Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Metal–Support Interactions Enhance the Ammonia Synthesis Activity over Ruthenium Supported on Zr-modified CeO_2 catalysts

Zhanwei Ma,[ab] Xumao Xiong,[a] Chengli Song[a], Bin Hu[a]* and Weiqiang Zhang[c]

[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Changchun Zhongke Haorong New Material Research Co., Ltd.

Corresponding author,

E-mail: Hcom@licp.cas.cn

1. Experimental section

1.1 Materials and Instruments

All chemicals were analytical grade and used directly without any further purification. They were purchased from Aladdin Industrial Corporation in China. Deionized water with a resistivity of 18.25 MΩ.cm was used in all reactions.

The crystalline structure of the samples was analyzed by X-ray powder diffraction (XRD) (X'pert, PANalytical, Dutch) using Cu Kα radiation (λ = 1.54050 Å). Transmission electron microscope (TEM) experiments were conducted in a JEM-2010 TEM with an accelerating voltage of 200 KV. Temperature programmed reduction (TPR) profiles of the samples were generated on a TP-5080 catalyst characterization instrument. H_2/Ar (10 % of H_2) mixture was used as the reducing gas and heated at a linear heating ramp of 10 K/min from 298 to 1173 K. UV-visible diffuse reflectance spectra were taken on a UV-2550 (Shimadzu) spectrometer using $BaSO_4$ as the reference. The element composition was detected by X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi). The photoluminescence (PL) spectra were detected with an F-7000 spectrofluorometer (Hitachi High-Technologies, Tokyo, Japan). Raman spectra of samples were recorded on Renishaw RM1000 (λ = 514.5 nm). The percentage composition of Ru was determined by XRF on MagixPW2403.

1.2 Support and catalyst preparation

$Ce_xZr_{1-x}O_2$ supports were synthesized with different Ce/(Ce+Zr) molar ratios (x = 0, 0.6, 0.8, and 1.0) via a citric acid sol-gel process using $Ce(NO_3)_3\cdot 6H2O$ and $Zr(NO_3)_4\cdot 4H_2O$ as precursors. First, the solutions of $Ce(NO_3)_3\cdot 6H_2O$ and $Zr(NO_3)_4\cdot 4H_2O$

in deionized water (total amount of Ce and Zr = 5 mmol,molar ratio of $Ce^{3+}/(Ce^{3+}+Zr^{4+})$ = x, 30 mL) were poured into a 100-mL beaker. A solution of citric acid in deionized water (0.5 mmol/mL, 10 mL) was then directly added with stirring. The mixture was stirred for a further 12 h at room temperature, and then the xerogel was obtained after the solvent was evaporated at 383K. The xerogel was then calcined at 823 K in air for 4 h. The support was heated at 2.3 K/min from room temperature to 573 K, held at 573 K for 30 min, then heated at a rate of 4 K/min from 573 to 823 K.

The supports $Ce_xZr_{1-x}O_2$ were stirred with a solution of ruthenium carbonyl in THF at room temperature for 12 h in a rotary evaporator. Then, the THF solvent was removed under reduced pressure at 303 K. The gray powder was calcined at 573 K for 3 h under hydrogen atmosphere, followed by cooling in hydrogen atmosphere to room temperature.

Measurements of catalytic activity

In ammonia synthesis reaction, 0.2 g catalyst samples were used for each experiment. A stainless steel reactor with an inner diameter of 6 mm was used. The catalyst was first heated in mixture of N_2:H_2 (1:3) to 673K at a heating rate of 5 K/min and then held at 673K for 2 h. Finally the temperature was adjusted to the required value for the ammonia synthesis reaction. The mixture of N_2:H_2 (1:3) with a flow rate of 60 mL/min was used as reactant. All the reactions were performed at presure 1 MPa. A Shimadzu GC-8A gas chromatograph equipped with a TCD was employed to measure the composition of product gas. Argon was used as the carrier gas.

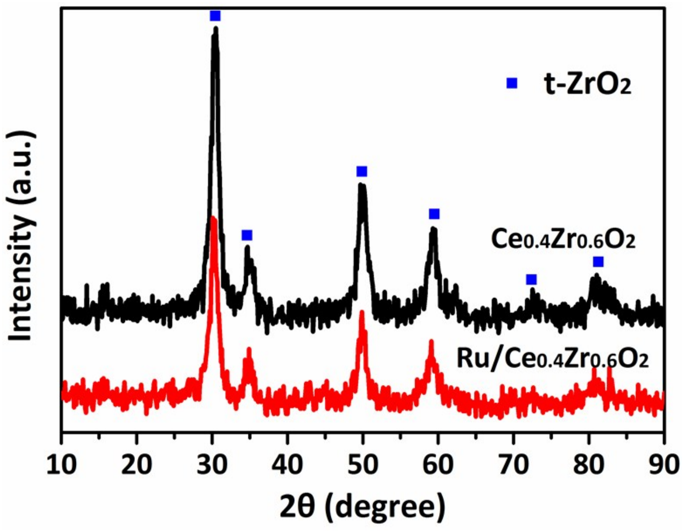

Figure S1. the XRD patterns of $Ce_{0.4}Zr_{0.6}O_2$ and $Ru/Ce_{0.4}Zr_{0.6}O_2$

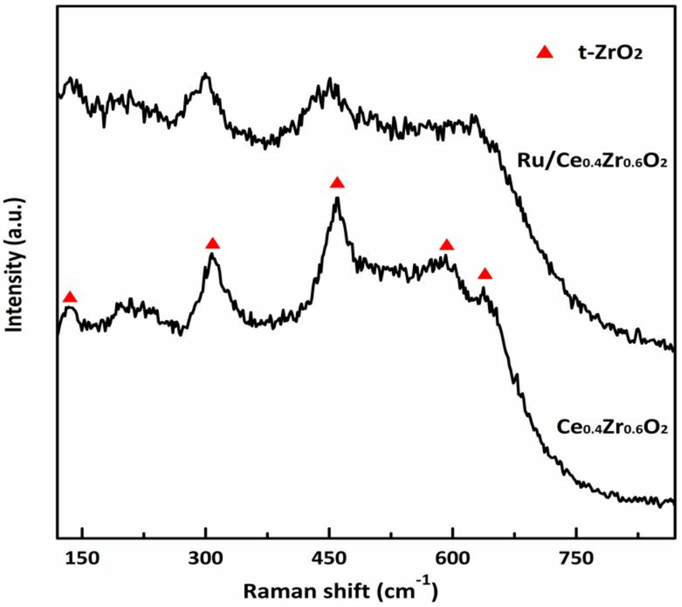

Figure S2. the Raman spectra of $Ce_{0.4}Zr_{0.6}O_2$ and $Ru/Ce_{0.4}Zr_{0.6}O_2$

Table S1. The microstrain of the $Ce_xZr_{1-x}O_2$ and Ru/$Ce_xZr_{1-x}O_2$

Sample	**Ru (wt%)**	**Microstrain (%)**		
		(1 1 1)	**(2 0 0)**	**(2 2 0)**
CeO_2		0.50	0.42	0.32
$Ce_{0.8}Zr_{0.2}O_2$		2.49	1.86	1.55
$Ce_{0.6}Zr_{0.4}O_2$		2.68	2.19	1.69
Ru/ CeO_2	3.84	0.46	0.39	0.3
Ru/$Ce_{0.8}Zr_{0.2}O_2$	3.92	2.25	1.62	1.52
Ru/$Ce_{0.6}Zr_{0.4}O_2$	3.87	2.52	1.94	1.60

The Results of microstrain (ε)obtained from the Equation[1] (1):

$$\frac{\beta\cos\theta}{\lambda}=\frac{1}{D}+4\varepsilon\frac{\sin\theta}{\lambda} \qquad (1)$$

$\boldsymbol{\beta}$**:** full width at half maximum (FWHM), $\boldsymbol{\theta}$: the Bragg angle

$\boldsymbol{D}$**:** size of coherently diffracting domains

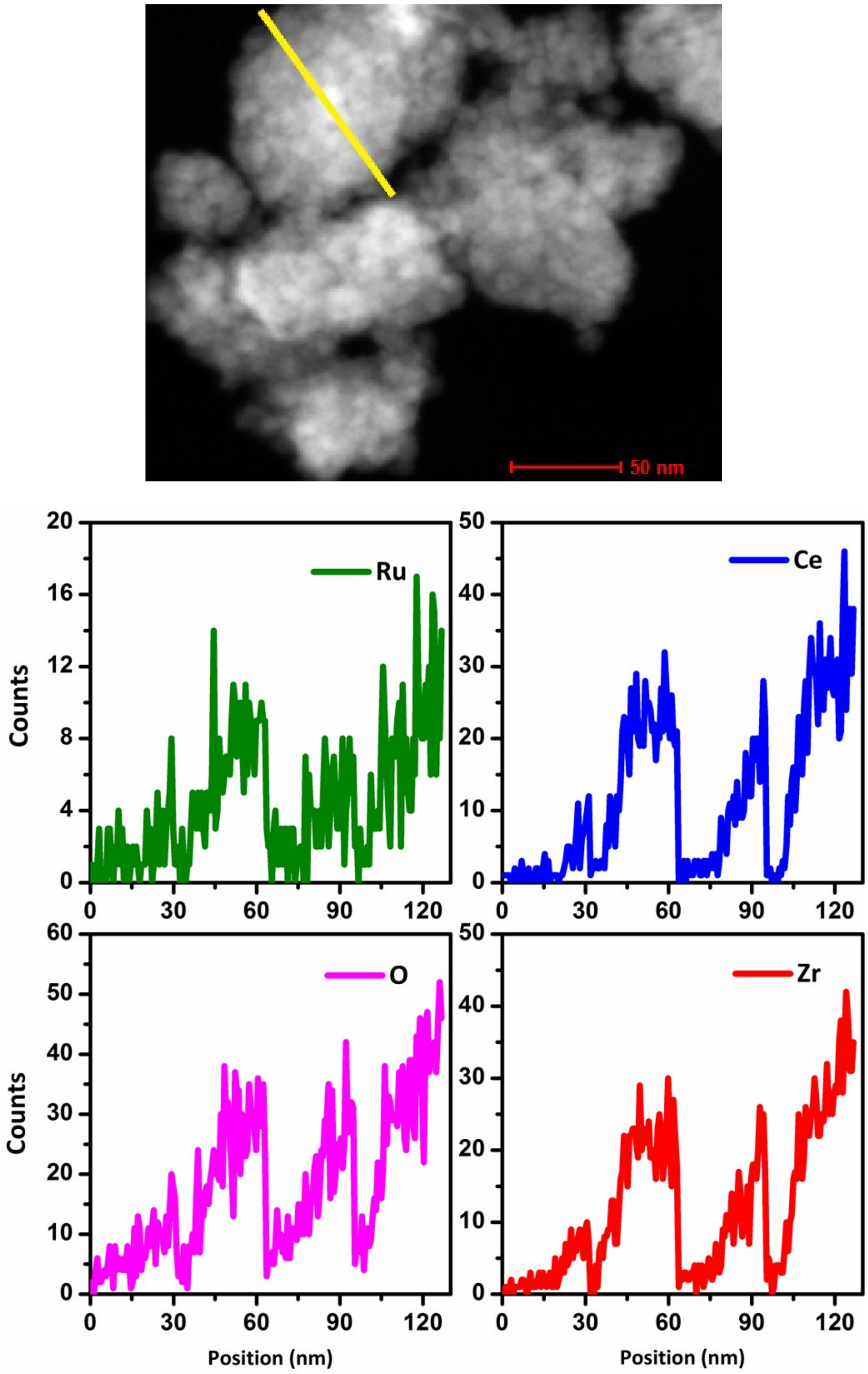

Figure S3. HAADF-STEM image of Ru/$Ce_{0.6}Zr_{0.4}O_2$ and distribution of components in randomly selected area in (a) by a line-scan EDS analysis.

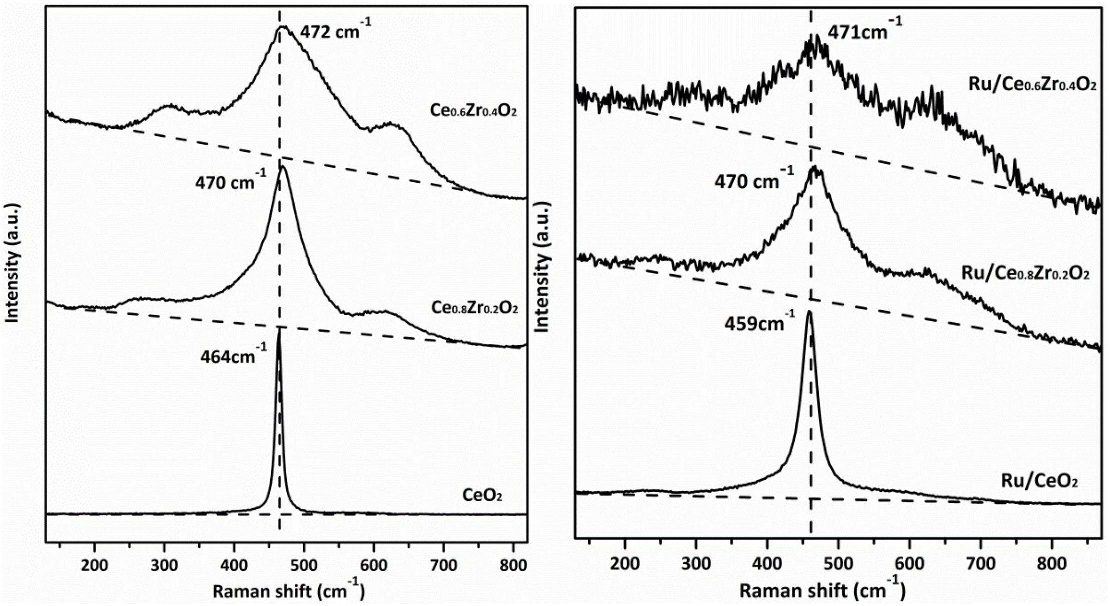

Figure S4. Raman spectra of the support $Ce_xZr_{1-x}O_2$ and the corresponding catalysts.

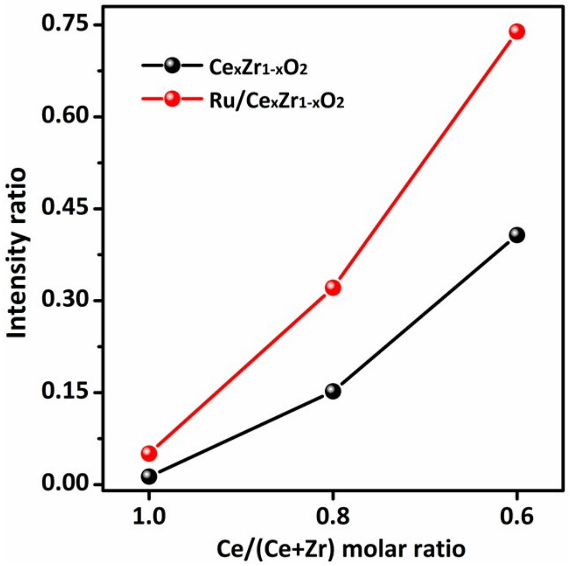

Figure S5. The I_D/I_{F2g} values of $Ce_xZr_{1-x}O_2$ and the corresponding catalysts

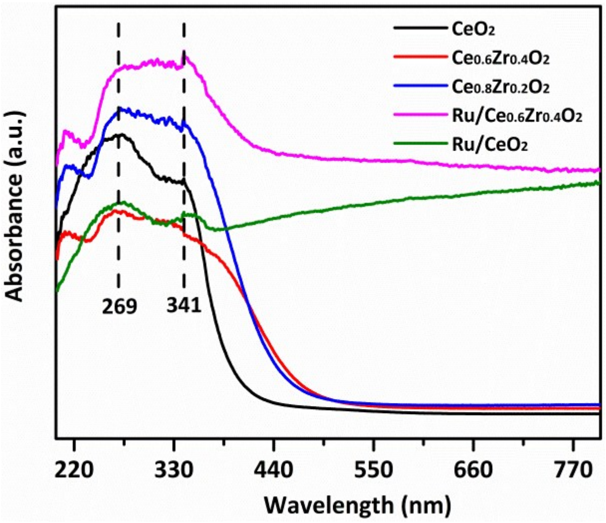

Figure S6. UV–vis diffuse reflectance spectra of the supports and the corresponding catalysts.

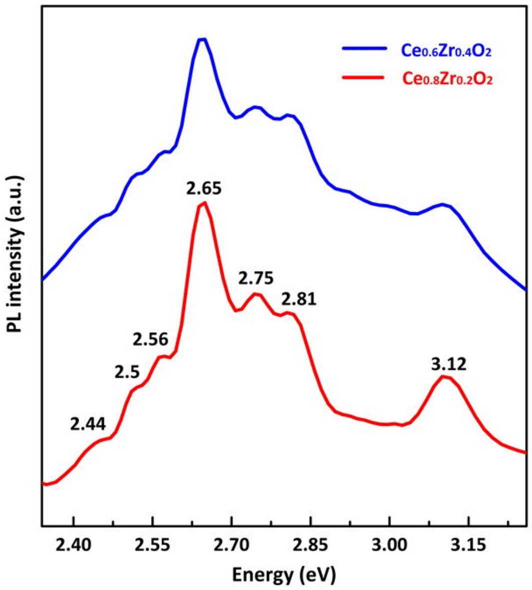

Figure S7. PL spectra of the supports and the corresponding catalysts.

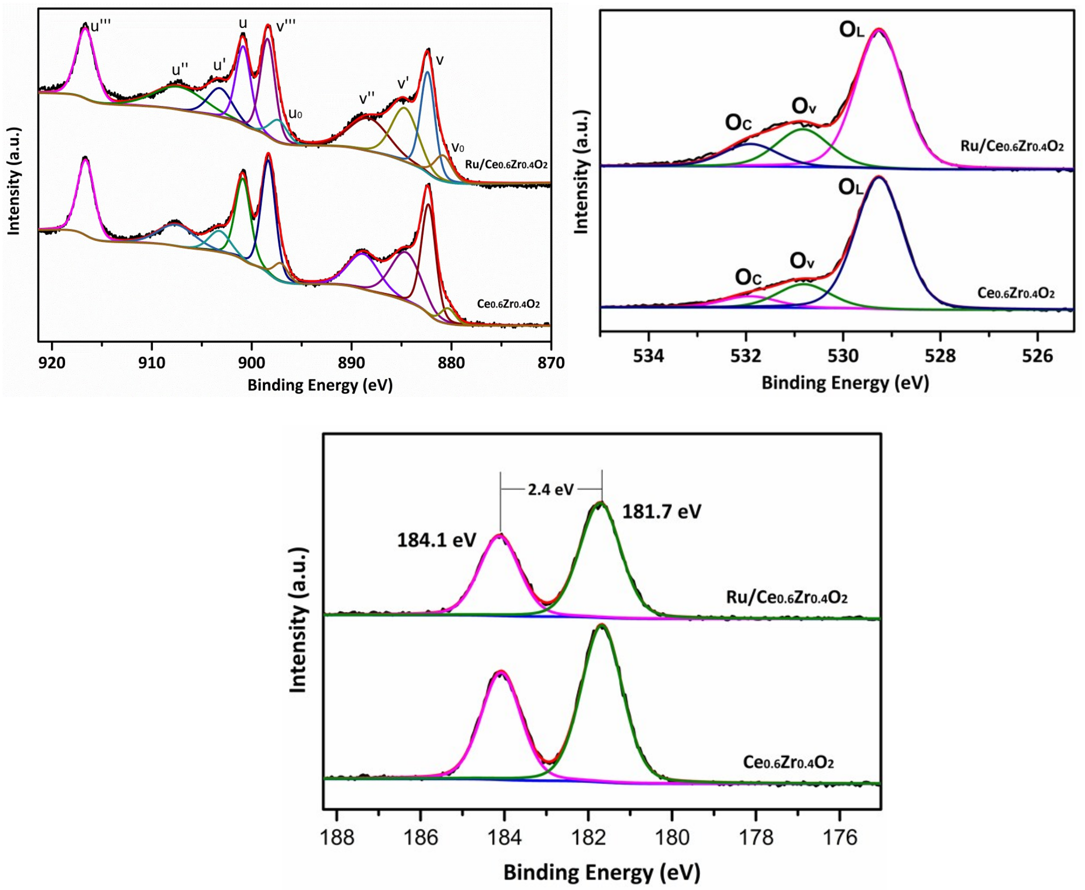

Figure S8. XPS spectra of $Ce_{0.6}Zr_{0.4}O_2$ and Ru/$Ce_{0.6}Zr_{0.4}O_2$.

The O 1s could be fitted with three peaks[2] at 529.3 eV (O_L), 530.8 eV (O_V) and 531.9 eV (O_c). The O_L component of the O 1s peak is attributed to lattice oxygen bound to metal cations, the Ov component at 530.8 eV is associated with O^{2-} in oxygen-deficient regions. And the Oc component is attributed to chemisorbed and dissociated oxygen species or OH. As could be observed in the Figure S8, the binding energies of Zr $3d_{5/2}$ and $3d_{3/2}$ were around 182.5 eV and 184.9 eV, which were in good agreement with previous reports[3] and corresponded to Zr in 4+ oxidation state.

Table S2. the relative amount of different components.

Sample	Ce^{4+}	Ce^{3+}	O_C	O_V	O_L	Ru^0	Ru_n^+	Ru_n^-
$Ce_{0.6}Zr_{0.4}O_2$	76.0%	24.0%	7.6%	15.4%	77.0%	-	-	-
$Ru/Ce_{0.6}Zr_{0.4}O_2$	70.2%	29.8%	12.5%	20.4%	67.1%	45.6%	34.1%	20.3%

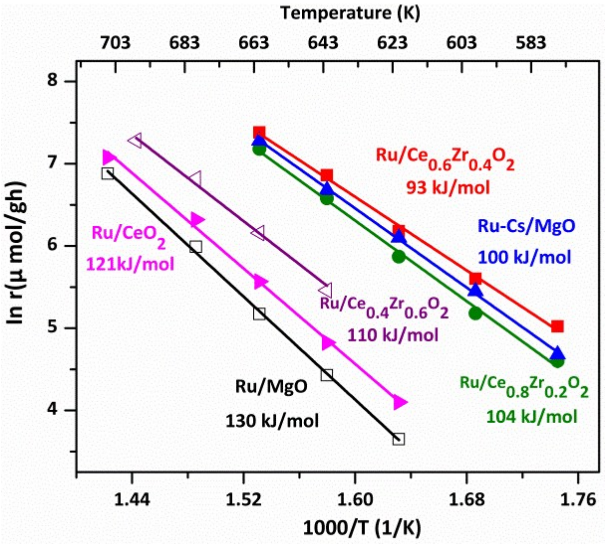

Figure S9. Apparent activation energies for ammonia synthesis over various 4 wt% Ru-loaded catalysts. Reaction conditions: catalyst, 0.2 g; H_2/N_2=3 with a flow rate of 60 ml/min; pressure, 1 MPa.

References

1. Y. Luo, A. Habrioux, L. Calvillo, G. Granozzi and N. Alonso-Vante, *ChemCatChem*, 2015, **7**, 1573-1582.

2. J. C. Dupin, D. Gonbeau, P. Vinatier and A. Levasseur, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1319-1324.

3. B. M. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Loridant and J. C. Volta, *J. Phys. Chem. B*, 2003, **107**, 11475-11484.