Promotional mechanism of activity of three-dimensionally ordered macroporous Cu-doped Ce-Fe mixed oxides for CO-SCR

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Catalyst performance

The catalytic performance of 3DOM $Ce_{0.7}Fe_{0.2}M_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalysts for NO_x is tested in a fixed-bed reactor. About 25 mg (40-60 mesh) of sample is put in a quartz tube (inner diameter 4 mm) and fixed with quartz cotton. The reaction gas is composed of 5 vol % NO (He as residual gas; 10 mL/min), 10 vol % CO (He as residual gas; 10 mL/min), 10% H₂O (when used), 500 ppm SO₂ (when used), and the space velocity (SV) is 90000 mL/(g·h). Before each test, each sample is pretreated in N₂ atmosphere at 110 °C for 1 h, and then converted into reaction gas after cooling to 25 °C. Then the catalytic performance of each catalyst at the corresponding temperature point during the heating process is tested. Furthermore, two chromatographic columns and two TCDs are used for on-line separation and analysis of outlet gases (N₂O, CO₂, N₂, NO and CO). NO conversion, N₂ selectivity and N₂ yield are calculated using the following formulas:

$$\begin{split} &\text{NO}_{\text{conversion}} (\%) = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) / [\text{NO}]_{\text{in}} \times 100\% \\ &\text{N}_{2\text{selectivity}} (\%) = 2[\text{N}_2]_{\text{out}} / ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) \times 100\% \\ &\text{N}_2\text{O}_{\text{selectivity}} (\%) = (1 - \text{N}_{2\text{selectivity}}) \times 100\% \\ &\text{N}_{2\text{vield}} (\%) = \text{NO}_{\text{conversion}} \times \text{N}_{2\text{selectivity}} \end{split}$$

The catalytic performance of 3DOM $Ce_{0.7}Fe_{0.2}M_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalysts for CO oxidation is also tested in a fixed-bed reactor. About 25 mg (40-60 mesh) of sample is put in a quartz tube (inner diameter 4 mm) and fixed with quartz cotton. The reaction gas is composed of 2 vol % CO (N₂ as residual gas; 10.4 mL/min), dry-air (21 vol % O₂, 79 vol % N₂; 8.2 mL/min), and the space velocity (SV) is 75000 mL/(g·h). Before each test, each sample is pretreated in N₂ atmosphere at 110 °C for 1 h, and then converted into reaction gas after cooling to 25 °C. Then the catalytic performance of each catalyst at the corresponding temperature point during the heating process is tested. The effluent gases are analysed with a gas chromatograph equipped with a flame ionization detector. The following formula is used to calculate CO conversion:

 $CO_{conversion}$ (%) = ([CO]_{in} - [CO]_{out}) / [CO]_{in} × 100%

Catalyst characterization

Scanning electron microscope/SEM (Hitachi S-3400N) is used to analyze the surface morphology of catalysts. Before the testing, the sample is sprayed with gold in vacuum. The energy-dispersive spectroscopy/EDS element analyzer (Hitachi S-3400N) is used to measure element composition and distribution. The bulk

compositions of catalysts are analyzed by inductively coupled plasma optical emission spectrometer (Agilent ICPOES720).

Microstructure and lattice fringes are measured by transmission electron microscope/TEM (FEI Tecnai G2 F20 S-TWIN). 1-2 mg of sample is dispersed with ethanol, and then dripped into copper mesh after 20 min of ultrasound for testing.

 N_2 adsorption-desorption isotherms and BJH measurements are obtained by a Micromeritics TriStar II 3flex instrument are conducted to study the texture characteristics of catalyst. Prior to the adsorption measurement, about 0.1 g of sample is firstly degassed in a N_2 /He mixture at 300 °C for 4 h.

Crystal structure and phase composition are measured by X-ray diffractometer/XRD (D/MAX-2600) with Cu K α radiation, which is operated at 40 kV and 120 mA, and XRD data are collected from 10 to 80 ° at a scanning rate of 8 °/min.

Raman spectra of the catalysts are collected in the wavenumber range of 100-1000 cm⁻¹ by using a LabRAM HR Evolution spectrometer with a He-Nd laser (excitation wavelength: 532 nm).

H₂-temperature programmed reduction/H₂-TPR measurement is carried out on a Finesorb-3010 chemisorber and a thermocouple is used for temperature test and control. Firstly, about 10 mg of fresh sample is pretreated at 110 °C for 1 h in N₂ atmosphere (30 mL/min), and then cooled to room temperature. Then N₂ is switched to a mixture of N₂ (30 mL/min) and 7.03% H₂ (10 mL/min, Ar as balance gas), and the catalyst is treated for 0.5 h. Finally, the catalyst is heated from 25 to 900 °C, and the effluent gas H₂ is analyzed by thermal conductivity detector.

 O_2 and NO-temperature programmed desorption (O_2 /NO-TPD) measurement is also carried out on Finesorb-3010 chemisorber and a thermocouple is used for temperature test and control. Firstly, 25 mg of the sample is pretreated in He (10 mL/min) from room temperature to 200 °C and held for 1 h, subsequently cooled to room temperature in a He atmosphere and switched to pure O_2 or 5 vol% NO/He (O_2 and NO-TPD, respectively; 10 mL/min) and held for 0.5 h. After that, it is purged by He for 0.5 h for removal of residual gas. Then the catalyst is heated from roomtemperature to 700 °C (O_2 -TPD) or 550 °C (NO-TPD) in He at a heating rate of 10 °C/min. The effluent gas O_2 and NO is continuously monitored using a thermal conductivity detector.

X-ray photoelectron spectroscopy/XPS is measured on a ESCALAB 250XI+

spectrometer with Al K α radiation (1486.8 eV) as X-ray source and C 1s (284.6 eV) as internal binding energy standard.

Quasi-in situ XRD, Raman, XPS are mainly used to observe the changes of the relevant species of the best catalyst in the reaction in order to better obtain the important information that may exist, and then support the proposition of some arguments.

In situ diffuse reflectance infrared fourier transform spectra/in situ DRIFTS of the catalysts are collected in the wavenumber range of 650-4000 cm⁻¹ by using a Nicolet iS50 FT-IR spectrometer equipped with a mercury cadmium telluride detector. An appropriate amount of the catalysts is placed in a quartz IR cell and pretreated for 1 h at 500 °C in N₂ atmosphere. The spectra are collected at each temperature point as background when the temperature drops from 500 to 25 °C. Subsequently, the gas is switched into CO or/and NO gas around 25 °C and keep time for 30-40 min. After that, the temperature is raised from 25 to 500 °C to obtain the adsorption gas spectrum for each target temperature point. All of the presented diffuse reflectance spectra are obtained by subtracting the corresponding background image.

Calculation of TOF

TOF is defined as the number of NO molecules converted per Cu per second, and calculated by the following equation¹:

$$TOF = \frac{\frac{PV}{RT} * x}{nCu}$$

Where P is the standard atmospheric pressure; V is the volume of NO passed through the catalyst bed per second; R is the ideal gas constant, 8.314 J/(mol·K); x is NO conversion and nCu is the mole number of surface Cu.

The numbers of surface Ce, Fe, Cu and O atoms are calculated depending on their surface concentrations obtained from the XPS data and BET surface area. Based on the assumption that the vertical projection area of all the surface atoms equals to the surface area and the XPS data in Table S1. For example, the number of Cu atom (X) on the surface of 0.1 g 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ is 8.63 × 10¹⁷ (1.43 ×10⁻⁶ mol), because of the Ce atom (4.26X), Fe atom (2.68X), O atom (27.52X) and $(4\pi r_{Ce}^2 \times 4.66X + 4\pi r_{Fe}^2 \times 2.68X + 4\pi r_{O}^2 \times 27.52X + 4\pi r_{Cu}^2 \times X = 39m^2/g \times 0.1g)$, r_{Ce} , r_{Fe} , r_{O} , r_{Cu} are the radius of Ce, Fe, O and Cu, and 182 pm, 126 pm, 73pm and 128 pm respectively.

At 150 °C, TOF over the 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ is calculated as follows: $TOF = \frac{101325Pa \times 10 \text{mL/min} \times 5\% \times 49.84\%}{8.314 \text{J/mol/k} \times 423 \text{k} \times 1.43 \times 10^{\circ}\text{-}6\text{mol}} = 0.837 \times 10^{\circ}\text{-}1 \cdot \text{s}^{\circ}\text{-}1$

The TOF values of bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ and 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ can be also calculated by the method above and the results are shown in Table S1. Clearly, the formation of 3DOM structure can increase the TOF value and the existence of 3DOM structure can effectively improve the catalytic performance of $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ nanoparticles.

Catalyst	S _{BET} (m²/g)	Ce/Cu ^a	Fe/Cu ^a	O/Cu ^a	NO conversion ^b	TOF (10 ⁻¹ s ⁻¹)
						NO + CO (150
						°C) ^c
3DOM	20	166	2.69	27.52	40 840/	0.837
$Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$	39	4.00	2.08	21.32	49.0470	0.837
Bulk	14	2 16	1 47	10.41	10.069/	0.412
$Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$	14	2.10	1.4/	10.41	19.00%	0.412

Table S1 Surface compositions and CO-SCR activity data of catalysts.

^a The atom ratio of Ce/Cu, Fe/Cu and O/Cu determined by XPS analysis.

^b The value of NO conversion corresponds to the value of conversion at 150 °C in Figure 2.

^c Gas composition: 5% NO and 10% CO (He as residual gas), the gas flow rates of NO and CO are 10 mL/min, respectively.



Figure S1. NO conversion of 3DOM $Ce_{0.7}Fe_{0.3}O_2$ and 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ (A); NO conversion under normal conditions and dilution conditions of high-purity He at different flow rates (B); NO conversion over the catalyst 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ at different SV= 45000, 90000, 225000 mL/(g·h) (C).

Catalyst	Reaction gas	Space velocity	Catalytic activity	Reference	
	ratio (CO:NO)		T ₅₀		
$Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$	2:1	00000 m L a-l h-l	150 °C	This work	
		90000 mL·g ··n ·	$(90\% \text{ NO} \rightarrow \text{N}_2\text{O})$	THIS WOLK	
	1:1	36000 h ⁻¹	235 °C	Ampl Sumf Sei 2010 462 425 444	
Cu/CeO_2			(80% NO→N ₂ O)	Appl. Surl. Sci. 2019, 463, 435-444	
	2:1	40000 h ⁻¹	83 °C	Chinese I. Cotal 2019, 20, 729, 725	
$CuO-CeO_2$			(90% NO→N ₂ O)	Chinese J. Catal. 2018, 39, 728-735	
CuACoN/CuNCoA	2:1	12000	210 °C	I Calleid Interf Sei 2019 500 224 24	
		$12000 \text{ mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$	(80% NO→N ₂ O)	J. Colloid. Interf. Sci. 2018, 509, 334-345	
0.6Cu/0.1SmAl	2:1	24000 mL \cdot g ⁻¹ \cdot h ⁻¹	290 °C	I Mal Catal A: Cham 2016 420 24 4	
			(n.m)	J. Mol. Catal. A. Chem. 2016, 420, 34-44	
	2:1	24000 mL \cdot g ⁻¹ \cdot h ⁻¹	290 °C	Annal Starf Soil 2017 426 270 286	
CuCeAI-SI			(87% NO→N ₂ O)	Appl. Surl. Sci. 2017, 426, 279-286	
	2:1	20000 h-1	110 °C	Appl. Catal. B: Environ. 2018, 239, 485-	
Cu ₄ /CF		30000 h ⁻¹	(90% NO→N ₂ O)	501	
CCA800	2:1	12000 h-1	185 °C	Evel 2018 224 206 204	
		12000 h ⁻¹	$(70\% \text{ NO} \rightarrow N_2\text{O})$	Fuel. 2018, 234, 290-304	
0.016MnFeCu	2:1	150000 mJ and had	200 °C	ACS Appl. Mater. Interf. 2018, 10, 40509-	
		130000 mL·g ··n ·	$(55\% \text{ NO} \rightarrow \text{N}_2\text{O})$	40522	
	1:1	80000 h ⁻¹	100 °C	CI	
Cu_5Pa/AI_2O_3			$(50\% \text{ NO} \rightarrow N_2\text{O})$	Cnem. Sci. 2019, 10, 8292-8298	

Table S2 Com	parison of CO	-SCR activity betwe	en 3DOM Ceo 7Fe	$e_0 \sim C u_0 + O_2 c_0$	atalyst and other	catalysts
	pullison of CO	DOIL double of the		$u_0 2 C u_0 1 C 2 C$	ataryst and other	cuturysts.

n.m.: Not mentioned.



Figure S2. SEM images of 3DOM $Ce_{0.7}Fe_{0.2}M_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalysts; $Ce_{0.8}Fe_{0.2}O_2(a), Ce_{0.7}Fe_{0.2}Mn_{0.1}O_2(b), Ce_{0.7}Fe_{0.2}Co_{0.1}O_2(c), Ce_{0.7}Fe_{0.2}Ni_{0.1}O_2(d), Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2(c)$ (e), and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2(f)$.



Figure S3. SEM image of PMMA microsphere template.



Figure S4. The EDS element-mapping images of Ce (pink), Fe (red), Cu (green) and O (blue) in 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ catalyst.



Figure S5. The CO oxidation activity test of 3DOM $Ce_{0.7}Fe_{0.2}M_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalysts.

In addition to CO-SCR reaction, a series of samples are also used for CO catalytic oxidation. The results are shown in Figure S5. All 3DOM catalysts have no catalytic activity at relatively low temperatures (50 °C). At the same time, it can be seen that the catalytic activity of 3DOM $Ce_{0.7}Fe_{0.2}M_{0.1}O_2$ (M =Mn, Co, Ni) catalyst is basically the same as that of $Ce_{0.8}Fe_{0.2}O_2$, demonstrating that the introduction of these elements has no effect on the improvement of activity. On the contrary, when Cu is introduced into $Ce_{0.8}Fe_{0.2}O_2$, 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalysts obviously promote CO oxidation, especially 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$, and it has the highest catalytic activity in the whole temperature range.



Figure S6. The cycle test of 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ catalyst.



Figure S7. The results of NO conversion (A), XRD (B), Raman (C), Cu2p (D) and O1s (E) in the two states of 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalyst (after cycle test (a); after cycle test and then oxidized in air at 700 °C for 1 h (b)).

We also carry out cyclic tests on the optimum catalyst because the recycling of

catalysts is very important. It can be seen from Figure S6 that the catalytic performance at lower temperatures decreases significantly, but the catalytic activity is not completely inactivated. And the negative effect is not obvious with the increase of temperature.

In order to explore the cause of the deactivation of the cycle test and the method of improving the cycle stability of the catalyst, we implement a certain characterization analysis of the two states of 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ catalyst (after cycle test (a); after cycle test and then oxidized in air at 700 °C for 1 h (b)), and this oxidation process is expected to improve the deactivation of the catalyst. The partial deactivation of the 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ catalyst after the cycle test may be related to the reduction of copper species to Cu⁰ in such a strong reduction environment, which is also consistent with the Cu2p results (Figure S7(D)). It can also be seen from the XRD and Raman results (Figure S7(B-C)) that the active species of the inactivated sample is obviously the coexistence of the main phase CeO₂ and the secondary phase CeFeO₃. After the oxidation process, it is obvious that this only improves the activity of the catalyst at the medium temperature stage, but it does not have much effect on the low temperature activity (Figure S7(A)). And CeFeO₃ phase disappears, combining with Raman and Cu2p, it can be known that the Cu⁰ on the surface and Fe form $CuFe_2O_4$ spinel. It is worth mentioning that the bands appearing at 219 cm⁻¹, 290 cm⁻¹, 339 cm⁻¹, 460 cm⁻¹, 643 cm⁻¹ and 688 cm⁻¹ are assigned as $T_{2g}(1)$, Eg(1), Eg(2), $T_{2g}(2)$, $A_{1g}(2)$ and $A_{1g}(1)$ modes of the CuFe₂O₄ spinel phase. Obviously, the active species at this time is composed of the main phase CeO2 and the highly dispersed second phase CuFe₂O₄, and the presence of the latter is conducive to the improvement of activity in the middle temperature range. The low-temperature activity has not been improved, which may be related to the phase change of the catalyst and the large amount of carbonate on the catalyst surface occupying the active site. The high stability of these carbonates can be reflected in the in situ DRIFTS analysis, which is obviously different from nitrates in that it is stable at 500 °C. It can also be seen that $(O_{\beta+\gamma})/(O_{\alpha+\beta+\gamma})$ has not been effectively increased (Table S3). In addition, the shift of O_{α} in O1s may also be related to the oxidation of Cu⁰, which further promotes the generation of CuFe₂O₄ (Figure S7(E)). These results once again prove that the presence of a large number of Cu⁺ species is propitious to the improvement of low-temperature activity, and the conversion of active species and the occupation of active sites by carbonates in the strongly reducing environment of the



reaction prevent the activity from returning to the initial state after the cycle test.

Figure S8. The activity stability test (A), H_2O resistance test (B), SO_2 resistance test (C) and (D) H_2O and SO_2 resistance test over 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalyst at 350 °C, FESEM image after activity stability test (E).



Figure S9. The results of DRIFTS (A), XRD (B), Raman (C), Cu2p (D) and O1s (E) in the two states of 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ catalyst (before SO₂ resistance test (a); after SO₂ resistance test (b)).

Moreover, the stability of catalytic activity is the key factor for its catalytic

application. Hence, we further test the optimum catalyst (3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$) in the prepared catalyst by significantly increasing SV at 350 °C to avoid the activity saturation. Figure S8(A) displays the corresponding catalytic performance curve of 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalyst at a high SV. It can be clearly observed that the increase of SV from 90000 to 225000 mL/(g·h) leads to a slight decrease in NO conversion and N₂ yield, which decreases by only about 10% at 350 °C. Meanwhile, there is little change in N₂ and N₂O selectivity. This also confirms that 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalyst has excellent catalytic activity at both low and high space velocities. Furthermore, the NO conversion drops only 2% during the 6 h test, which indicates that 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalyst has good activity stability. Simultaneously, from the FESEM image of 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ after the activity stability test, it can be found that the catalyst is slightly agglomerated, but its morphology is not much affected, indicating that the 3DOM structure also has a certain degree of stability (Figure S8(E)).

As is known to all, H₂O and SO₂ have important effects on the catalytic performance of catalyst. Meanwhile, since the NO conversion of 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ catalyst is 100% in the temperature range of 350-700 °C, H₂O (10%) and SO₂ (500 ppm) resistance tests are carried out at 350 °C to avoid the influence of excessive high temperature on H₂O. When H₂O is introduced (Figure S8(B)), it is clear that the catalyst is hardly affected. Figure S8(C) shows the results of catalytic performance over 3DOM Ce_{0.7}Fe_{0.2}Cu_{0.1}O₂ catalyst in the presence of SO₂. When SO₂ is added, the NO conversion of the catalyst decreases from 100% to 40% and tends to be stable. After removing SO₂ from the reaction gas, the NO conversion increases slightly and recovers to 43%. When the reaction temperature is raised to 375 °C, the NO conversion can be restored to 100%, and then slightly decreased to 95% when the reaction temperature is cooled to 350 °C. At the same time, the existence of SO2 at this temperature (350 °C) makes NO not completely converted to N₂, but partly to N_2O . When H_2O and SO_2 are added to the reaction gas at the same time (Figure S8(D)), the results are basically similar to Figure S8(C), except that the decline is slightly greater. The results show that SO₂ has a great influence on the catalyst, but it is easy to be affected by temperature changes and will not be permanently deactivated.

In order to further clarify the effect of SO_2 , the catalyst before and after SO_2 tolerance test at 350 °C are also tested by DRIFTS, XRD, Raman, and XPS. As exhibited in Figure S9(A), it can be seen that a wide band appears in the range of 900-

1300 cm⁻¹ after sulfur resistance test, which is caused by the overlap of a series of bands at 981, 1054, 1123 and 1204 cm⁻¹, and these bands belong to sulfate species.² The results show that a large amount of sulfate specie is deposited on the catalyst surface after SO₂ tolerance test, which obviously affects the reaction of reaction gas on the catalyst surface, thus leading to deactivation of the catalyst to a certain extent. It can be seen from Figure S9(A) and S9(B) that the SO₂ tolerance test does not have much effect on the CeO₂ main phase. It can be seen from the oxidation of Cu in Cu2p (Figure S9(C)) that the addition of SO₂ inhibits the reduction of CO and promotes the formation of sulfate, which in turn occupies a large number of active sites leading to a significant reduction in catalytic activity. Although $(O_{\beta+\gamma})/(O_{\alpha+\beta+\gamma})$ can be found to increase significantly after the SO₂ tolerance test (Table S3), due to the lack of active sites for the CO-SCR reaction, there is no improvement in catalytic activity. Hence, the influence of SO₂ on the catalyst is greater than that of H₂O, mainly because of the reduction of active sites due to the deposition of large amounts of sulfate.

Catalyst	Surfac	e O	Lattice O	ratio ^a
	$O_{\beta}(O^{-}/O_{2}^{2-})$ (%)	$O_{\gamma}(O_{2})$ (%)	$O_{\alpha}(O^{2-})$ (%)	
3DOM Ce _{0.7} Fe _{0.2} Cu _{0.1} O ₂ (350°C: NO+CO)	29.1	4.4	66.5	0.335
3DOM Ce _{0.7} Fe _{0.2} Cu _{0.1} O ₂ (350°C: NO+CO+SO ₂)	48.3	5.6	46.1	0.539
3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ (After cycle test)	26.5	4.8	68.7	0.313
3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ (Oxidized at 700 °C for 1 h)	30.6	5.3	64.1	0.359

Table S3 The chemical composition of 3DOM $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalyst under different conditions.

^a Ratio of surface adsorbed oxygen and surface total oxygen.



Figure S10. The in situ DRIFT spectra of NO adsorption (5%) over 3DOM $Ce_{0.7}Fe_{0.2}M_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalysts as a function of temperature; $Ce_{0.8}Fe_{0.2}O_2$ (A), $Ce_{0.7}Fe_{0.2}Mn_{0.1}O_2$ (B), $Ce_{0.7}Fe_{0.2}Co_{0.1}O_2$ (C), $Ce_{0.7}Fe_{0.2}Ni_{0.1}O_2$ (D) and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ (E).



Figure S11. The in situ DRIFT spectra of CO and NO adsorption (10% and 5%, respectively) over 3DOM $Ce_{0.7}Fe_{0.2}M_{0.1}O_2$ and bulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ catalysts as a function of temperature; $Ce_{0.8}Fe_{0.2}O_2(A)$, $Ce_{0.7}Fe_{0.2}Mn_{0.1}O_2(B)$, $Ce_{0.7}Fe_{0.2}Co_{0.1}O_2(C)$, $Ce_{0.7}Fe_{0.2}Ni_{0.1}O_2$ (D)andbulk $Ce_{0.7}Fe_{0.2}Cu_{0.1}O_2$ (E).

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