Effect of ceria on copper/γ-alumina catalysts for carbon monoxide and n-hexane oxidation

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Abstract——In this paper, oxidation activity of $CuO/\gamma\text{-}Al_2O_3$ catalysts and the addition of CeO_2 on $CuO/\gamma\text{-}Al_2O_3$ catalysts for oxidation reaction of n-hexane ($n\text{-}C_6H_{14}$) and carbon monoxide (CO) were studied by means of the flow method techniques, XRD and TPD-MS. Experimental results indicated that (1) the addition of CeO_2 improving disperse degree of CuO on $CuO/\gamma\text{-}Al_2O_3$ catalysts which caused a large increase in activity; (2) the addition of CeO_2 may increase oxygen supplying ability and oxygen recovery ability of catalyst surface.

Keywords: ceria; copper/γ-alumina; carbon monoxide; hydrocarbon; catalytic activity.

1   Introduction

In recent years, air pollution is recognized as a crucial problem in urban and heavily industrialized areas. Carbon monoxide, a product of incomplete combustion or partial oxidation of carbonaceous materials, is the most widely spread gaseous hazard. One of many ways for reducing air pollution is to eradicate carbon monoxide. An important reaction for cleaning up of emissions from automotive exhausts is the oxidation of carbon monoxide and hydrocarbon. The three way catalysts containing precious metal oxide Pt, Pd and Rh to control automotive exhaust have been studied and were used for this reaction, among which Rh has been selectively used to reduce NO_x into N_2, instead of NH_3. Because the precious metal are relatively rare and expensive, therefore some transition metal oxide and rare earth oxide catalysts for purifying automotive exhaust have been studied. $CuO/\gamma\text{-}Al_2O_3$ was widely used in complete oxidation reactions of CO and RH (Friedman, 1978; Strohmeier, 1985; Huang, 1989; Praserthdam, 1994). The rare earth oxide combined with the transition metal oxide, can adjust the performance of catalyst surface, were found with an excellent redox behavior and thermal stability (Yao, 1984). In this paper, the effect of addition of CeO_2 on $CuO/\gamma\text{-}Al_2O_3$ activities have been investigated by means of the flow method techniques, XRD and TPD-MS.

2   Experimental

2.1   Catalyst preparation

The catalyst was prepared by the method of impregnation with $Cu(NO_3)_2$ and $Ce(NO_3)_3$ aqueous solution of desired concentration. The catalysts were dried at 120℃ followed by calcination with air stream for 4h at 500℃ (Content of active component were calculated using by pure γ-Al_2O_3 support). For the series of CuO/γ-Al_2O_3 catalysts, the content of CuO decrease with the order: 25%CuO > 20%CuO > 15%CuO > 10%CuO > 5%CuO > 1% CuO; for CeO_2/γ-Al_2O_3 catalysts, the content of CeO_2 decrease with the order: 18%CeO_2> 14%CeO_2> 10%CeO_2> 6%CeO_2> 2%CeO_2; for CuO-CeO_2/γ-Al_2O_3 catalysts, content of all CuO are same, the content of CeO_2 decrease with the order: 18%CeO_2—15%CuO > 14% CeO_2—15%CuO > 10%CeO_2—15%CuO > 6%CeO_2— 15%CuO > 2%CeO_2—15%CuO.

2.2 Measurement of oxidation activity of n-Hexane(n-C_6H_{14})

Literature (Jiang, 1992) was referenced as process chart of activity measurement to n-C_6H_{14}.

2.3 XRD analysis of crystal phase

Measurement of X-ray powder diffraction (XRD) was conducted by Riggku D/Max-IIIB.

2.4 Measurement of oxidation activity of carbon-monoxide (CO)

The catalyst (0.5 ml) was placed in a quartz glass fixed-bed reactor (ϕmm), and was activated with O_2 stream for 1h at 500℃, the catalyst was then cooled to a proper reaction temperature. Reactive tail gas was analyzed by GC, experimental data were calculated by a CR-6A data processing instrument. The condition of Gas Chromatography, GC column: Propark Q column to separation CO, temperature of column: 34℃; flow of carrier gas H_2: 30 ml/min.

2.5 TPD-MS

Surface oxygen desorption: the sample (100 mg) was activated with O_2 stream for 0.5h at 600℃, cooled to 50℃, changed into He stream 0.5h, then was conducted surface oxygen desorption at flow of He (β=20 K/min).
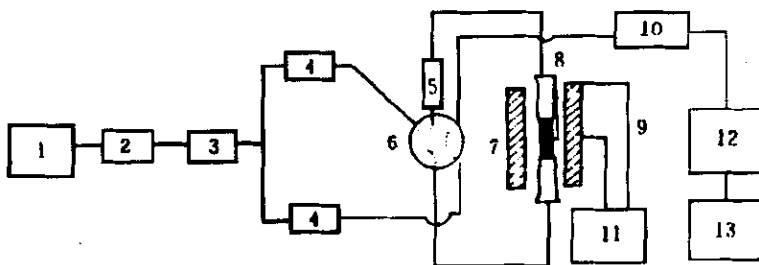

Fig. 1   Process chart of TPD-MS tester systems

1. He steel bottle 2. Pressure reducer 3. Deoxidation tube

4. Flowmeter 5. Sampler 6. Six-way pipe 7. Heater

8. Quartz glass reactor 9. Thermocouple 10. GC-MS separator

11. Temperature controller 12. MS tester 13. Data processing instrument

Surface oxygen recovery: the sample (100 mg) was activated with He stream for 0.5h at 650℃, cooled to 400℃, this moment, sample surface adsorption oxygen has been com-

pletely desorbed, changed into O_2 stream 0.5h, cooled to 50℃; changed into He stream 0.5h, then conducted surface oxygen recovery ($\beta=20$ K/min). TPD-MS equipment was refitted by the GC-MS of type ZHD-OIS. The process chart is shown in Fig. 1.

3 Results and discussion

3.1 Correlation between CeO_2, CuO-contents and oxidation activity

The minimum reaction temperature of reactant conversion efficiency$\geqslant99\%$ may be used as activity target of evaluation for oxidative catalyst. It is shown by T_{99}(℃). The higher the activity is the smaller value of T_{99}. The order of activity of CuO/γ-Al_2O_3 and CeO_2/γ-Al_2O_3 were respectively: CuO/γ-Al_2O_3 systems, 15%CuO > 20%CuO > 25%CuO > 10%CuO > 5%CuO > 1%CuO; CeO_2/γ-Al_2O_3 systems, $10\%CeO_2$> $6\%CeO_2$> $14\%CeO_2$> $18\%CeO_2$ > $2\%CeO_2$. The results are shown in Fig. 2 (A,B). But as the addition of CeO_2 on CuO/γ-Al_2O_3 catalysts, from Fig. 2(C), it can be seen that the value of T_{99} for 15%CuO catalyst decreased a range from 70-80℃. The results are shown in Fig. 2.
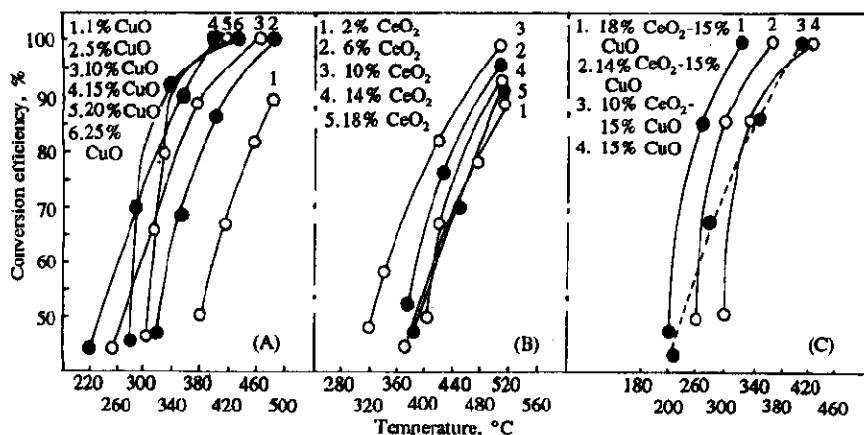

Fig. 2 Oxidation activity of catalysts to n-C_6H_{14}

(A,B): the order of activity of CuO, CeO_2/γ-Al_2O_3 for oxidation reaction of n-C_6H_{14}

(C): effect of the addition of CeO_2 on oxidation reaction of n-C_6H_{14}

The correlation between CeO_2, CuO-contents and oxidation activity were investigated by means of the flow method techniques and XRD. Results showed that CuO are highly dispersed on carrier. It did not appear diffraction peaks of CuO on XRD spectra for 1% CuO, 5%CuO and 10%CuO. But as the CuO-content increases to 15%CuO, there begins to appear several diffraction peaks which correspond to the crystal state CuO on catalysts. This moment, the oxidation activity of 15%CuO was the highest. Further increasing CuO-content, diffraction peaks of CuO increased gradually, oxidation activity becomes lower. Thus it can be seen that the oxidation activity was mainly attributed to the quantity of uncrystallized state CuO. The more production of crystal state CuO, may block some aperture of catalysts, or covered a part of surface of uncrystallized state CuO, thus resulted in decrease of activity with increasing the CuO- content.
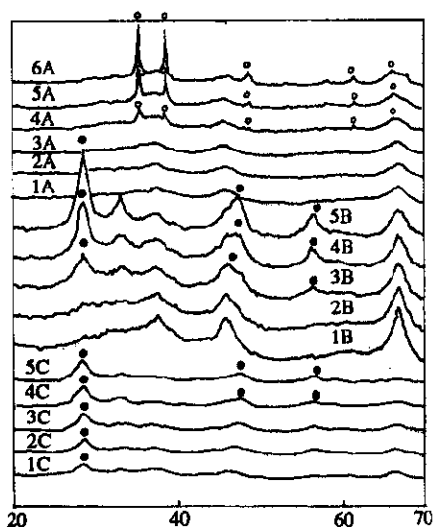
Fig. 3   XRD spectra of CuO, CeO$_2$ and CeO$_2$-CuO/γ-Al$_2$O$_3$

          ∘ CuO   ∙ CeO$_2$

1A. 1%CuO, 2A. 5%CuO, 3A. 10%CuO, 4A. 15%CuO, 5A. 20%CuO, 6A. 25%CuO ; 1B. 2%CeO$_2$, 2B. 6%CeO$_2$, 3B. 10%CeO$_2$, 4B. 14%CeO$_2$ 5B. 18%CeO$_2$; 1C. 2%CeO$_2$-15%CuO, 2C. 6%CeO$_2$-15%CuO, 3C. 10%CeO$_2$-15%CuO, 4C. 14%CeO$_2$-15%CuO, 5C. 18%CeO$_2$-15%CuO

It is well known that CeO$_2$ is more chemical stable and oxidation activity was lower for itself. XRD spectra of CeO$_2$ have also explained that correlation between oxidation activity and content. As the CeO$_2$-content are between 2%CeO$_2$-18%CeO$_2$, appeared all CeO$_2$ diffraction peaks with different shape. It indicates that CeO$_2$ form crystal state CeO$_2$ very easy. After mixing CuO and CeO$_2$, the great majority of CuO on catalysts existed in the uncrystallized state. Because the uncrystallized state dispersed highly on catalysts, so the activity of catalysts may be improved quickly after mixing CuO and CeO$_2$ (Fig. 3).

3. 2   The activity of CeO$_2$-CuO/γ-Al$_2$O$_3$ for oxidation of CO

T_{99} (℃) of CeO$_2$-CuO/γ-Al$_2$O$_3$ for oxidation of CO under the condition of lean O$_2$ (CO 3.1%, O$_2$ 1.8%) and abundant O$_2$ (CO 3.3%, O$_2$ 9%) are shown in Table 1.

Table 1   Correlation between CO conversion and reaction temperature of catalysts

Catalysts	Lean O$_2$, T_{99}(℃)	Abundant O$_2$, T_{99}(℃)	ΔT^*, (℃)
15% CuO	220	180	40
2%CeO$_2$—15%CuO	170	150	20
6%CeO$_2$—15%CuO	130	120	10
10%CeO$_2$—15%CuO	120	110	10
14%CeO$_2$—15%CuO	110	100	10
18%CeO$_2$—15%CuO	100	100	0

* $\Delta T = T_{99}$(lean O$_2$)-T_{99}(abundant O$_2$)

From Table 1, it may be seen that the oxidation activity of CeO$_2$-CuO/γ-Al$_2$O$_3$ catalysts for CO at the condition of lean O$_2$ were lower than the abundant O$_2$, ΔT(20→10)℃, as content of active component increased gradually from 2%CeO$_2$—15%CuO to 14%CeO$_2$—15% CuO. But as the CeO$_2$-content increased to more than 14%CeO$_2$—15%CuO, $\Delta T = 0$℃. It indicates that the addition of CeO$_2$ improving catalytic activity at lean O$_2$ state. Because of oxidation activity of catalysts for CO is dependent on the adsorption state oxygen of catalyst

surface to a great extent. From the range of descent of lean O_2 activity (ΔT), it can be seen that the increasing of content of CeO_2, may decrease the value of ΔT. It indicates that when the oxygen concentration of gaseous phase decreases, the oxygen supplying ability of catalyst surface for oxidation reaction of CO becomes apparently. In addition, the effect of oxygen concentration on oxidation activity becomes smaller, if oxygen supplying ability of catalyst surface is getting better.

3.3 Effect of CeO_2 on surface oxygen desorption and recovery of $CuO/\gamma-Al_2O_3$

The activity of catalysts is decided by the adaptability of groups structure of reactant molecule and the oxygen supplying ability of surface active centers, the oxygen supplying ability is composed by the number of oxygen supplying centers and activity. The surface oxygen desorption and recovery of catalyst under the condition of non-reaction were investigated by means of the TPD-MS technique. The determine of the O^{32+} signal may show the information of surface oxygen desorption and recovery. Fig. 4 shows the information of surface oxygen desorption of catalysts. Fig. 5 shows the information of surface oxygen recovery of catalysts.

From Fig. 4 it can be seen that there are three O_2-TPD feature peaks, by inference the peaks of low and middle temperature is adsorption oxygen peak of CuO, the peak of high temperature is the lattice oxygen peaks of CuO. The desorption oxygen feature peaks of CeO_2 is not apparent. With CeO_2-content increasing, the third O_2-TPD feature peaks of CuO decreases gradually, it indicates that

Fig. 4 O_2-TPD spectra of catalysts
1. 10%CeO_2 2. 15%CuO
3. 2%CeO_2-15%CuO
4. 10%CeO_2-15% CuO
5. 18%CeO_2-15%CuO

Fig. 5 O_2-TPD spectra of catalysts
1. 15%CuO 2. 18%CeO_2-15% CuO

the addition of CeO_2 restrains the desorption of lattice oxygen of CuO. In addition, from Fig. 4, it can been clearly seen that the addition of CeO_2, and with CeO_2-content increasing, make peak temperature location of adsorption oxygen to move forward to the direction of lower temperature, it indicates that the correlation between active increasing and advance of peaks temperature of adsorption oxygen. In order to explain the correlation, we have also studied the surface oxygen recovery ability of catalyst. It is usual considered that the surface adsorption oxygen of higher activity catalyst can be recovered after it was desorbed. From Fig. 5, it can be seen that though surface adsorption oxygen can not recover to original level after the addition of CeO_2, but it makes the areas of des-
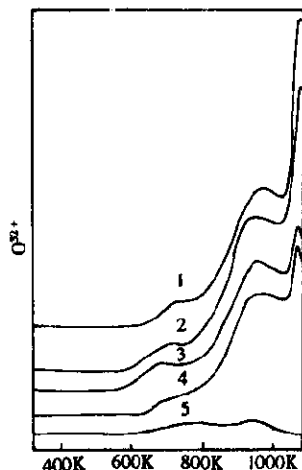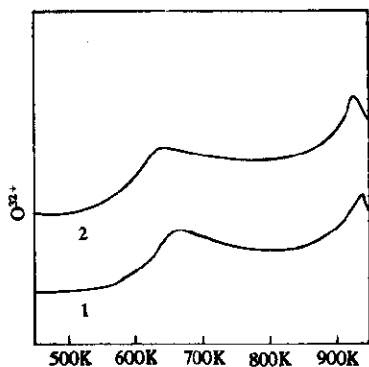
orption peaks of adsorption oxygen to become bigger than $CuO/\gamma-Al_2O_3$ catalyst and peaks temperature advances. It shows that catalyst active contribution is mainly that the surface adsorption oxygen can be recovered after it was desorbed.

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