

# Effect of Cesium Modification on CuO/CeO<sub>2</sub> Catalysts for the Catalytic Decomposition of N<sub>2</sub>O

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**Abstract** A series of Cs-modified CuO/CeO<sub>2</sub> mixed oxide catalysts was prepared for enhancing the stable activity of N<sub>2</sub>O decomposition. It was found that Cs modification promoted the catalytic performance of CuO/CeO<sub>2</sub> catalysts significantly. The 1%Cs-CuO/CeO<sub>2</sub> catalyst exhibited the best activity, and the conversion of N<sub>2</sub>O reached 100% at 380 °C in the presence of 2% O<sub>2</sub>. The catalytic behaviors were investigated by means of XRD, N<sub>2</sub> adsorption isotherms, XPS, H<sub>2</sub>-TPR (TPR: temperature-programmed reduction), CO-IR, O<sub>2</sub>-TPD (TPD: temperature-programmed desorption) and diffused reflectance infrared Fourier transform spectroscopy (DRIFTS). The results revealed that Cs modification promoted the activity and the oxygen resistance by enhancing the desorption of surface oxygen species and increasing the content of Ce<sup>3+</sup>. CO-DRIFTS revealed that Ce<sup>3+</sup> could efficiently facilitate the regeneration of active Cu<sup>+</sup> sites by an oxygen migration step. The possible reaction mechanism was also discussed.

**Keywords** Cs-Modified CuO/CeO<sub>2</sub>; N<sub>2</sub>O decomposition; Reaction mechanism

## 1 Introduction

Nitrous oxide (N<sub>2</sub>O) is a major greenhouse gas with a long lifetime of approximately 150 years in the atmosphere. The global warming potential (GWP) of N<sub>2</sub>O is 310 times higher than CO<sub>2</sub><sup>[1,2]</sup>. Furthermore, it contributes to stratospheric ozone depletion<sup>[3]</sup>. The concentration of N<sub>2</sub>O in the atmosphere has been increasing recently mainly because of human activities, particularly chemical manufacturing. Thus, it is urgent to develop efficient methods for N<sub>2</sub>O removal from industrial exhaust gases. Considering efficiency and cost, direct catalytic N<sub>2</sub>O decomposition technology is a superior choice.

Various types of catalysts have been investigated to promote N<sub>2</sub>O degradation, such as noble metals<sup>[3–5]</sup>, metal oxides<sup>[6–8]</sup>, and zeolites<sup>[9–11]</sup>. Among them, Ce-based mixed metal oxides have a great advantage because of low cost and excellent catalytic activity. They have been widely applied for N<sub>2</sub>O decomposition in forms, such as CuCe, NiCe and FeCe catalysts<sup>[12–18]</sup>.

In our previous work, CuCe mixed oxide catalysts exhibited high efficiency for N<sub>2</sub>O decomposition<sup>[13]</sup>, and we also revealed that Cu<sup>+</sup> is the active site. The desorption of generated oxygen was considered as the rate-determining step for N<sub>2</sub>O decomposition:  $2\text{Cu}^{2+}\text{-O} \longrightarrow 2\text{Cu}^{+} + \text{O}_2$ . Zabitskiy *et al.*<sup>[16,17]</sup> synthesized various CuO/CeO<sub>2</sub> catalysts with different nano-CeO<sub>2</sub> supports and proposed another pathway, in which Ce<sup>3+</sup> participated in the regeneration of the active Cu<sup>+</sup> sites:  $\text{Cu}^{2+}\text{-O} + \text{Ce}^{3+} \longrightarrow \text{Cu}^{+} + \text{Ce}^{4+}\text{-O}$ . Konsolakis *et al.*<sup>[18]</sup> investi-

gated the catalytic decomposition of N<sub>2</sub>O over CuO-CeO<sub>2</sub> catalysts prepared by different synthesis routes, and coprecipitation was found to be the best route. However, few of the CuCe mixed oxide catalysts were effective enough for commercial application because their activities were severely inhibited by other gases, such as O<sub>2</sub><sup>[15–18]</sup>. Therefore, the issue of activity improvement and oxygen resistance should be solved promptly.

Alkali doping was found to be an efficient method to improve the activity of N<sub>2</sub>O decomposition over single-metal oxide catalysts (CuO, NiO and Co<sub>3</sub>O<sub>4</sub>)<sup>[18–22]</sup>. It was revealed that alkali modification improved the reducibility of the transition metal and enhanced the regeneration of active sites. Additionally, Cs showed the best promotion effect among alkali metals<sup>[23]</sup>. To the best of our knowledge, there is little research on the effect of alkali modification over CuO/CeO<sub>2</sub> mixed metal oxide catalysts. Furthermore, the reaction pathway of N<sub>2</sub>O decomposition over CuO/CeO<sub>2</sub> catalysts is inconsistent<sup>[13–18]</sup>.

In the present work, Cs modification was applied to improve the activity and oxygen resistance of the CuO/CeO<sub>2</sub> catalyst. The effects of Cs promotion and a possible reaction pathway were also discussed.

## 2 Experimental

### 2.1 Materials

CuO/CeO<sub>2</sub> was prepared by the citric acid method<sup>[13]</sup>, and

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a series of Cs-modified CuO/CeO<sub>2</sub> catalysts with Cs of 0, 0.25%, 0.5%, 1.0%, 2.0% and 4.0%(molar fraction) were prepared by the impregnation method<sup>[19]</sup>. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and citric acid(1:1:4, molar ratio) were dissolved in water under continuous stirring. An amorphous precursor was acquired after the solution was dried at 80 °C overnight, then dried at 120 °C for 6 h. The precursor was calcined at 550 °C for 4 h to acquire the mixed oxide. Cs-modified CuO/CeO<sub>2</sub> catalysts were obtained by impregnation with an aqueous solution of CsNO<sub>3</sub>·H<sub>2</sub>O. The samples were dried at 120 °C, then the catalysts were calcined at 550 °C for 4 h in air. The Cs to (Cu+Ce) molar ratio was varied from 0 to 4.0%, and the catalysts were denoted as y%Cs-CuO/CeO<sub>2</sub>(y=0.25—4).

## 2.2 Characterization

A Bruker D8 powder X-ray diffractometer was operated at 40 kV and 40 mA to record XRD patterns. The patterns were taken over a 2θ range from 10° to 80° with a step size of 0.02°. The surface areas of the BET model were measured on a Micromeritics TRISTAR 3000 apparatus. XPS results were recorded on a Perkin Elmer PHI5000C system, and the binding energy was calibrated by the carbonaceous C<sub>1s</sub> line(284.6 eV).

A Micromeritics AutoChem II 2920 equipped with a TCD detector was used to obtain the H<sub>2</sub>-TPR(TPR: temperature-programmed reduction) data. A sample of 0.05 g was pretreated in He at 200 °C for 1 h and cooled to 25 °C. Next, the sample was reduced in H<sub>2</sub>/Ar(5% H<sub>2</sub>, volume fraction) with a heating rate of 10 °C/min. O<sub>2</sub>-TPD(TPD: temperature-programmed desorption) was also carried out on the AutoChem II 2920. Samples were pretreated in a helium stream at 400 °C for 1 h, and then an O<sub>2</sub>-He mixture(5% O<sub>2</sub>, volume fraction) was introduced into the reactor for 1 h after cooling down to 30 °C in helium. Afterwards, the samples were heated to 600 °C in helium to analyze the effluent gases.

The CO-IR and diffused reflectance infrared Fourier

transform spectroscopy(DRIFTS) were carried out on an FTIR(Nicolet 6700) spectrometer. For CO-DRIFTS, samples were pretreated under corresponding conditions, then cooled down to 50 °C in He flow. Spectra were collected after the 1% CO-He mixture had been introduced into the system for 30 min. For *in situ* N<sub>2</sub>O-DRIFTS, spectra were collected after the samples had reacted with 2600 μL/L N<sub>2</sub>O-He mixture at various temperatures for 1 h.

## 2.3 Activity Tests

An automated 8-flow reactor system was used to evaluate activities for N<sub>2</sub>O catalytic decomposition. Approximately 250 mg of catalyst(40—60 mesh) was packed in the middle part of a quartz reactor. The sample was pretreated in helium at 400 °C for 1 h and then cooled down to 260 °C. The activity was tested in a gas mixture(2600 μL/L N<sub>2</sub>O in He) with a gas flow of 60 mL/min(GHSV=19000 h<sup>-1</sup>). The products were analyzed by a Finnigan Trace GC Ultra. The activity tests under an O<sub>2</sub>-containing atmosphere were carried out under the same conditions, except for an extra 2% O<sub>2</sub> in the reaction gas.

## 3 Results and Discussion

### 3.1 Textural Properties of Cs-Modified CuO/CeO<sub>2</sub> Catalysts

XRD patterns of Cs-modified CuO/CeO<sub>2</sub> catalysts are shown in Fig.S1(see the Electronic Supplementary Material of this paper). There were no Cs species(Cs<sub>2</sub>O, CsOH) observed, indicating that the Cs species were well-dispersed on the surface. The average crystal sizes and specific surface areas of the Cs-modified CuO/CeO<sub>2</sub> catalysts are listed in Table 1. It was found that both the crystal size and the surface area of the mixed oxides changed little, indicating that the effect of Cs modification on phase and morphology was slight.

**Table 1 Textural properties of the Cs-modified CuO/CeO<sub>2</sub> catalysts**

Catalyst	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	Size of CuO <sup>a</sup> /nm	Size of CeO <sub>2</sub> <sup>b</sup> /nm	H <sub>2</sub> uptake of peak $a/(\text{mmol} \cdot \text{g}^{-1})$	Area of Cu <sup>+</sup> -CO <sup>c</sup> /a.u.	$n(\text{Cs})/n(\text{Cu}+\text{Ce})^d$	Ce <sup>3+</sup> (%)	Concentration of surface oxygen <sup>e</sup> (μmol·g <sup>-1</sup> )	Reaction rate <sup>f</sup> (μmol·s <sup>-1</sup> ·g <sup>-1</sup> )
CuO/CeO <sub>2</sub>	34	27	11	2.00	15.6	—	13.2	277	18.9
0.25%Cs-CuO/CeO <sub>2</sub>	36	28	10	3.01	17.8	—	15.7	286	35.6
0.5%Cs-CuO/CeO <sub>2</sub>	40	29	10	3.34	19.5	0.004	19.0	364	87.6
1%Cs-CuO/CeO <sub>2</sub>	34	31	10	1.10	10.2	0.009	26.5	413	132.9
2%Cs-CuO/CeO <sub>2</sub>	28	30	10	0.59	7.7	0.022	23.3	336	51.2
4%Cs-CuO/CeO <sub>2</sub>	32	28	11	0.35	5.0	0.048	16.7	289	44.2

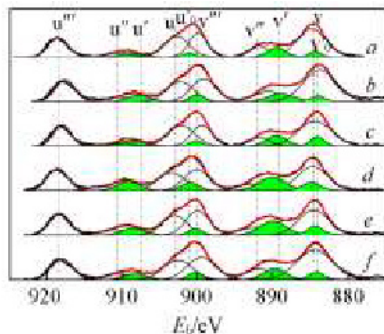
*a.* Calculated from the CuO phase(2θ=35.4°) by Scherrer's equation; *b.* calculated from the CeO<sub>2</sub> phase(2θ=28.5°) by Scherrer's equation; *c.* areas of the IR peak of Cu<sup>+</sup>-CO at 2100 cm<sup>-1</sup>; *d.* calculated from XPS analysis; *e.* calculated from the peak area of O<sub>2</sub>-TPD; *f.* calculated at 300 °C.

It has been reported that small amounts of alkali ions can stabilize lower valence states<sup>[20,21]</sup>. XPS experiments were conducted to obtain information on the valence states of Cu and Ce. Fig.S2(see the Electronic Supplementary Material of this paper) exhibits the Cu<sub>2p</sub> spectra obtained from catalysts with various Cs contents. The peaks at a binding energy of 934.0 eV, assigned to Cu<sub>2p<sub>3/2</sub></sub>, barely changed, indicating that Cu mainly existed in the form of Cu<sup>2+</sup> and was not influenced by Cs modification<sup>[13]</sup>.

Fig.1 shows the XPS spectra of Ce<sub>3d</sub>. According to the reported data<sup>[24,25]</sup>, peaks labeled v, v'' and v''' are attributable to

the Ce<sub>3d<sub>5/2</sub></sub> photoelectron emission of Ce<sup>4+</sup>, while peaks labeled u, u'' and u''' are due to the Ce<sub>3d<sub>3/2</sub></sub> of Ce<sup>4+</sup>. Peaks labeled v', v'<sub>0</sub> and u', u'<sub>0</sub>(green color-filled curves) are attributable to the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> electrons of Ce<sup>3+</sup>, respectively. The Ce<sup>3+</sup> percentages of various Cs-modified CuO/CeO<sub>2</sub> were calculated from the corresponding peak areas(the green area/the whole area) and have been listed in Table 1. The Ce<sup>3+</sup> percentage significantly increased with the modification of Cs, and 1%Cs-CuO/CeO<sub>2</sub> contained the highest Ce<sup>3+</sup> percentage, which was almost twice as much as CuO/CeO<sub>2</sub>, indicating that the Cs electron donor had a strong interaction with the CeO<sub>2</sub> and effectively

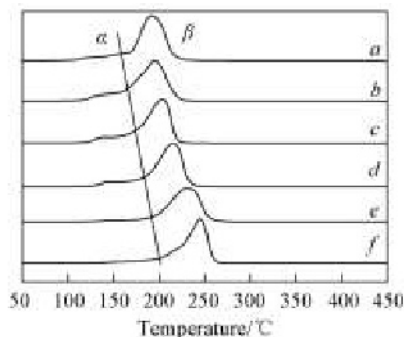
improved the stability of  $Ce^{3+}$ [25]. The increase in  $Ce^{3+}$  content produced more oxygen vacancies, which could enhance oxygen migration. The further increase in Cs content led to the decrease of  $Ce^{3+}$ , probably due to the inhibiting counter effect as reported[21].



**Fig.1 XPS spectra of  $Ce_{3d}$  obtained on Cs-modified  $CuO/CeO_2$  catalysts**

a.  $CuO/CeO_2$ ; b. 0.25%Cs- $CuO/CeO_2$ ; c. 0.5%Cs- $CuO/CeO_2$ ;  
d. 1%Cs- $CuO/CeO_2$ ; e. 2%Cs- $CuO/CeO_2$ ; f. 4%Cs- $CuO/CeO_2$ .

The reducibility change caused by Cs modification was visualized by  $H_2$ -TPR(Fig.2). According to previous works[15,16,26], the peaks from 100 °C to 300 °C related to the reduction of various  $CuO$  species; peak  $\alpha$  corresponded to the reduction of highly dispersed  $CuO$  that had a strong synergic effect with  $CeO_2$ , and this  $CuO$  species was regarded as the main active site[13,15]; peak  $\beta$  corresponded to the reduction of larger  $CuO$  clusters or bulk  $CuO$ , which had weak or no interactions with  $CeO_2$ . The  $H_2$  consumption of peak  $\alpha$  is shown in Table 1. We found that the addition of Cs slightly influenced the strong effect between  $CuO$  and  $CeO_2$ . With the increase in Cs content, the area of peak  $\alpha$  increased at first and the reduction temperatures of both peaks did not change until the Cs content reached 0.5%, indicating the improvement of reducibility by Cs modification. However, the area of peak  $\alpha$  decreased dramatically, and peak  $\beta$  shifted to a higher temperature upon excessive Cs loading. This indicated a decrease of reducibility because excessive Cs could migrate to the  $Cu$  surface, leading to reduction-inhibiting effects[27].

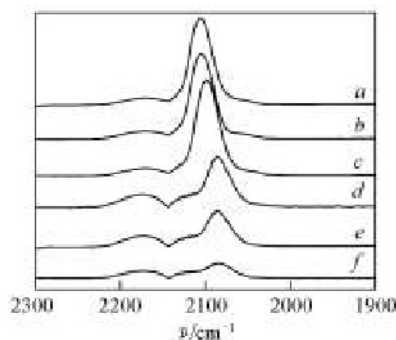


**Fig.2  $H_2$ -TPR profiles of Cs-modified  $CuO/CeO_2$  catalysts**

a.  $CuO/CeO_2$ ; b. 0.25%Cs- $CuO/CeO_2$ ; c. 0.5%Cs- $CuO/CeO_2$ ;  
d. 1%Cs- $CuO/CeO_2$ ; e. 2%Cs- $CuO/CeO_2$ ; f. 4%Cs- $CuO/CeO_2$ .

Previous works[13,15–18] revealed that the catalytic decomposition of  $N_2O$  over  $Cu-Ce$  mixed oxide catalysts took place on  $Cu^+$  sites. IR was used as a powerful method to detect and measure the number of  $Cu^+$  active sites[13,16]. Fig.3 exhibits the

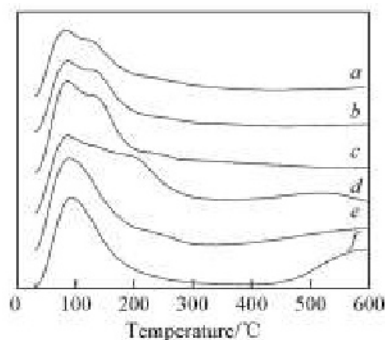
$CO$ -IR spectra of Cs-modified  $CuO/CeO_2$  catalysts at 50 °C after being heated in He at 400 °C for 1 h. The peaks at approximately 2080  $cm^{-1}$  are related to  $Cu^+-CO$ [13,16], and the peak areas are listed in Table 1. It was found that the amount of  $Cu^+$  increased at first with the addition of Cs and reached a maximum level at 0.5%Cs- $CuO/CeO_2$ , then decreased with higher Cs content. The amount of  $Cu^+$  was proportional to the  $H_2$  consumption of peak  $\alpha$ , suggesting that the active  $Cu^+$  came from the reduction of highly dispersed  $CuO$ , which had a strong synergic effect with  $Ce^{16}$ . However, the peak area increased by only 25% at maximum, meaning the promotion effect on the amount of  $Cu^+$  by Cs modification was fairly limited.



**Fig.3 IR spectra recorded of adsorbed  $CO$  on Cs-modified  $CuO/CeO_2$  catalysts**

a.  $CuO/CeO_2$ ; b. 0.25%Cs- $CuO/CeO_2$ ; c. 0.5%Cs- $CuO/CeO_2$ ;  
d. 1%Cs- $CuO/CeO_2$ ; e. 2%Cs- $CuO/CeO_2$ ; f. 4%Cs- $CuO/CeO_2$ .

It is well-known that  $O_2$  desorption is the rate-limiting step in  $N_2O$  decomposition, and more  $Ce^{3+}$  is generally considered to promote this step[2,3,13–18]. Thus, temperature-programmed desorption (TPD) of  $O_2$  was carried out to investigate the character change of  $CeO_2$  by Cs modification (shown in Fig.4). According to previous works[28,29], the peaks at 100 and 140 °C corresponded to the surface  $O_2$  molecule species, and the peak at approximately 220 °C was assigned to the surface oxygen atom. Both the surface oxygen species were considered to correlate with the activity of  $N_2O$  decomposition. Additionally, the lattice oxygen from  $CeO_2$  would desorb at approximately 450 °C. The addition of Cs shifted the surface atom oxygen peak toward lower temperatures and resulted in a massive increase in the peak area (Table 1), indicating that the Cs promoter enhanced the oxygen mobility effectively. The maximum surface-active oxygen was observed with the 1%Cs- $CuO/CeO_2$



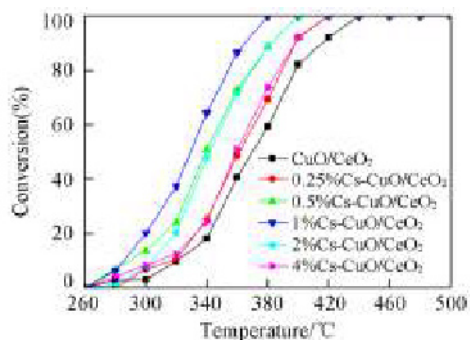
**Fig.4  $O_2$ -TPD profiles of Cs-modified  $CuO/CeO_2$  catalysts**

a.  $CuO/CeO_2$ ; b. 0.25%Cs- $CuO/CeO_2$ ; c. 0.5%Cs- $CuO/CeO_2$ ;  
d. 1%Cs- $CuO/CeO_2$ ; e. 2%Cs- $CuO/CeO_2$ ; f. 4%Cs- $CuO/CeO_2$ .

catalyst.

### 3.2 Catalytic Performance

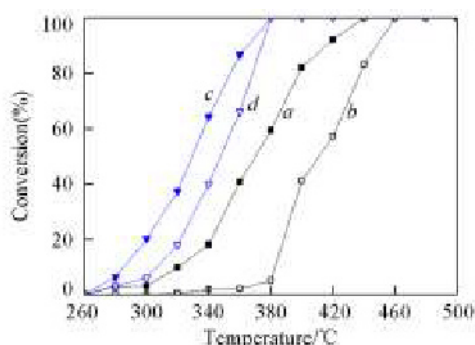
The catalytic performances of the catalysts with different Cs contents for N<sub>2</sub>O decomposition are shown in Fig.5, and the reaction rates are listed in Table 1. The selectivity for generating N<sub>2</sub> and O<sub>2</sub> was 100%. It was found that the activity for N<sub>2</sub>O decomposition was drastically enhanced by Cs modification. It was also found that the activity was related to the content of Ce<sup>3+</sup>, as the 1%Cs-CuO/CeO<sub>2</sub> with the highest Ce<sup>3+</sup> percentages showed the best performance, and complete conversion of N<sub>2</sub>O was achieved at 380 °C. A further increase in the Cs content resulted in a decrease in the activity, which was also observed over alkali-doped Co<sub>3</sub>O<sub>4</sub> catalysts and NiO catalysts<sup>[19,20]</sup>.



**Fig.5 Conversion of N<sub>2</sub>O over different Cs-modified CuO/CeO<sub>2</sub> catalysts**

Conditions: 2600 μL/L N<sub>2</sub>O, balance He, 0.3 MPa, GHSV: 19000 h<sup>-1</sup>.

To evaluate the effect of Cs modification on oxygen resistance, the conversion of N<sub>2</sub>O over CuO/CeO<sub>2</sub> and 1%Cs-CuO/CeO<sub>2</sub> at different reaction conditions is shown in Fig.6. It is obvious that Cs modification exhibited a great promotion effect on oxygen resistance. The conversion of N<sub>2</sub>O reached 100% in the presence of O<sub>2</sub> at 380 °C over 1%Cs-CuO/CeO<sub>2</sub>, but only reached 5% over CuO/CeO<sub>2</sub> in the same amount of time.

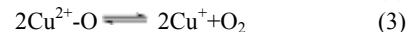
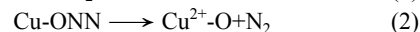
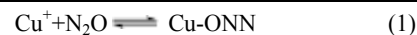


**Fig.6 Conversion of N<sub>2</sub>O over CuO/CeO<sub>2</sub> and 1%Cs-CuO/CeO<sub>2</sub> under different reaction conditions**

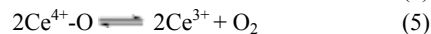
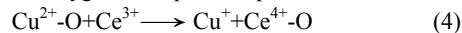
a. CuO/CeO<sub>2</sub>; b. CuO/CeO<sub>2</sub>-O<sub>2</sub>; c. 1%Cs-CuO/CeO<sub>2</sub>; d. 1%Cs-CuO/CeO<sub>2</sub>-O<sub>2</sub>. a, c. 2600 μL/L N<sub>2</sub>O+He; b, d. 2600 μL/L N<sub>2</sub>O+2%O<sub>2</sub>+He.

### 3.3 DRIFTS

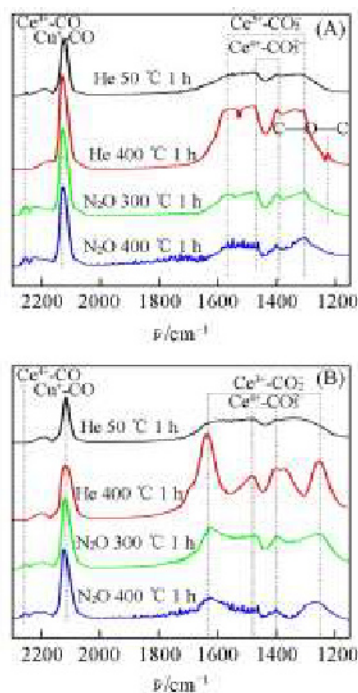
It is commonly believed that N<sub>2</sub>O decomposition over CuO/CeO<sub>2</sub> catalysts mainly proceeds through the following mechanism<sup>[13,16]</sup>:



However, a recent work<sup>[17]</sup> proposed a new reaction pathway with a different oxygen desorption step:



To better understand the relationship between textural properties and catalytic performance, CO-DRIFT was used to investigate the reaction pathway over Cs-modified CuO/CeO<sub>2</sub>. Fig.7 exhibits the CO-DRIFTS of the CuO/CeO<sub>2</sub> and 1%Cs-CuO/CeO<sub>2</sub> through different pretreatments. As shown in Fig.7, the peaks at 2120 and 2270 cm<sup>-1</sup> belonged to the linearly adsorbed Cu<sup>+</sup> and Ce<sup>4+</sup> ions, respectively<sup>[30–32]</sup>, while the signal at 2200 cm<sup>-1</sup> was attributed to gaseous CO. The several peaks in the range from 1200 cm<sup>-1</sup> to 1700 cm<sup>-1</sup> belonged to a monodentate carbonate species (1390 and 1480 cm<sup>-1</sup>) over Ce<sup>4+</sup> and an asymmetrical inorganic carboxylate species (at approximately 1600 and 1280 cm<sup>-1</sup>) over Ce<sup>3+</sup><sup>[30–34]</sup>. The shift of the peaks of asymmetrical inorganic carboxylate should be attributed to the electron donation effect of the Cs modification, which caused a weaker C—O bond. These carbon species were considered the products of a CO disproportionation reaction taking place on Ce<sup>3+</sup> ions, which can be confirmed by the appearance of a coke peak at 1250 cm<sup>-1</sup><sup>[34]</sup>.



**Fig.7 CO-DRIFTS of CuO/CeO<sub>2</sub>(A) and 1%Cs-CuO/CeO<sub>2</sub>(B) in 1% CO-He at 50 °C for 30 min after different pretreatments**

It is obvious that the amounts of Cu<sup>+</sup> and Ce<sup>3+</sup> both increased when heated in He, indicating the desorption of active surface oxygen species. After reaction with N<sub>2</sub>O, the amount of Ce<sup>3+</sup> decreased greatly, and the signal of CO-Ce<sup>4+</sup> appeared over both catalysts, indicating that the Ce<sup>3+</sup> species were oxidized. We noticed that the CeO<sub>2</sub> did not show any activity at 300 °C, and the Ce-N<sub>2</sub>O peak was not detected by *in situ*

N<sub>2</sub>O-DRIFTS(Fig.S3, see the Electronic Supplementary Material of this paper)<sup>[16,32]</sup>. Thus, the oxygen should come from the N<sub>2</sub>O decomposition taking place on Cu<sup>+</sup>, demonstrating the existence of an oxygen migration step[Eq.(4)].

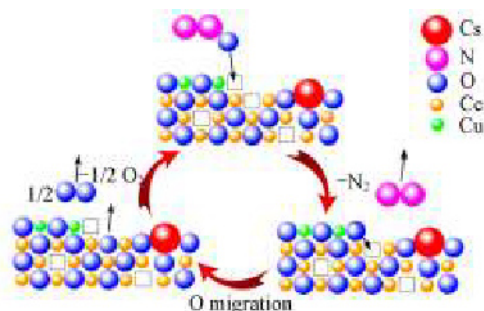
Peak areas of Cu<sup>+</sup>-CO after different pretreatments are shown in Table 2. After a reaction at 300 °C or 400 °C for 1 h, the amount of Cu<sup>+</sup> did not change over that of 1%Cs-CuO/CeO<sub>2</sub>, indicating that the oxygen migration, which regenerates Cu<sup>+</sup> from Cu<sup>2+</sup>-O, can compensate for the loss of Cu<sup>+</sup>. On the contrary, the amount of Cu<sup>+</sup> decreased greatly after a reaction in N<sub>2</sub>O over unmodified CuO/CeO<sub>2</sub>, demonstrating that the oxygen migration step should be the rate limiting step.

**Table 2 Peak areas of Cu<sup>+</sup>-CO after different pretreatments**

Pretreatment	CuO/CeO <sub>2</sub>	1%Cs-CuO/CeO <sub>2</sub>
He, 50 °C for 1 h	8.2	7.3
He, 400 °C for 1 h	15.6	10.2
1% N <sub>2</sub> O, 300 °C for 1 h	14.0	10.4
1% N <sub>2</sub> O, 400 °C for 1 h	12.7	10.1

### 3.4 A Possible Reaction Pathway

Based on previous results, the N<sub>2</sub>O decomposition over Cs-modified CuO/CeO<sub>2</sub> proceeded along the following pathway: N<sub>2</sub>O was reversibly deposited on the active Cu<sup>+</sup> sites[Eq.(1)], then the activated N—O bond broke, released N<sub>2</sub> and oxidized the Cu<sup>+</sup> to Cu<sup>2+</sup>-O[Eq.(2)]. Afterwards, Cu<sup>2+</sup>-O was reduced by Ce<sup>3+</sup>, Cu<sup>+</sup> was regenerated and formed Ce<sup>4+</sup>-O[Eq.(4)], and finally, Ce<sup>4+</sup>—O bonds broke to form O<sub>2</sub>[Eq.(5)] as shown in Scheme 1<sup>[16]</sup>:



**Scheme 1 Possible oxygen migration mechanism over Cs-modified CuO/CeO<sub>2</sub> catalysts**

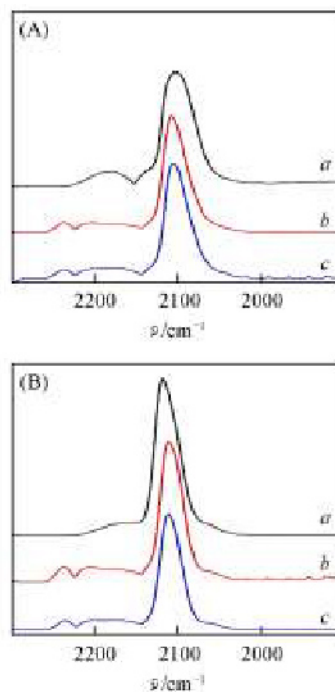
The desorption of generated oxygen was considered as the rate-determining step for N<sub>2</sub>O decomposition, so the Ce<sup>3+</sup> played a key role in the reaction, which was supported by the activity test. Cs modification increased the content of Ce<sup>3+</sup> dramatically, improved the oxygen mobility and provided more migration sites[Eq.(4)]. Furthermore, it stabilized Ce<sup>3+</sup> by the electron-donating effect and contributed to the desorption of O<sub>2</sub>[Eq.(5)]. Thus, the activity was significantly facilitated. The desorption of generated oxygen is the rate-determining step, and it decides the turnover frequency of Cu<sup>+</sup> sites. Thus, the 1%Cs-CuO/CeO<sub>2</sub> with the best ability of oxygen desorption exhibited the highest activity. Excessive Cs loading resulted in the decrease in Cu<sup>+</sup> and Ce<sup>3+</sup>, reducing the number and turnover frequency of active sites, finally leading to a reduction in activity.

### 3.5 Oxygen Inhibition

O<sub>2</sub> is usually present in the N<sub>2</sub>O-containing gas stream, and it is known that O<sub>2</sub> will inhibit the activity of N<sub>2</sub>O decomposition over a catalyst *via* competitive adsorption with N<sub>2</sub>O<sup>[14,19]</sup>. The 1%Cs-CuO/CeO<sub>2</sub> catalyst exhibited a good performance of oxygen resistance, and it is necessary to explore the reason behind this observation.

Fig.S4(see the Electronic Supplementary Material of this paper) shows the *in situ* N<sub>2</sub>O-DRIFTS of 1%Cs-CuO/CeO<sub>2</sub> and CuO/CeO<sub>2</sub> in the presence or absence of O<sub>2</sub>. The peak at approximately 2200 cm<sup>-1</sup> is related to the N<sub>2</sub>O absorbed on Cu<sup>+</sup><sup>[13,16]</sup>. It was found that the competitive adsorption between O<sub>2</sub> and N<sub>2</sub>O existed over both catalysts, and it was barely affected by Cs modification, indicating that competitive adsorption was not the main reason for oxygen inhibition. As discussed above, we proposed that the oxygen migration step is the rate-determining step, and O<sub>2</sub> may affect the reaction by inhibiting this step.

CO-DRIFTS through different reactions are shown in Fig.8. It is obvious that the amount of active Cu<sup>+</sup> sites decreased greatly after the reaction with the presence of oxygen over CuO/CeO<sub>2</sub>, indicating that oxygen migration was certainly inhibited by O<sub>2</sub>. In contrast, the very slight change of Cu<sup>+</sup> over 1%Cs-CuO/CeO<sub>2</sub> indicated an excellent oxygen migration ability, accounting for its great oxygen resistance.



**Fig.8 CO-DRIFTS of 1%Cs-CuO/CeO<sub>2</sub>(A) and CuO/CeO<sub>2</sub>(B) through different reactions**  
a. He; b. 2600 μL/L N<sub>2</sub>O+He; c. 2600 μL/L N<sub>2</sub>O+2%O<sub>2</sub>+He.

## 4 Conclusions

In summary, Cs modification improved stable activity significantly over the CuO/CeO<sub>2</sub> catalysts, and the 1%Cs-CuO/CeO<sub>2</sub> catalyst exhibited the best catalytic performance. CO-DRIFTS revealed that Ce<sup>3+</sup> could efficiently



facilitate the regeneration of active  $\text{Cu}^+$  sites by an oxygen migration mechanism. Cs modification resulted in an increase in  $\text{Ce}^{3+}$  content and a promotion of oxygen desorption, which facilitated the regeneration rate of active  $\text{Cu}^+$  sites, thus improving the catalytic activity and oxygen resistance over  $\text{CuO/CeO}_2$  catalysts for  $\text{N}_2\text{O}$  decomposition.

### Electronic Supplementary Material

Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s40242-019-8295-2>.

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