes at 20 mL min⁻¹ and in-situ sample spectra were recorded. After 15 minutes, H₂ gas was then passed at 20 mL min⁻¹ and in-situ spectra were recorded. The presented spectra are the difference spectra of the in-situ spectra from the background spectra.

Computational details.

In density function theory (DFT) calculations, we employed projector-augmented waves (PAW)^{5,6} generalized gradient approximation (GGA)⁷. In the plane wave calculations, cutoff energy of 500 eV was applied, which was automatically set by the total energy convergence calculation for Mg-terminated MgO(111) (Mg-MgO(111)) and oxygen-terminated MgO(111) (O-MgO(111)), MgO(110) and MgO(001) slab systems. The surface is constructed as a slab within the three dimensional periodic boundary conditions and models are separated from their images in the direction perpendicular to the surface by a 14 Å vacuum layer. 3 × 3 × 1 k-Point mesh was used in the super cell in all MgO slab systems. During all calculations, the bottom two layers were kept fixed to the bulk coordinates and full atomic relaxations were allowed for the top three

layers. Corresponding supercells were found $8.933 \times 8.933 \times 20.078 \text{ \AA}^3$ for Mg-MgO(111), $11.911 \times 11.911 \times 18.862 \text{ \AA}^3$ for O-MgO(111), $12.633 \times 8.933 \times 19.955 \text{ \AA}^3$ for MgO(110) and $8.933 \times 8.933 \times 24.528$ for MgO(100) to calculate the adsorption of hydrogen. The atoms in the cell were allowed to relax until the forces on unconstrained atoms are less than 0.02 eV/Å. The adsorption energy of H in Mg-MgO(111) system, E_{ad} , is defined as the sum of interactions between the capping molecule and slab system, and it is given as $E_{ad} = E_{total} - E_{Mg-MgO(111)} - 0.5E_{H_2}$, where E_{total} , $E_{Mg-MgO(111)}$ and E_{H_2} are the energy of total system, Mg-MgO(111) slab and H_2 molecule, respectively. Notice that the negative sign of E_{ad} corresponds to the energy gain of the system due to molecular adsorption. The calculation of O-MgO(111), MgO(110) and MgO(100) systems were carried out similarly.

To further explain the remarkable activity of the oxygen-terminated MgO (111) system (O-MgO(111) system), first-principles calculations were employed to investigate the charge transfer and adsorption energy between H molecule and O-MgO(111) surface. The surface is constructed as a slab within the three dimensional periodic boundary conditions and models are separated from their images in the z direction perpendicular to the surface by a 14 Å vacuum layer (the x and y directions being parallel to the surface), see Figure S11. To find the suitable dimension of supercell, the H adsorption on O-MgO (111) slab system with the stable structure is used as an example to perform calculations in $8.93 \times 8.93 \times 21.29 \text{ \AA}^3$ system. Geometry optimizations and charge analysis calculations were performed using the Vienna ab initio simulation package (VASP), and calculations were based on density functional theory (DFT) and PAW of generalized gradient approximation (GGA)^{5,7}. The ion-electron interaction was modeled by the non-local real space, ultrasoft pseudopotential⁸⁻¹⁰ with a cutoff of 500 eV. The O-MgO(111) slab was initially constructed on a MgO with bulk Mg-O bond lengths and then optimized with the total energy convergence of 1×10^{-2} eV, as shown in Figure S11. The

adsorption energies (E_{ads}) are defined as $E_{ads} = E_{H-MgO_2(111)} - (E_{MgO_2(111)} + \frac{1}{2}E_{H_2})$,

where $E_{H-MgO_2(111)}$ represents the total energy of the H adsorbed on the O-MgO(111) slab,

$E_{MgO_2(111)}$ is the total energy of the O-MgO(111) slab and $E_{\frac{1}{2}H_2}$ is the total energy of the isolated H molecule.

To model the surface we adopted slabs with seven layers with nine atoms per layer. The bottom two layers are kept fixed to the bulk coordinates and full atomic relaxations were allowed for the top five layers, as shown in Figure S12. For these calculations, a $3 \times 3 \times 1$ k-Point mesh was used in the 3×3 supercell.

Chemisorption measurements

The chemisorption uptake of CO and H were measured to examine the effect of hydrogen spillover where the ratio of Ru: CO/H = 1 is assumed^{11,12}. The samples were measured on a Micromeritics ASAP 2020 (M+C) analyzer. The samples were pre-reduced at 773 K and evacuated for 1 h at 773 K to ensure a high surface cleanness. An isotherm was measured in an adsorbate pressure range of 100-600 Torr at a precisely controlled temperature of 308 K.

Conductivity measurements

The current-voltage test (I-V test) is done to probe the proton conductivity of the catalyst under a flowing hydrogen atmosphere. To merge the grain boundary and to amplify the difference, 10 weight % silver added to some of the catalyst powder by means of ball-milling. Prior to measurement the powder (with or without silver) was pressed into a pellet under 5000 kg force and was maintained for 3 minutes. After that it was transferred to a furnace where 10% H_2 in He was passed at 300 °C for 3 hours. The measurement was conducted at 50 °C and 150 °C

on a Keithley 4200 A-SCS semiconductor analyser using a 4-point probe system and a 2-point probe system under 5% H₂ in He. The voltage bias was set to be -1.0-1.0 V with a scan rate of 0.01 Vs⁻¹.

Operando Ambient-Pressure XPS (AP-XPS) measurements

The study of the dynamic change of [OH] concentration under different gas conditions was performed by means of operando XPS measurements, at the Diamond Light Source B07 beamline. The powdered samples were dissolved in acetone and mounted on a silicon wafer, which were subsequently heated by a heat plate at 110 °C to remove the solvent. The temperature was maintained at a constant throughout the experiment at 350 °C. The measurements were performed either under 1 mbar Ar or 1 mbar H₂. The gas composition was continuously monitored by online mass spectrometry (MS). If not otherwise stated O 1s, spectra were recorded using a fixed photon energy of 980 eV. The binding energy (BE) scale was calibrated with respect to the Mg 2s (88.1 eV) as internal standard.

The depth profiling by XPS is determined by the attenuation function of the emitted electrons. In homogenous materials, the intensity from a depth z is approximation as follow:

$$I(z) = I(z=0) \exp(-z/\lambda \cos\theta) \quad \text{Eq: 1}$$

θ represents angle between normal surface and analyser direction (emission)
 λ - inelastic mean free path of the photoelectrons (IMFP).

As a result, the IMFP decay function to deviate from exponential law, it is clear that the measured intensities will arise also from locations deeper than $z = \lambda$. In this model the signal intensity of an element A at an excitation energy $h\nu$ is proportional to a Laplace transformation of the depth-dependent concentration¹³.

As for the depth profiling measurement taken in B07 of Diamond light source, the photon energy was varied at 980 eV, 1280 eV and 1880 eV, which corresponded to a penetration depth of 21.3 Å, 26.2 Å, and 35.5 Å respectively. The diode current was also recorded for each photon energy so as to normalise the spectra. The number of atomic layer was estimated using the IMFP-TPP2M software.

From our XPS we obtained the identical BEs of our reduced Ru (3d_{5/2} = 280.0 eV, 3d_{3/2} = 284.2 eV) over MgO(111), (110) and (100) indicated that there is no significant difference in the electronic influence from these MgO supports to Ru nanoparticle. In addition, it is well-accepted that the N-N dissociation, which is the rate-determining step in ammonia synthesis occurs at the Ru B5 sites of Ru nanoparticle. Given a very similar nitrogen rate order among the three facets and the randomness of the Ru nanoparticle distribution on these samples (TEM). We assume that the N-N cleavage still takes place on these electronic unperturbed Ru sites but clearly the H poisoning on these sites varies in using different MgO support facets indicating that the hydrogen on Ru active sites can be uniquely converted to protons on MgO(111) support to reduce the surface poisoning of the Ru sites.

Supplementary Materials

Table S1: BET, CO₂-TPD and corresponding basic site concentration of various MgO supports.

Table S2 H charge transfer model on MgO(111) oxygen terminated surface.

Fig. S1: TEM and HRTEM images of various MgO facets.

Fig. S2: SEM images of various MgO facets.

Fig. S3: XRD profiles of various MgO facets.

Fig. S4: Kinetic Studies of faceted Cs-Ru/MgO catalysts.

Fig. S5: EPR spectra of various MgO facets.

Fig. S6: TEM images and size histograms of faceted Cs-Ru/MgO catalysts.

Fig. S7: CO₂-TPD profile of various MgO facets.

Fig. S8: Hydrogen rate order study for Ru/MgO(111), Ru/MgO(110), and Ru/MgO(100) at 673K and 1.0 MPa

Fig. S9: Stability test of ammonia production rate of faceted Cs-Ru/MgO catalysts.

Fig. S10: Deconvoluted ¹H NMR spectra of various MgO facets.

Fig. S11: Time resolved FTIR spectra of various faceted Ru/MgO catalysts.

Fig. S12: DFT calculations on H adsorption energies on polar MgO(111).

Fig. S13: H configuration models on polar MgO(111).

Fig. S14: DFT calculations on H adsorption energies on different sites of polar MgO(111).

Fig. S15-S19: Deconvoluted O1s AP-XPS spectra under various reaction conditions.

Fig. S20: STEM image and EELS of freshly prepared Ru/MgO(111).

Fig. S21: STEM image for the post-mortem analysis of Ru/MgO(111).

Table S1: BET, CO₂-TPD and corresponding basic site concentration of various MgO supports.

Supports	BET (m ² /g)	CO ₂ - TPD (mmol/g)	Basic site concentration (μmol/m ²)
MgO(111)	128.6	4.93	38.3
MgO(110)	170.6	4.37	25.6
MgO(100)	13.4	0.26	19.4

Table S2 H charge transfer model on MgO(111) oxygen terminated surface.

System	Charge (e)	Charge difference (e)
O-terminated MgO(111)	O (surface): 6.99 O (sub-surface): 7.59 O (bottom): 6.88 Mg: 6.29	---
H ₂	H: 0.94	---
H adsorbed on the O-terminated MgO(111) slab	O (surface): 7.74 O (sub-surface): 7.62 O (bottom): 6.88 Mg: 6.28 H: 0.00	O (surface): 6.99-7.74=-0.75 O (sub-surface): 7.59-7.62=-0.03 O (bottom): 6.88-6.88=0 Mg: 6.29-6.28 = +0.01 H: 0.94-0.00 = + 0.94

Fig. S1 TEM and HRTEM images of (a) MgO(111), (b) MgO(110) and (c) MgO(100). Inset: ten lattices of each sample were measured as 2.44, 1.48 and 2.14 nm, which correspond to the lattice spacing 0.244, 0.148 and 0.214 nm of MgO (111), (110) and (100) facets.

Fig. S2 High (first row) and low (second row) resolution SEM images of (a) MgO(111), (b) MgO(110) and (c) MgO(100).

Fig. S3 XRD of MgO(111), MgO(110) and MgO(100).

Fig. S4 Kinetic Studies of Cs-Ru/MgO(111), Cs-Ru/MgO(110) and Cs-Ru/MgO(100). (a) Arrhenius Plot, (b) NH_3 rate order. Reaction conditions: 370 °C, 1.0 MPa, flow rate: 60 mL min^{-1} .

We deliberately chose the testing temperature and pressure (370 °C and 10 bar) such that the measured conversion was less than 15% of the equilibrium conversion. As a result, the outlet ammonia concentration was maintained at a low level such that the reverse reaction was minimised.

Similar order of reaction measurement by Aika was performed at below 1 bar (ref. 23 in main text) while ours were performed at 10 bars. Under the enhanced pressure, hydrogen would pre-adsorb much more readily on the Ru active sites, which would significantly amplify the hydrogen poisoning effect. As a result, we chose 10 bar to do the rate order study in order to demonstrate the effect more clearly.

Fig. S5 EPR X-band EPR spectra of MgO(111), MgO(110) and MgO(100). EPR is employed to evaluate MgO defects by monitoring the unpaired electron spins ¹⁴. The signal at $g=2.0$ has commonly been assigned to the unpaired electrons deeply trapped in surface defect via adsorbed oxygen species from air (O_2^-) and the signal at $g=1.98$ represents unpaired electrons trapped by paramagnetic center in bulk. MgO(110) and MgO(100) reveal intense signal at around $g= 2.0$ and $g=1.98$ respectively, while no surface or internal defects can be detected for MgO(111).

Fig. S6 TEM images and corresponding size histograms of Cs-promoted Ru supported on (a) MgO(111), (b) MgO(110) and (c) MgO(100). 100 particles were counted in each histogram.

After careful checking, some larger Ru nanoparticles could occasionally be seen from the TEM images in MgO(100) sample. (seen the particles count above). This can be accounted for its lower value of chemisorption results shown in Fig. 1d of the main text. This suggests that the smaller average Ru size in the case of MgO(111) can be a contributing factor to the difference in activity when compared to MgO(100). However, the comparable surface area of MgO(111) with (110) and the Ru average size (measured by CO chemisorption) can clearly attribute to the significant hydrogen spillover effect (higher H chemisorption) to the MgO(111) facet to account for reduction in hydrogen poisoning on active Ru sites in the former case.

Fig. S7 CO₂-temperature programmed desorption (TPD) profiles of MgO(111), MgO(110) and MgO(100) supports (enlarged Fig. shown in the right).

Fig. S8 Hydrogen rate order study for Ru/MgO(111), Ru/MgO(110), and Ru/MgO(100) at 673K and 1.0 MPa (the measured activities of Ru/MgO(111), Ru/MgO(110), and Ru/MgO(100) are 2.6, 1.5, 0.7 μmol metal·mol⁻¹ h⁻¹, respectively in the same conditions as Table 1).

The resultant trend of the hydrogen rate order for Ru on MgO catalysts agrees well with those Cs-Ru/MgO catalysts (Table 1 in main manuscript), which has shown a distinct positive order for MgO(111)

and a negative order for the remaining 2 facets. Thus, the Cs-modification does not seem to alter the characteristic properties of MgO(111). This result again confirms the excellent hydrogen removal ability (the intrinsic higher H affinity) offered by the oxygen terminated surface of the MgO(111) facet.

On the other hand, it is well accepted that the N-N dissociation, which is the rate determining step in ammonia synthesis, occurs at the Ru B5 sites, which are mainly on Ru nanoparticle. Given a similar nitrogen rate order among the 3 facets and the randomness of the Ru nanoparticle distribution on these samples (TEM), we assume that the N-N cleavage still takes place on the Ru nanoparticle but the H poisoning varies in using different MgO support facets.

Fig. S9 Stability test of ammonia production rate (activity) over Cs-Ru/MgO(111) at (a) 370 °C, (b) 400 °C and 1.0 MPa. WHSV is 36,000 $\text{mLg}^{-1}\text{h}^{-1}$.

Fig. S10 Deconvoluted ^1H NMR spectra of (a) $\text{MgO}(111)$, (b) $\text{MgO}(110)$ and (c) $\text{MgO}(100)$.

Fig. S11 Time resolved in-situ FTIR spectra (Difference spectra with background subtraction) of Ru supported on (A) $\text{MgO}(111)$, (B) $\text{MgO}(110)$ and (C) $\text{MgO}(100)$ under 15 minutes of flowing N_2 and H_2 respectively under room temperature.

Fig. S12 The H adsorption on the O-MgO(111) slab system of the (a) top-view and (b) side-view.

Fig. S13 (a) Adsorption site of H on O-MgO(111) and the optimized H on the O-MgO(111) slab structures in the (b) atop configurations.

(a)

H adsorption energy on
atop O site: -3.83 eV

(b)

H adsorption energy on
bridging O site: -3.76 eV

Fig. S14 H adsorption energy on (a) atop oxygen site; (b) bridging oxygen site on the oxygen terminated polar MgO(111) surface.

111-
1. Ar

	Peak Position (eV)	Area (%)	FWHM
[OH]	531.5	13.6	1.7
[O ²⁻]	529.5	86.4	1.8

Fig. S15. O1s spectra of Ru/MgO(111) under first pass of Ar at 350 °C.

111-
H₂

Fig. S16. O1s spectra of Ru/MgO(111) under H₂ (second step) at 350 °C.

111-
3. Ar

Fig. S17. O1s spectra of Ru/MgO(111) under second pass of Ar at 350 °C.

	Peak Position (eV)	Area (%)	FWHM
[OH]	531.6	18.7	1.6
[O ²⁻]	529.6	81.2	1.9

Fig. S18. Depth profiling O1s spectra of Ru/MgO(111) under H₂ at 350 °C at a photon energy of 1280 eV (6 atomic layer with penetration depth 26.2 Å).

	Peak Position (eV)	Area (%)	FWHM
[OH]	531.7	12.3	1.7
[O ²⁻]	529.5	87.7	1.8

Fig. S19. Depth profiling O1s spectra of Ru/MgO(111) under H₂ at 350 °C at a photon energy of 1880 eV (8 atomic layer with penetration depth 26.2 Å).

As observed in the ambient pressure XPS (Figure 4 in the main manuscript), the concentration of [OH] species increased when gaseous H₂ was used and decreased when it was removed from the system.

This suggests the reversibility of the protons on MgO(111) and H₂ on Ru with their rapid interactions at the interface. Given the facile ability for the protons to travel across the O²⁻ surface (as evidenced by the excellent proton conductivity of Ru/MgO(111) and a low activation barrier (0.1 eV) for the H⁺ to hop across the O²⁻ sites), we believe that a dynamic behaviour on the H⁺/H₂ should be viewed. For example, active Ru sites to sustain N₂ fixation can be poisoned by H_{ads} which can rapidly migrate to other remote Ru particles of different facets/sites for H₂ recombination in form of the hopping H⁺ via the O²⁻ surface of the MgO(111). Under such dynamic gas flow during the reaction, it is possible that H⁺ on the MgO(111) surface undergoes reverse hydrogen spillover at an instant on other type of Ru sites hence H does not hinder the Ru active sites for N₂ fixation (B5 sites). As a result, the steady state of H adsorption, migration and desorption allows a continuous removal of hydrogens from the active Ru surface. Meanwhile, the stability test of 100-hour continuous reaction with minimal drop of catalytic activity also suggests a continuous removal of hydrogen adatoms from Ru active sites.

(a)

(b)

Fig. S20 (a) A typical STEM image showing freshly made Ru clusters on MgO (111) facet with no surface reconstruction of the MgO(111) with lattice spacing of 0.244 nm; (b) The corresponding M3 & M2-edge of Ru could be seen clearly from the Ru clusters.

Fig. S21 A typical STEM image showing post-mortem analysis of Ru clusters on MgO (111) facet with no surface reconstruction of the MgO(111) with lattice spacing of 0.244 nm after testing for ammonia synthesis.

We have performed additional STEM analysis on the post-mortem Ru/MgO(111) sample after a 5-hour reaction of passing N_2 and H_2 at 673 K and 1.0 MPa. Results in Fig. S21 have clearly demonstrated that the dominant exposed facet is still MgO(111).

It is noted that the stability ionic crystal packing depends on some important factors such as Madelung constants, charges, polarizability and covalence, etc. For their surfaces, charge, packing density and structural factors (facet) are the important parameters. Wander et al. have calculated the surface energies of some slab rocksalt polar surfaces and concluded the MgO(111) is unstable compared to (110) and (100)¹⁵. As mentioned above, the unique atomic arrangement of the O^{2-} layer and the Mg^{2+} layer with the same charges and Madelung constants as (110) and (100) in a simple ionic MgO (111) facet results in a net dipole moment, which gives rise to the electrical polarity as the key factor. As a result, the structure has a high tendency to cancel the polarity. Due to the rigid oxidation state of Mg^{2+} and O^{2-} as well as the absence of the ability to generate oxygen vacancies, the only possible method to cancel the polarity is to invoke foreign cations, in this case protons, to adsorb onto the charged O^{2-} surface. This has the same conclusion in the cited paper quoted¹⁵. In this work we make use of this property to capture the adsorbed hydrogen species stuck on the Ru active sites which can on one hand stabilise the unstable polar surface and alleviate the hydrogen poisoning in ammonia synthesis on the other. The surface roughness may have even lower energy than flat surfaces hence at elevated temperature surface reconstruction could have happened. However, as seen from our post-mortem analysis in Fig. S21, the dominant exposed facet appeared to be maintained at the rigid ionic MgO(111) surface initial synthesised without severe reconstruction during the ammonia synthesis.

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