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Monolayer Dispersive Supported CuO/ γ -Al₂O₃ Catalysts Studied by XAFS

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Abstract

The local structures of supported CuO/ γ -Al₂O₃ monolayer dispersive catalysts with different CuO loadings have been investigated by XAFS. For the CuO/ γ -Al₂O₃ catalyst with CuO loading of 0.4 mmol/100 m², the XAFS results indicate that only one peak corresponding to the Cu-O first shell appears in the radial structural function of Cu atoms, and that the bond length $R_{\text{Cu-O}}$ and coordination number N are 1.95 Å and 3.8, respectively. We consider that the CuO active species on the surface of γ -Al₂O₃ are in the form of isolated atomic clusters (CuO₄)_mⁿ⁺ with distorted structure for the CuO/ γ -Al₂O₃ (0.4 mmol/100 m²) catalyst. It has been found that small amount of CuO nano-grains is formed on the surface of γ -Al₂O₃ for CuO/ γ -Al₂O₃ (0.8 mmol/100 m²) catalyst while the CuO loading is just equal to the threshold 0.8 mmol/100 m². For the catalyst with CuO loading of 1.2 mmol/100 m², the local structure of Cu atoms in CuO/ γ -Al₂O₃ is similar to that of CuO powder. On the basis of the XAFS results, a schematic monolayer dispersion model has been proposed for CuO/ γ -Al₂O₃ catalysts.

1. Introduction

The elimination of atmosphere pollutants and automobile exhaustions, such as the reduction of NO and CO concentrations, have attracted considerable attention in the last two decades [1–4]. Although the noble metals catalysts of Pt/ γ -Al₂O₃ and Pd/ γ -Al₂O₃ show a nice catalytic property in reduction of NO in the presence of CO or oxidation of CO [3, 4], they are not widely used due to their expenses. Hence, one needs to find a cheaper catalyst. A number of studies by Kummer [5], Kapteijn *et al.* [6], and Chen *et al.* [7] have indicated that the supported CuO/ γ -Al₂O₃ monolayer-dispersed catalysts possess higher catalytic activity at room temperature for the reduction of NO in the presence of CO or oxidation of CO. Especially, CuO/ γ -Al₂O₃ catalyst has a lower price than those of the noble metal catalysts [8, 9]. It means that CuO/ γ -Al₂O₃ is a promising candidate for applications in controlling environmental pollutions.

Xie *et al.* [10], Chen *et al.* [7, 11] and Friedman *et al.* [12] have reported that under proper calcination conditions, the copper oxide species can be spontaneously dispersed as a monolayer on the surface of γ -Al₂O₃ support. The threshold for CuO monolayer dispersion on the surface of γ -Al₂O₃ is about 0.8 ~ 1.6 mmol/100 m² [7, 11]. The monolayer dispersion has been confirmed by X-ray diffraction (XRD). No peaks corresponding to the crystalline CuO phase appear in the XRD pattern of CuO/ γ -Al₂O₃ when the CuO loading is lower than its monolayer dispersive threshold. However, peaks of crystalline CuO phase can be observed in CuO/ γ -Al₂O₃ while the CuO loading is higher than its monolayer dispersive threshold. Unfortunately, even if a lot of studies have been done on CuO/ γ -Al₂O₃ monolayer dispersive

catalysts, the occupations of Cu²⁺ ions on the surface of γ -Al₂O₃ support are not clear enough yet [7, 11–13].

In this present approach, the local structures of supported CuO/ γ -Al₂O₃ monolayer dispersive catalysts prepared via impregnations have been investigated by XAFS. Three different CuO loadings of 0.4, 0.8 (equal to the monolayer dispersion threshold of 0.8 mmol/100 m²) and 1.2 mmol/100 m² are used to study the local structures of CuO/ γ -Al₂O₃ catalysts. On the basis of the XAFS results, a simple monolayer dispersion model has been proposed to interpret the structures of CuO/ γ -Al₂O₃ catalysts.

2. Experimental

γ -Al₂O₃, obtained from Fusun Petrochemical Institute in China, had been calcined at 973 K for 5 hours before using for preparing supported catalysts; the BET surface area was 195 m²·g⁻¹. The supported CuO/ γ -Al₂O₃ catalyst was prepared by incipient wetness impregnation of γ -Al₂O₃ support with an aqueous solution containing the requisite amount of copper nitrate hexahydrate. The catalyst was dried at 373 K for 24 hours, and subsequently calcined at 923 K in air for 3.5 hours. The CuO/ γ -Al₂O₃ catalysts with different CuO loadings were as follows, CuO/ γ -Al₂O₃ (0.4 mmol/100 m²), CuO/ γ -Al₂O₃ (0.8 mmol/100 m²) and CuO/ γ -Al₂O₃ (1.2 mmol/100 m²).

The Cu K-edge absorption spectra of CuO/ γ -Al₂O₃ catalysts were measured at the XAFS station of 4W1B beamline of Beijing Synchrotron Radiation Facility. The electron beam energy was 2.2 GeV and the maximum stored current was about 80 mA. Fixed-exit Si (111) flat double crystals were used as monochromator. The X-ray harmonics were minimized by detuning the two flat Si (111) crystals to about 70% of the maximum incident light intensity. Data were collected in transmission mode using ion chambers with mixed Ar/N₂ fill gas at room temperature. XAFS data were analyzed by using USTCXAFS3.0 [14] and UWXAFS3.0 codes [15].

3. Results and Discussion

The Cu K-edge EXAFS functions $k^3\chi(k)$ and their Fourier transformations (FT) for CuO powder and CuO/ γ -Al₂O₃ catalysts with different CuO loadings are shown in Figure 1 and Figure 2, respectively. The FT is performed using the k region from 2.5 to 12 Å⁻¹ and a Hanning window. It can be observed that several stronger oscillations as shown in Figure 1 appear in the high- k region extended to 12 Å⁻¹ for the CuO powder. The oscillation feature of CuO/ γ -Al₂O₃ catalyst with CuO loading

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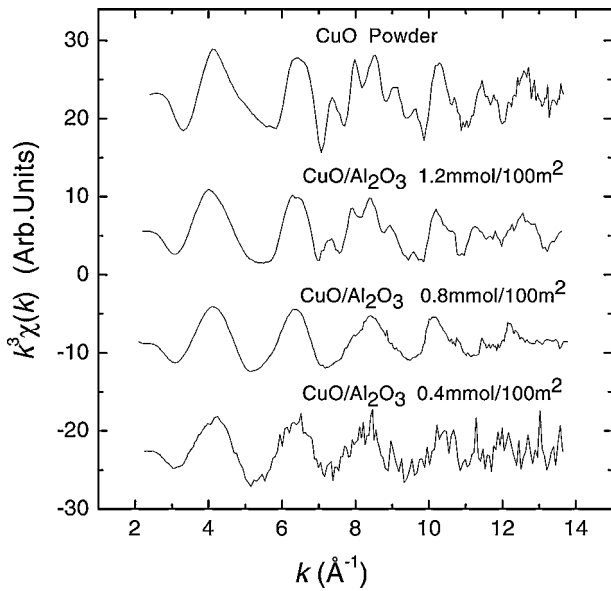


Fig. 1. $k^3\chi(k)$ functions of CuO powder and CuO/ γ -Al₂O₃ with different CuO loadings.

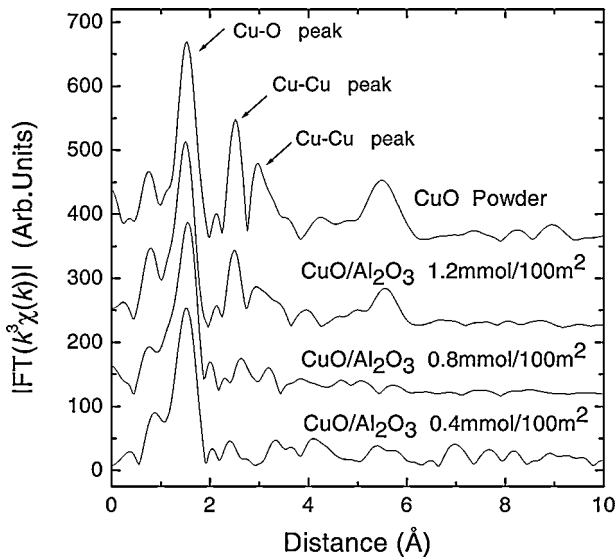


Fig. 2. RSF curves of CuO powder and CuO/ γ -Al₂O₃ with different CuO loadings.

of 1.2 mmol/100 m² is similar to that of CuO powder, unless its magnitude in the high- k region is slightly deceased. With the CuO loadings decreasing to 0.8 or 0.4 mmol/100 m², the magnitude of the oscillation peaks for the CuO/ γ -Al₂O₃ catalyst is further deceased by compared with that of CuO/ γ -Al₂O₃ (1.2 mmol/100 m²). Figure 2 demonstrates that there are three stronger peaks located at about 1.5, 2.5 and 3.4 Å in the FT curve of the CuO powder. The first and second peaks correspond to the first shell of four Cu-O pairs with bond length of 1.96 Å, the second shell of two Cu-O pairs with bond length of 2.78 Å and ten Cu-Cu pairs with an average bond length of 3.03 Å, respectively. With the CuO loading changing from 1.2 to 0.4 mmol/100 m², only the peak of the first shell exists and the peaks of the higher shells disappear for the monolayer dispersive CuO/ γ -Al₂O₃ catalyst.

For obtaining the structural parameters of CuO/ γ -Al₂O₃ catalysts, least-squares curve fit was performed for the data analysis by using the USTCXA3.0 code [14]. The theoretical amplitude functions and phase shifts were calculated by FEFF7.0

Table I. The structural parameters of CuO powder and CuO/ γ -Al₂O₃ with different CuO loadings.

Sample	Bond type	$R/\text{\AA}$	$\sigma^2/\text{\AA}^2$	N	$\Delta E/\text{eV}$
CuO/ γ -Al ₂ O ₃ (0.4 mmol/100 m ²)	Cu-O	1.95	0.0052	3.8	-1.9
	Cu-O	2.78	0.0161	0.1	-1.9
	Cu-Cu	2.97	0.0220	0.2	-1.9
CuO/ γ -Al ₂ O ₃ (0.8 mmol/100 m ²)	Cu-O	1.95	0.0050	3.9	-1.6
	Cu-O	2.78	0.0153	0.2	-1.6
	Cu-Cu	2.97	0.0214	3.4	-1.6
CuO/ γ -Al ₂ O ₃ (1.2 mmol/100 m ²)	Cu-O	1.95	0.0049	4.0	-1.9
	Cu-O	2.78	0.0139	2.0	-1.9
	Cu-Cu	2.97	0.0221	8.1	-1.9
CuO Powder	Cu-O	1.95	0.0042	3.9	2.1
	Cu-O	2.78	0.0050	2.0	2.1
	Cu-Cu	2.97	0.0220	9.6	2.1

[15]. The curve fits, based on single-scattering theory, were performed in R -range between 1.0 and 2.9 Å for the two first nearest Cu-O sub-shells ($R_1 = 1.96$, $R_2 = 2.78$ Å) and one Cu-Cu second shell ($R_3 = 3.03$ Å). The fitting results are summarized in Table I.

Seen from Table I, the structural parameters of the Cu-O first sub-shell are almost the same for all the CuO/ γ -Al₂O₃ catalysts with CuO loadings of 0.4, 0.8 and 1.2 mmol/100 m². Their bond lengths R and the coordination numbers N are 1.95 Å and 3.8, 1.95 Å and 3.9, 1.95 Å and 4.0, respectively. However, the N of the Cu-O second sub-shell ($R = 2.78$ Å) is about 2.0 for CuO/ γ -Al₂O₃ (1.2 mmol/100 m²) while those of CuO/ γ -Al₂O₃ (0.8 or 0.4 mmol/100 m²) are close to zero, and the N of the Cu-Cu second shell ($R = 2.97$ Å) are 8.1, 3.4 and 0.2 for CuO loadings of 1.2, 0.8 and 0.4 mmol/100 m², respectively. These structural parameters have clearly shown that only the XAFS signal corresponding to the Cu-O first shell appears in the CuO/ γ -Al₂O₃ (0.4 mmol/100 m²) catalyst that is lower than the monolayer dispersion threshold of 0.8 mmol/100 m². When the CuO loading is increased to the monolayer dispersion threshold or exceeds it, the peaks of their higher shells appear in the FT curves as shown in Figure 2. It is noteworthy that the bond lengths ($R = 1.95$ Å) and coordination numbers ($N = 3.8$) of the Cu-O first shell of CuO/ γ -Al₂O₃ (0.4 mmol/100 m²) catalyst is almost the same as those ($R = 1.95$ Å and $N = 4.0$) of CuO powder, CuO/ γ -Al₂O₃ (0.8 mmol/100 m²) and CuO/ γ -Al₂O₃ (1.2 mmol/100 m²) catalysts. This feature implies that the first nearest neighbors of Cu²⁺ in CuO/ γ -Al₂O₃ catalysts are similar to that of crystalline CuO powder, which is independent of the CuO loadings. Xie *et al.* [10], Chen *et al.* [7, 11] and Friedman *et al.* [12] have considered that CuO species are highly dispersed (or monolayer dispersive) on the surface of γ -Al₂O₃ under the monolayer dispersive threshold of CuO, since their XRD patterns indicate that no diffraction peaks corresponding to crystalline CuO were observed for CuO loadings of 0.8 mmol/100 m². In fact, there are two possible reasons for the disappearance of CuO diffraction peaks. One is that CuO species are monolayer dispersive on the surface of γ -Al₂O₃, which is just as the results reported by Xie *et al.* [10] and Chen *et al.* [7, 11]. The other is that CuO species are much smaller clusters with high dispersion on the surface of γ -Al₂O₃. XRD technique is difficult for detecting the diffraction signals while the grain sizes of the particles are small enough [16]. Our XAFS results indicate that Cu²⁺ ions are in the form of atomic clusters (CuO₄)_{*n*}^{*n*+}

with distorted structure on the surface of γ -Al₂O₃, even for the CuO/ γ -Al₂O₃ catalyst in which CuO loading is lower than the threshold of 0.8 mmol/100 m². Meanwhile, the disappearance of higher Cu-O and Cu-Cu coordination shells for CuO/ γ -Al₂O₃ (0.4 mmol/100 m²) catalyst indicates that there are no Cu²⁺ ions existing in incorporated form on the surface vacant sites of the γ -Al₂O₃ support, or in other words, there are no Cu-Cu or Cu-Al second coordination shells in CuO/ γ -Al₂O₃ (0.4 mmol/100 m²). Otherwise, the peak associated with the Cu-Cu or Cu-Al second shell should appear in the monolayer-dispersed CuO/ γ -Al₂O₃ catalysts [12]. This result suggests that CuO species on the surface of γ -Al₂O₃ do not exist in the form of Cu₂O [17] or spinal CuAl₂O₄ [18]. In addition, the present results seem to indicate that it is impossible to have Cu²⁺ coordinated by 5 oxygen atoms in the first nearest neighbor as claimed in Refs. [11] and [12]. In order to well interpret the XAFS results, we consider that the CuO active species on the surface of γ -Al₂O₃ are in the form of isolated atomic clusters (CuO₄)_mⁿ⁺ with distorted structure. This result means that the (CuO₄)_mⁿ⁺ cluster as a basic structural element occupies the surface vacant site of the γ -Al₂O₃ support for the monolayer-dispersed supported CuO/ γ -Al₂O₃ catalyst after calcined at a lower temperature of 723 K.

The weak peaks of the higher coordination shells for the CuO/ γ -Al₂O₃ catalyst with CuO loading of 0.8 mmol/100 m² show that most of the Cu²⁺ ions are in the form of isolated atomic clusters (CuO₄)_mⁿ⁺, but there is also a small amount of CuO nano-grains forming on the surface of γ -Al₂O₃ support. For the CuO/ γ -Al₂O₃ catalyst with CuO loading of 1.2 mmol/100 m², Cu²⁺ ions on the surface of the γ -Al₂O₃ support are mainly in the form of poly-crystalline CuO. Our results are consistent with those reported by Shi *et al.* [19]. They have studied the local structures around Mo for monolayer-dispersed MoO₃/ γ -Al₂O₃ catalysts with XAFS, and show that below the monolayer dispersive threshold of MoO₃ loadings, the dispersion phase of MoO₃ active species on the surface of γ -Al₂O₃ support consists of [MoO₄] polyhedrons that are not connected to each other.

In summary, we propose a schematic mechanism to interpret the local structural change for monolayer dispersive

CuO/ γ -Al₂O₃ catalyst during the preparation by impregnation. After the mixture of γ -Al₂O₃ support and copper nitrate aqueous solution is dried, Cu²⁺ ions exist in the form of Cu(NO₃)₂ absorbed randomly onto the surface of γ -Al₂O₃ support. Then, the Cu(NO₃)₂ compound with the crystal water are probably decomposed at the calcinating temperature of 723 K in air for 3.5 hours, the CuO species are in the form of atomic clusters (CuO₄)_mⁿ⁺ (or (Cu(OH)₄)_mⁿ⁺) with distorted structure as a basic cluster element occupying the surface vacant sites of the γ -Al₂O₃ support.

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