

Supporting Information

Acid-Promoter-Free Ethylene Methoxycarbonylation over Ru-Clusters/Ceria: the Catalysis of Interfacial Lewis Acid-Base Pair

Jinghua An,^{†,||,‡} Yehong Wang,^{†,‡} Jianmin Lu,[†] Jian Zhang,[†] Zhixin Zhang,[†] Shutao Xu,[†] Xiaoyan Liu,[†] Tao Zhang,[†] Martin Gocyla,[§] Marc Heggen,[§] Rafal E. Dunin-Borkowski,[§] Paolo Fornasiero,[¶]
and Feng Wang^{†*}

[†] State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

^{||} University of Chinese Academy of Sciences, Beijing 100049, China

[§] Ernst Ruska Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Juelich GmbH, Juelich 52425, Germany

[¶] Department of Chemical and Pharmaceutical Sciences, INSTM, Center of Excellence for Nanostructured Materials (CENMAT), University of Trieste, Via L. Giorgieri 1, Trieste 34127, Italy

[‡] These authors contributed equally

* Correspondence author: F. Wang (*): wangfeng@dicp.ac.cn

General Characterizations. X-ray powder diffraction (XRD) analyses were conducted on a Rigaku D/Max 3400 powder diffraction system with CuK α radiation ($\lambda = 0.1542$ nm). The 2θ scans were taken from 10° to 80° with a step size of 0.04° . Phase purity and crystal structures were confirmed by powder X-ray diffraction profiles using the EXPGUI, GSAS package. Hydrogen temperature-programmed reduction (H $_2$ -TPR) was performed by using a Micromeritics AutoChem II 2920 device with a thermal conductivity detector (TCD). Before measurement, the sample (200 mg) was placed in a quartz U-tube reactor and was purged with flowing Ar gas ($50 \text{ mL}\cdot\text{min}^{-1}$) at 200°C for 30 min. For TPR measurement, the sample was reduced in a stream of H $_2$ /Ar (1:9, v/v; the total flow rate is $50 \text{ mL}\cdot\text{min}^{-1}$) with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ up to 600°C . Temperature-programmed desorption (TPD) of ethylene was conducted on a GSD320 Thermostar instrument. In a typical TPD experiment, 200 mg of dried sample material was placed in a quartz tube and reduced in flowing H $_2$ ($20 \text{ mL}\cdot\text{min}^{-1}$) at 350°C for 30 min. Then it was purged with flowing Ar gas ($20 \text{ mL}\cdot\text{min}^{-1}$) for 30 min after cooling down to room temperature. Subsequently, the sample was exposed to ethylene gas for three times through a 5.0 mL injection syringe. After ethylene adsorption, the sample was purged with flowing Ar gas ($20 \text{ mL}\cdot\text{min}^{-1}$). Finally, the TPD was carried out by heating the sample from room temperature to 300°C with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in flowing Ar gas ($20 \text{ mL}\cdot\text{min}^{-1}$). Raman spectra were recorded on a micro-Raman spectrometer (Renishaw) equipped with a CCD detector using a He/Ne laser with a wavelength of 532 nm.

Table S1. Detail list of the chemicals and reagents

Chemicals	Purity	Corporation
RuCl ₃	36.0-38.0% metal basis	the Non Ferrous Metal Institute of Shenyang
Methanol	AR	Sinooharm Chemical Reagent Co., Ltd CINOR chemical Aladdin Industrial Corporation
NiO	AR	
ZrO ₂	AR	
Ce(NO ₃) ₃ ·6H ₂ O	AR	
TiO ₂ (anatase)	99.8% metal basis	
WO ₃	99.9% metal basis	
MoO ₃	99.9% metal basis	
SiO ₂	99.5% metal basis	
MgO	>98%	Beijing fine chemicals Co., Ltd
Na ₃ PO ₄ ·6H ₂ O	AR	Tianjin Kemiou Chemical Reagent Co., Ltd
NaOH	AR	
NH ₄ OH	AR	
Ethylene	99.9%	Dalian Guangming Special Gas Products Co., Ltd
CO,	99.9999%	Dalian Institute of Chemical Physics
Millipore-purified water	18 MΩ·cm	

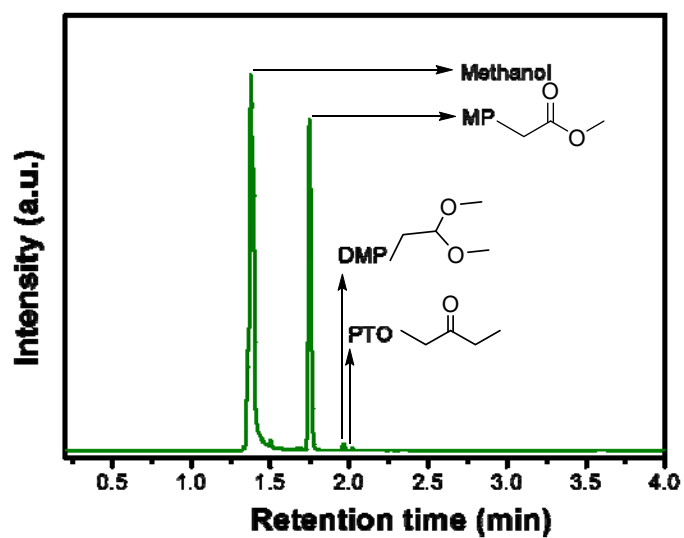


Fig. S1. GC-MS signal of the product after reaction. Reaction conditions: Ru/ceria (0.15 g, 0.03 mmol as Ru), ethylene (7.5 mmol), 1.0 MPa CO, methanol (4 mL), 165 °C, 6 h. MP: methyl propionate, PTO: pentan-3-one, DMP: 1, 1-dimethoxypropane.

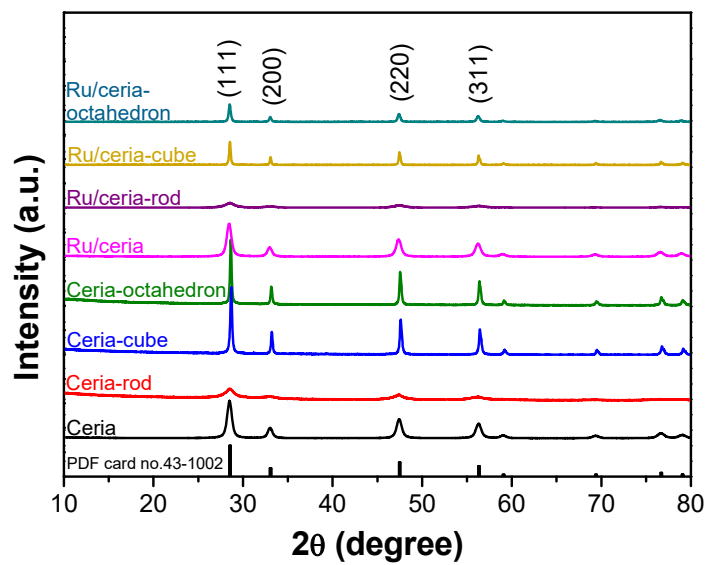


Fig. S2. Powder XRD patterns of ceria with various shapes and ceria-supported Ru catalysts. The loading amount of Ru is 2 wt%.

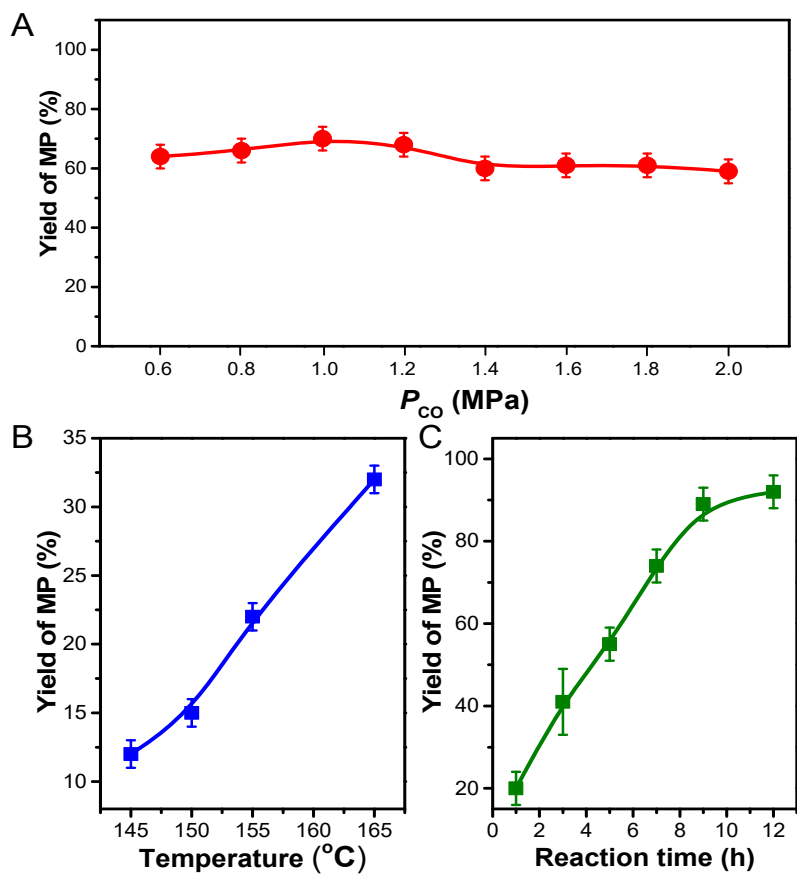


Fig. S3. (A) Effect of CO partial pressure on MP yield in EMC reaction over Ru/ceria. Reaction conditions: Ru/ceria (0.15 g, 0.03 mmol as Ru), ethylene (7.5 mmol), methanol (4 mL), 165 °C, 8 h, P_{CO} is the partial pressure of CO. (B) The effect of reaction temperature. Reaction conditions: Ru/ceria (0.15 g, 0.03 mmol as Ru), ethylene (7.5 mmol), CO (1.4 MPa), methanol (4 mL), 2 h. (C) Time-on-stream profile at 165 °C. Reaction conditions: Ru/ceria (0.15 g, 0.03 mmol as Ru), ethylene (4.0 mmol), CO (0.5 MPa), methanol (4 mL).

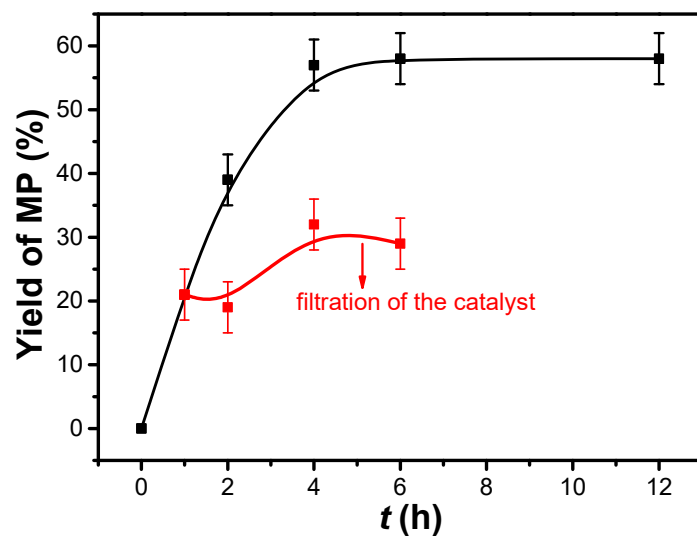


Fig. S4. Filtration reaction. Reaction conditions: Ru/ceria (0.15 g, 0.03 mmol as Ru), CO (7.5 mmol), ethylene (0.6 MPa), methanol (4 mL), 165 °C. The yield of MP is calculated based on CO.

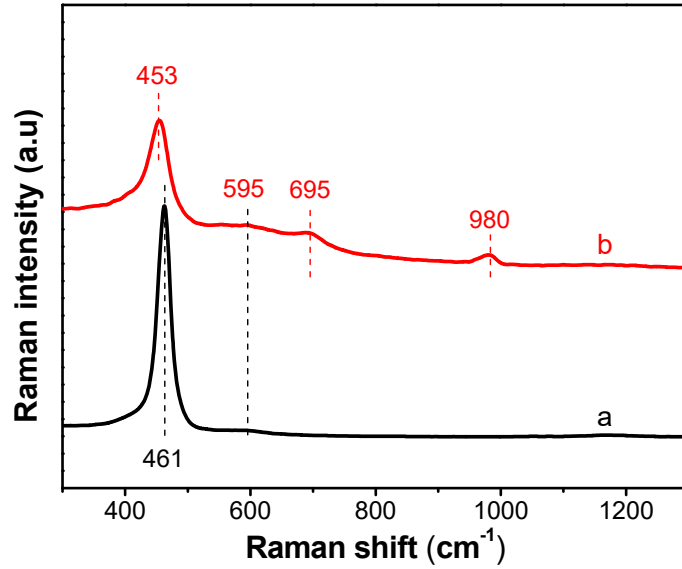


Fig. S5. Raman spectra of ceria (a) and Ru-clusters/ceria (b).

In the Raman spectra of pristine ceria, two peaks are observed. The sharp peak at 461 cm⁻¹ is assigned to the F_{2g} vibrational mode of the ceria fluorite-type structure.¹ Another peak at 595 cm⁻¹ is assigned to the defect induced (D) mode of ceria.^{1b} When 2wt % of Ru was impregnated on ceria, those Raman peaks still remained but with the peak assigned to F_{2g} red-shifted and broadened compared with pristine ceria. This may be due to the presence of V_o derived from the introduction of Ru into the ceria.² In addition to those Raman peaks observed on pristine ceria, two peaks at 695 cm⁻¹ and 980 cm⁻¹ are also observed on Ru-clusters/ceria, which are assigned to the existence of Ru-O-Ce or Ru=O stretching.²⁻³

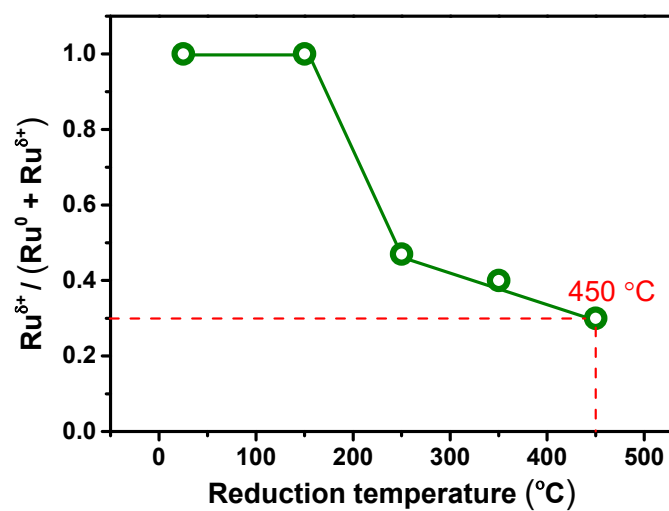


Fig. S6. $Ru^{\delta+} / (Ru^0 + Ru^{\delta+})$ calculated with using the XPS data in Fig. 2. $Ru^{\delta+} / (Ru^0 + Ru^{\delta+})$ is calculated according to the following Eq. S1.

$$\frac{Ru^{\delta+}}{Ru^{\delta+} + Ru^0} = \frac{\frac{Ru^{\delta+}}{Ru^0}}{1 + \frac{Ru^{\delta+}}{Ru^0}} \quad \text{Eq. S1.}$$

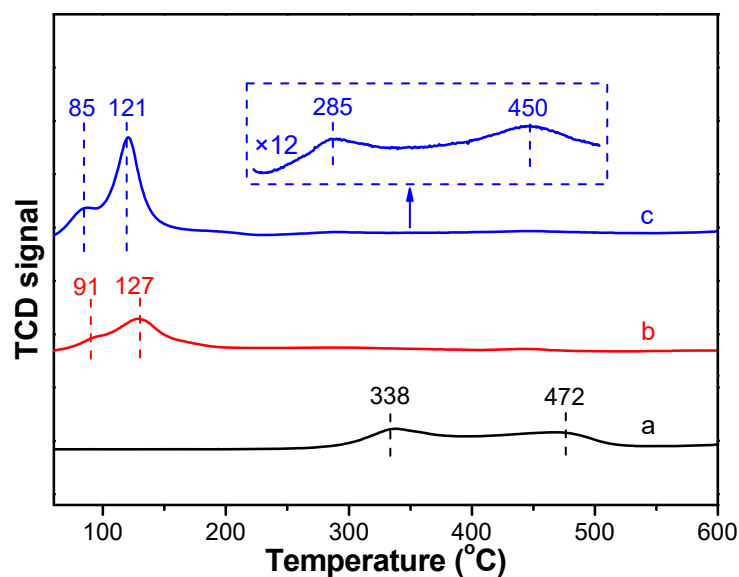


Fig. S7. H₂-TPR of ceria (a), RuO₂/SiO₂ (b) and RuO₂/ceria (c).

H₂-TPR of RuO₂/ceria is conducted and shown in Fig. S7. The pristine ceria and inactive catalyst RuO₂/SiO₂ are also investigated for compared. For pristine ceria, two peaks at 338 °C and 472 °C are assigned to the removal of the surface oxygen.^{1a, 4} For Ru catalyst, the oxidized RuO₂ has been reduced even at < 150 °C for either RuO₂/ceria or RuO₂/SiO₂. On RuO₂/ceria, the peaks at 285 °C and 450 °C are probably due to the removal of the surface oxygen of the ceria support, which shift to lower temperature compared with pristine ceria, indicating the promotion of Ru addition for the ceria reduction.^{4a, 5} Further, the H₂ consumption of RuO₂/ceria (11.7 mmol per gram supported RuO₂, Ru 2.0 wt% relative to ceria) is lower than that of the stoichiometrically-demanded H₂ consumption considering a full reduction of RuO₂ to Ru⁰ (15.1 mmol per gram RuO₂), indicating the presence of partially oxidized Ru species.

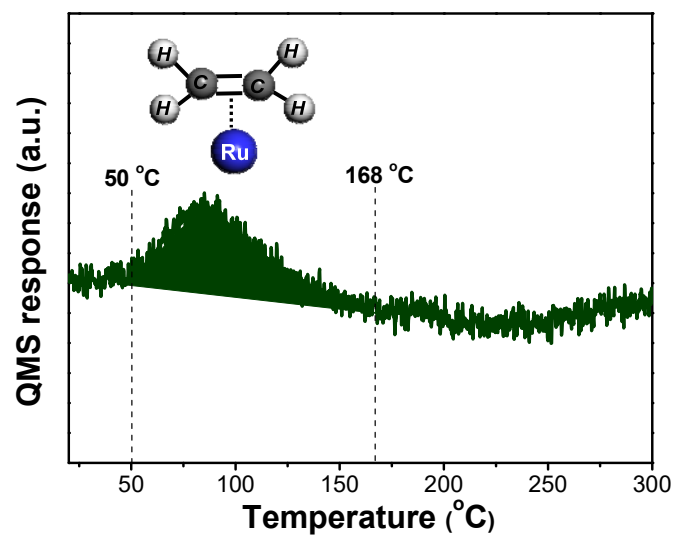


Fig. S8. Ethylene-TPD profiles of Ru-clusters/ceria.

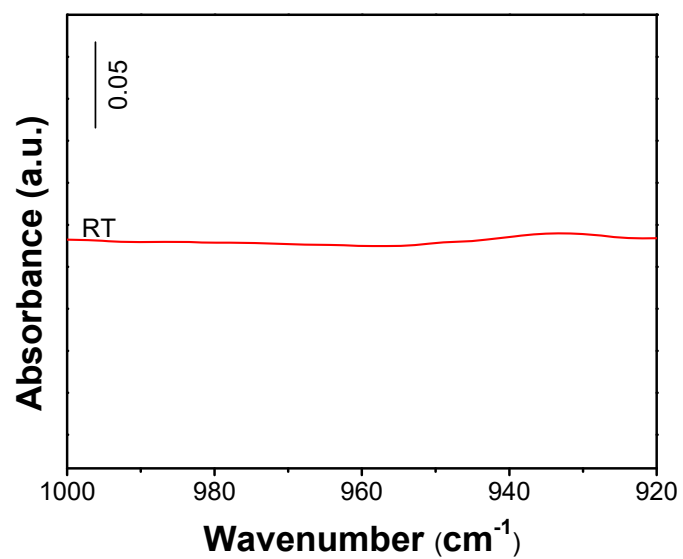


Fig. S9. In situ IR spectra of ethylene adsorption on pristine ceria recorded after desorption at room temperature for 30 min.

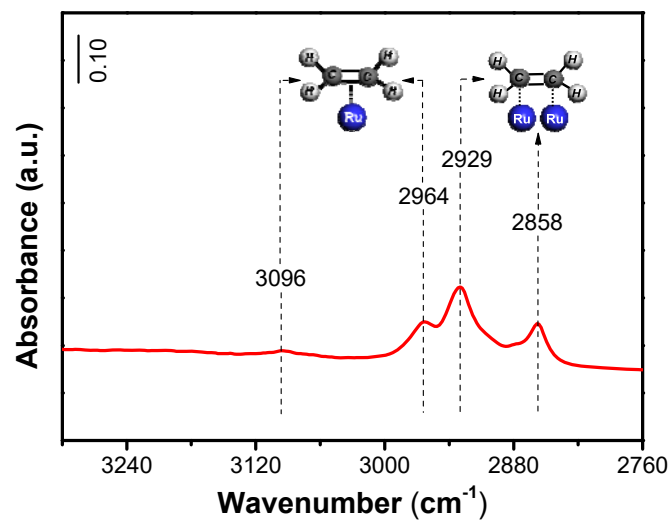


Fig. S10. In situ IR of ethylene adsorption on Ru/silica in the regions of 3300 cm⁻¹–2760 cm⁻¹. The spectra are collected after ethylene desorption at room temperature.

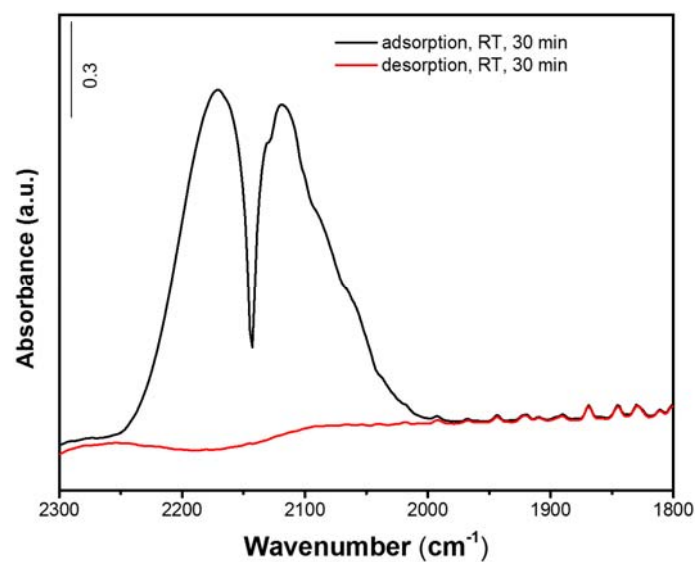


Fig. S11. In situ IR spectra of CO adsorption on pristine ceria recorded after desorption at room temperature for 30 min.

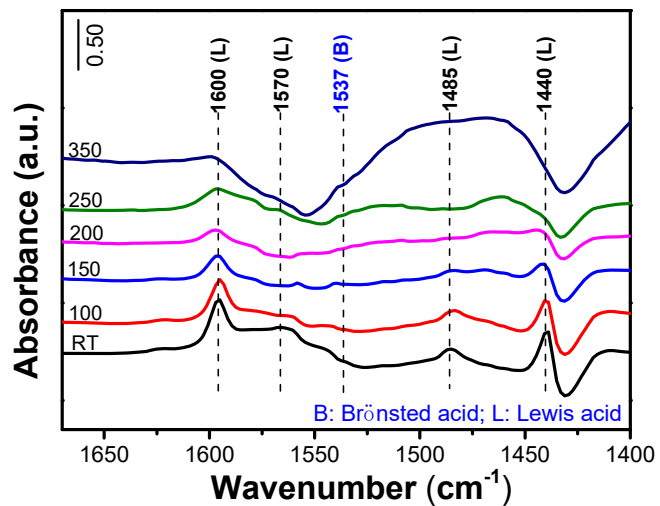


Fig. S12. In situ pyridine-IR after methanol adsorption on ceria.

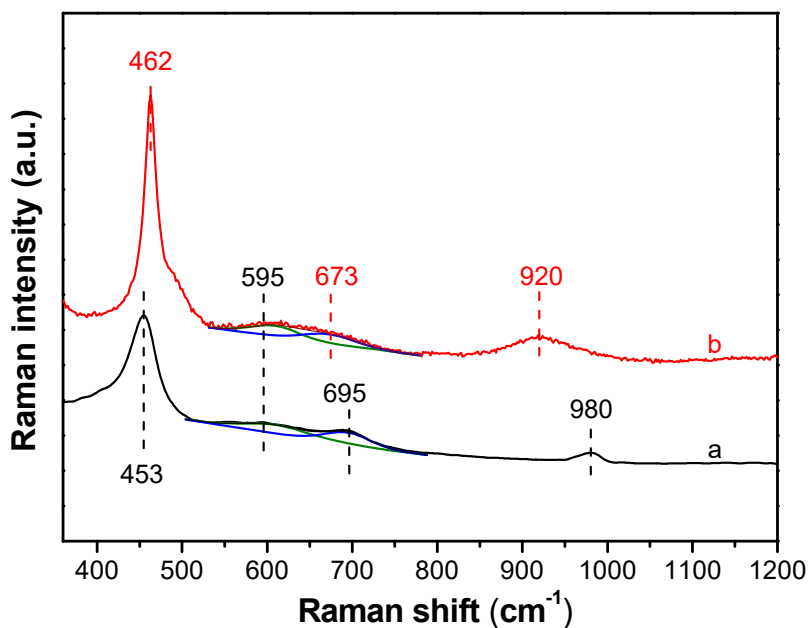
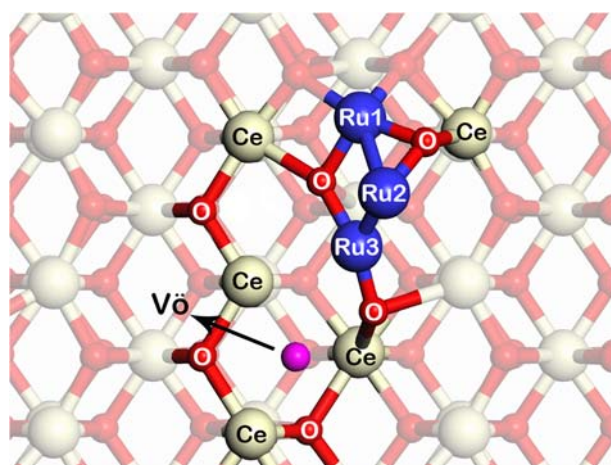


Fig S13. Raman spectra of fresh Ru-clusters/ceria (a) and the catalyst used for three times (b).

The ratio of the integrated peak areas around the bands at 595 and 460 cm^{-1} (A_{595}/A_{460}) can be used to quantify the relative surface concentration of oxygen vacancies.⁶ The concentration of oxygen vacancies in Ru-clusters/ceria catalyst decreased after used for three times (0.1654 for fresh catalyst and 0.1083 for the deactivated catalyst). In addition, for the deactivated catalyst, the peaks assigned to Ru-O-Ce red-shifted compared with fresh Ru-clusters/ceria, indicating the blocking of interface of by organic species.⁷



Ru atom	Bader charge
Ru1	0.30
Ru2	1.10
Ru3	0.38

Fig. S14. Bader charge of the three Ru atoms in the model.

Reference:

1. (a) Wang, F.; Li, C.; Zhang, X.; Wei, M.; Evans, D. G.; Duan, X. *J. Catal.* **2015**, *329*, 177-186. (b) Huang, H.; Dai, Q.; Wang, X. *Appl. Catal. B* **2014**, *158-159*, 96-105.
2. Tamura, M.; Satsuma, A.; Shimizu, K.-i. *Catal. Sci. Technol.* **2013**, *3*, 1386-1393.
3. Lin, W.; Herzing, A. A.; Kiely, C. J.; Wachs, I. E. *J. Phys. Chem. C* **2008**, *112*, 5942-5951.
4. (a) Zhao, G.; Yang, F.; Chen, Z.; Liu, Q.; Ji, Y.; Zhang, Y.; Niu, Z.; Mao, J.; Bao, X.; Hu, P.; Li, Y. *Nat. Commun.* **2017**, *8*, 14039. (b) Aneggi, E.; Wiater, D.; De Leitenburg, C.; Llorca, J.; Trovarelli, A. *ACS Catal.* **2014**, *4*, 172-181. (c) Shen, Q.; Wu, M.; Wang, H.; He, C.; Hao, Z.; Wei, W.; Sun, Y. *Catal. Sci. Technol.* **2015**, *5*, 1941-1952.
5. Acerbi, N.; Tsang, S. C.; Jones, G.; Golunski, S.; Collier, P. *Angew. Chem. Int. Ed.* **2013**, *52*, 7737-7741.
6. (a) Wang, R.; Wang, Y.; Ren, M.; Sun, G.; Gao, D.; Chin Chong, Y. R.; Li, X.; Chen, G. *Int. J. Hydrog. Energy* **2017**, *42*, 6757-6764. (b) Wang, Y.; Wang, F.; Song, Q.; Xin, Q.; Xu, S.; Xu, J. *J. Am. Chem. Soc.* **2013**, *135*, 1506-1515.
7. (a) Mar, S. Y.; Chen, C. S.; Huang, Y. S.; Tiong, K. K. *Appl. Surf. Sci.* **1995**, *90*, 497-504. (b) Wang, F.; He, S.; Chen, H.; Wang, B.; Zheng, L.; Wei, M.; Evans, D. G.; Duan, X. *J. Am. Chem. Soc.* **2016**, *138*, 6298-6305. (c) Hardcastle, F. D.; Wachs, I. E. *J. Mol. Catal.* **1988**, *46*, 173-186. (d) Xu, C. Y.; Zhang, P. X.; Yan, L. *J. Raman Spectrosc.* **2001**, *32*, 862-865.