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Influence of ferric oxide modification on the properties of copper oxide supported on γ-alumina

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ABSTRACT

X-ray diffraction (XRD), Mössbauer spectroscopy, and temperature-programmed reduction (TPR) were employed to investigate the dispersion and reduction behaviors of the $Fe_2O_3/CuO/\gamma\text{-}Al_2O_3$ system. The results indicated that: (1) the crystalline CuO particle in the $CuO/\gamma\text{-}Al_2O_3$ samples was redispersed during impregnating $CuO/\gamma\text{-}Al_2O_3$ samples with $Fe(NO_3)_3$ solutions; (2) two different dispersion states of surface iron species could be observed, i.e., State I corresponding to the iron(III) species located in the D layer on the surface of $\gamma\text{-}Al_2O_3$ and State II corresponding to those in the C layer. The dispersed states of surface iron(III) species were closely related to the iron loading amount; (3) the copper species located in the D layer of alumina surface was easily reduced and the copper species located in the C layer were more stable, which could be due to the influence of the iron(III) species in the different layers; (4) in the NO + CO reaction, the catalytic performances were enhanced due to the Cu–Fe synergism and the main active species in this system should be the surface-dispersed copper oxide species.

1. Introduction

Supported metal oxide catalysts have attracted much attention due to their wide applications in a variety of industrially important reactions, such as hydrodesulfurization, cracking, polymerization, and partial oxidation of hydrocarbons and the selective reduction of nitrogen oxides [1–6]. It is well established that the chemical properties and activities of supported metal oxide catalysts can be dramatically influenced by the nature of the carrier [7–10]. Therefore, knowledge of the local structure of the catalyst surface and insight into the factors that determine the surface structure play an important role in further development and optimization of supported metal oxide heterogeneous catalytic systems. Accordingly, a large number of studies have been devoted to exploring the interaction between the support and the dispersed oxide species, and various explanations of models concerning the nature of the interaction have been proposed [11–17].

In the past, primary attention has been focused on the interaction between the monocomponent active component and the support in the catalysts. Correspondingly, reports about the multicomponent-supported catalysts are rare, partly because of the complex compositions and interactions of these species. Due to the complexity of the multicomponent-supported catalysts, though many correlative research studies have been carried out, there is still a lack of general agreement on the intrinsic interactions among the components. For example, in $CuO/CeO_2/TiO_2$ catalysts, the interactions should involve all the species including dispersed copper oxide, crystalline copper oxide, dispersed ceria species, crystalline CeO, and TiO_2 support. However, in fact, the catalysts, commonly used in the chemical industry, are binary or multiple component catalysts, such as the $Fe\text{–}K/\gamma\text{-}Al_2O_3$ catalyst for CO_2 hydrogenation [18], $V_2O_5\text{–}WO_3/TiO_2$ catalyst in the reduction of NO_x by NH_3, and WO_3-modified $NiO\text{–}ZrO_2$ for the dimerization of ethylene [19,20]. Hence, the interaction between multiple metal oxides in those catalysts is wide open for study.

$\gamma\text{-}Al_2O_3$, copper oxide, and ferric oxide are important components in automotive exhaust emission control and industrial catalysts. For example, $CuO/\gamma\text{-}Al_2O_3$ catalysts show a potential catalytic activity for the elimination of NO_x and CO oxidation and special attention has been paid to the substitution of noble metal catalysts in these systems [21], and iron-containing catalysts have been widely used in alkylation and oxidation reactions [22,23]. Comparatively, the supported $Fe_2O_3/CuO/\gamma\text{-}Al_2O_3$ system has received little attention in the past. In the present work, Mössbauer spectroscopy, X-ray diffraction (XRD), and temperature-programmed reduction (TPR) have been employed to study the structure of iron and copper species of $Fe_2O_3/CuO/\gamma\text{-}Al_2O_3$ samples

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prepared by the stepwise impregnation method, and the activity of the removal of NO by CO has been tested. Attention has been focused on: (1) the influence of the impregnation of ferric oxide on the dispersion and reduction of copper oxide species in CuO/γ-Al_2O_3, (2) the dispersion and reduction of ferric oxide and copper oxide on copper oxide premodified γ-Al_2O_3 support, and (3) the catalytic performances of Fe_2O_3/CuO/γ-Al_2O_3 samples.

2. Materials and methods

2.1. Sample preparation

γ-Al_2O_3, obtained from Fusun Petrochemical Institute (China), was calcined at 750 °C for 5 h before being used for preparing supported samples. The BET surface area is about 216 $m^2\ g^{-1}$.

Supported copper oxide samples with fixed CuO loadings (0.7 mmol/100 m^2 γ-Al_2O_3, close to the dispersion capacity [24]) were prepared by incipient wetness impregnation of γ-Al_2O_3 supports with an aqueous $Cu(NO_3)_2$ solution. The samples were dried at 100 °C for 24 h, and then calcined at 450 °C in air for 5 h. The same procedure was used for the preparation of Fe_2O_3-supported samples.

Fe_2O_3/CuO/γ-Al_2O_3 samples were prepared by incipient wetness impregnation of CuO/γ-Al_2O_3 samples with an aqueous $Fe(NO_3)_3$ solution of different concentrations. The samples were dried at 100 °C for 24 h, and then calcined at 450 °C in air for 5 h. For simplicity, the Fe_2O_3/CuO/γ-Al_2O_3 samples were assigned as Fxy; i.e., F01 corresponds to a sample with Fe^{3+} loading amount of 0.1 mmol/100 m^2 γ-Al_2O_3 and fixed CuO loading amounts of 0.7 mmol/100 m^2 γ-Al_2O_3.

Fe_2O_3–CuO sample, containing 3 mol Fe_2O_3 and 1 mol CuO, was prepared by coprecipitation of aqueous $Fe(NO_3)_3$ and $Cu(NO_3)_2$ solution, dried at 100 °C for 24 h, and then calcined at 450 °C in air for 5 h.

2.2. Characterization

XRD patterns were obtained with a Philips X'pert Pro diffractometer employing Ni-filtered Cu*K*α radiation (0.15418 nm); the X-ray tube was operated at 40 kV and 40 mA.

The surface area of γ-Al_2O_3 was determined via nitrogen adsorption at 77 K with the Brunauer–Emmet–Teller (BET) method using a Micrometrics ASAP-2000 adsorption apparatus.

Mössbauer spectra were measured at room temperature, using a constant acceleration spectrometer with a 20 mCi source of ^{57}Co in rhodium, and the isomer shifts were given relative to α-Fe at room temperature. The absorption lines in the Mössbauer spectra were fitted to Lorentzian lines employing a least-squares method by the MOSFUN program [25].

TPR profiles were carried out in a quartz U-tube reactor, and a 30 mg sample was used for each measurement. Prior to the reduction, the sample was pretreated in a N_2 stream at 100 °C for 1 h and then cooled to room temperature. After that, a H_2–Ar mixture (7.3% by volume) was switched on. The temperature was increased linearly at a rate of 10 °C min^{-1}, and the consumption of H_2 in the reactant stream was detected by a thermal conductivity cell.

The activities for "NO + CO" reaction were determined under steady state, involving a feed steam with a fixed composition, NO 5%, CO 10%, and He 85% by volume as diluents. A quartz U-tube with a requisite quantity of catalyst (∼50 mg) was used. The catalysts were pretreated in N_2 stream at 100 °C for 1 h and then cooled to room temperature, after that, the mixed gases were switched on. The reactions were carried out at different temperatures with a space velocity of 12,000 h^{-1}. Two volumes and thermal conduction detections (TCDs) were used for the purpose of analyzing the production, with volume A packed with Paropak Q for the separation of N_2O and CO_2, and volume B packed with a 5A molecular sieve (40–60 M) for separating N_2, NO, and CO.

3. Results and discussion

3.1. XRD results

XRD results of Fe_2O_3/CuO/γ-Al_2O_3 samples with constant copper oxide loadings (0.7 mmol Cu^{2+}/100 m^2 γ-Al_2O_3) and different ferric oxide loadings are shown in Fig. 1. For Fe_2O_3/CuO/γ-Al_2O_3 samples with the ferric oxide loadings are lower than 0.9 mmol Fe^{3+}/100 m^2 γ-Al_2O_3, no characteristic peaks of crystalline Fe_2O_3 (typically at $2\theta = 33.21°$ and 35.63°) have been observed, which suggest that ferric oxide species have been highly dispersed on the surface of CuO/γ-Al_2O_3. However, characteristic peaks of crystalline Fe_2O_3 have been found in high ferric oxide loading samples (⩾1.1 mmol Fe^{3+}/100 m^2 γ-Al_2O_3) and the intensities of the peaks increase with increase in ferric oxide loading amount, indicating the formation of crystalline Fe_2O_3. Therefore, the dispersion capacity of ferric oxide on the surface of CuO/γ-Al_2O_3 is about 0.9 mmol Fe^{3+}/100 m^2 γ-Al_2O_3.

Furthermore, for samples with extreme low ferric oxide loadings (⩽0.3 mmol Fe^{3+}/100 m^2 γ-Al_2O_3), the peaks corresponding to crystalline CuO ($2\theta = 35.55°$ and 38.74°) can be observed. Their intensities decrease with increase in ferric oxide loadings, and disappear at last when the loading amounts of ferric oxide reach 0.5 mmol Fe^{3+}/100 m^2 γ-Al_2O_3. Because the theoretical dispersion capacity of CuO on γ-Al_2O_3 surface is about 0.75 mmol Cu^{2+}/100 m^2 γ-Al_2O_3 [24], the peaks corresponding to crystalline CuO in samples F00, F01, and F03 indicate that the copper oxide species have not dispersed on the γ-Al_2O_3 surface completely. As CuO/γ-Al_2O_3 was reimpregnated with a concentrated $Fe(NO_3)_3$ solution, the crystalline CuO particles became soluble, and then redisperses on the surface of γ-Al_2O_3. Thus, crystalline CuO peaks disappear

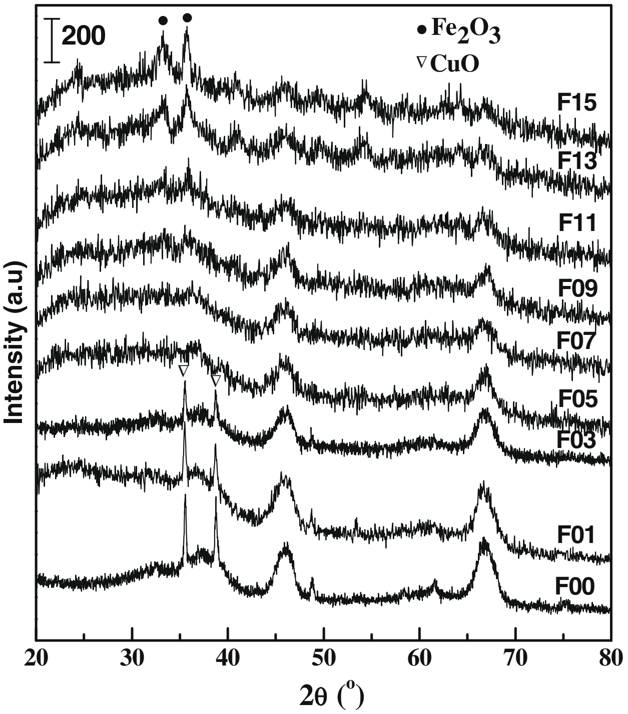

Fig. 1. XRD patterns of Fe_2O_3/CuO/γ-Al_2O_3 samples with fixed CuO loadings (0.7 mmol/100 m^2 γ-Al_2O_3) and Fe_2O_3 loadings of 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, and 1.5 mmol Fe^{3+}/100 m^2 γ-Al_2O_3.