

## ARTICLE

**Comparative Study of CuO Species on CuO/Al<sub>2</sub>O<sub>3</sub>, CuO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and CuO/La<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> Catalysts for CO Oxidation**

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(Dated: Received on January 25, 2007; Accepted on April 5, 2007)

CuO/Al<sub>2</sub>O<sub>3</sub>, CuO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and CuO/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> (denoted as Cu/Al, Cu/CeAl, and Cu/LaAl) catalysts were prepared by an impregnation method. CuO species and CuO/Al<sub>2</sub>O<sub>3</sub> thermal solid-solid interaction were characterized by *in situ* XRD, Raman spectroscopy and H<sub>2</sub>-TPR techniques. For the Cu/Al catalyst, a CuAl<sub>2</sub>O<sub>4</sub> phase exists between the CuO and Al<sub>2</sub>O<sub>3</sub> layer and the CuO phase exists on the surface in both highly dispersed and bulk forms. For the Cu/CeAl catalyst, there is highly dispersed and bulk CuO on the surface, but most of the CuO has transferred into the internal layer of CeO<sub>2</sub> as bulk CuO and CuAl<sub>2</sub>O<sub>4</sub>. For the Cu/LaAl catalyst, only bulk CuO is present on the surface of the catalyst and no CuAl<sub>2</sub>O<sub>4</sub> is formed. The catalytic activity order for CO oxidation is Cu/CeAl>Cu/Al>Cu/LaAl. The highly dispersed CuO on the catalyst surface may be the active phase for CO oxidation. The results show that the addition of CeO<sub>2</sub> not only promotes both the transference of CuO and the formation of CuAl<sub>2</sub>O<sub>4</sub> but also favors the CO oxidation due to the association of highly dispersed CuO with CeO<sub>2</sub>, while La<sub>2</sub>O<sub>3</sub> hinders the transference of CuO and the formation of CuAl<sub>2</sub>O<sub>4</sub>.

**Key words:** CuO/Al<sub>2</sub>O<sub>3</sub>, CuO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CuO/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, *in situ* XRD, Raman, TPR**I. INTRODUCTION**

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> is regarded as a suitable support for a variety of catalysts used in various reactions such as alkane dehydrogenation, NO<sub>x</sub> and SO<sub>2</sub> reduction [1-5]. The CuO/Al<sub>2</sub>O<sub>3</sub> catalysts exhibit comparable activities as precious metals catalysts for carbon monoxide oxidation [6]. However, a spinel structure of CuAl<sub>2</sub>O<sub>4</sub> is formed as a result of the CuO/Al<sub>2</sub>O<sub>3</sub> interaction at high temperatures and its catalytic activities are apparently lower than the metal oxide itself [7]. The strong CuO/Al<sub>2</sub>O<sub>3</sub> interaction indicates that it is necessary for the CuO/Al<sub>2</sub>O<sub>3</sub> catalyst to add other oxides Cr<sub>2</sub>O<sub>3</sub> [8], Sm<sub>2</sub>O<sub>3</sub> [9] and ZrO<sub>2</sub> [10] for inhibiting the interaction and improving the catalytic activities of CO oxidation [11-13]. ZnO-doped CuO/Al<sub>2</sub>O<sub>3</sub> suppressed the formation of CuAl<sub>2</sub>O<sub>4</sub> calcined at 600 °C but accelerated the formation at 800 °C. However, the catalytic activity for CO oxidation did not decrease at 800 °C due to the enhanced dispersion of CuO [14].

Rare earth oxides have been widely applied as co-catalysts because of their specific oxidation activity and the variability of the metal ionic valance [15,16]. It is well known that CeO<sub>2</sub> can improve the oxygen storage capacity and the thermal stability, and it has been widely used as an essential part in various industrial heterogeneous catalysts and in the automotive three-way converter. The addition of La<sub>2</sub>O<sub>3</sub> improves the

thermal stability of the catalyst and supporter [17-19]. The CuO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst and the CuO/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst have become the object of several investigations [20-23].

In this work, the effect of CuO distribution and the addition of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> on the catalytic properties for CO oxidation was investigated. It was shown that the distribution of CuO and thermal CuO/Al<sub>2</sub>O<sub>3</sub> solid-solid interaction can be effectively confirmed by *in situ* XRD, Raman spectroscopy and H<sub>2</sub>-TPR techniques. The catalytic activity for CO oxidation is related to the highly dispersed CuO on the catalyst surface.

**II. EXPERIMENTS****A. Catalyst preparation**

CuO/Al<sub>2</sub>O<sub>3</sub>, CuO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and CuO/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> (denoted as Cu/Al, Cu/CeAl, and Cu/LaAl) catalysts were prepared using an impregnation method. CeO<sub>2</sub> or La<sub>2</sub>O<sub>3</sub> modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (denoted CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>) was prepared as follows: an appropriate amount of Ce(NO<sub>3</sub>)<sub>3</sub> or La(NO<sub>3</sub>)<sub>3</sub> was dissolved in deionized water, and the support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.3-0.4 mm, 240 m<sup>2</sup>/g) was added into the solution. The mixture was constantly stirred at 95 °C until the water totally evaporated, and the resulting solid was finally calcined at 500 °C for 4 h. The content of CeO<sub>2</sub> or La<sub>2</sub>O<sub>3</sub> was 40wt% in the CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, respectively.

For the preparation of supported Cu catalysts, the as-prepared supports (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or La<sub>2</sub>O<sub>3</sub>-

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Al<sub>2</sub>O<sub>3</sub>) were impregnated with certain amount of Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solution. The catalysts were stirred constantly at 95 °C until the water totally evaporated, and further dried at 120 °C overnight, which was followed by calcinations at 800 °C for 4 h. The content of CuO in these catalysts was 33.3wt%.

## B. Characterization

X-ray diffraction (XRD) patterns were collected on a PHILIPS PW3040/60 powder diffractometer using Cu K $\alpha$  radiation. The working voltage of the instrument was 40 kV and the current was 40 mA. The intensity data were collected at room temperature in a  $2\theta$  range from 25° to 65° with a scan rate of 0.1°/s. The high-temperature *in situ* XRD measurements were carried out on the same instrument equipped with an X-ray reactor chamber (XRK-900 Anton Paar). 200 mg of catalyst was placed in the chamber, and a mixed gas containing 5%H<sub>2</sub> and 95%N<sub>2</sub> was introduced at a total flow rate of 20 mL/min. When the sample was reached the desired temperature, it was held there for 10 min and the intensity data were collected in a  $2\theta$  range from 25° to 65° with a scan rate of 0.2°/s.

Raman spectra were obtained with a Renishaw RM1000 confocal microscope. The exciting wavelength was 632.8 nm from a He-Ne laser with a power of ca. 3 mW on the catalyst.

UV-visible absorption spectra were recorded on a JASCO V-550 spectrophotometer equipped with an integrating sphere.

The reduction properties of the catalysts were determined by means of temperature programmed reduction (TPR) technique. 10 mg of catalyst was placed in a quartz reactor. The reactor was heated from room temperature to 900 °C at a heating rate of 20 °C/min under flowing H<sub>2</sub>:N<sub>2</sub> (5:95) with a total flow rate of 20 mL/min (room temperature and 101.3 kPa). The amount of H<sub>2</sub> consumption was determined by a gas chromatograph with a TCD detector.

## C. Catalytic activity of CO oxidation

Catalytic activity measurements were carried out in a fixed bed reactor (i.d.=6 mm) using 150 mg catalyst. A mixed gas of 3.0%CO and 3.0%O<sub>2</sub> in N<sub>2</sub> was introduced to the catalysts at a total flow rate 80 mL/min without any pretreatment. The analysis of the CO<sub>2</sub> concentration in the reactor effluent was performed by means of a GC equipped with a thermal conductivity detector (TCD).

FIG. 1 XRD patterns of Cu/Al (a), Cu/CeAl (b), and Cu/LaAl (c) catalysts.

FIG. 2 Laser Raman spectra of Cu/Al (a), Cu/CeAl (b), and Cu/LaAl (c) catalysts.

## III. RESULTS AND DISCUSSION

### A. XRD and Raman characterization

Figure 1 shows the XRD patterns of the Cu/Al, Cu/CeAl, and Cu/LaAl catalysts. For the Cu/Al catalyst, peaks due to CuO and CuAl<sub>2</sub>O<sub>4</sub> are present; for the Cu/CeAl catalyst, peaks due to CuO, CeO<sub>2</sub>, and CuAl<sub>2</sub>O<sub>4</sub> are present, while for the Cu/LaAl catalyst only the CuO phase peak is observed. The intensities of the CuO diffraction peaks are weaker in the Cu/Al catalyst and the Cu/CeAl catalyst than that in the Cu/LaAl catalyst, but strong peaks of CuAl<sub>2</sub>O<sub>4</sub> formed in these two catalysts. CuAl<sub>2</sub>O<sub>4</sub> formed as a result of the following thermal solid-solid reaction: CuO+Al<sub>2</sub>O<sub>3</sub>→CuAl<sub>2</sub>O<sub>4</sub>. The XRD results indicate that the addition of La<sub>2</sub>O<sub>3</sub> can prevent the formation of CuAl<sub>2</sub>O<sub>4</sub>. For Cu/Al, Cu/CeAl, and Cu/LaAl catalysts, the crystalline sizes of CuO are 17.2, 17.9, and 14.0 nm, respectively, suggesting among the three different catalysts, the crystalline sizes of CuO hardly change.

The Laser Raman spectra of the Cu/Al, Cu/CeAl, and Cu/LaAl catalysts are shown in Fig.2. Three typical bands at 285, 330, and 620 cm<sup>-1</sup> are observed for the Cu/Al and the Cu/LaAl catalysts. These bands are characteristics of CuO phase [24], while only a strong band centered at 465 cm<sup>-1</sup> attributed to cubic CeO<sub>2</sub> [25] are observed for the Cu/CeAl catalyst.

XRD and Raman techniques provide information from both the bulk and the surface of a solid catalyst. However, the signal from the bulk is attenuated for Raman scattering, particularly when the catalyst absorbs the excitation laser light and the scattering light. Therefore, compared with the bulk of the catalysts, Raman scattering mainly comes from the surface top region [26,27]. UV-Visible diffuse reflectance

FIG. 3 UV-Visible diffuse reflectance spectra of Cu/Al (a), Cu/CeAl (b), and Cu/LaAl (c) catalysts.

FIG. 4 TPR profiles of Cu/Al (a), Cu/CeAl (b), and Cu/LaAl (c) catalysts.

spectra of the Cu/Al, Cu/CeAl, and Cu/LaAl catalysts shown in Fig.3 clearly suggest that for all these catalysts there is absorption at 632.8 nm, which is the wavelength of the excitation laser for Raman spectra in this work. This suggests that the information detected by Raman comes from the surface region of these catalysts and the surface region contains bulk CuO for the Cu/Al and Cu/LaAl catalysts and bulk CeO<sub>2</sub> for the Cu/CeAl catalyst. Combined with the XRD pattern, it can be concluded that a CuAl<sub>2</sub>O<sub>4</sub> layer is between the CuO and Al<sub>2</sub>O<sub>3</sub> layers for the Cu/Al catalyst [26]. The crystalline phase of CuO and CeO<sub>2</sub> for the Cu/CeAl catalyst are present in the XRD pattern, which allows the conclusion that CuO has transferred into the internal layer of CeO<sub>2</sub> and interacts with the support Al<sub>2</sub>O<sub>3</sub> to produce CuAl<sub>2</sub>O<sub>4</sub> [28]. The authors propose that this is because CuO easily combines with CeO<sub>2</sub> to form Cu-Ce-O solid solution [29], which is favorable for the transference of CuO.

### B. *In situ* XRD and TPR characterizations of CuO species

Figure 4 shows the TPR profiles of the Cu/Al, Cu/CeAl, and Cu/LaAl catalysts. For the Cu/Al catalyst, there are three large reduction peaks at about 210 °C ( $\alpha$ ), 300 °C ( $\beta_1$ ), and 470 °C ( $\gamma_1$ ) and a broad and weak peak at about 800 °C ( $\gamma_2$ ). For the Cu/CeAl catalyst, besides the same reduction peaks ( $\alpha$ ,  $\beta_1$ , and  $\gamma_1$ ) in the Cu/Al catalyst, a reduction peak ( $\beta_2$ ) at 380 °C is present as well. Furthermore, the intensities of the  $\alpha$  and  $\beta_1$  peaks sharply decrease while that of the  $\gamma_1$  peak obviously increases in the Cu/CeAl catalyst compared with the Cu/Al catalyst. For the CuO/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, only a strong reduction peak  $\beta_1$  ( $\sim$ 300 °C) is observed.

In order to further confirm the attribution of the TPR peaks, *in situ* XRD experiments were carried out. The *in situ* XRD patterns of the Cu/Al, Cu/CeAl, and Cu/LaAl catalysts recorded under the same reduction condition as the TPR experiments are shown in Fig.5. It can be seen that the XRD patterns obtained under 250 °C are the same as those of at room temperature for these catalysts. For the Cu/Al catalyst (Fig.5(a)), the CuO phase disappears at 300 °C, while the peaks due to CuAl<sub>2</sub>O<sub>4</sub> phase gradually decrease in intensity while the temperature increases to 500 °C and completely disappears at 800 °C. The decrease in the intensities of the CuO and CuAl<sub>2</sub>O<sub>4</sub> phases is accompanied by growing peaks of metallic Cu phase starting from 300 °C. The metallic Cu is the only phase in the catalyst at 800 °C. For the Cu/CeAl catalyst (Fig.5(b)), the CuO phase disappears at 400 °C, and the peak intensity of CuAl<sub>2</sub>O<sub>4</sub> phase gradually decreases at 500 °C and disappears at 800 °C. Again, the decrease is accompanied by growing peaks of metallic Cu phase starting from 400 °C. The peaks of CeO<sub>2</sub> phase are present during the whole temperature program. For the Cu/LaAl catalyst (Fig.5(c)), the peak intensity of CuO phase disappears at 300 °C, with the appearance of peaks due to Cu, Cu<sub>2</sub>O phase is present simultaneously. In addition, metallic Cu is the only phase in the catalyst with further increasing temperature.

By comparing the TPR profiles with the *in situ* XRD patterns, assignment of the reduction peaks in TPR could be made. There is a reduction peak  $\alpha$  at 250 °C in the Cu/Al and Cu/CeAl catalysts (Fig.4(a) and (b)), while there is no change in their structures according to the *in situ* XRD results (Fig.5(a) and (b)). Therefore, the reduction peak  $\alpha$  can be assigned to the reduction of the highly dispersed CuO particles on the catalysts surface. For the Cu/LaAl catalyst, there is only one reduction peak  $\beta_1$  at 300 °C (Fig.4(c)), and only CuO phase changes during the temperature program (Fig.5(c)), so it is clear that the reduction peak  $\beta_1$  is due to the reduction of bulk CuO on the catalyst surface. This is consistent with the results for the Cu/Al catalyst (Fig.5(a)). In Fig.5, the diffraction peaks of Cu<sub>2</sub>O can be observed, probably due to the incomplete reduction of CuO. For the Cu/Al and Cu/CeAl catalysts (Fig.5(a) and (b)), CuAl<sub>2</sub>O<sub>4</sub> is the only phase that changes with increasing temperatures, so both the  $\gamma_1$  and  $\gamma_2$  peaks are the reduction of CuAl<sub>2</sub>O<sub>4</sub> species ( $\text{CuAl}_2\text{O}_4 + \text{H}_2 \rightarrow \text{Cu} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$ ).

Table I lists the proportion of each peak area in the total areas of TPR profile for the Cu/Al, Cu/CeAl, and Cu/LaAl catalysts. The proportion of the areas of  $\gamma_1 + \gamma_2$  peaks in the Cu/CeAl catalyst is larger than that in the Cu/Al catalyst, indicating that CuAl<sub>2</sub>O<sub>4</sub> content in the former is higher than that in the latter. This fact suggests that the addition of CeO<sub>2</sub> into Cu/Al catalysts can promote the formation of CuAl<sub>2</sub>O<sub>4</sub> while La<sub>2</sub>O<sub>3</sub> can suppress it.

Based on all of the above results, it is concluded that

FIG. 5 *In situ* XRD patterns of Cu/Al (a), Cu/CeAl (b) and Cu/LaAl (c) catalysts during the programmed elevating temperature.

TABLE I Proportions of each peak area in the total area of TPR profile for Cu/Al (a), Cu/CeAl (b) and Cu/LaAl (c) catalysts

Catalysts	Proportion of each peak area/%			
	$\alpha$	$\beta_1$	$\beta_2$	$\gamma_1+\gamma_2$
Cu/Al	9.3	38.8	—	51.9
Cu/CeAl	5.6	3.5	13.1	77.8
Cu/LaAl	—	100	—	—

for the Cu/Al catalyst, both highly dispersed and bulk CuO species exist on the surface and  $\text{CuAl}_2\text{O}_4$  exists between CuO and  $\text{Al}_2\text{O}_3$  layer. For the Cu/CeAl catalyst, the main phase on the surface is  $\text{CeO}_2$ , most of CuO has transferred into the internal layer of  $\text{CeO}_2$ . For the Cu/LaAl catalyst, CuO presents as bulk phase on the surface and  $\text{La}_2\text{O}_3$  exists between CuO and  $\text{Al}_2\text{O}_3$  layer.

### C. Catalytic activity for CO oxidation

Figure 6 shows catalytic activities of the Cu/Al, Cu/CeAl, and Cu/LaAl catalysts for CO oxidation. It can be seen that the catalytic performance follows the order: Cu/CeAl > Cu/Al > Cu/LaAl. The TPR results show that the Cu/Al and Cu/CeAl catalysts contain both highly dispersed and bulk CuO, while the Cu/LaAl catalyst only contains bulk CuO. Therefore, the difference in catalytic performance is possibly related to the contents of highly dispersed CuO phase on the catalyst surface, as revealed in the authors' previous work [29,30]. However, the conflicting results of the activities between the Cu/Al and Cu/CeAl catalysts are most likely owing to the effect of  $\text{CeO}_2$ . From the refer-

FIG. 6 Catalytic activity of Cu/Al (a), Cu/CeAl (b), and Cu/LaAl (c) catalysts for CO oxidation.

ence, the increased activity by the addition of  $\text{CeO}_2$  to the alumina can primarily be related to the association of CuO with  $\text{CeO}_2$  rather than increased dispersion of CuO [31]. It has been shown that a very little amount of CuO doped to  $\text{CeO}_2$  can promote the catalytic activity for CO oxidation extensively, due to the activation of oxygen by  $\text{CeO}_2$  [32,33].

### IV. CONCLUSION

This research investigated the effect of CuO distribution in Cu/Al, Cu/CeAl, and Cu/LaAl catalysts and the addition of  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$  on the catalytic properties for CO oxidation. For the Cu/Al catalyst, CuO presents as highly dispersed and bulk CuO on the surface. For the Cu/CeAl catalyst, most of CuO has transferred into the internal and CuO- $\text{Al}_2\text{O}_3$  interaction can be promoted. For the Cu/LaAl catalyst, all of CuO presents as bulk CuO on the surface. The results of CO oxidation activity indicate that the catalytic activities are related to the highly dispersed CuO species. The addition of  $\text{La}_2\text{O}_3$  can hinder the transference of CuO and consequently prevent the formation of  $\text{CuAl}_2\text{O}_4$ . Also, the addition of  $\text{CeO}_2$  to the alumina can improve the CO oxidation. For the Cu/Al catalyst system, it is most desirable that the transference of CuO should be hindered in order to improve the catalytic activity.

### V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.20473075).

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