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Catalytic performance of Ag–Co/CeO$_2$ catalyst in NO–CO and NO–CO–O$_2$ system

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Abstract

A new bimetallic catalyst (Ag–Co/CeO$_2$) was studied for simultaneously catalytic removal of NO and CO in the absence or presence of O$_2$. CeO$_2$ prepared by homogeneous precipitation method was optimized as supports for the active components. The addition of Ag on CeO$_2$ greatly improved the catalytic activities in the lower temperature regions ($\leqslant 300\,°C$), and the introduction of Co on CeO$_2$ increased the activities at higher temperatures ($\geqslant 250\,°C$). The bimetallic Ag–Co/CeO$_2$ catalyst combined the advantages of the corresponding individual metal supported catalysts and showed superior activity due to the synergetic effect. The effect of support, temperature, loading amount, GHSV and oxygen on catalysis was investigated. NO and CO could be completely removed in the temperature range of 200–600 °C at a very high space velocity of 120 000 h^{-1}. No deactivation was observed over 4% Ag–0.4% Co/CeO$_2$ catalyst even after 50 h test.
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1. Introduction

Air pollution caused by release of nitric oxide (NO) and carbon monoxide (CO) from stationary or mobile sources can be effectively controlled using heterogeneous catalysts, especially noble metal supported materials. Among these metals, Rh is the main component in the TWC (three-way catalyst) converter responsible for the elimination of CO and NO. Although Rh performs high activity in this reaction, the presence of O$_2$ decreases its activity even at a high ratio of carbon monoxide to nitric oxide [1,2]. Recently, numerous studies attempt to diminish or replace these noble metals with cheap elements [3–7]. Among these alternatives, copper-containing materials such as copper-exchanged zeolites or supported copper oxide draw much

attention, but the catalytic activities of these catalysts are poor at low temperatures [8–11].

Recent research indicated that there exists silver–oxygen interaction when NO adsorbed on silver surface [12–17]. NO molecular could dissociate on reduced silver catalysts even at room temperature by oxidizing silver atoms and desorbing N$_2$O according to the formula (1) described in Ref. [16]. Lambert and co-workers

$$Ag_s + 2NO_{(g)} \rightarrow Ag_s - O + N_2O(g) \qquad (1)$$
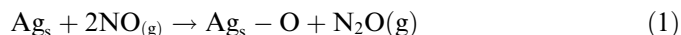
further reported that in the presence of Na, NO was more strongly adsorbed and underwent surface dissociation to yield adsorbed O and N atoms whose subsequent reactions led to the formation N$_2$ and N$_2$O as gaseous products [18,19]. The adsorbed oxygen produced by NO dissociate was strongly bound on silver surface to form different kinds of active oxygen species(O$_\alpha$, O$_\beta$, O$_\gamma$), which have been utilized to catalyze the partial oxidation of methanol [20]. Hence these strongly bound oxygen species formed from NO dissociation may be applied to CO oxidation and the

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catalytic activity of silver superior to copper-containing materials at low temperatures is expected.

Herein, we want to utilize the active oxygen species produced by NO dissociation on silver surface to catalyze CO oxidation at lower temperatures, a novel bimetallic catalyst (Ag–Co/CeO$_2$) was prepared and its catalytic activity was evaluated for the simultaneous catalytic removal of NO and CO in the absence or presence of O$_2$.

2. Experiment

2.1. Catalyst preparation

The support (CeO$_2$) was prepared by three kinds of methods: CeO$_2$(1) was obtained by the calcination of Ce(NO$_3$)$_3$ · 6H$_2$O in air at 500 °C for 3 h; CeO$_2$(2) was synthesized by precipitation method: Ammonia (26–28 wt%) was added to a 0.5 M aqueous solution of Ce(NO$_3$)$_3$ · 6H$_2$O and adjusted pH to 10 at room temperature. The precipitate was filtrated and washed with deionized water to pH < 8, then washed with ethanol and dried at 100 °C overnight, followed by calcination at 500 °C in air for 3 h; CeO$_2$(3) was prepared by homogenous precipitation: 0.3 M urea and 0.05 M Ce(NO$_3$)$_3$ · 6H$_2$O solution were added to a three neck flask equipped with a cooler after stirred for 10 h at 80 °C, white precipitation appeared and the system was heated at 80 °C for additional 2–3 h for aging the precipitation. The following procedure was the same as shown for CeO$_2$(2).

The catalysts were all prepared by impregnation method with the corresponding nitrate salts. Ag was initially impregnated using AgNO$_3$ as the precursor salt, and the sample was dried at 120 °C for over 5 h, and then Co impregnation followed and dried again, catalysts obtained after calcination at 500 °C for 1 h in He atmosphere were denoted as wt% Ag–wt% Co/CeO$_2$ and tested directly.

2.2. Activity measurement

The catalytic activity test was carried out in a fixed-bed flow reactor at atmospheric pressure. Hundred milligram of catalyst (40–60 mesh) was placed in a quartz reactor (i d : 4 mm). Gas feed for the reaction was typically (1) NO: CO = 0.25: 0.25% with He balance, and the total gas flow rate was 20 cm^{3}min^{-1} (space velocity was 30 000 h^{-1}); (2) NO:CO:O$_2$ = 0.25:1.25:0.5% with He balance, and total gas flow rate was 75 cm^3 min^{-1} (space velocity was 120 000 h^{-1}). Before reaction, the catalysts were heated to 500 °C at a heating rate of 15 °C min^{-1} in a He stream and held for 1 h. The gas concentration was analyzed by GC with TCD detector after 25 min reaction at a certain temperature. The catalytic activity was calculated using the following formula:

$$CO_{conv.} = \{([CO]_{in} - [CO]_{out})/[CO]_{in}\} \times 100\% \qquad (2)$$

$$NO_{conv.} = \{2[N_2]_{out}/[NO]_{in}\} \times 100\% \qquad (3)$$

The subscript "in" refers to initial concentration whereas "out" means after reaction, [N$_2$]$_{out}$ refers to the concentration of N$_2$ produced.

2.3. Characterization of catalysts

The BET specific surface areas of CeO$_2$ were determined by N$_2$ adsorption using a Micromeritics ASAP-2010 instrument.

X-ray diffraction (XRD) patterns of CeO$_2$ and Ag/CeO$_2$ catalysts were recorded on a Rigaku Dmax-rA powder diffractometer using Cu Kα radiation with a scan rate of 1.2° min^{-1}.

Temperature programmed reduction (TPR) was performed in an in situ reaction device equipped with a TCD detector using 3% H$_2$ in nitrogen as reducing gas at a flow rate of 50 cm^3 min^{-1}. A 20 mg catalyst was pretreated in He stream at 500 °C for 1 h and then cooled to the room temperature. For TPR measurements, the temperature range investigated was 25–900 °C and the heating rate was 15 °C min^{-1}.

3. Results and discussion

3.1. Properties of CeO$_2$ support

The XRD patterns of CeO$_2$ obtained by three different kinds of preparation methods are shown in Fig. 1. They are all crystal diffraction peaks of pure CeO$_2$ in a fluorite structure and the crystallite sizes calculated from the Debye–Scherrer method are in the range 9–15 nm.

Table 1 shows BET results of CeO$_2$ supports. It is clear that the surface area of CeO$_2$ decreased in the order of CeO$_2$(2) > CeO$_2$(3) > CeO$_2$(1). CeO$_2$ prepared by the direct decomposition of Ce(NO$_3$)$_3$ · 6H$_2$O in air has the lowest surface area of 76.0 m^2 g^{-1}. Comparatively, CeO$_2$ prepared by precipitation method shows the highest surface area of 94.7 m^2 g^{-1}.
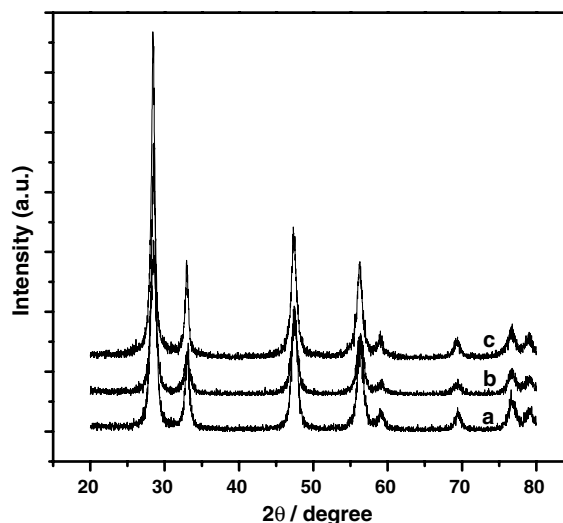

Fig. 1. XRD patterns of (a) CeO$_2$(1), (b) CeO$_2$(2) and (c) CeO$_2$(3).

Table 1
BET specific surface area of three kinds of CeO_2

Sample	BET surface area/m^2g^{-1}
$CeO_2(1)$	76.0
$CeO_2(2)$	94.7
$CeO_2(3)$	84.9

3.2. Interaction between Ag and CeO_2

Seven wt% Ag was impregnated on CeO_2 supports, and the sample's TPR results were shown in Fig. 2. Fig. 2A shows the TPR profiles of $CeO_2(1)$, $CeO_2(2)$ and $CeO_2(3)$. Two reduction peaks, i.e., one peaking around 505–534 °C, the other in the range of 787–817 °C, were observed. The first peak should be assigned to the H_2-reduction of surface oxygen species of CeO_2, and the second one corresponds to the reduction of bulk oxygen by H_2 and formation of lower oxides of cerium [21–23]. Fig. 2B shows the TPR profiles of Ag doped CeO_2. Compared to Fig. 2A, it is clear that the presence of Ag modifies the features of TPR profiles greatly (Fig. 2B(a–c)). By adding Ag on CeO_2, an obvious shift toward lower temperatures is observed for the low temperature signal due to the interaction between silver and ceria, epically on $CeO_2(3)$. While for the second peak, the site almost does not change.

The catalytic activities of 7 wt% Ag/CeO_2 catalysts were evaluated for NO–CO reaction, and the results are shown in Table 2. The presence of silver on CeO_2 greatly enhanced the catalytic activities, especially in the lower temperature regions ($\leqslant300$ °C). Moreover, the "light-off" temperature (the temperature at which NO conversion is over 5%) was decreased apparently by addition of silver, especially on $CeO_2(3)$. The "light-off" temperature for $CeO_2(3)$ was 250 °C, while that for 7 wt% Ag/$CeO_2(3)$ was 100 °C. The results indicate that the catalytic activity for NO–CO reaction was greatly enhanced by addition of Ag on $CeO_2(3)$, especially at lower temperatures.

Combine Fig. 2 with Table 2, we can conclude that the preparation methods of CeO_2 have great effect on the interaction between Ag and CeO_2. Higher catalytic activities
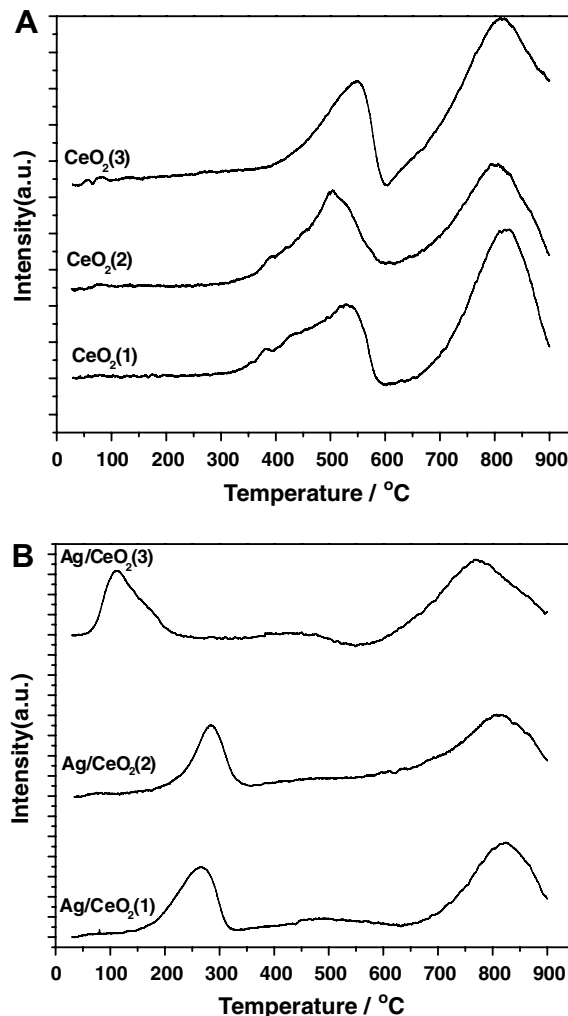

Fig. 2. H_2-TPR spectra of CeO_2 supports (A) and Ag/CeO_2 catalysts (B) pretreated in He stream at 500 °C for 1 h.

Table 2
The activity of CeO_2 and Ag/CeO_2 for NO reduction with CO

T (°C)	Conversion (%)											
	Catalyst											
	$CeO_2(1)$		Ag/$CeO_2(1)$		$CeO_2(2)$		Ag/$CeO_2(2)$		$CeO_2(3)$		Ag/$CeO_2(3)$	
	NO	CO	NO	CO	NO	CO	NO	CO	NO	CO	NO	CO
100	0	0	0	6	0	0	0	13	0	0	8	17
150	0	0	5	15	0	0	17	27	0	0	35	40
200	0	5	25	29	0	0	34	42	0	9	57	64
250	0	7	39	46	7	13	46	62	14	22	72	81
300	16	17	50	66	22	24	50	72	34	44	64	88
350	37	45	59	78	44	52	59	82	56	75	68	100
400	62	78	76	89	71	80	76	93	75	100	85	100
450	78	100	88	100	89	100	88	100	96	100	100	100
500	88	100	100	100	100	100	100	100	100	100	100	100

Reaction conditions: catalyst weight: 0.1 g; total flow rate: 20 cm^3 min^{-1}; GHSV = 30 000 h^{-1}.

correlate well with the stronger interaction between Ag and CeO_2, which is evidenced by the existence of easily reduced oxygen species.

3.3. Effect of Ag loading on CeO_2

We prepared a series of $Ag/CeO_2(3)$ samples of different Ag loading (1 wt%, 4 wt%, 7 wt%, 10 wt%), and their XRD patterns were shown in Fig. 3. Before XRD measurements, the samples were pretreated in He stream at 500 °C for 1 h. In Fig. 3, the XRD patterns of 1 wt% and 4 wt%Ag/ $CeO_2(3)$ samples show the diffraction lines agree well with $CeO_2(3)$ in a fluorite structure and there are no reflections corresponding to Ag metal or oxide in the patterns. While for the 7 wt% and 10 wt% $Ag/CeO_2(3)$ samples, there are Ag metal diffraction lines at 38.2° in 2θ, and with the Ag loading increases, the diffraction lines also intensify. These results indicate that with the increasing Ag loading on $CeO_2(3)$, the silver particle sizes increase.

Effect of the amount of silver loading on the catalytic activities of $Ag/CeO_2(3)$ was investigated, and the results are shown in Fig. 4. Fig. 4A showed that the highest NO conversion to N_2 was at 250 °C in the temperature range of 100–300 °C over $Ag/CeO_2(3)$ catalysts, and then decreased with the increasing of temperature. Over $CeO_2(3)$, the conversion for NO was only 14 wt% at 250 °C, while it reached 74% over 1 wt% $Ag/CeO_2(3)$. With increasing the amount of Ag loading from 1 wt% to 4 wt%, the conversion of NO was further increased to 81%. The conversion of NO to N_2 did not increase with the further increasing of Ag loading from 4 wt% to 10 wt%, and 10 wt% $Ag/CeO_2(3)$ catalyst showed the lowest NO conversion compared with other silver catalysts. At temperatures above 350 °C, loading silver on ceria had no obvious influence on NO conversion, as shown in Fig. 4A. It means that
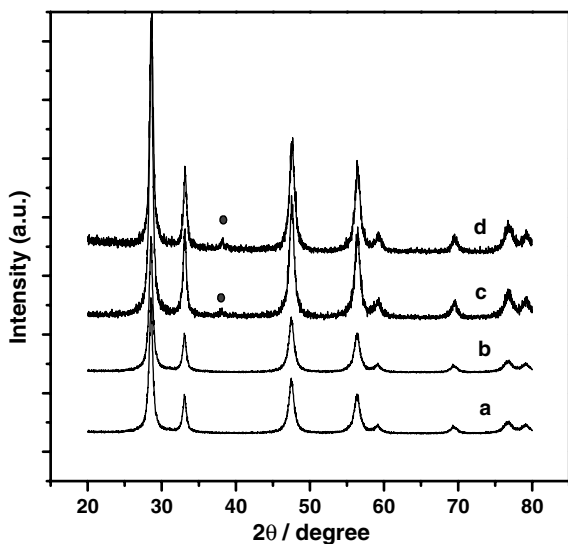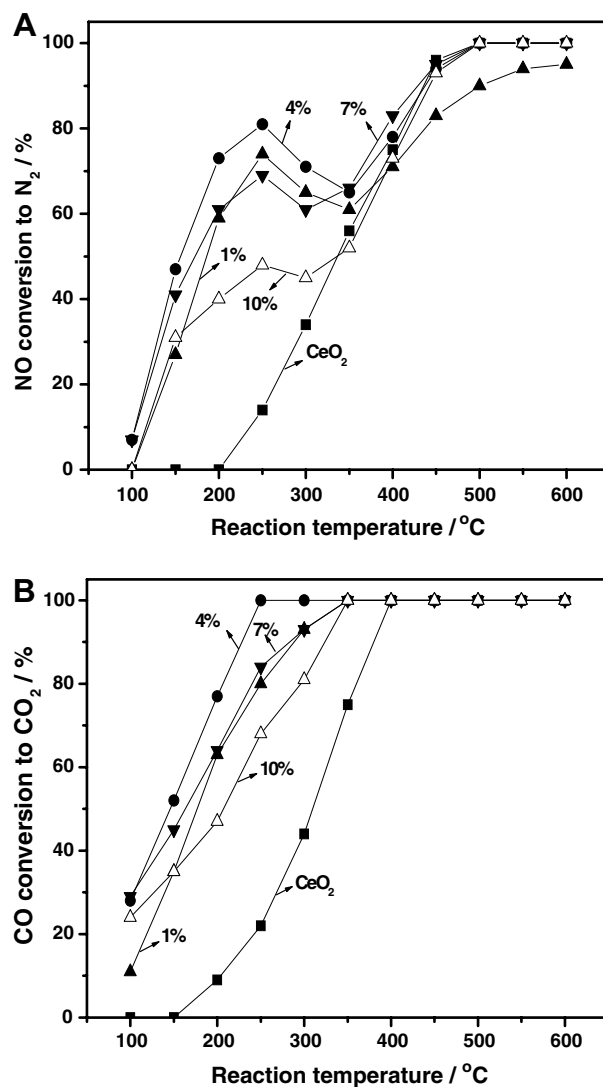

Fig. 4. The effect of the amount of Ag loading on the activity of $CeO_2(3)$ in NO–CO reaction: (■) $CeO_2(3)$; (▲) 1 wt% $Ag/CeO_2(3)$; (●) 4 wt% $Ag/CeO_2(3)$; (▼) 7 wt% $Ag/CeO_2(3)$; (△) 10 wt% $Ag/CeO_2(3)$. Gas composition: 2500 ppm NO, 2500 ppm CO and the balance of He. Reaction conditions: catalyst weight: 0.1 g; total flow rate: 20 cm^3 min^{-1}; GHSV = 30 000 h^{-1}.

the catalytic activity of $CeO_2(3)$ itself played a dominant role for NO–CO reaction at higher temperature regions ($\geqslant$ 350 °C), while silver had apparent catalytic functions in the lower temperature regions. The conversion of CO to CO_2 increased monotonously with the increasing temperature, and reached 100% at 250 °C over 4 wt% $Ag/$ $CeO_2(3)$, and at 400 °C over CeO_2 support, shown in Fig. 4B. It is noted that the additional CO consumption due to the reduction of CeO_2 should not be excluded, which resulted in the higher CO conversion than NO conversion to N_2 at a same temperature. From the results of Fig. 4, it was clear that the proper amount of silver loading on $CeO_2(3)$ for NO–CO reaction was 4%. Further increase in the amount of Ag loading caused a decrease in catalytic activity. Correlated the results with XRD characterizations
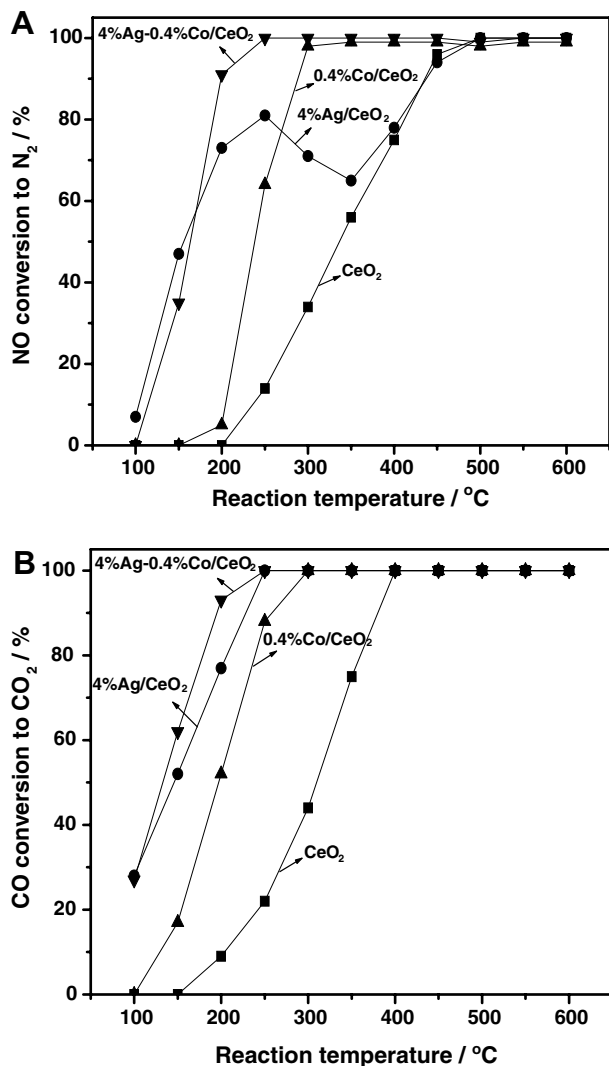

Fig. 3. XRD patterns of $Ag/CeO_2(3)$ catalysts pretreated in He stream at 500 °C for 1 h: (a) 1 wt% $Ag/CeO_2(3)$, (b) 4 wt% $Ag/CeO_2(3)$, (c) 7 wt% $Ag/CeO_2(3)$ and (d) 10 wt %$Ag/CeO_2(3)$.

temperature range of 100–250 °C. While comparison with 4 wt% Ag/CeO$_2$(3), its activity at higher temperature regions ($\geqslant$200 °C) was greatly enhanced. It is obvious that the 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalyst has higher catalytic activities for NO–CO reaction, and 100% conversions of both NO and CO were obtained at lower temperature of 250 °C, complete conversion lasted until 600 °C.

3.5. Effect of GHSV

The catalytic performance of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalyst was also studied under different space velocity, as shown in Fig. 6. When the space velocity was increased from 30 000 h^{-1} to 80 000 h^{-1}, the NO and CO conversions were not obviously affected, and that is, the catalytic activity of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) at the
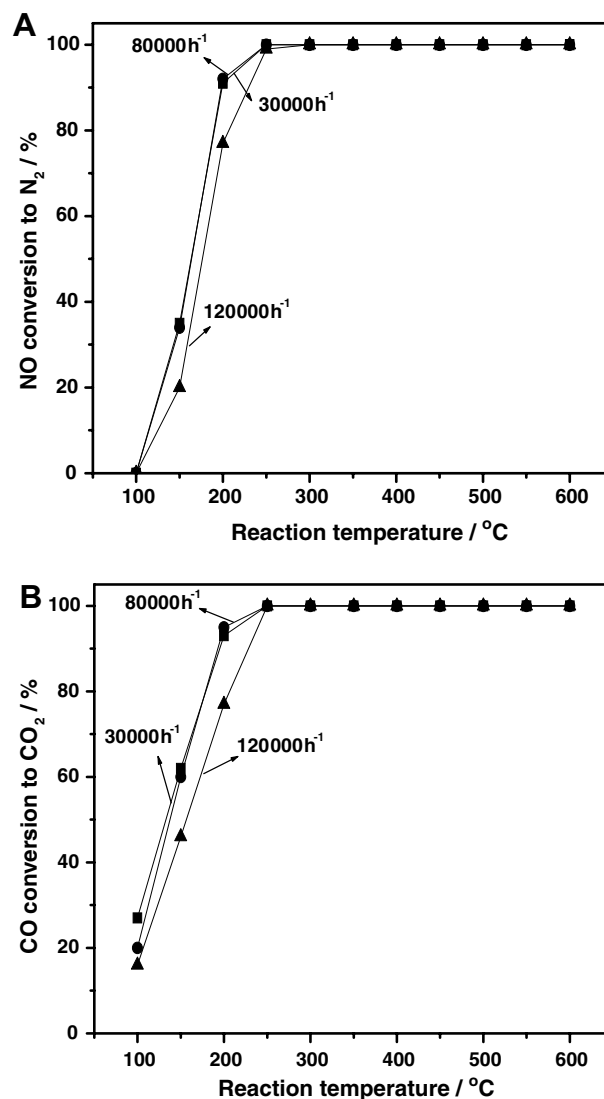

Fig. 5. NO and CO conversions of NO–CO reaction over (■) CeO$_2$(3); (●) 4 wt% Ag/CeO$_2$(3); (▲) 0.4 wt% Co/CeO$_2$(3); (▼) 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalysts. Gas composition: 2500 ppm NO, 2500 ppm CO and the balance of He. Reaction conditions: catalyst weight: 0.1 g; total flow rate: 20 cm^3 min^{-1}; GHSV = 30 000 h^{-1}.

(Fig. 3), it is clear that the decreased activity for higher Ag loading samples is due to the aggregation of silver on CeO$_2$ surface.

3.4. Effect of Co addition

As shown in Fig. 5, loading 0.4 wt% cobalt on CeO$_2$(3), the catalyst showed very high activity at temperatures over 250 °C. (*note*: the optimal loading of Co on CeO$_2$(3) was 0.4 wt%) Both NO and CO conversions reached 100% over 300 °C. This suggests that the combination of silver and cobalt as active components on CeO$_2$(3) might create a synergetic effect for NO–CO reaction, and the catalytic activity of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) had proved it. Compared with 0.4 wt% Co/CeO$_2$(3), 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalyst had especially higher activity in the lower

Fig. 6. The effect of GHSV on the catalytic activity of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) for NO–CO reaction: (■) 30 000 h^{-1}; (●) 80 000 h^{-1}; (▲) 120 000 h^{-1}. Gas composition: 2500 ppm NO, 2500 ppm CO and the balance of He. Reaction conditions: catalyst weight: 0.1 g.

space velocity of 80 000 h^{-1} remained the same level as that at 30 000 h^{-1}. Further increase in the space velocity from 80 000 h^{-1} to 120 000 h^{-1} caused a slightly decrease in catalytic activity. But from the activity curves shown in Fig. 6, we can see that even at a space velocity 120 000 h^{-1}, 100% conversions of NO and CO were also obtained at 250 °C.

3.6. Activity measurement of Ag–Co/CeO$_2$(3) catalyst in the presence of O$_2$

The catalytic activity of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalyst was further investigated in the NO–CO–O$_2$ system, and the results are shown in Fig. 7. At a space velocity of 120 000 h^{-1}, the presence of O$_2$ decreased the catalytic activity at lower temperatures. Until 200 °C, NO reduction was lighted-off, and at 250 °C, NO conversion to N$_2$ was decreased to 68% by the presence of oxygen. While both

NO and CO conversions still could reach 100% at 300 °C.The results indicate the higher catalytic performance of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalyst for NO–CO–O$_2$ system at such a high space velocity of 120 000 h^{-1}.

3.7. Durability of Ag–Co/CeO$_2$(3) catalyst in the absence or presence of O$_2$

The durability of the 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalyst in the NO–CO and NO–CO–O$_2$ systems were evaluated, and the results are shown in Fig. 8. The reactions carried out continuously for 50 h at 250 °C for the NO–CO system and at 300 °C for the NO–CO–O$_2$ system. As evidenced in Fig. 8, the catalyst remained its activity well during the test, and no deactivation was observed both in the absence or presence of O$_2$.
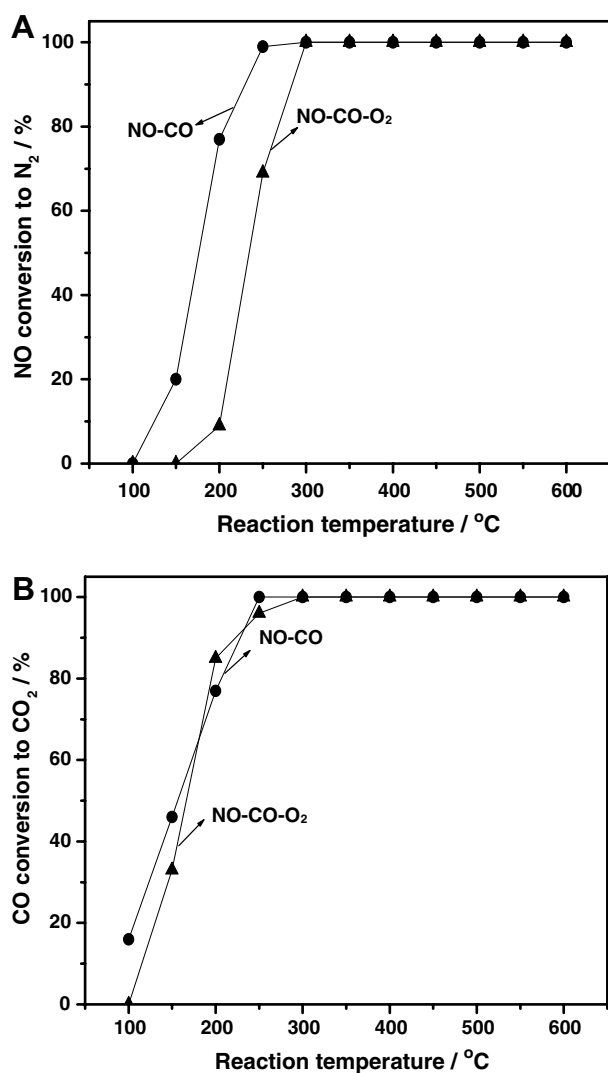

Fig. 7. The effect of oxygen on the catalytic activity of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) catalyst: (●) NO–CO; (▲) NO–CO–O$_2$. Feed gas: 2500 ppm NO, 2500 ppm CO and the balance of He; 2500 ppm NO, 12 500 ppm CO, 5000 ppm O$_2$ and the balance of He. Reaction conditions: catalyst weight: 0.1 g; total flow rate: 75 cm^{3}min^{-1}; GHSV = 120 000 h^{-1}.
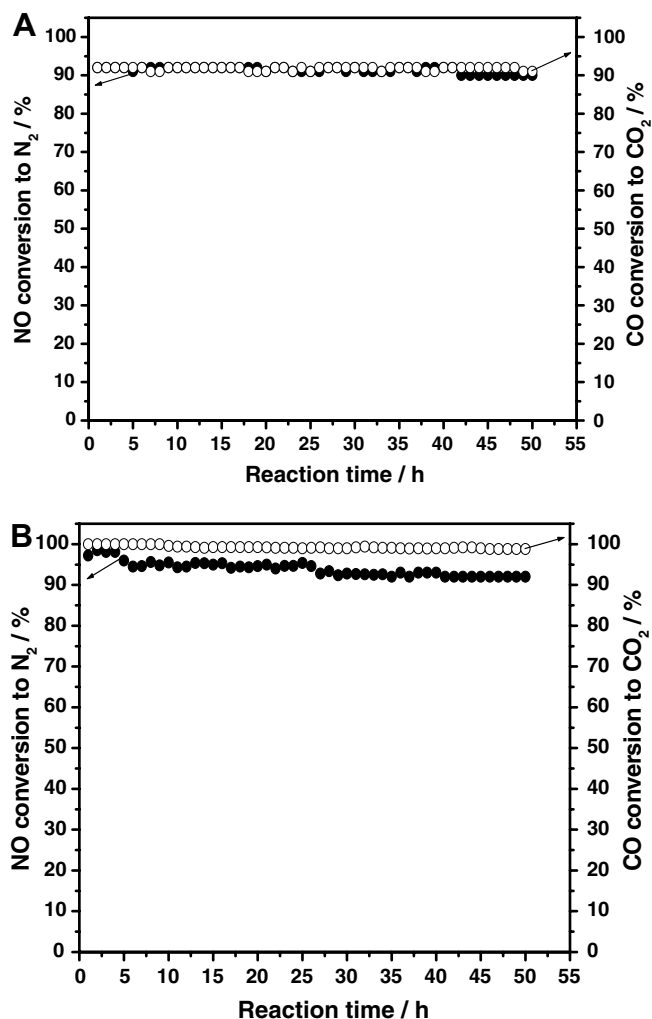

Fig. 8. Stability of 4 wt% Ag–0.4 wt% Co/CeO$_2$(3) in the oxidation of CO and the reduction of NO in the following systems: (A) NO–CO (B) NO–CO–O$_2$ at temperatures of 250 °C and 300 °C, respectively. Feed gas: (A) 2500 ppm NO, 2500 ppm CO and the balance of He. (B) 2500 ppm NO, 12 500 ppm CO, 5000 ppm O$_2$ and the balance of He. Reaction conditions: catalyst weight: 0.1 g; total flow rate: 75 cm^{3}min^{-1}; GHSV = 120 000 h^{-1}.

4. Conclusions

Some specific conclusions from the present work can be drawn as follows:

(1) Preparation methods for CeO_2 supports have great effect on the catalytic activity of Ag/CeO_2 catalyst for NO/CO reaction. $Ag/CeO_2(3)$ catalyst using the support prepared by homogeneous precipitation shows the highest catalytic activity due to the stronger interaction between Ag and CeO_2.

(2) The addition of Ag on CeO_2 greatly improved the catalytic activities in the lower temperature regions ($\leqslant 300\ ^\circ C$), and the introduction of Co on CeO_2 increased the activities at higher temperatures ($\geqslant 250\ ^\circ C$). The bimetallic $Ag–Co/CeO_2$ catalyst combined the advantages of the corresponding individual metal supported catalysts and showed superior activity due to the synergetic effect.

(3) $Ag–Co/CeO_2$ catalyst shows higher catalytic activity and good stability in NO–CO reaction. NO and CO can be completely removed at $250\ ^\circ C$, at a space velocity of $120\ 000\ h^{-1}$. The presence of oxygen has little effect on its catalytic performance and stability.

Acknowledgements

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