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Comparative Study of CuO Species on CuO/Al₂O₃, CuO/CeO₂-Al₂O₃ and CuO/La₂O-Al₂O₃ Catalysts for CO Oxidation

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CuO/Al₂O₃, CuO/CeO₂-Al₂O₃, and CuO/La₂O₃-Al₂O₃ (denoted as Cu/Al, Cu/CeAl, and Cu/LaAl) catalysts were prepared by an impregnation method. CuO species and CuO/Al₂O₃ thermal solid-solid interaction were characterized by *in situ* XRD, Raman spectroscopy and H₂-TPR techniques. For the Cu/Al catalyst, a CuAl₂O₄ phase exists between the CuO and Al₂O₃ 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 CeO₂ as bulk CuO and CuAl₂O₄. For the Cu/LaAl catalyst, only bulk CuO is present on the surface of the catalyst and no CuAl₂O₄ 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 CeO₂ not only promotes both the transference of CuO and the formation of CuAl₂O₄ but also favors the CO oxidation due to the association of highly dispersed CuO with CeO₂, while La₂O₃ hinders the transference of CuO and the formation of CuAl₂O₄.

Key words: CuO/Al₂O₃, CuO/CeO₂-Al₂O₃, CuO/La₂O₃-Al₂O₃, *in situ* XRD, Raman, TPR**I. INTRODUCTION**

γ -Al₂O₃ is regarded as a suitable support for a variety of catalysts used in various reactions such as alkane dehydrogenation, NO_x and SO₂ reduction [1-5]. The CuO/Al₂O₃ catalysts exhibit comparable activities as precious metals catalysts for carbon monoxide oxidation [6]. However, a spinel structure of CuAl₂O₄ is formed as a result of the CuO/Al₂O₃ interaction at high temperatures and its catalytic activities are apparently lower than the metal oxide itself [7]. The strong CuO/Al₂O₃ interaction indicates that it is necessary for the CuO/Al₂O₃ catalyst to add other oxides Cr₂O₃ [8], Sm₂O₃ [9] and ZrO₂ [10] for inhibiting the interaction and improving the catalytic activities of CO oxidation [11-13]. ZnO-doped CuO/Al₂O₃ suppressed the formation of CuAl₂O₄ 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 CeO₂ 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 La₂O₃ improves the

thermal stability of the catalyst and supporter [17-19]. The CuO/CeO₂-Al₂O₃ catalyst and the CuO/La₂O₃-Al₂O₃ catalyst have become the object of several investigations [20-23].

In this work, the effect of CuO distribution and the addition of CeO₂ and La₂O₃ on the catalytic properties for CO oxidation was investigated. It was shown that the distribution of CuO and thermal CuO/Al₂O₃ solid-solid interaction can be effectively confirmed by *in situ* XRD, Raman spectroscopy and H₂-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/Al₂O₃, CuO/CeO₂-Al₂O₃, and CuO/La₂O₃-Al₂O₃ (denoted as Cu/Al, Cu/CeAl, and Cu/LaAl) catalysts were prepared using an impregnation method. CeO₂ or La₂O₃ modified γ -Al₂O₃ support (denoted CeO₂-Al₂O₃ or La₂O₃-Al₂O₃) was prepared as follows: an appropriate amount of Ce(NO₃)₃ or La(NO₃)₃ was dissolved in deionized water, and the support γ -Al₂O₃ (0.3-0.4 mm, 240 m²/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 CeO₂ or La₂O₃ was 40wt% in the CeO₂-Al₂O₃ or La₂O₃-Al₂O₃, respectively.

For the preparation of supported Cu catalysts, the as-prepared supports (Al₂O₃, CeO₂-Al₂O₃ or La₂O₃-

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Al₂O₃) were impregnated with certain amount of Cu(NO₃)₂ 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 α 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 2θ 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%H₂ and 95%N₂ 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 2θ 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 H₂:N₂ (5:95) with a total flow rate of 20 mL/min (room temperature and 101.3 kPa). The amount of H₂ 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%O₂ in N₂ was introduced to the catalysts at a total flow rate 80 mL/min without any pretreatment. The analysis of the CO₂ 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 CuAl₂O₄ are present; for the Cu/CeAl catalyst, peaks due to CuO, CeO₂, and CuAl₂O₄ 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 CuAl₂O₄ formed in these two catalysts. CuAl₂O₄ formed as a result of the following thermal solid-solid reaction: CuO+Al₂O₃→CuAl₂O₄. The XRD results indicate that the addition of La₂O₃ can prevent the formation of CuAl₂O₄. 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⁻¹ 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⁻¹ attributed to cubic CeO₂ [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 CeO₂ for the Cu/CeAl catalyst. Combined with the XRD pattern, it can be concluded that a CuAl₂O₄ layer is between the CuO and Al₂O₃ layers for the Cu/Al catalyst [26]. The crystalline phase of CuO and CeO₂ for the Cu/CeAl catalyst are present in the XRD pattern, which allows the conclusion that CuO has transferred into the internal layer of CeO₂ and interacts with the support Al₂O₃ to produce CuAl₂O₄ [28]. The authors propose that this is because CuO easily combines with CeO₂ 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 (α), 300 °C (β_1), and 470 °C (γ_1) and a broad and weak peak at about 800 °C (γ_2). For the Cu/CeAl catalyst, besides the same reduction peaks (α , β_1 , and γ_1) in the Cu/Al catalyst, a reduction peak (β_2) at 380 °C is present as well. Furthermore, the intensities of the α and β_1 peaks sharply decrease while that of the γ_1 peak obviously increases in the Cu/CeAl catalyst compared with the Cu/Al catalyst. For the CuO/La₂O₃-Al₂O₃ catalyst, only a strong reduction peak β_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 CuAl₂O₄ 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 CuAl₂O₄ 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 CuAl₂O₄ 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 CeO₂ 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, Cu₂O 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 α 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 α 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 β_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 β_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 Cu₂O can be observed, probably due to the incomplete reduction of CuO. For the Cu/Al and Cu/CeAl catalysts (Fig.5(a) and (b)), CuAl₂O₄ is the only phase that changes with increasing temperatures, so both the γ_1 and γ_2 peaks are the reduction of CuAl₂O₄ 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 CuAl₂O₄ content in the former is higher than that in the latter. This fact suggests that the addition of CeO₂ into Cu/Al catalysts can promote the formation of CuAl₂O₄ while La₂O₃ 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/%			
	α	β_1	β_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 CuAl_2O_4 exists between CuO and Al_2O_3 layer. For the Cu/CeAl catalyst, the main phase on the surface is CeO_2 , most of CuO has transferred into the internal layer of CeO_2 . For the Cu/LaAl catalyst, CuO presents as bulk phase on the surface and La_2O_3 exists between CuO and Al_2O_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 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 CeO_2 to the alumina can primarily be related to the association of CuO with CeO_2 rather than increased dispersion of CuO [31]. It has been shown that a very little amount of CuO doped to CeO_2 can promote the catalytic activity for CO oxidation extensively, due to the activation of oxygen by 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 CeO_2 and La_2O_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- Al_2O_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 La_2O_3 can hinder the transference of CuO and consequently prevent the formation of CuAl_2O_4 . Also, the addition of 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.

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