Supporting Information:

Metal-Support Interactions on Ru/CaAlO_x Catalysts Derived

from Structural Reconstruction of Ca-Al Layered Double

Hydroxides for Ammonia Decomposition

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Experimental Section

Material

 $Ca(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. $RuCl_3 \cdot xH_2O$ and CNTs was purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd. All reagents were used as received without further purification.

CaAl-LDHs preparation

The Ca-Al LDHs were prepared from aqueous solutions containing $Ca(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. The atomic ratio, $y = Ca^{2+}/Al^{3+}$ was equal to 2. An aqueous solution of 2 mol/L of NaOH was used as a precipitating agent. The pH was maintained at 12 throughout the process. The obtained precipitates were transferred to a teflon vessel and aged in an oven at 100 °C for 36 h, following which the slurry was separated by centrifugation, washed with deionized water and dried overnight at 50 °C to obtain the Ca-Al LDHs.

Catalyst preparation

The supported Ru catalyst precursors was prepared by the impregnation method using $RuCl_3 \cdot xH_2O$ as the ruthenium source. The chloride ruthenium was dissolved in either the deionized water or ethanol and mixed with the LDHs. The mixture was stirred for 12 hours, then separated. The obtained slurry was dried overnight at 50 °C. The Ru metal loading was varied with the Ru:Ca:Al molar ratio. The catalyst precursor was named as Ru/LDHs-w or Ru/LDHs-e, depending on the solvent used.

Ru/CNTs precursor preparation

The raw CNTs were purified in 16 M aqueous HNO₃ solution for 2 h by refluxing at 120 °C, followed by washing with deionized water and drying overnight. Then the

purified CNTs were impregnated with the aqueous solution of $RuCl_3 \cdot xH_2O$. The mixture was stirred for 12 hours, then filtered. The obtained slurry was dried overnight at 50 °C.

Ru/SiO₂ precursor preparation

The home-made SiO_2 were impregnated with the aqueous solution of $RuCl_3 \cdot xH_2O$. The mixture was stirred for 12 hours. Then the obtained slurry was dried overnight at 50 °C.

Catalyst pretreatment and ammonia decomposition

Prior to the catalytic reaction, the dried catalyst precursors were loaded in a continuous fixed-bed flow quartz reactor (100 mg, 25–50 mesh) and pretreated in a 50 mL/min $H_2/N_2 = 1:9$ gas flow from room temperature to 500 °C with a heating rate of 10 °C/min. The resulting catalyst was named as Ru/CaAlOx-w or Ru/CaAlOx-e.

The activity tests of the Ru/CaAlOx catalysts used NH₃ (gas flowrate of 10 mL/min) and were conducted in the temperature range of 300–500 °C under atmospheric pressure with a gas hourly space velocity (GHSV) of 6,000 mL·g_{cat}⁻¹·h⁻¹. The gas composition was analyzed using a GC-2020 on-line gas chromatograph (Hengxin) equipped with a thermal conductivity detector (TCD), with Ar as the carrier gas.

Catalyst characterization

During catalyst precursor preparation, the concentrations of the Ca, and Al metal ions in the supernatant fraction in the mixture of LDHs and the deionized water or ethanol were determined using a 7700 Series ICP-MS (Agilent, USA).

The prepared catalyst was characterized using the following methods: The specific surface (BET) area of the sample was measured using an Autosorb IQ surface area

analyzer (Quantachrome). The morphologies of the catalysts were observed using a JSM-5510 LV SEM (JEOL, Japan). TEM images were measured on a JEM-2000EX microscope (JEOL, Japan). Thermogravimetry/differential thermal analyses (TG-DTA) of the LDHs were performed using an STA-449-F3 instrument (NETZSCH, Germany) at a heating rate of 10 °C/min in Ar atmosphere. XRD patterns were obtained by means of a D8 Advance instrument (Bruker, Germany) using Cu Ka radiation, with a scanning speed of 10 °C/min. Temperature-programmed reduction (H₂-TPR) measurements were performed under a 1:9 H₂/Ar gas mixture at a flowrate of 30 mL/min. Using this method, 50 mg of catalyst was heated from 50 °C to 700 °C at a rate of 10 °C/min. Hydrogen uptake was monitored using a TCD. Raman spectra were acquired using a DXR Raman microscope (Thermo Fisher, USA). The Ru dispersion was determined using an AutoChem II Chemisorption Analyzer (Micromeritics). Prior to the measurement, the catalyst precursor was reheated to 500 °C (at a rate of 10 °C/min) in a 1:9 H₂/Ar gas mixture at a flowrate of 30 mL/min. After cooling down, the CO pulse was performed at 25 °C and the CO gas was monitored using a TCD. Electronic binding energy analysis of each element on the catalyst surface was conducted using an ESCALAB 250XI XPS (Thermo Company, USA). In situ DRIFTS investigations were conducted using a high temperature reaction chamber (Harrick Scientific Products Inc., USA) coupled with a Nicolet IS50 FTIR spectrometer (Thermo Fisher, USA) equipped with a mercury cadmium telluride detector. Samples were placed without packing on a screen through which gas could pass. The gas flowrate was controlled using a mass flow controller (Beijing Sevenstar Electronics Ltd., China). Prior to the tests, the sample was pretreated at 500 °C for 1 h in a 8:2 H₂/Ar gas mixture at a flowrate of 50 mL/min. After pretreatment, the sample was cooled down to 30 °C in Ar and the background spectra

were recorded. CO desorption infrared spectroscopy measurements were acquired on the pre-adsorption Ru/CaAlOx. After flowing 1:9 CO/He at 30 °C until sample saturation was reached, the catalyst was purged with Ar. The reaction experiments were carried out at 300 °C by feeding NH₃ at 10 mL/min. Subsequently, desorption of ammonia was carried out at a higher temperature (e.g. 350 or 400 °C) under Ar flow. All DRIFTS spectra were recorded by accumulating 32 scans at a resolution of 4 cm⁻¹.

1. Results



Figure S1 X-ray diffraction patterns of the Ru/LDHs catalyst precursors. The ◆ symbol indicates peaks corresponding to LDH structure.



Figure S2. TG-DTA analysis of LDHs from room temperature to 500 °C.



Figure S3. X-ray diffraction patterns of the Ru/CaAlOx catalysts after H₂ reduction at 500 °C for 1 h with Ru loading of (a) 0.5 wt%, (b)1.5 wt%, (c)2.5 wt%, (d)3.5 wt%, (e) 3.5wt%. The symbols \checkmark and \approx correspond to CaO and Ca(OH)₂, respectively.



Figure S4. H₂-TPR profiles of Ru/LDHs-w and Ru/LDHs-e.



Figure S5. (a) N₂ sorption isotherms and (b) pore size distribution curves of the catalyst precursors.

| sample | Surface Area | Pore Volume | Pore Diameter | CO adsorption (|
|-------------|----------------------|---------------------|---------------|------------------------|
| | $(m^2 \cdot g^{-1})$ | $(mL \cdot g^{-1})$ | (nm) | $mmol \cdot g^{-1})$ |
| CaAlOx | 3.7 | 0.013 | 4.321 | - |
| Ru/CaAlOx-e | 11.3 | 0.038 | 4.316 | 2.335×10 ⁻³ |
| Ru/CaAlOx-w | 11.8 | 0.069 | 3.825 | 2.567×10 ⁻³ |

Table S1. Surface area, pore volume, pore diameter, and CO adsorption data forCaAlOx, Ru/CaAlOx-e, and Ru/CaAlOx-w.



Figure S6. Selected DRIFTS spectra of CO adsorbed on (A) Ru/CaAlOx-w and (B)

Ru/CaAlOx-e.



Figure S7. *In situ* Drifts results of purging NH_3 -presorbed $Ru/CaAlO_x$ -w (a) and $Ru/CaAlO_x$ -e (b) with Ar at different reaction temperature.



Figure S8. Time on stream of NH_3 conversion over Ru/LDHs-w. Temperature, 500 °C; space velocity, 12000 mL·g_{cat}⁻¹·h⁻¹.



Figure S9 SEM images of $Ru/CaAlO_x$ -e-o (a) and $Ru/CaAlO_x$ -w-o(b).