View Article Online View Journal

INORGANIC CHEMISTRY

FRONTIERS

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: X. Wang, X. Fu, W. Yu, C. Ma, C. Jia and R. Si, *Inorg. Chem. Front.*, 2017, DOI: 10.1039/C7QI00470B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.





rsc.li/frontiers-inorganic



INORGANIC CHEMISTRY FRONTIERS

RESEARCH ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Synthesis of Ceria Supported Iron-Ruthenium Oxide Catalyst and Its Structural Transformation from Subnanometer Clusters to Single Atoms during Fischer-Tropsch Synthesis Reaction

Xu Wang,^{a,b} Xin-Pu Fu,^c Wen-Zhu Yu,^c Chao Ma,^{*d} Chun-Jiang Jia,^{*c} Rui Si,^{*a}

Formation of supported metal/metal oxide single-atom catalysts (SAC), as well as their structural evolutions during catalytic reactions, have attracted much research interest in the fields of both inorganic chemistry and catalysis recently. In this work, we report the synthesis of iron (ca. 10 at.%) oxide catalysts with the doping of small-amount (0.5–0.6 at.%) ruthenium oxide, which have been deposited onto the surface of ceria nanorods by an optimized deposition-precipitation (DP) route. Multiple characterizations including X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and nitrogen adsorption/desorption confirmed the identically structural and textural properties of ceria support after the DP step. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with electron energy loss spectroscopy (EELS) observed the formation of subnanometer iron species in the fresh samples. Furthermore, the X-ray absorption fine structure (XAFS) technique by the aids of related data-analysis verified the generation of noncrystalline iron oxide clusters composed by Fe3+ ions dominantly. Here, the addition of secondary metal (ruthenium) greatly promoted the dispersion of Fe over the ceria nanorods. After the catalytic reaction of Fischer-Tropsch synthesis (FTS), the transformation from subnanometer iron oxide species to ionic Fe $^{\delta_{1}}$ single atoms has been revealed and confirmed by the corresponding profile fits on the extended X-ray absorption fine structure (EXAFS) spectra. In contrast to the normal coarsening process, the FTS conditions (up to 300 °C, 2 MPa, $CO/H_2 = 1/1$) did drive the creation of such iron single atoms solely coordinated by oxygen ions.

Introduction

Published on 12 October 2017. Downloaded by University of Windsor on 12/10/2017 11:54:05.

Recently, supported metal/metal oxide single-atom catalysts (SAC) have attracted much research interest because of their unique electronic and/or local coordination structure, as well as their potential applications in multiple catalytic processes, which is probably due to 100% exposed active sites and/or new reaction pathways.¹⁻²³ So both developing the fabrication of SAC and deepening the understanding of formation mechanism on such single-atom species, are of significant importance in heterogeneous catalysis. Various wet chemical approaches with optimized synthetic parameters have been realized to controllably prepare diverse SAC such as Pt^{1,4,6,7,9-11,14,16}, Au^{3,8,15,20}, Pd¹³, Rh^{17,18}, Co¹⁹, etc. For instance, Qiao et al. synthesized 0.17wt.% Pt₁/FeO_x catalyst via a coprecipitation method with optimized precipitating agent and final pH value.¹ However, the formation mechanism of these SAC

remained unknown or controversial, since only a few examples have been investigated thoroughly.

On the other hand, due to the complexity in structure of metal/metal oxide single atoms, as well as the relatively much lower signals compared to common nanoparticles, advanced characterization techniques are required to precisely detect the electronic and local coordination structures of these single atoms. Among them, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)^{1-6,8-20} and X-ray absorption fine structure (XAFS)^{1-3,6-10,12-14,16-20} play crucial roles for determining SAC at the atomic scale, either giving microscopic direct observations or providing macroscopic averaged electronic and local coordination structural information. For example, Guo et al. identified three different gold species (single atoms, subnanometer clusters and nanoparticles) on the surface of ceria nanorods by using both HAADF-STEM and XAFS measurements.²⁰

Supported iron (Fe) catalysts have been widely applied, particularly for the Fischer-Tropsch synthesis (FTS) reaction.²¹⁻²⁶ The previous assignments on the important active species of iron were determined to be either metallic Fe particles^{22,26} or iron carbide (Fe_xC_y) phases such as χ -Fe₅C₂²⁴ and ε -Fe₂C^{23,24}. However, till now, the investigations on the effect of ultra-fine iron oxide species, which may also be stable and catalytically active for FTS reaction, are still very limited. Meanwhile, nanosized cerium oxide (CeO₂) has been used as a reducible oxide support to deposit different metals

^{a.} Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China. sirui@sinap.ac.cn.

^{b.} University of Chinese Academy of Science, Beijing 10049, China.

^{c.} Key Laboratory for Colloid and Interface Chemistry, Key Laboratory of Special Aggregated Materials, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China. jiacj@sdu.edu.cn

^d Center for High Resolution Electron Microscopy, College of Materials Science and Engineering, Hunan University, Changsha 410082, China. cma@hnu.edu.cn. † Electronic supplementary information (ESI) available: comparison of the

activities, EXAFS result, XANES linear combination fitting result and XPS result. See DOI: 10.1039/x0xx00000x

Journal Name

ARTICLE

or metal oxides, because of its easily reversible transformation between Ce³⁺ and Ce⁴⁺.^{27, 28} Previously, our group have prepared finely dispersed iron catalysts on the surface of ceria nanorods via a coprecipitation approach, and demonstrated that the Fe-O-Fe coordination structure in the form of subnanometer iron oxide clusters as active species for FTS.²⁹

Here we report the creation of single atoms in ceria-supported ironruthenium oxide catalysts with the help of catalytic process of FTS. The harsh reaction conditions (up to 300 °C, 2 MPa, CO/H₂ = 1/1), normally coarsened small-size clusters into large-size particles, did re-dispersed the subnanometer iron oxide clusters (Fe_xO_y) to generate iron single atoms solely coordinated by oxygen ions. In addition, the introduction of low-concentration (0.5–0.6 at.%) Ru effectively accelerated the transformation from the Fe_xO_y clusters to Fe SAC. In this work, the structural evolutions on ionic iron single atoms and subnanometer iron oxide clusters have been accurately monitored by not only the HAADF-STEM technique but also the XAFS characterization with the corresponding data-analysis.

Results and discussion

Published on 12 October 2017. Downloaded by University of Windsor on 12/10/2017 11:54:05.

In our work, the ceria nanorods were prepared via a hydrothermal synthesis. The bimetallic iron-ruthenium oxides sample (FeRu Ce), as well as the corresponding single metal (Fe or Ru) oxide counterpart (Fe Ce or Ru Ce), was anchored onto the surface of ceria nanorods via a deposition-precipitation (DP) approach. Table 1 shows that the metal concentrations of Fe are ~10 at.%, in good agreement with the designed value. Furthermore, the concentrations of more expensive ruthenium have been determined as 0.5-0.6 at.%, which is much lower than that of cheaper iron. Table 1 also shows that the BET specific surface areas of as-calcined (air, 400 °C) samples are 92-97 m²g⁻¹, well consistent with those of doped ceria nanorods (80-97 m²g⁻¹)³⁰. It indicates that the doping of metal (Fe and/or Ru) ions did not modify the textural properties of the CeO₂ support. The X-ray diffraction (XRD) patterns in Figure 1 verify a pure fcc Fluorite-type CeO₂ (JCPDS card no: 34-394) crystal structure for all the ceria-supported iron-ruthenium catalysts after DP, and no phases of Fe/Fe₃O₄/Fe₂O₃ or Ru/RuO₂ can be identified. The calculated lattice constants (a) of CeO_2 is 5.40–5.41 Å (see Table 1), very close to that of pure ceria nanorods (~ 5.41 Å) in the previous report.³¹

Table 1. Metal concentrations of Fe and Ru, BET specific surface areas (S_{BET}), lattice constants (*a*) and averaged particle size (*D*) of CeO₂ in ceria-supported iron-ruthenium oxide samples.

Sample	Fe (at.%) ^a	Ru (at.%) ^a	S _{BET} (m ² g ⁻¹) ^b	а (Å) ^с	D (nm) ^d
FeRu_Ce	9.9	0.6	92	5.399	8.9±1.5
				5.405 ^e	8.6 ± 1.4^{e}
Fo Co	07		06	5.401	8.4±1.7
re_Ce	9.7		90	5.410^{e}	8.6±1.6 ^e
Ru_Ce		0.5	07	5.407	8.5±1.7
			97	5.418 ^e	8.8+1.7 ^e

^{*a*} Determined by ICP-AES; ^{*b*} Calculated from nitrogen adsorptiondesorption results; ^{*c*} Calculated from XRD patterns; ^{*d*} Determined from the HRTEM images with over 100 particles; ^{*e*} For used samples. The high-resolution transmission electron microscope (HBTEM) images in Figures 2a-2c exhibit that all of the fresh samples, either single metal oxide (Fe_Ce and Ru_Ce) or bimetallic oxides (FeRu Ce), are composed by rod-like nanocrystals with an averaged width (D) varied from 8.4 to 8.9 nm (see Table 1), in good agreement with that of pure ceria nanorods (8.6 nm)³¹. The HRTEM images also identify that these nanorods have been highly crystallized by determining that the *d*-spacing values match the interplanar distances for CeO₂ (111) planes. Meanwhile, a large number of surface voids can be observed for ceria nanorods in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Figures 2d-2f), possibly caused by the dehydration process during the hydrothermal growth of CeO2.²⁰ Nevertheless, no iron (Fe/Fe3O4/Fe2O3) or ruthenium (Ru/RuO₂) crystallized particles were observed in HRTEM, which is consistent with the XRD results.







Figure 2. HRTEM (a-c) and HAADF-STEM (d-f) images of fresh ceriasupported iron-ruthenium oxide samples: (a,d) Fe_Ce; (b,e) Ru_Ce; (e,f) FeRu_Ce.

The aberration-corrected HAADF-STEM combining with electron energy-loss spectroscopy (EELS) measurements were performed to obtain the spatial distribution of Fe in the fresh catalysts. From Figure 3a, we can see that the Fe-rich microdomains up to ca. 1 nm display for Fe_Ce, which can be attributed to subnanometer iron oxide clusters supported on the surface of ceria.²⁹ For bimetallic iron-ruthenium oxides sample (FeRu_Ce), the distribution of Fe seems more uniform (Figure 3b), possibly due to the smaller size of iron oxide species with the aids of introduced ruthenium. Since the distinctly lower z value of Fe (z = 26) than that of Ce (z = 58), as well as the limited amount of iron (~ 10 at.%) and ruthenium (~ 0.5 at.%) in the measured samples, the HAADF-STEM/EELS skills can only reach a low spatial resolution of ca. 2-3 Å in this work. So, the iron single atoms were possibly missing from the microscopic view. Thus, other characterization techniques are required to obtain the specific structure of Fe.



Figure 3. Aberration-corrected HAADF-STEM/EELS results for fresh ceria-supported iron-ruthenium oxide samples: (a) Fe_Ce; (b) FeRu_Ce.

X-ray absorption fine structure (XAFS) technique, which is elementally sensitive and very powerful to determine both electronic structure and local coordination structure (distance *R*, coordination number *CN*, etc.) of investigated metal by the aids of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) parts, respectively. From the XANES profiles in Figure 4a, with the help of different references (Fe foil for Fe⁰, Fe₃O₄ for Fe²⁺/Fe³⁺ and Fe₂O₃ for Fe³⁺), we have run liner combination fits³² on the fresh catalysts (Figures S1a and S1b). Table 2 shows that fully oxidized Fe³⁺ ions, without any fraction of reduced components of Fe²⁺/Fe⁰, can be determined for both single metal (Fe) oxide and bimetallic (Fe, Ru) oxides samples. Besides, the averaged oxidation states of ruthenium in **Ru_Ce** and **FeRu_Ce** are also close to that of ionic Ru³⁺ (Figures 5a, S2a and S2b; Table 3).

On the basis of EXAFS spectra in *R* space of Fe K edge (Figure 4b), as well as the corresponding fitting results (see Table 2), the local coordination structure around iron can be obtained as below: (1) A strong peak at 1.96 Å (*CN* = 4.1-4.5) is assigned to the first shell (Fe-O) for the fresh catalysts; (2) Two weak peaks centered at 2.96 and 3.45 Å can be attributed to the second (Fe-Fe) and third shells (Fe-Ce), which are originated from Fe-O-Fe and Fe-O-Ce interaction,²⁹ respectively. These contributions are involved in the Fe_xO_y clusters strongly interacting with the ceria support; (3) The *CN* of Fe-Fe in **FeRu_Ce** (0.9) is much lower than that in **Fe_Ce** (2.1), revealing the presence of less fraction or smaller size of Fe_xO_y clusters with the introduction of ruthenium. Furthermore, the EXAFS spectra of our ceria-supported iron-ruthenium oxide catalysts are clearly different



from those of standards (Fe/Fe₂O₃/Fe₃O₄ and Ru/RuQ₂) in Respace (Figure S3), which is caused by their small-size cluster hat the 0470B



Figure 4. XANES profiles (a) and EXAFS fitting results in *R* space (b) for ceria-supported iron-ruthenium oxide samples: Fe K edge.



Figure 5. XANES profiles (a) and EXAFS fitting results in *R* space (b) for ceria-supported iron-ruthenium oxide samples: Ru K edge.

Journal Name

Table 2. Averaged oxidation state of iron (δ) and Fe K-edge EXAFS fitting results (*R*: distance; *CN*: coordination number; σ^2 : Debye Waller DOI: 10.1039/C7QI00470B factor; ΔE_0 : inner potential correction) of ceria-supported iron-ruthenium oxide samples.

Sample	δ^a	Fe-O		Fe-Fe		Fe-Ce		-2 (\$ 2)	
		<i>R</i> (Å)	CN	<i>R</i> (Å)	CN	<i>R</i> (Å)	CN	<i>σ</i> ⁼ (A²)	$\Delta E_0 (eV)$
Fe_Ce (fresh)	3.0	1.96±0.01	4.5±0.3	2.96±0.01	2.1±0.5	3.45±0.02	1.6±0.8		11.2±0.9
Fe_Ce (used)	2.4	1.97±0.01 2.59±0.02	3.1±0.3 2.2±0.6	3.07±0.04	0.7±0.4		_	0.003(O)	9.7±0.9
FeRu_Ce (fresh)	3.0	1.96±0.01	4.1±0.2	2.96±0.01	0.9±0.3	3.45±0.02	1.5±0.5	0.005(Fe)	11.2±0.9
FeRu_Ce (used)	2.7	1.94±0.01 2.64±0.02	3.4±0.2 1.1±0.5			_		0.000(00)	9.7±0.9
Fe ^b	0	_	_	2.464 2.843	8 6				
Fe ₂ O ₃ ^b	3	1.983 2.062	6 6	2.889 2.969	1 3				
$Fe_3O_4{}^b$	8/3	2.096 3.630	6 8	2.964 3.476	6 6	—	_	_	_

^a Determined by linear combination analysis on the XANES profiles with references of Fe foil (δ = 0) and α -Fe₂O₃ (δ = 3); ^b From Crystallography Open Database (nos. 9006603, 1011240 and 1513301 for Fe, Fe_2O_3 and Fe_3O_4 , respectively).

Table 3. Averaged oxidation state of ruthenium (δ) and Ru K-edge EXAFS fitting results (*R*: distance; *CN*: coordination number; σ^2 : Debye-Waller factor^{*a*}; ΔE_0 : inner potential correction^{*b*}) of ceriasupported iron-ruthenium oxide samples.

	δ^c	Ru-	0	Ru-Ru		
Sample		<i>R</i> (Å)	CN	<i>R</i> (Å)	CN	
Ru_Ce (fresh)	3.2	2.00±0.01	4.2±0.4	_	_	
Ru_Ce (used)	1.8	2.01±0.02	2.9±0.4	2.71±0.02	1.8±0.4	
FeRu_Ce (fresh)	3.1	2.01±0.01	4.4±0.4	_	_	
FeRu_Ce (used)	1.3	2.02±0.02	2.4±0.3	2.69±0.02	1.4±0.5	
Ru ^d	0	—	_	2.665 2.727	6 6	
		1.942	2			
RuO ₂ ^d	4	1.986	4	3.105	2	
		3.412	4	3.539	8	
		3.662	4			

^a Set to be 0.003 and 0.006 for Ru-O and Ru-Ru paths, respectively; ^b Determined as 5.3±1.8 and 4.0±2.7 eV for fresh and used samples, respectively; ^c Determined by linear combination analysis on the XANES profiles with references of Ru foil ($\delta = 0$) and RuO₂ ($\delta = 4$); ^d From Crystallography Open Database (nos. 1512537 and 1000058 for Ru, RuO₂, respectively).

According to the EXAFS spectra in R space of Ru K edge (Figure 5b), as well as the corresponding fitting results (see Table 3), the local coordination structure around ruthenium can be obtained. A strong peak at 2.00–2.01 Å (CN = 4.2-4.4) is attributed to the Ru-O first shell for both of the fresh catalysts, either single metal oxide (Ru_Ce) or bimetallic oxides (FeRu Ce). No other shells at longer distance can be decided in the EXAFS spectra. It indicates that the ultra-fine ruthenium oxide species are highly dispersed over the ceria nanorods.

In this work, Fischer-Tropsch synthesis (FTS) reaction was tested for different ceria-supported iron-ruthenium oxide catalysts. Table 4 shows that Ru_Ce has zero CO conversion at both temperatures of 250 and 300 °C under the FTS conditions. It has been well known that supported ruthenium catalysts are active for FTS. Carballo et al. observed an increased TOF values for FTS on 1.8 wt.% Ru/Al₂O₃ with an increased Ru particle size from 4 to 16 nm.³³ Recently, Gonzalez-Carballo et al. reported a TOF of 0.02 s⁻¹ for FTS on Al₂O₃ supported 3 wt.% Ru.³⁴ In this work, the very low concentration (ca. 0.3 wt.%) of Ru in the form of ultrafine clusters (< 1-2 nm) prevented the conversion of CO in FTS. Also, the ceria nanorods may not be a good support for the active ruthenium sites in our study, and the catalytic performance of bimetallic oxides catalyst should be contributed by the active iron sites only. Figure 6a and Table 4 also show that the CO conversions of FeRu_Ce are significantly higher than those of Fe_Ce (7.1% vs 0.8% at 250 °C and 15.7% vs 8.7% at 300 °C), nearly one order magnitude at 250 °C and twice at 300 °C. Table 4 also presents that the selectivity of desired products catalyzed by two different iron-containing samples in FTS at 300 °C. Specifically, single iron oxide sample (Fe_Ce) displays better selectivity than bimetallic oxide catalyst (FeRu_Ce), e. g. higher fraction of C5+, lower percentage of CO₂ and CH₄, as well as nearly identical C₂-C₄. It has been reported that small Ru clusters favor the formation of methane³⁵. So, the addition of ruthenium did increase the selectivity of methane for our ceria-supported iron oxide catalyst (Table 4). On the other hand, the methane selectivity of iron catalysts supported on inert oxide (e. g. Al_2O_3) increases at the higher temperature.²¹ However, we used a reducible oxide (CeO₂) support, and thus the methane selectivity slightly decreased (FeRu_Ce) or maintained (Fe_Ce) from 250 to 300 °C.²⁹ As discussed as above, the distribution of the products on our ceria-supported iron-ruthenium oxide catalysts is modest (see Table S1 for details) and should have no special sites. However, the major motivation of this work is to trace the structural evolutions on different species in

Chemisti

Published on 12 October 2017. Downloaded by University of Windsor on 12/10/2017 11:54:05.

ARTICLE

ceria-supported iron-ruthenium oxide catalysts before and after the FTS reaction.

Table	4.	Catalytic	reactivity	of	ceria-supported	iron-ruthenium
sample	es f	or FTS.				

Sample	<i>Т</i> (°С)	Conv. (%) ^a	CO ₂	So CH4	electivity C ₂ -C ₄	(%) ^b C ₅₊	olefin ^c
FeRu_Ce	250	7.1	47	34	52	14	3.1
	300	15.7	45	27	45	28	2.0
Fe_Ce	250	0.8	25	16	41	43	2.6
	300	8.7	26	13	37	50	2.7
Ru_Ce	250 300	0 0		—		—	—

^{*a*} Based on carbon calculation under the following reaction conditions: 110 mg, H₂/CO = 1/1, 2.0 MPa, 21.5 ml·min⁻¹, time-on-stream of 5h; ^{*b*} Calculation of CO conversion is based on carbon calculation for all hydrocarbons (exclude CO₂); ^{*c*} Olefin selectivity is calculated by $C_2=C_4 / C_2-C_4$.



oxide samples for FTS: (a) CO conversion; (b) Selectivity of CO_2 , CH_4 , C_2 - C_4 and C_{5+} products.

For the used samples after FTS, we carried out different characterizations to monitor the structural evolution of ceriasupported iron-ruthenium oxide catalysts. The XRD data (Figure 1b) determine that the crystal structure of *fcc* Fluorite-type CeO₂ was maintained for the FTS process. There is an minor increase of ceria lattice constants from 5.399-5.407 Å to 5.405-5.418 Å (see Table 1), giving a hint that the surface Fe³⁺ ions may be extracted out of the sub-surface of ceria nanorods under the FTS reaction conditions.²⁹ The HRTEM and HAADF-STEM images (Figure 7) verify the similar morphologies of used iron-ruthenium oxide catalysts as their fresh counterparts. Meanwhile, the averaged widths of ceria nanorods show no changes before and after the FTS reaction (see Table 1). Still, no lattice fringes of Fe/Fe₃O₄/Fe₂O₃ or Ru/RuO₂ can be determined.

The aberration-corrected HAADF-STEM/EELS results in Figure 8 confirm that subnanometer iron oxide species and ruthenium species were dominant in both of the iron-containing samples after FTS. The XANES profiles (Figure 4a and Figure 5a) reveal that both iron and ruthenium species were partially reduced after FTS, with the averaged oxidation states of Fe^{2.4+}, Ru^{1.8+} and Fe^{2.7+}/Ru^{1.3+} for **Fe_Ce Ru_Ce** and **FeRu_Ce**, respectively (see Tables 2 and 3). Here, we found that more oxidized iron species and more reduced ruthenium species were present for the bimetallic oxides sample (**FeRu_Ce**) than those in the single metal oxide counterparts (**Fe_Ce**

and **Ru_Ce**). In another word, the relatively lower reduction degree of iron formed at the expense of the relatively higher reduction degree of ruthenium in the used ceria-supported iron-ruthenium oxides catalysts, and thus the introduction of Ru³⁺ could help the stabilization of Fe³⁺ species during FTS. The profiles of XANES linear combination fits for Fe K edge and Ru K edges have been included (Figures S1c, S1d, S2c and S2d).



Figure 7. HRTEM (a,b,c) and HAADF-STEM (d,e,f) images of used ceria-supported iron-ruthenium oxide samples: (a,d) **Fe_Ce**; (b,e) **Ru_Ce**; (e,f) **FeRu_Ce**.



Figure 8. Aberration-corrected HAADF-STEM/EELS results for used ceria-supported iron-ruthenium oxide samples: (a) Fe_Ce; (b) FeRu_Ce.

From Figure 4b and Table 2, the EXAFS analysis of Fe K edge for the used catalysts provides the following results: (1) The first shell (Fe-O) is similar as the fresh samples, i. e. R = 1.94-1.97 Å and CN = 3.1-3.4; (2) Another shell of Fe-O at the longer distance around 2.6 Å can be determined for both **Fe_Ce** and **FeRu_Ce** after FTS (CN = 1.1-2.2). The sum of CN values for the above two Fe-O shells is nearly

equal to those for the first Fe-O shell before the FTS process, indicating the separation of Fe-O shell in the used catalysts. This peak-split could be due to the harsh FTS conditions (high pressure and high concentrations of CO/H_2 ; (3) For the used Fe Ce, the second Fe-Fe shell caused by the Fe-O-Fe interaction is weakened (CN = 0.7) and the third Fe-Ce shell around 3.5 Å by the Fe-O-Ce interaction completely disappears, revealing the shrink and loose of Fe_xO_y clusters during the FTS reaction for the single metal (Fe) oxide catalyst; (4) For the used FeRu_Ce, both Fe-Fe and Fe-Ce shells were lost after FTS. Besides the first Fe-O shell, no contributions in the range of 3-4 Å can be identified. Therefore, for ceria-supported bimetallic iron-ruthenium oxides clusters, Fe single atoms coordinated by oxygen ions only (FeO_x, R = 1.94 and 2.64 Å; CN =3.4 and 1.1) formed during the FTS process (reaction conditions: up to 300 °C, H₂/CO=1/1, 2 MPa). Here, the iron oxide clusters observed in HAADF-STEM/EELS image (Figure 8b) could be in minor fraction, and averaged in the EXAFS signals. Furthermore, the missing of Fe-Fe metallic bond around 2.5 Å identifies the absence of formation of any iron carbides reported by Ribeiro et al. previously³⁶. So, just like the previous studies on the atomically dispersed Pd and cerium oxide,³⁷ the EXAFS analysis is determining to probe the short-range (< 4 Å) coordination structure around Fe, as well as to identify the iron SAC in this work. On the other hand, the EXAFS spectra (Figure 5b) and the related fitting results (Table 3) confirm that both Ru-O shell (~ 2.0 Å, CN = 2.4–2.9) and metallic Ru-Ru bond (~ 2.7 Å, CN = 1.4-1.8) presents for Ru K edge in the used Ru_Ce and FeRu_Ce, indicating the formation of metallic Ru-Ru bond in FTS.

It is widely believed that iron carbide (e. g. Fe_5C_2) is the active species for FTS.^{23,24,38} In our study, no such Fe_5C_2 species can be determined for the used catalysts, which have been confirmed by the totally different EXAFS spectra to the previous report³⁸, as well as the almost identical XPS C 1s spectra on **Fe_Ce** and **FeRu_Ce** before and after the reaction (Figure S4). The absence of iron carbide is probably due to the low concentration of Fe (ca. 10 at.%) for our samples than that for pure Fe_5C_2 , and thus the coordinated oxygen species could not be eliminated by carbon during FTS.



Scheme 1. Demonstration on the formation of Fe single atoms for ceria-supported iron-ruthenium oxide samples.

As discussed as above, the formation of Fe single atoms for ceriasupported bimetallic iron-ruthenium oxides (refer to Scheme 1) was actually governed by the following two key factors: (1) Catalytic reaction (FTS) could weaken both Fe-O-Fe and Fe-O-Ce interactions, i. e. the former generates iron oxide clusters; while the latter Page 6 of 8

connects them with CeO₂ support. Here, the real driving forces may be due to the high-concentration CO or H_D and the bigh pressure (ca. 2 MPa); (2) Addition of ruthenium could tune the specific structure of Fe_xO_y clusters, as well as scarify itself (Ru³⁺ \rightarrow Ru⁰) to prevent the reduction of iron species (Fe³⁺ \rightarrow Fe⁰).

Conclusions

In conclusion, we have discovered a spontaneous formation of SAC during the FTS process. The electronic and local coordination structures of iron single atoms have been determined by the related XANES analysis and EXAFS fittings, respectively. The high-concentration CO or H₂ and high pressure during FTS could weaken both Fe-O-Fe and Fe-O-Ce interactions for the transformation from iron oxide clusters to iron single atoms. The addition of small-amount ruthenium could have positive effect on both catalyst preparation and catalytic reaction steps. All the above factors drove the generation of iron single atoms, which are composed by slightly reduced Fe^{δ +} (δ = 2.7) species coordinated by two different types of oxygen ions at ca. 2.0 and 2.6 Å and anchored onto the surface of ceria nanorods.

Experimental

Materials

All the chemicals used in this work were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd without any further purification.

Synthesis

Preparation of ceria nanorods: The ceria nanorods were synthesized according to the hydrothermal method³⁹. Ce(NO₃)₃·6H₂O (4.5 mmol) was added into an aqueous NaOH (6 M, 60 mL) solution under vigorous stirring. After the precipitation process was completed (about 10 min), the stock solution was transferred into a Teflon bottle, and further tightly sealed in a stainless-steel autoclave. The hydrothermal procedure was carried out in a temperature-controlled electric oven at 100 °C for 24 h. The precipitates were separated by centrifugation and then washed by deionized water four times and ethanol once. The ceria support was obtained by drying as-washed product in air under 70 °C overnight.

Deposition of iron-ruthenium oxide: Ceria-supported ironruthenium oxide samples were synthesized via a depositionprecipitation method. (NH₄)₂CO₃ (2.4 g) and the as-calcined CeO₂ nanorods (1 g) were suspended in 100 mL Millipore (> 18 MΩ) water under vigorously stirring. Then, Fe(NO₃)₃·9H₂O (0.7 mmol) and RuCl₃·H₂O (0.07 mmol) aqueous solution (15 ml) were dropped into the above solution until the final pH value of ~ 9. After the generation of greenish slurries, the stock solution was further aged at room temperature for another 2 h. The as-obtained precipitates were filtered and then washed by Millipore water for three Times. The as-washed powders were dried in vacuum at 80 °C overnight and then calcined in air at 400 °C for 4 h (ramping rate: 2 °C/min).

Characterizations

The metal ratios of Fe/Ru/Ce were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer (40 kV, 40 mA) with a scanning rate of 4 ° min⁻¹, using Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å). The diffraction patterns were collected from 20 to 80 ° with a step of 0.02 °. The 2 θ angles were calibrated with a μ m-scale Alumina disc. The powder sample after grinding was placed inside a quartz sample holder for each test. With the software "LAPOD" of least-squares refinement of cell dimensions of cubic CeO₂ from powder data by Cohen's method^{40, 41}.

The nitrogen adsorption-desorption measurements were performed on an ASAP2020-HD88 analyzer (Micromeritics Co. Ltd.) at 77 K. The measured powders were degassed at 250 C under vacuum (< 100 μ mHg) for over 4 h. The BET specific surface areas (S_{BET}) were calculated from data in the relative pressure range between 0.05 and 0.20.

The aberration-corrected high-resolution TEM (HRTEM) or highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and electron energy-loss spectroscopy (EELS) measurements were performed on JEOL ARM200F microscope equipped with probe-forming spherical-aberration corrector and Gatan image filter (Quantum 965). In order to obtain the good signal-noise ratio, iron distribution was mapped by Fe L_{2,3} edges in EELS spectra.

The X-ray photoelectron spectroscopy (XPS) analysis was performed on an Axis Ultra XPS spectrometer (Kratos, U.K.) with 225 W of Al K_{α} radiation (1487 eV). The C 1s line at 284.8 eV was used to calibrate the binding energies.

X-ray absorption fine structure

The X-ray absorption fine structure (XAFS) spectra at Fe K (E_0 = 7112 eV) edge and Ru K (E_0 = 22117 eV) edge were performed at BL14W1 beamline⁴² of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under "top-up" mode with a constant current of 260 mA. The XAFS data were recorded under fluorescence mode with a 7-element Ge solid state detector. The energy was calibrated accordingly to the absorption edge of pure Fe foil and Ru foil.

Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as function of energies $\mu(E)$ were processed by background subtraction and normalization procedures, and reported as "normalized absorption". Based on the normalized XANES profiles, the chemical valence of iron or ruthenium was determined by comparison to the corresponding references of Fe/Fe₂O₃ and Ru/RuO₂.

For the extended X-ray absorption fine structure (EXAFS) part, the Fourier transformed (FT) data in R space of Fe and Ru were analyzed by applying quick first shell model for Fe-O, FeO model for Fe-Fe contributions and applying quick first model for Ru-O, Ru model for Ru-Ru contributions. The passive electron factor, S_0^2 , was determined by fitting the experimental data on Fe and Ru foil and fixing the coordination number (*CN*) of Fe-Fe to be 8 + 6, and fixing the *CN* of Ru-Ru to be 12, and then fixed for further analysis of the measured samples. The parameters describing the electronic properties (e.g., correction to the photoelectron energy origin, E_0) and local structure environment including *CN*, bond distance (*R*)

Journal Name

and Debye-Waller (*D.W.*) factor around the absorbing atoms were allowed to vary during the fit process. The fitted Panges for Randra spaces were selected to be k = 2.7–9.7 Å⁻¹ with R = 0.8–3.6 Å (k^3 weighted) for Fe K edge and k = 3–10 Å⁻¹ with R = 0.8–3.3 Å (k^2 weighted) for Ru K edge. To distinguish the effect of Debye-Waller factor from coordination number, we set σ^2 to be 0.003, 0.005 and 0.006 Å² for all the analyzed Fe-O, Fe-Fe and Fe-Ce shells, according to the fitted results of iron standards. We also set σ^2 to be 0.003 and 0.006 Å² for all the analyzed Ru-O and Ru-Ru shells, according to the fitted results of ruthenium standards. To distinguish the effect of correction to the photoelectron energy origin from distance, we set ΔE_0 to be 11.2/9.7 eV for fresh/used **Fe_Ce** and **FeRu_Ce** (Fe K edge); 5.3/4.0 eV for fresh/used **Ru_Ce** and **FeRu_Ce** (Ru K-edge), which were obtained from the linear combination fits on XANES profiles and the fitting results of standards.

Catalytic tests

The catalytic activity of Fischer-Tropsch synthesis (FTS) reaction of ceria-supported iron-Ruthenium oxide samples were investigated in a fixed-bed flow reactor using 110 mg of sieved (40–60 mesh) powders diluted with 0.5g SiO₂ in a gas mixture of 47 vol.% CO, 47 vol.% H₂ and 6 vol.% N₂ (from Jinan Deyang Corporation, 99.997% purity) at a flow rate of 21.7 mL/min, corresponding to a space velocity of 12,000 mL·h⁻¹·g_{cat}⁻¹. The FTS measurements at multiple temperature (250-300 °C) were carried out under a high pressure of 2 MPa with a pretreatment at 350 °C for 3h in 10% H₂/Ar.

The product and reactant in the gas phase were detected online using a gas chromatograph (GC-9160, Shanghai, China). C_1 - C_4 range hydrocarbons were analyzed using a Plot Al₂O₃ capillary column with a flame ionization (FID); however, CO, CO₂, CH₄, and N₂ were analyzed by using a Porapak Q and 5A molecular sieve-packed column with a thermal conductivity detector (TCD). To calculate the CO conversion, the 6% N₂ in syngas was used as an internal standard. All hydrocarbons were analyzed using a GC-9160 with a PONA capillary column and a flame ionization detector (FID). The selectivity of the products was based on the basis of all used CO, whereas the selectivity of CH₄, C_2 - C_4 , and C_{5+} is calculated on the basis of all hydrocarbons produced.

Acknowledgements

Financial supported from the National Science Foundation of China (NSFC) (grant no. 21373259), the Excellent Young Scientists Fund from the NSFC (21622106), the Hundred Talents project of the Chinese Academy of Sciences, the Strategic Priority Research Program of the Chinese Academy of Sciences (grant no. XDA09030102), the Taishan Scholar project of Shandong Province (China), the Fundamental Research Funds for the Central Universities (China).

Notes and references

- B. T. Qiao, A. Q. Wang, X. F. Yang, L. F. Allard, Z. Jiang, Y. T. Cui, J. Y. Liu, J. Li and T. Zhang, *Nat. Chem.*, 2011, 3, 634-641.
- X. G. Guo, G. Z. Fang, G. Li, H. Ma, H. J. Fan, L. Yu, C. Ma, X. Wu, D. H. Deng, M. M. Wei, D. L. Tan, R. Si, S. Zhang, J. Q. Li, L. T. Sun, Z. C. Tang, X. L. Pan and X. H. Bao, *Science*, 2014, **344**, 616-619.
- 3 M. Yang, S. Li, Y. Wang, J. A. Herron, Y. Xu, L. F. Allard, S. Lee, J. Huang, M. Mavrikakis and M. Flytzani-stephanopoulos, *Science*, 2014, **346**, 1498-1501.

Journal Name

- ARTICLE
- 4 M. Yang, J. L. Liu, S. Lee, B. Zugic, J. Huang, L. F. Allard and M. Flytzani-Stephanopoulos, J. Am. Chem. Soc., 2015, 137, 3470-3473.
- 5 J. Jones, H. F. Xiong, A. T. Delariva, E. J. Peterson, H. Pham, S. R. Challa, G. S. Qi, S. Oh, M. H. Wiebenga, X. I. P. Hernandez, Y. Wang and A. K. Datye, *Science*, 2016, **353**, 150-154.
- L. L. Lin, W. Zhou, R. Gao, S. Y. Yao, X. Zhang, W. Q. Xu, S. J. Zheng,
 Z. Jiang, Q. L. Yu, Y. W. Li, C. Shi, X. D. Wen and D. Ma, *Nature*, 2017,
 544, 80-83.
- 7 H. Itoi, H. Nishihara, S. Kobayashi, S. Ittisanronnachai, T. Ishii, R. Berenguer, M. Ito, D. Matsumura and T. Kyotani, *J. Phys. Chem. C*, 2017, **121**, 7892-7902.
- S. Yao, X. Zhang, W. Zhou, R. Gao, W. Xu, Y. Ye, L. Lin, X. Wen, P. Liu, B. Chen, E. Crumlin, J. Guo, Z. Zuo, W. Li, J. Xie, L. Lu, C. J. Kiely, L. Gu, C. Shi, J. A. Rodriguez and D. Ma, *Science*, 2017, 10.1126/science.aah4321.
- 9 B. Zhang, H. Asakura, J. Zhang, J. G. Zhang, S. De and N. Yan, Angew. Chem. Int. Ed., 2016, 55, 8319-8323.
- 10 S. G. Yang, J. Kim, Y. J. Tak, A. Soon and H. Lee, Angew. Chem. Int. Ed., 2016, 55, 2058-2062.
- Z. P. Chen, S. Mitchell, E. Vorobyeva, R. K. Leary, R. Hauert, T. Furnival, Q. M. Ramasse, J. M. Thomas, P. A. Midgley, D. Dontsova, M. Antonietti, S. Pogodin, N. Lopez and J. Perez-Ramirez, *Adv. Funct. Mater.*, 2017, 27, 1605785.
- 12 H. Yan, H. Cheng, H. Yi, Y. Lin, T. Yao, C. L. Wang, J. J. Li, S. Q. Wei and J. L. Lu, *J. Am. Chem. Soc.*, 2015, **137**, 10484-10487.
- 13 P. X. Liu, Y. Zhao, R. X. Qin, S. G. Mo, G. X. Chen, L. Gu, D. M. Chevier, P. Zhang, Q. Guo, D. D. Zang, B. H. Wu, G. Fu and N. F. Zheng, *Science*, 2016, **352**, 797-801.
- 14 S. G. Yang, Y. J. Tak, J. Kim, A. Soon and H. Lee, ACS Catal., 2017, 7, 1301-1307.
- 15 B. Qiao, J. X. Liu, Y. G. Wang, Q. Q. Lin, X. Y. Liu, A. Q. Wang, J. Li, T. Zhang and J. Liu, ACS Catal., 2015, 5, 6249-6254.
- H. Huang, K. Li, Z. Chen, L. Luo, Y. Gu, D. Zhang, C. Ma, R. Si, J. Yang,
 Z. Peng and J. Zeng, J. Am. Chem. Soc., 2017, 139, 8152-8159.
- L. B. Wang, W. B. Zhang, S. P. Wang, Z. H. Gao, Z. H. Luo, X. Wang, R. Zeng, A. W. Li, H. L. Li, M. L. Wang, X. S. Zheng, J. F. Zhu, W. H. Zhang, C. Ma, R. Si and J. Zeng, *Nat. Commun.*, 2016, **7**, 14036.
- 18 L. B. Wang, H. L. Li, W. B. Zhang, X. Zhao, J. X. Qiu, A. W. Li, X. S. Zheng, Z. P. Hu, R. Si and J. Zeng, *Angew. Chem. Int. Ed.*, 2017, 56, 4712-4718.
- P. Q. Yin, T. Yao, Y. Wu, L. R. Zheng, Y. Lin, W. Liu, H. X. Ju, J. F. Zhu, X. Hong, Z. X. Deng, G. Zhou, S. Q. Wei and Y. D. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 10800-10805.
- 20 L. W. Guo, P. P. Du, X. P. Fu, C. Ma, J. Zeng, R. Si, Y. Y. Huang, C. J. Jia, Y. W. Zhang and C. H. Yan, *Nat. Commun.*, 2016, **7**, 13481.
- 21 H. H. Dong, M. J. Xie, J. Xu, M. F. Li, L. M. Peng, X. F. Guo and W. P. Ding, *Chem. Commun.*, 2011, **47**, 4019-4021.
- 22 H. M. T. Galvis, J. H. Bitter, T. Davidian, M. Ruitenbeek, A. I. Dugulan and K. P. de Jong, J. Am. Chem. Soc., 2012, **134**, 16207-16215.
- 23 R. P. Mogorosi, N. Fischer, M. Claeys and E. van Steen, J. Catal., 2012, 289, 140-150.
- 24 K. Xu, B. Sun, J. Lin, W. Wen, Y. Pei, S.-R. Yan, M.-H. Qiao, X.-X. Zhang and B.-N. Zong, *Nat. Commun.*, 2014, 5, 5783.
- 25 J. Z. Lu, L. J. Yang, B. L. Xu, Q. Wu, D. Zhang, S. J. Yuan, Y. Zhai, X. Z. Wang, Y. N. Fan and Z. Hu, *ACS Catal.*, 2014, **4**, 613-621.
- 26 V. lablokov, Y. Xiang, A. Meffre, P.-F. Fazzini, B. Chaudret and N. Kruse, ACS Catal., 2016, 6, 2496-2500.
- 27 Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science*, 2003, 301, 935-938.
- 28 S. Carrettin, P. Concepcion, A. Corma, J. M. L. Nieto, V. F. Puntes, Angew. Chem. Int. Ed., 2004, 43, 2538-2540.
- 29 Q. Yang, X.-P. Fu, C.-J. Jia, C. Ma, X. Wang, J. Zeng, R. Si, Y.-W. Zhang and C.-H. Yan, ACS Catal., 2016, 6, 3072-3082.
- W. W. Wang, P. P. Du, S. H. Zou, H. Y. He, R. X. Wang, Z. Jin, S. Shi, Y. Y. Huang, R. Si, Q. S. Song, C. J. Jia and C. H. Yan, *ACS Catal.*, 2015, 5, 2088-2099.

- 31 R. Si, J. Raitano, N. Yi, L. Zhang, S.-W. Chan, M. Flytzani-View Article Online Stephanopoulos, Catal. Today, 2012, 180, 68:180.1039/C7QI00470B
- A. I. Frenkel, Q. Wang, N. Marinkovic, J. G. Chen, L. Barrio, R. Si, A. L. Camara, A. M. Estrella, J. A. Rodriguez and J. C. Hanson, *J. Phys. Chem. C*, 2011, **115**, 17884-17890.
- J. M. G. Carballo, J. Yang, A. Holmen, S. Garcia-Rodriguez, S. Rojas, M. Ojeda and J. L. G. Fierro, J. Catal., 2011, 284, 102-108.
- J. M. Gonzalez, F. J. Perez-Alonso, F. J. Garcia-Garcia, M. Ojeda, J. L. G. Fierro and S. Rojas, *J. Catal.*, 2015, **332**, 177-186.
- 35 M. C. Bahome, L. L. Jewell, K. Padayachy, D. Hildebrandt, D. Glasser, A. K. Datye and N. J. Coville, *Appl. Catal. A*, 2007, **328**, 243-251.
- 36 M. C. Ribeiro, G. Jacobs, B. H. Davis, D. C. Cronauer, A. J. Kropf and C. L. Marshall, J. Phys. Chem. C, 2010, **114**, 7895-7903.
- 37 P.-P. Du, X.-C. Hu, X. Wang, C. Ma, M. Du, J. Zeng, C.-J. Jia, Y.-Y. Huang and R. Si, *Inorg. Chem. Front.*, 2017, 4, 668-674.
- 38 C. Yang, H. B. Zhao, Y. L. Hou, and D. Ma, J. Am. Chem. Soc., 2012, 134, 15814-15821.
- 39 H.-X. Mai, L.-D. Sun, Y.-W. Zhang, R. Si, W. Feng, H.-P. Zhang, H.-C. Liu and C.-H. Yan, J. Phys. Chem. B, 2005, **109**, 24380-24385.
- 40 J. I. Langford, J. Appl. Cryst., 1971, 4, 259-260.
- 41 J. I. Langford, J. Appl. Cryst., 1973, 6, 190-196.
- 42 H. S. Yu, X. J. Wei, J. Li, S. Q. Gu, S. Zhang, L. H. Wang, J. Y. Ma, L. N. Li, Q. Gao, R. Si, F. F. Sun, Y. Wang, F. Song, H. J. Xu, X. H. Yu, Y. Zou, J. Q. Wang, Z. Jiang and Y. Y. Huang, *Nucl. Sci. Tech.*, 2015, **26**, 050102.

8 | J. Name., 2012, 00, 1-3