

Dispersion of copper oxide supported on γ -alumina and its sulfation properties

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Abstract: CuO/ γ -Al₂O₃ catalysts were prepared by impregnation with different CuO loadings. The dispersion of CuO supported on γ -Al₂O₃ support was studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), and temperature programmed reduction (TPR). The dispersion threshold of CuO in γ -Al₂O₃ determined by X-ray quantitative analysis was 0.275 g/g, i.e., 0.275CuAl. Highly dispersed CuO or crystalline CuO would appear on the γ -Al₂O₃ support when CuO loading was below or more than its dispersion threshold. TPR experiments show that reduction peak temperature ranges of 0.1CuAl and pure CuO are 420–690 °C and 290–380 °C, respectively. 0.1CuAl is not easily reduced due to interaction between CuO and γ -Al₂O₃. 0.5CuAl shows a two-step reduction range during 210–300 °C and 410–730 °C, which confirms the existence of highly dispersed CuO and crystalline CuO. The sulfation experiments show the optimal CuO loading amount is far below its dispersion threshold, and copper oxide supported on γ -Al₂O₃ is in the form of submonolayer.

Key words: copper oxide; dispersion; submonolayer

1 Introduction

Copper oxide has been received considerable attention in recent years for the removal of soot from diesel engine exhaust, the selective oxidation of CO in excess hydrogen, SO₂ removal from stack gas [1–4], etc. The active ingredient copper oxide is generally dispersed on porous supports of inert metal oxides such as γ -Al₂O₃ and SiO₂ to augment its catalytic activity. Many metal oxides have a much higher capacity for the formation of atomically dispersed surface species on supports, and the physical and chemical properties of highly dispersed surface species are usually drastically different from those of the corresponding bulk phases. The interaction between copper oxide and support has been of interest in heterogeneous catalysis for many years, not only because of their importance in catalytic applications, but also because of the diversity of explanations of the nature and structure of the dispersed metal oxides on various

supports [5–8].

For supported copper oxide catalysts, it has been found that the dispersion state of copper oxide on the support significantly influenced its catalytic properties. YAO et al [9] studied catalytic decomposition of nitrous oxide on CuO/ γ -Al₂O₃ catalysts prepared by grafting, and they found that the properties of these catalysts changed with the amount of deposited metal oxide. HU et al [10] carried out a series work on the dispersion of metal oxides on supports and pointed out that Cu²⁺ ions occupy the surface octahedral vacant sites of γ -Al₂O₃ at the pre-impregnation procedure. WANG et al [11] proposed that a great many oxides and salts could disperse spontaneously onto the surfaces of supports to form a monolayer or submonolayer, because in these cases the monolayer was a thermodynamically stable form. The utmost dispersion capacity was called dispersion threshold.

Despite of the studies mentioned above, the effect of the loading amount on activity of copper oxide

supported on γ -Al₂O₃ and desulfurization properties have rarely been reported. In the present work, a series of CuO/ γ -Al₂O₃ catalysts were prepared and the effect of loading amount was studied.

2 Experimental

CuO/ γ -Al₂O₃ sample was prepared by wet impregnation with a known mass of γ -Al₂O₃ (BET surface area 277.8 m²/g) and solution containing a calculated amount of Cu(NO₃)₂·3H₂O. Followed by evaporation at 90 °C with stirring, the samples were dried in an oven at 120 °C for 12 h, and subsequently calcined at 450 °C in stagnant air for 5 h in a muffle furnace. In this way, samples containing 0.07 g CuO, 0.10 g CuO, 0.12 g CuO, 0.12 g CuO, 0.15 g CuO, 0.35 g CuO, and 0.40 g CuO, 0.45g CuO, 0.55g CuO per gram γ -Al₂O₃ were obtained, respectively, which were labeled as 0.07 CuAl, 0.10 CuAl, etc.

Temperature-programmed reduction (TPR) experiments were carried out in a thermogravimetric setup with a 5% (volume fraction) H₂/Ar mixture and a heating rate of 10 °C/min. Desulfurization experiments were carried out in the same setup as in TPR experiments. The calculated gas composition was 2×10⁻³ SO₂, 5% O₂, and 3% H₂O, with N₂ as the balance. Chemical reactions occurring during the reduction of CuO by H₂ and desulfurization of CuO were as follows:



Due to the consumption of H₂, SO₂ and O₂, and the production of H₂O gas in these two reactions, the total mass of sample was changed continuously during reaction. Mass change could be used to evaluate the activity of sample. Mass gain ($\Delta m = m_t - m_0$) plotted as a function of time was obtained from thermogravimetry results, where m_t and m_0 were actual and initial catalyst masses, respectively. Correspondingly, the mass loss, plotted as a function of temperature, was negative.

X-ray diffraction (XRD) for identification of crystalline phases in the catalysts was performed in a D/MAX diffractometer with Cu K α radiation (40 kV, 50–100 mA). XRD patterns were recorded in the range 10° ≤ 2θ ≤ 80°. A scanning electron microscope was used to follow the surface morphology.

3 Results and discussion

3.1 XRD analysis of CuO supported on γ -Al₂O₃

XRD patterns of CuO/ γ -Al₂O₃ sorbents with different copper loadings are shown in Fig. 1. For samples with lower CuO loadings, evident peaks corresponding to the crystalline CuO are not observed in Fig. 1(a), which implies that the copper oxide species

are highly dispersed on the surface of γ -Al₂O₃ support. When the CuO loading exceeds a critical value, i.e., dispersion threshold, crystalline CuO presents increasing intensity with loading as shown in patterns (b), (c), (d), and (e) in Fig. 1.

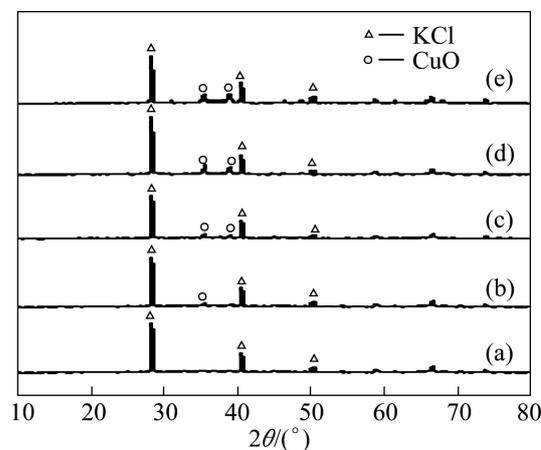


Fig. 1 XRD patterns of CuO/ γ -Al₂O₃ samples with different CuO loadings and reference material KCl: (a) 0.1 CuAl+KCl; (b) 0.35 CuAl +KCl; (c) 0.4 CuAl +KCl; (d) 0.50 CuAl +KCl; (e) 0.55 CuAl +KCl

The dispersion threshold determination was done by X-ray quantitative analysis with internal-standard material KCl [12]. For a binary mixture of compound CuO and matrix γ -Al₂O₃, the relation between X-ray diffraction intensities and mass fraction of CuO is shown in Fig. 2.

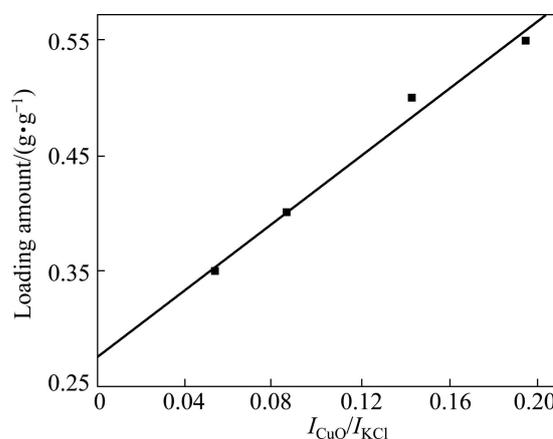


Fig. 2 Diffraction intensity ratio of CuO to KCl versus CuO loading amount

The intercept in Fig. 2 is the dispersion threshold of 0.275CuAl. As metal loading increases, X-ray diffraction of CuO appears, and microparticles of CuO form on the γ -Al₂O₃ support. The theoretical dispersion value of CuO is 0.529 according to O²⁻ anion radius of 0.132 nm, which means that CuO is dispersed on γ -Al₂O₃ in the form of submonolayer.

3.2 Scanning electron microscopy (SEM) analysis

In order to examine the dispersion of CuO on γ -Al₂O₃ support, stereographic pictures of 0.1CuAl and 0.5CuAl taken from a scanning electron microscope are shown in Fig. 3. The even surface shown in Fig. 3(a) means that copper oxide supported on γ -Al₂O₃ is highly dispersed. On the other hand, the higher CuO loaded sample 0.5CuAl shows clearly differentiated nano-CuO in Fig. 3(b). Dispersion states of CuO with loading amount below and above its dispersion threshold coincide with the XRD results above.

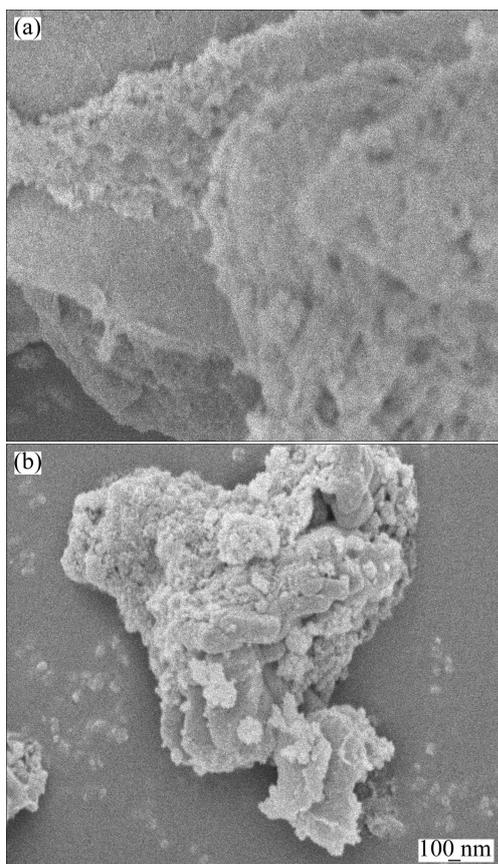


Fig. 3 SEM images of 0.1CuAl (a) and 0.5CuAl (b)

3.3 TPR analysis

The reduction characteristics of the prepared samples were studied over the temperature range of 100–900 °C by temperature-programmed-reduction (TPR) given in Fig. 4.

Mass loss of pure CuO in the temperature range of 290–380 °C shows that unsupported CuO is easily reduced by H₂. A gentle mass loss of 0.1CuAl in the temperature range of 420–690 °C shows that reduction of copper oxide is difficult due to its interaction with the support as CuO loading amount is below its dispersion threshold. The mass loss of 0.1CuAl approximates to the theoretical value following Eq. (1), which means that the reduction product is Cu. X-ray diffraction measurements for the residual products were conducted,

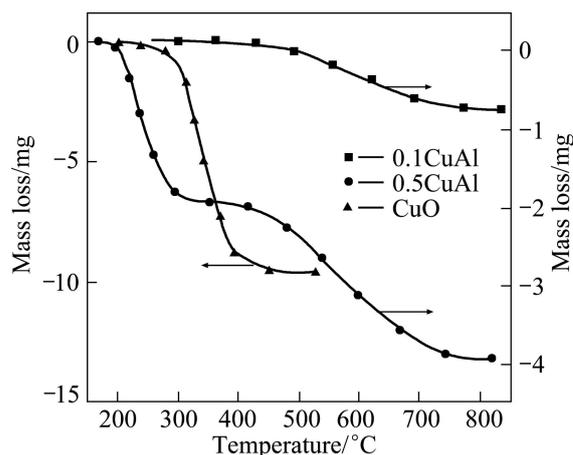


Fig. 4 TPR profiles of 0.1CuAl, 0.5CuAl and CuO

and no evidence was obtained for the presence of Cu₂O. However, the mass loss of 0.5CuAl occurs in a two-step temperature range of 210–300 °C and 410–730 °C, respectively, which shows that there are two reduction processes. The first one denotes the reduction of crystallite CuO on the support. The lower reduction temperature of crystalline CuO means that nano-CuO is more active than normal size CuO. The higher one denotes the reduction of amorphous CuO on γ -Al₂O₃ support, which coincides with the reduction of 0.1CuAl. Above dispersion threshold, copper oxide would exist in the form of highly dispersed and crystalline states on γ -Al₂O₃ support, and CuO in crystalline state can be detected by XRD, such as 0.5CuAl shown in Fig. 1.

3.4 Sulfation experiment

In order to understand the catalytic oxidation of copper oxide supported on γ -Al₂O₃, sulfation of CuO/ γ -Al₂O₃ with different CuO loading amounts is performed. Mass gain caused by the reaction of CuO/ γ -Al₂O₃ sorbents with SO₂ at 350 °C as a function of time is shown in Fig. 5(a). With increasing CuO loading amount, the mass gain should increase until CuO loading amount reaches its dispersion threshold. However, the specific rate of sulfation passes through a maximum for a defined surface coverage of copper oxide on alumina, i.e., 0.12 g CuO per gram γ -Al₂O₃ shown in Fig. 5(b), much lower than its dispersion threshold.

From a microscopic point, metal oxide surfaces are mainly composed of oxygen atoms and hydroxyl groups. According to the close-packed monolayer model [11], a great many oxides and salts can disperse spontaneously onto the surfaces of supports to form a monolayer or submonolayer. This model is on the assumption that O²⁻ anions form a close-packed monolayer, and metal cation occupies the vacant between O²⁻ anions. The schematic diagram is shown in Fig. 6.

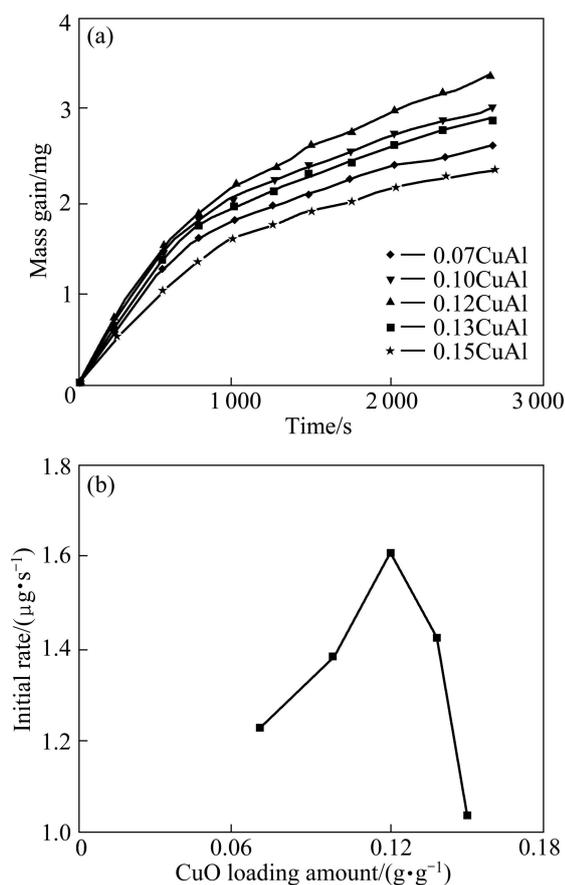


Fig. 5 Sulfation of CuO/ γ -Al₂O₃ with different CuO loading amounts: (a) Effect of CuO loading amount versus time; (b) Initial rate versus CuO loading amount

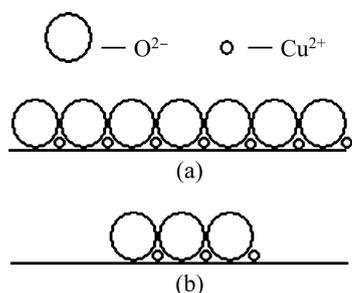


Fig. 6 Schematic diagram of close-packed model: (a) Monolayer; (b) Submonolayer

The dispersion threshold gave a meaningful explanation of highly dispersed oxides and crystalline oxides from thermodynamic point. If all the surface of γ -Al₂O₃ support is covered with CuO, γ -Al₂O₃ support will not participate in catalytic reaction. However, further study showed that the surface of γ -Al₂O₃ support participated in sulfation reaction under condition of a long sulfation time [13]. The amount introduced onto the porous support depends on the equilibrium concentration of the impregnating solution, the porous volume of the γ -Al₂O₃ support and the adsorption isotherm which

describes the binding of the precursor onto the support surface [14]. Considering these factors, it seems impossible that γ -Al₂O₃ is covered by CuO thoroughly uniformly. CuO in the form of submonolayer is more reasonable.

TWU [15] reported three structures about surface of sulfates as shown in Fig. 7, and one sulfur atom lines two or three oxygen atoms. When a CuO molecule is transformed into CuSO₄, the SO₄²⁻ ionic group may cover the adjacent CuO molecules, which may cause the optimal CuO loading amount far below its theoretical dispersion threshold.

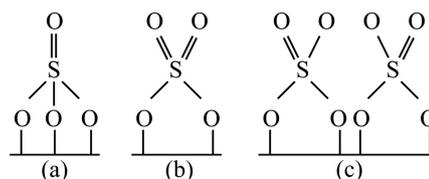


Fig. 7 Structure diagram of sulfates

4 Conclusions

1) The dispersion threshold of CuO supported on γ -Al₂O₃ support is 0.275CuAl. Scanning electronic micrographs show that highly dispersed CuO or crystalline CuO will exist on the γ -Al₂O₃ support when CuO loading amount is below or above its dispersion threshold.

2) Reduction peak temperature ranges of 0.1CuAl and pure CuO are 420–690 °C and 290–380 °C, respectively, which means that 0.1CuAl is not easily reduced due to the interaction between CuO and γ -Al₂O₃. 0.5CuAl shows a two-step reduction range of 210–300 °C and 410–730 °C, which confirms the existence of highly dispersed CuO and crystalline CuO. The lower reduction temperature of crystalline CuO denotes that nano-CuO is more active than normal size CuO.

3) Catalytic oxidation experiments show that the optimal CuO loading amount is 0.12CuAl, which is much lower than its dispersion threshold.

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氧化铜在 γ -Al₂O₃ 载体表面的分布及其硫化性能

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摘要: 采用浸渍方法制备不同氧化铜含量的 CuO/ γ -Al₂O₃ 催化剂。使用 XRD、SEM 和程序控制升温还原(TPR)方法研究 γ -Al₂O₃ 载体表面氧化铜的分布情况。用 X 射线定量分析方法得到氧化铜在 γ -Al₂O₃ 中的分散阈值为 0.275 g/g, 即 0.275CuAl。当氧化铜负载量小于或大于其分散阈值时, 高度分散或结晶状氧化铜将会出现在 γ -Al₂O₃ 载体表面。TPR 实验表明 0.1CuAl 和纯 CuO 还原温度范围分别为 420–690 °C 和 290–380 °C。氧化铜与载体之间的相互作用导致 0.1CuAl 不易被还原。0.5CuAl 呈现 2 个分步还原温度范围, 分别为 210–300 °C 和 410–730 °C, 证实了 γ -Al₂O₃ 载体表面高度分散和结晶状分布的氧化铜。硫化实验表明, 最佳氧化铜负载量小于其分散阈值, 氧化铜以亚单层形式分布在 γ -Al₂O₃ 载体表面。

关键词: 氧化铜; 分散; 亚单层

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