Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Conversion of CO_2 on a Highly Active and Stable Cu/FeOx/CeO_2 Catalyst: Tuning Catalytic Performance by Oxide-Oxide Interactions

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Supplementary Tables and Figures

Table S1. The physicochemical properties of 5CuxFe/CeO_2 catalysts

Sample	Cu loading	Fe loading	BET surface area (m^2/g)
CeO_2	--	--	40
5Cu/CeO_2	5.26+/-0.01	--	39
5Cu0.8Fe/CeO_2	4.91+/-0.04	0.76+/-0.01	40
5Cu1.6Fe/CeO_2	5.43+/-0.03	1.59+/-0.01	42
5Cu3.2Fe/CeO_2	5.01+/-0.02	3.00+/-0.01	40
5Cu5Fe/CeO_2	4.93+/-0.01	4.23+/-0.01	38
1.6Fe/CeO_2	--	1.57+/-0.01	41

Table S2. The affiliation of the major diffraction peaks and related crystal phase of Fe and Cu species[a].

Species	Diffraction peaksº (related crystal phase)	
Fe	6.82 (110)	9.65 (200)
FeO	5.56 (110)	6.41 (11-1)
Fe_3O_4	4.66 (220)	5.46 (311)
Fe_2O_3	5.12 (104)	5.49 (2-10)
$CuFe_2O_4$	5.72 (202)	6.74 (220)
Cu	6.59 (111)	7.65 (200)
CuO	5.47 (002)	5.97 (111)

a. the incident X-ray wavelength was 0.24121 Å.

When the temperature increases during XRD data collection, the lattice thermal expansion will happen and cause the shift of the diffraction peaks shifting to lower 2θ. The peak centered at 5.49º was used to determine the diffraction of Fe_2O_3, as the strongest line was overlapped by the one of the peaks of CeO_2. So the peak centered at 5.44 º appeared at 180 ºC was attributed the diffraction of Fe_2O_3 species.

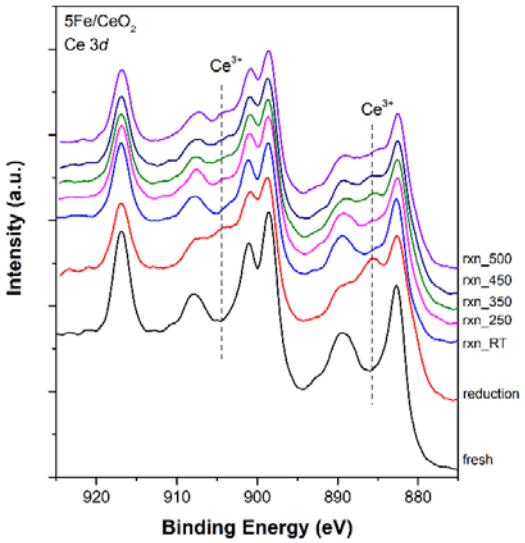

Figure S1. AP-XPS characterization of Ce 3*d* profiles of 5Cu1.6Fe/CeO_2 catalyst under varied conditions.

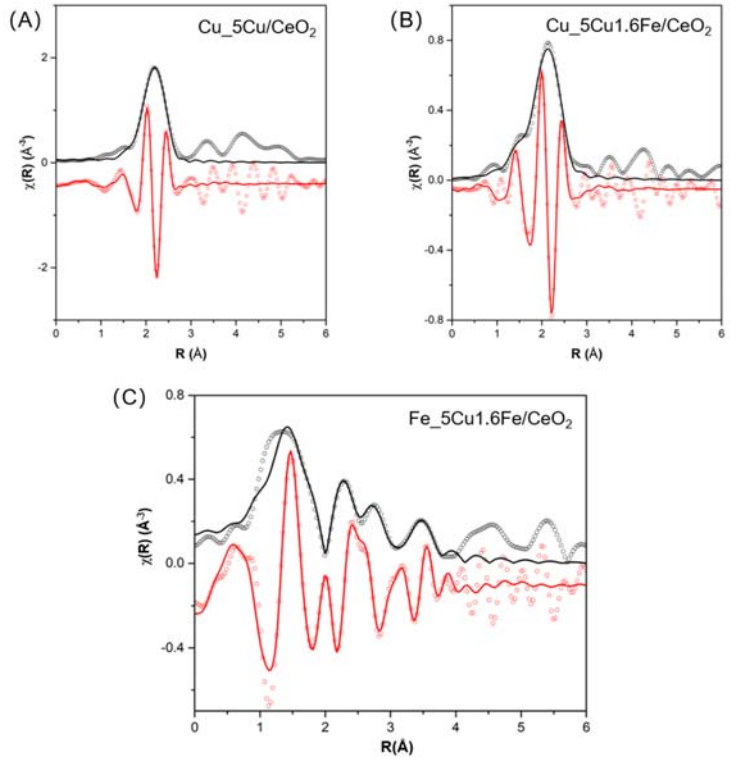

Figure S2. The EXAFS fitting results in R space of the **(A)** 5Cu/CeO_2; **(B)** 5Cu1.6Fe/CeO_2 in Cu K edge and **(C)** 5Cu1.6Fe/CeO_2 in Fe K edge. The black line and dot are the R magnitude spectra while the red ones are the R real spectra.

Table S3. The EXAFS fitting results of Cu K edge and Fe K edge of $Cu5Fe1.6/CeO_2$ catalyst.

Edge	Sample	Shell	Bond length (Å)	Coordination	σ^2	E_0 shift
Cu K	$5Cu/CeO_2$	Cu-Cu	2.52±0.01	9.0+/-0.9	0.011	0.8
	$5Cu1.6Fe/CeO_2$-RED	Cu-Cu	2.50±0.01	5.3+/-0.4	0.015	0.1
	$5Cu1.6Fe/CeO_2$-RXN	Cu-Cu	2.50±0.03	5.3+/-0.8	0.015	-0.4
Fe K edge	$5Cu1.6Fe/CeO_2$-RXN	Fe-O	1.96±0.03	2.2+/-0.5	0.008	3.2
		Fe-O	2.16±0.04	2.2+/-0.6	0.008	
		Fe-Fe(Cu)	2.52±0.02	1.6+/-0.2	0.009	
		Fe-(O)-Fe	3.13±0.02	1.2+/-0.3	0.009	
		Fe-(O)-Fe	3.66±0.02	0.4+/-0.1	0.009	
		Fe-Ce	3.83±0.04	0.3+/-0.2	0.005	

Table S4. The linear combination of Fe_2O_3, Fe_3O_4, FeO and Fe species in the $5Cu1.6Fe/CeO_2$ catalyst under reaction condition

Catalyst	Fe_2O_3	Fe_3O_4	FeO	Fe
$5Cu1.6Fe/CeO_2$-rxn	31.4+/-3.5	24.2+/-3.9	45.6+/-0.7	0

The necessary of including the Fe-Ce shell in the fitting of $5Cu1.6Fe/CeO_2$ catalysts

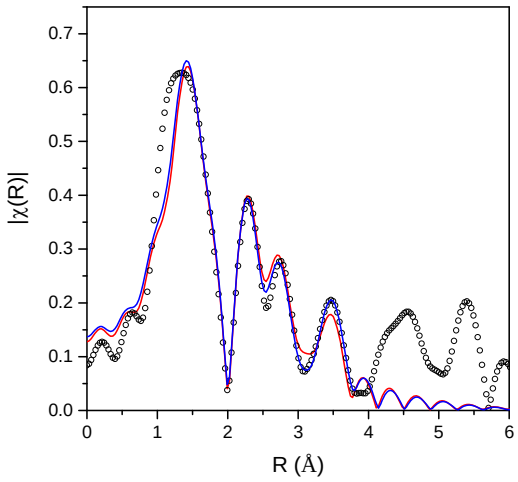

Figure S3. The comparison of the fitting results in R space of the one without Fe-Ce shell (red) and with Fe-Ce shell (blue).

As shown in the Figure S3, it could be seen that if the Fe-Ce shell is not included in the fitting of the Fe K edge spectrum, the quality of the fitting in the range of 3-4 Å will get worse. In the meantime, the fitting parameters of

the longest Fe-Fe shell became meaningless when there is no Fe-Ce path in the fitting, such as the negative σ^2 value. This phenomenon suggests that the Fe-Ce and Fe-Fe shells are correlating shells that should both be included in the fitting processes.

Table S5. The Fe-Fe parameter comparison of the fitting with Fe-Ce and without Fe-Ce path

	Bond length	Amplitude	σ^2	E0 shift
Without Fe-Ce	3.67	0.07	**-0.002**	4.0
With Fe-Ce	3.66	0.10	0.003	3.2

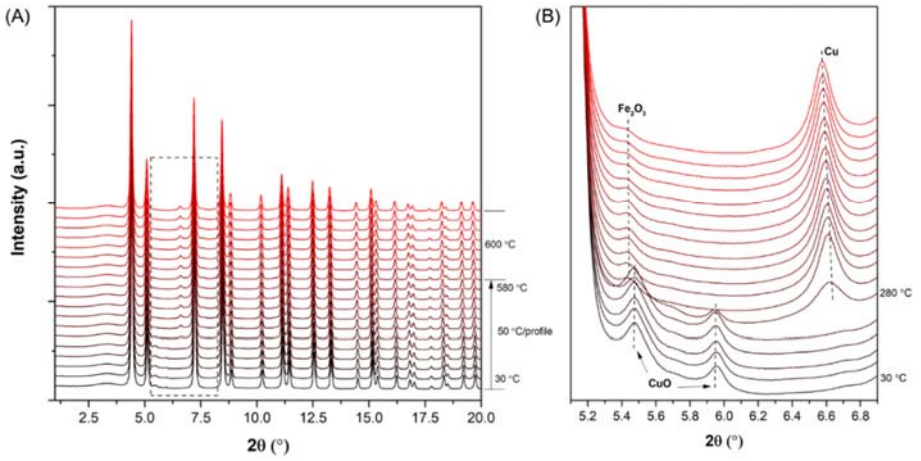

Figure S4. The crystal phase evolution of **(A)** 5Cu1.6Fe/CeO_2 in the reaction atmosphere (CO_2:H_2=1:1) from room temperature, **(B)** the enlarged figure of Figure A in dash square from 5.1 to 6.9°.