# Supporting Information

# Enhanced Ammonia Synthesis Performances of Ceria-supported Ru Catalysts via Introduction of Titanium

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1. Eepermental section

1.1. Preparation of Samples

Ti-load CeO<sub>2</sub> (Ti-Ce-S): 3.472 g of Ce(NO)<sub>3</sub>·6H<sub>2</sub>O was dispersed into 20 mL deionized water , followed by adding 140 mL of NaOH aqueous solution (38.4 g NaOH) at room tempreature with stirring for 30 min. After hydrothermally treated at 100 °C for 24 h, The precipitate was separated by centrifugation and washed with deionized water and ethanol until pH=7. Titanium butoxide and ethanol mixed solution consisted of 2 mL titanium butoxide and 10 mL ethanol was added into above gel, and the pH of the mixture solution was adjusted to about 10 with ammonia solution (25%-28%). It was continually stirred for an additional 30 min, and then heated at 80 °C for 2 h. The as-obtained precipitate was separated by centrifugation, and then washed with deionized water and ethanol until pH=7. Finally, the sample was dried at 60 °C overnight, then calcined in air at 550 °C for 4 h, and the as-prepared oxide was labelled as Ti-Ce-S.

Ti-embedded CeO2 (Ti-Ce-E): 3.472 g of Ce(NO)3·6H2O and 2 mL of titanium(IV) butoxide

(97%, Sigma-Aldrich) were dispersed into 20 mL anhydrous ethanol, then 140 mL NaOH aqueous solution containing 38.4 g NaOH was added drop by drop with stirring at room tempreature. After continuously stirring for 30 min, the mixed solution was transferred into a Teflon-lined stainless steel autoclave, heated at 100 °C for 24 h, while the subsequent procedure steps are the same as the ones discussed above. The as-obtained sample was named as Ti-Ce-E.

CeO<sub>2</sub>: 3.472 g of Ce(NO)<sub>3</sub>·6H<sub>2</sub>O was dispersed into 20 mL anhydrous ethanol, then 140 mL NaOH aqueous solution containing 38.4 g NaOH was added with stirring at room tempreature. After continuously stirring for 30 min, the mixed solution was transferred into a Teflon-lined stainless steel autoclave, heated at 100 °C for 24 h. while the subsequent procedure steps are the same as the ones described above. The as-obtained sample was named as CeO<sub>2</sub>.

TiO<sub>2</sub>: 4 mL of titanium(IV) butoxide was dissolved in 20 mL anhydrous ethanol, then 140 mL NaOH aqueous solution containing 38.4 g NaOH was added with stirring at room tempreature. After continuously stirring for 30 min, the mixed solution was transferred into a Teflon-lined stainless steel autoclave, heated at 100 °C for 24 h. while the subsequent procedure steps are the same as the ones described above. The as-obtained sample was named as  $TiO_2$ .

Ru catalysts were prepared by incipient wetness impregnation of support with ruthenium(III) nitrosyl nitrate solution (Aldrich) to achieve a Ru-to-support ratio of approximately 3 wt %. Then the as-prepared catalysts were reduced in hydrogen at 550 °C for 6 h, and the samples using Ti-Ce-E, Ti-Ce-S, CeO<sub>2</sub> and TiO<sub>2</sub> were named hereinafter as Ru/Ti-Ce-E, Ru/Ti-Ce-S, Ru/CeO<sub>2</sub> and Ru/TiO<sub>2</sub>, respectively.

#### 1.2. Characterization

Nitrogen adsorption-desorption isotherms measurements at -196 °C were performed over a

Micromeritics ASAP 2020 apparatus. XRD patterns of samples were obtained using a PANalytical X'Pert3 powder diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field emission scanning electron microscope. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai G2 F20 microscope. X-ray phototoelectron spectroscopy (XPS) was conducted using an ESCALAB 250Xi photoelectron spectrometer (Thermo Fisher Scientific). To acquire spectra of reduced Ru catalysts, samples were reduced at 450 °C for 4 h under 5% H<sub>2</sub>/Ar mixture (30 mL/min) in a pretreatment chamber (Highlight Tech Corp.) attached to the spectrometer. The XPS binding energies were calibrated against the C 1s peak at 284.6 eV of adventitious carbon.

Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) of samples was performed on a Micromeritics AutoChem II 2920 equipped with a mass spectrometer (Hiden Analytical HPR-20). Prior to a H<sub>2</sub>-TPR run, 100 mg of catalyst (sieve fraction 0.30–0.56 mm) was pretreated at 150 °C for 60 min in Ar and then cooled to room temperature. Afterward, reduction was carried out by heating the sample from room temperature to 900 °C at a rate of 10 °C min<sup>-1</sup> under a flow of 10% H<sub>2</sub>/Ar mixture (30 mL min<sup>-1</sup>). Temperature-programmed oxidation (TPO) experiments were carried out on the same instrument. The samples were heated in 9% O<sub>2</sub>/Ar mixture (30 mL/min) from room temperature to 900 °C at a rate of 10 °C (m/z =28) and CO<sub>2</sub> (m/z =44) were recorded. Temperature-programmed desorption (TPD) experiments were performed using the same apparatus as well. Prior to a TPD run, 100 mg of a sample was reduced in hydrogen at 450 °C for 4 h and then purged with Ar and cooled to 400 °C. Subsequently, hydrogen (H<sub>2</sub>-TPD), nitrogen (N<sub>2</sub>-TPD), or 3.3% N<sub>2</sub>-10% H<sub>2</sub>-Ar gas mixture (H<sub>2</sub>+N<sub>2</sub>-TPD) was introduced to the catalyst at 400 °C for 1 h. Then the catalyst was cooled down to 50 °C and purged with Ar for 1 h before being heated from 50 to 900 °C at

a rate of 10 °C/min. The evolution of  $H_2$ ,  $N_2$ , and  $H_2O$  was monitored by mass spectrometry. Prior to  $H_2$ -TPR, CO-TPR, and TPSR studies for reduced samples, a catalyst was treated in hydrogen at 450 °C and then purged with Ar. After cooling down to 50 °C, the sample was heated to 900 °C (10 °C/min) in 10%  $H_2$ /Ar mixture ( $H_2$ -TPR), CO (CO-TPR), or 3.3%  $N_2$ -10%  $H_2$ -Ar gas mixture (TPSR).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Nicolet 6700 spectrometer. The sample was in situ reduced in hydrogen at 450 °C for 4 h and purged with He for 30 min. Then the catalyst was cooled down to room temperature, and background spectrum was taken. The DRIFTS experiments were carried out by feeding 5% CO/He (50 mL min<sup>-1</sup>) to the as-treated sample for a designated period. Finally, the sample was purged with He for 10 min before spectrum acquisition. All spectra were recorded by 32 scans accumulation at 4 cm<sup>-1</sup> resolution in succession.

#### 1.3. Ammonia synthesis measurement

Ammonia synthesis was carried out in a fixed-bed flow reactor. Prior to measurement, the samples (0.2 g, 32–60 mesh) were treated in a stoichiometric  $H_2$ – $N_2$  gas mixture at 550 °C for 4 h, and then cooled down to a designated reaction temperature. After the designated pressure was adjusted, the ammonia in the outlet gas was trapped by a dilute sulfuric acid solution (0.02 mol L<sup>-1</sup>), and then analyzed using an ion chromatography (Thermo Scientific, ICS-600) equipped with the Dionex IonPac<sup>TM</sup> CS16 column and DS5 conductivity detector. Subsequently, the NH<sub>3</sub> concentration and the ammonia synthesis rates can be calculated.

## Mass and Heat Transfer Calculations for Ammonia Synthesis on Ru/Ti-Ce-S

## Mears Criterion for External Diffusion (Fogler, p841; Mears, 1971)

If 
$$\frac{-r_A' \rho_b Rn}{k_c C_{Ab}} < 0.15$$
, then external mass transfer effects can be neglected.

 $-r_A'$  = reaction rate of nitrogen, kmol/kg-cat·s

n = reaction order with respect to N<sub>2</sub> (e.g. K. Aika et al, Appl. Catal., 28(1986) 57–68).

R = catalyst particle radius, m

 $\rho_b$  = bulk density of catalyst bed, kg/m<sup>3</sup>

 $C_{Ab}$  = bulk gas concentration of nitrogen, kmol/m<sup>3</sup>

 $k_c$  = mass transfer coefficient, m/s

$$\frac{-r_{A}' \rho_{b} Rn}{k_{c} C_{Ab}} = [8 \times 10^{-8} \text{ kmol-N}_{2}/\text{kg-cat} \cdot \text{s}] [910 \text{ kg/m}^{3}][3 \times 10^{-4} \text{ m}][1]/([1.7 \text{ m/s}]*[0.045])]$$

 $kmol/m^{3}$ ])= 2.9x10<sup>-7</sup> <0.15 {Mears for External Diffusion}

#### Weisz-Prater Criterion for Internal Diffusion (Fogler, p839)

If 
$$C_{WP} = \frac{-r'_{A} \rho_{c} R^{2}}{D_{e} C_{Ab}} < 1$$
, then internal mass transfer effects can be neglected.

 $-r_A'$  = reaction rate of nitrogen, kmol /(kg-cat·s)

 $\rho_c$  = solid catalyst density (kg m<sup>-3</sup>)

R = catalyst particle radius, m

 $\rho_b$  = bulk density of catalyst bed, kg/m<sup>3</sup>

 $C_{Ab}$  = bulk gas concentration of nitrogen, kmol/m<sup>3</sup>

 $k_c$  = mass transfer coefficient, m/s

 $D_e$  = effective gas-phase diffusivity, m<sup>2</sup>/s

$$C_{WP} = \frac{-r'_{A} \rho_{c} R^{2}}{D_{e} C_{Ab}} = [8 \times 10^{-8} \text{ kmol-N}_{2}/\text{kg-cat} \cdot \text{s}] \times [4 \times 10^{3} \text{ kg-cat/m}^{3}] \times [3 \times 10^{-4} \text{ m}]^{2} / ([3.34 \times 10^{-6} \text{ m}]^{2})$$

 $10^{-6} \text{ m}^2/\text{s} \ge (0.045 \text{ kmol/m}^3) = 1.9 \times 10^{-4} < 1$  {Weisz-Prater Criterion for Internal Diffusion}

Mears Criterion for External (Interphase) Heat Transfer (Fogler, p842)

$$\left|\frac{-\Delta H_r(-r_A')\rho_b RE}{h_t T_b^2 R_g}\right| < 0.15$$

 $[136.9 \text{ kJ/mol} \times 8 \text{ x } 10^{-8} \text{ kmol} \text{-N}_2/(\text{kg-cat} \cdot \text{s}) \times 910 \text{ kg-cat/m}^3 \times 3 \text{ x } 10^{-4} \text{ m} \times 150 \text{ kJ/mol}] / [185.3 \text{ kJ/m}^2.\text{K.s} \times 673^2 \text{ K}^2 \times 8.314 \times 10^{-3} \text{ kJ/mol}.\text{K}] = 6.4 \text{x} 10^{-7} < 0.15 \text{ {Mears Criterion for External for the external f$ 

## (Interphase) Heat Transfer}

## Mears Criterion for Combined Interphase and Intraparticle Heat and Mass Transport

(Mears, 1971)

$$\frac{-r'_{A}R^{2}}{C_{Ab}D_{e}} < \frac{1+0.33\gamma\chi}{|n-\gamma_{b}\beta_{b}|(1+0.33n\omega)}$$

$$\gamma = \frac{E}{R_{g}T_{s}}, \quad \gamma_{b} = \frac{E}{R_{g}T_{b}}, \quad \beta_{b} = \frac{(-\Delta H_{r})D_{e}C_{Ab}}{\lambda T_{b}}, \quad \chi = \frac{(-\Delta H_{r})-r'_{A}R}{h_{t}T_{b}}, \quad \omega = \frac{-r'_{A}R}{k_{c}C_{Ab}}$$

 $\gamma$  = Arrhenius number;  $\beta_b$  = heat generation function;

 $\lambda$  = catalyst thermal conductivity, W/m.K;

 $\chi$  = Damköhler number for interphase heat transport

 $\omega$  = Damköhler number for interphase mass transport

$$\frac{-r'_{A} \rho_{b} R^{2}}{C_{Ab} D_{e}} = [8 \text{ x } 10^{-8} \text{ kmol-N}_{2}/\text{kg-cat} \cdot \text{s} \times 910 \text{ kg-cat/m}^{3} \times (3 \text{ x } 10^{-4})^{2} \text{ m}^{2}]/([3.34 \text{ x } 10^{-6} \text{ m}^{2}/\text{s}] \times 10^{-6} \text{ m}^{2}/\text{s})$$

 $[0.045 \text{ kmol/m}^3])=4.4 \text{x} 10^{-5}$ 

$$\frac{1 + 0.33\gamma\chi}{\left|n - \gamma_b \beta_b\right| (1 + 0.33n\omega)} = 1.1$$

Left member < Right member {Mears Criterion for Interphase and Intraparticle Heat and

Mass Transport }

Samples	Na (wt%) <sup>a</sup>	Na (wt%) <sup>b</sup>	$TiO_2$ (wt%) <sup>b</sup>	CeO <sub>2</sub> (wt%) <sup>b</sup>
Ti-Ce-E	1.8	1.1	15.8	83.1
Ti-Ce-S	1.2	0.9	14.2	84.9

Table S1 The compositions of Ce-Ti-E and Ce-Ti-L

<sup>a</sup>Obtained from ICP analysis.

<sup>b</sup> Obtained by XRF analysis.

Samples	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	Pore volume ( $cm^3g^{-1}$ )	Average pore size (nm)
Ti-Ce-E	28	0.09	18.4
Ti-Ce-S	61	0.12	12.6
CeO <sub>2</sub>	44	0.25	35.9
TiO <sub>2</sub>	12	0.03	13.7
Ru/Ti-Ce-E	30	0.08	16.2
Ru/Ti-Ce-S	62	0.12	11.8
Ru/CeO <sub>2</sub>	13	0.04	18.2
Ru/TiO <sub>2</sub>	4	0.02	38.2

Table S2 Textural properties of oxides and oxides-supported Ru catalysts

 Samples
  $d_{CO}$  (nm)
  $D_{CO}$  (%) <sup>a</sup>
  $d_{TEM}$  (nm) <sup>b</sup>

 Ru/Ti-Ce-E
 3.4
 32.9
 3.6

 Ru/Ti-Ce-S
 1.7
 64.8
 1.5

Table S3 Particle sizes and dispersion of Ru catalysts

<sup>a</sup> obtained by CO chemisorption,

<sup>b</sup> measured by TEM study.

Samples	Rate	TOF <sup>a</sup>	Reaction	SV	Ref.
	$(\mu mol g^{-1} h^{-1})$	(Ru atom <sup><math>-1</math></sup> s <sup><math>-1</math></sup> )	conditions	$(mL g^{-1} h^{-1})$	
Ru/Ti-Ce-E	10861	10.5×10 <sup>-3</sup>	1 MPa, 400 °C	36000	This
Ru/Ti-Ce-S	14580	14.1×10 <sup>-3</sup>	1 MPa, 400 °C	36000	work
Ru/CeO <sub>2</sub>	4394	$4.2 \times 10^{-3}$	1 MPa, 400 °C	36000	This
Ru/TiO <sub>2</sub>	836	$8.0 \times 10^{-4}$	1 MPa, 400 °C	36000	work
Ru/TiO <sub>2</sub> -anatase	324	3.1×10 <sup>-4</sup>	1 MPa, 400 °C	36000	This
Ru/TiO <sub>2</sub> -rutile	530	$5.1 \times 10^{-4}$	1 MPa, 400 °C	36000	work
Ru(9.1%)-Ba/AC	8285	2.6×10 <sup>-3</sup>	1 MPa, 400 °C	18000	1
Ru(6%)-Cs/MgO	12117	5.7×10 <sup>-3</sup>	1 MPa, 400 °C	18000	1
Ru(4%)/C12A7:e <sup>-</sup>	6089	4.3×10 <sup>-3</sup>	1 MPa, 400 °C	18000	1
Ru(5%)/CeO <sub>2</sub>	7200	4.0×10 <sup>-3</sup>	0.9 MPa, 400 °C	18000	2
Ru(5%)/MgO	1800	$1.0 \times 10^{-3}$	0.9 MPa, 400 °C	18000	2
Ru(7.8%)/Y5Si3	4100	$1.5 \times 10^{-3}$	1 MPa, 400 °C	18000	3
Ru(4%)/r-CeO <sub>2</sub>	3830	$2.7 \times 10^{-3}$	1 MPa, 400 °C	18000	4
Ru(4%)/c-CeO <sub>2</sub>	1289	0.9×10 <sup>-3</sup>	1 MPa, 400 °C	18000	4
Ru(4%)/p-CeO <sub>2</sub>	529	0.4×10 <sup>-3</sup>	1 MPa, 400 °C	18000	4
Ru(5%)/La <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>1.75</sub>	65000	36.5×10 <sup>-3</sup>	1 MPa, 400 °C	72000	5
Ru(10%)/Ba-Ca(NH <sub>2</sub> ) <sub>2</sub>	60400	16.9×10 <sup>-3</sup>	0.9 MPa, 360 °C	36000	6
	50000	14.0×10 <sup>-3</sup>	0.9 MPa, 400 °C	36000	
Ru(6%)-Cs/MgO	23000	$6.5 \times 10^{-3}$	0.9 MPa, 400 °C	36000	6

Table S4 Catalytic performance of Ru catalysts on various supports

Cs-Ru(1%)/MgO	2700	1.0×10 <sup>-3</sup>	5MPa, 400 °C	66000	7
Ru(1%)/BaTiO <sub>3</sub>	4100	1.5×10 <sup>-3</sup>	5MPa, 400 °C	66000	7
Ba-Ru/Al <sub>2</sub> O <sub>3</sub> -980	7217	4.5×10 <sup>-3</sup>	1 MPa, 400 °C	60000	8
Ba-Ru/Al <sub>2</sub> O <sub>3</sub>	2796	$1.7 \times 10^{-3}$	1 MPa, 400 °C	36000	9
Ba-Ru/gC-Al <sub>2</sub> O <sub>3</sub>	5611	3.5×10 <sup>-3</sup>	1 MPa, 400 °C	36000	9
Ba-Ru/Al <sub>2</sub> O <sub>3</sub>	2083	1.3×10 <sup>-3</sup>	1 MPa, 400 °C	18000	9
Ba-Ru/gC-Al <sub>2</sub> O <sub>3</sub>	4219	2.6×10 <sup>-3</sup>	1 MPa, 400 °C	18000	9

<sup>a</sup> based on total number of Ru atoms

Ce-Ti-E	Ce	TI	0
1			
2 a			
_200 nm	200 nm	200 nm	200 nm
Ce-Ti-S	Се	Ti	0
W.c.v			
CHER !!			
100 nm	<u>100 nm</u>	100 nm	100 nm

Fig. S1 SEM-EDS mapping of oxides (Top) Ti-Ce-E and (Bottom) Ti-Ce-S.



Fig. S2 TEM images of (a, b) Ru/Ti-Ce-E and (c, d) Ru/Ti-Ce-S.



Fig. S3 STEM-HAADF image of Ru catalysts and the corresponding EDX elemental mapping images (Top) Ru/Ti-Ce-E and (Bottom) Ru/Ti-Ce-S.



Fig. S4 XRD patterns of samples.



Fig. S5 XPS spectra of Ti-Ce-E and Ti-Ce-S (a) Ce 3d, (b) Ti 2p and (c) O 1s.



Fig. S6 IR spectra of Ru catalysts obtained after exposing the reduced samples to CO at 50  $^{\circ}$ C for 10 min followed by He purging for 10 min.



Fig. S7 TPR profiles of (a) the fresh samples and (b) the reduced catalysts pre-exposed to air



Fig. S8 MS signals of  $H_2$  and  $N_2$  during TPD studies of oxides and oxides-supported Ru catalysts after exposure to a  $H_2$ - $N_2$  mixture.



Fig. S9 MS signals of water during TPD studies of oxides and oxides-supported Ru catalysts after exposure to a  $H_2$ - $N_2$  mixture.

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