

Copper Oxide Clusters Stabilized by Ceria for CO, C₃H₆, and NO Abatement

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Abstract: A strong interaction between a metal oxide and support has long been indicative of its promotion of catalytic activities. In connection with this, we investigated the interaction of CuO with γ -Al₂O₃ and CeO₂ for producing highly efficient catalysts for CO, C₃H₆, and NO abatement. In particular, the dispersion and thermal aging resistance of CuO clusters on different supports were studied. CuO clusters can be stabilized by interaction with CeO₂, while on γ -Al₂O₃ they aggregated into larger particles at high CuO loadings. On the other hand, due to the poor thermal stability of CeO₂, CuO clusters dispersed on it were sintered during an aging treatment at 950 °C. Accordingly, by pre-dispersing CeO₂ on γ -Al₂O₃ followed by CuO dispersion, stabilized CuO clusters were obtained that were based on the superior aging resistance of the γ -Al₂O₃ support. Therefore, better catalytic performance and thermal aging properties were obtained with a CuO/CeO₂/ γ -Al₂O₃ catalyst as compared with CuO/ γ -Al₂O₃ and CuO/CeO₂ samples.

Key words: CuO clusters; stability; surface interaction; carbon monoxide, propene; nitric oxide; catalytic abatement

A surface interaction between the active component and the support influences the catalytic behavior of a supported catalyst. The dispersion of an active component is different when it is supported on different materials [1–3]. In general, a strong metal oxide/support interaction would result in a high dispersion of metal oxide, and vice versa. In addition, factors such as charge transfer, coordination environment, and redox properties should also be considered. Based on XPS analysis, An et al. [4] found that Pt on fluorinated carbon (FC) was more electron rich than Pt supported on fluorine-free supports, which was due to electron transfer from FC to Pt. Better activity and selectivity were found for the reaction of NO with NH₃ over the Pt/FC catalysts, which was attributed to the enhanced availability of electrons. The electron-rich Pt sites can donate electrons to NO antibonding orbitals and thereby promote dissociative chemisorption and reaction of NO. Dong and coworkers [5,6] observed that the dispersion capacity of CuO on γ -Al₂O₃ was roughly half of that on MO/ γ -Al₂O₃ (MO = NiO, ZnO, CdO,

and MgO, etc.). They suggested that there was a preference incorporation of copper into the surface octahedral vacancies of γ -Al₂O₃ during catalyst calcination at 450 °C. In an extreme case, Park et al. [7] observed the formation of the CuAl₂O₄ species when a CuO/ γ -Al₂O₃ catalyst was calcined in air at 1000 °C for 24 h. They attributed the result to Cu²⁺ incorporation into the tetrahedral vacancies of the γ -Al₂O₃ surface. Jacobs et al. [8] reported that the reducibility of CoO species decreased in the order of Co/Al₂O₃ > Co/TiO₂ > Co/SiO₂, which was in line with the strength of interaction between CoO and the supports. In a comparison study of Cu/Al₂O₃ and Cu/CeO₂/Al₂O₃ catalysts, Martinez-Arias et al. [9] observed the easier reduction of copper species with the latter and attributed the result to copper interaction with ceria entities that were well dispersed on Al₂O₃ in a two dimensional manner. They believed that the copper species with better redox properties were responsible for the catalytic oxidation of CO. In summary, a relative study based on surface interaction is

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helpful for understanding the catalytic activity of differently supported catalysts.

In recent years, copper-based catalysts have been extensively investigated for their superior de-NO_x properties [10–12]. In the present study, we focused on the dispersion stability and thermal stability of CuO clusters on CuO/ γ -Al₂O₃, CuO/CeO₂, and CuO/CeO₂/ γ -Al₂O₃ catalysts. CO, NO, and C₃H₆ abatement was employed as the probe reaction. This is the key reaction system in the control of automotive exhaust emission. By correlating the stability of the copper species with catalytic behavior, the significance of CuO clusters was identified. It was found that CuO clusters can be stabilized by interaction with CeO₂, and the thermal stability of CeO₂ was enhanced by its interaction with γ -Al₂O₃. Therefore, pre-dispersing CeO₂ on γ -Al₂O₃ followed by CuO deposition allowed CuO clusters to exist at high temperatures, and a good catalytic performance was achieved.

1 Experimental

1.1 Catalyst preparation

CeO₂ was purchased from Rare-Chem Hi-Tech Co. Ltd., and γ -Al₂O₃ from Nanjing Catalyst Factory, China. The γ -Al₂O₃ material was calcined at 600 °C for 4 h before use. The CeO₂/ γ -Al₂O₃ binary support was prepared by incipient wetness impregnation of γ -Al₂O₃ with an aqueous solution of Ce(NO₃)₃·6H₂O. The material obtained was dried at 110 °C for 8 h and subsequently heated to 800 °C, with holding for 1 h after every rise of 100 °C.

Supported CuO catalysts were prepared by incipient wetness impregnation of the supports with an aqueous Cu(NO₃)₂ solution that would result in a designated CuO loading. After drying at 110 °C, the catalysts were calcined at 500 °C for 3 h in dry air. The CuO/ γ -Al₂O₃, CuO/CeO₂, and CuO/10%CeO₂/ γ -Al₂O₃ catalysts were denoted as CuA, CuC, and CuCA, respectively. With *x* (wt%) CuO loading based on the total mass of the sample, the catalysts were denoted as *x*CuA, *x*CuC, and *x*CuCA. A portion of the 7%CuA, 7%CuC, and 7%CuCA catalysts was subject to aging at 950 °C in air for 4 h. The resulting materials were denoted as CuA-a, CuC-a, and CuCA-a, respectively.

1.2 Catalyst tests

Activity test of the catalysts was carried out using a fixed bed quartz reactor equipped with a coaxial thermocouple. The catalyst (ca. 0.2 g) was pretreated in a N₂ stream (flow rate = 60 ml/min) at 500 °C for 1 h and then put in contact with a gas feed (0.1% NO + 0.1% C₃H₆ + 1% CO + 0.9% O₂, N₂ balance) at a gas hourly space velocity (GHSV) of 50000 h⁻¹. The effluent was analyzed online by a Foshan FGA-4100 analyzer.

1.3 Catalyst characterization

X-ray diffraction (XRD) analysis was carried out on a X-ray diffractometer (Rigaku D-Max Rotaflex) using Cu K α radiation (λ = 0.15404 nm). UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded in the range of 200–800 nm on a JASCO V-550 spectrometer. Temperature-programmed reduction (TPR) experiments were performed with a TCD system. The sample (50 mg) was first pretreated in an Ar stream (flow rate = 50 ml/min) at 500 °C for 1 h and cooled to room temperature (RT). The sample was then heated (10 °C/min) from 30 to 600 °C in a flow (rate = 50 ml/min) of 5 vol% H₂ in Ar for TPR characterization.

2 Results and discussion

2.1 Dispersion stability of copper oxide clusters

Figure 1 shows the XRD patterns of the catalysts with different CuO loadings on γ -Al₂O₃, CeO₂, and CeO₂/ γ -Al₂O₃. As can be seen in Fig. 1(a), the catalyst with the smallest CuO loading (3 wt%) showed no CuO peaks, implying that the copper species were highly dispersed. At or above 7 wt% loading, peaks attributable to CuO crystallites were clearly seen at 2θ = 35.44° and 38.78°. The results revealed that the higher copper oxide loading (i.e. 7 wt%) resulted in the formation of bulk CuO on the CuA catalysts. The crystallite sizes were calculated by the Scherrer equation and are listed in Table 1. For the CuA catalysts, the CuO particle grew from 22 to 24 nm, indicating the continual aggregation of metal oxide with increasing loading amount.

The UV-Vis DR spectra (Fig. 2(a)) of CuA showed that the catalyst with 3 wt% CuO loading had two main absorption bands: one at 235 nm and the other at 600–800 nm. According to Praliaud et al. [13], Chary et al. [14], and Chen et al. [15], the band at 210–270 nm can be attributed to the O²⁻→Cu²⁺ ligand-to-metal charge transfer that is characteristic of Cu²⁺ occupancy of isolated sites on γ -Al₂O₃. The broad band at 600–800 nm can be ascribed to the ²E_g→²T_{2g} spin-allowed transition of Cu²⁺ situated in a distorted octahedral symmetry. The results indicated that at 3 wt% loading, the Cu²⁺ ions were highly dispersed on the surface of γ -Al₂O₃. At higher loadings (\geq 7 wt%), the spectra showed the gradual development of an absorption edge at 740–800 nm ascribable to bulk CuO, in agreement with the XRD investigation (Fig. 1(a)). It should be noted that a broad band at around 450 nm was also observed, which was probably related to the formation of (Cu-O-Cu)²⁺ clusters highly dispersed on γ -Al₂O₃ [16]. According to Chen et al. [15], bulk-like CuAl₂O₄ also shows strong absorption in this region (400–500 nm). Nonetheless, in the present case the existence of CuAl₂O₄ was considered highly unlikely because the catalysts were calcined at a relatively lower temperature of 500 °C.

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