氧化铈稳定的 CuO 簇在 CO, C₃H₆ 和 NO 消除中的催化性能石 川^{1,2,*}, 徐 力^{1,2}, 朱爱民^{1,2}, 张玉卓^{1,2}, 区泽棠³¹大连理工大学工业生态与环境工程重点实验室, 辽宁大连 116024²大连理工大学等离子体物理化学实验室, 辽宁大连 116024³香港浸会大学化学系, 香港九龙塘 999077

摘要: 研究了 CuO 与 γ -Al₂O₃ 和 CeO₂ 的相互作用, 并由此制备出能有效脱除 CO, C₃H₆ 和 NO 的催化剂, 考察了不同载体表面 CuO 簇的分散稳定性和耐老化性能. 结果发现, 随 CuO 负载量的增加, CuO 簇因与 CeO₂ 载体的强相互作用而稳定存在; 而在 γ -Al₂O₃ 表面, CuO 簇易聚集成较大的颗粒. 另一方面, 由于 CeO₂ 本身较差的热稳定性, 表面分散的 CuO 在 950 °C 高温处理后烧结. 因此, 基于 γ -Al₂O₃ 载体优越的耐老化性能, 在 γ -Al₂O₃ 载体分散 CeO₂, 然后再担载 CuO, 从而得到了稳定的 CuO 簇, 所得催化剂比 CuO/ γ -Al₂O₃ 和 CuO/CeO₂ 具有更好的催化性能和抗热老化性能.

关键词: 氧化铜簇; 稳定性; 表面相互作用; 一氧化碳; 丙烯; 一氧化氮; 催化消除

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Copper Oxide Clusters Stabilized by Ceria for CO, C₃H₆, and NO AbatementSHI Chuan^{1,2,*}, XU Li^{1,2}, ZHU Aimin^{1,2}, ZHANG Yuzhuo^{1,2}, AU Chak Tong³¹Key Laboratory of Industrial Energy and Environmental Engineering (MOE), Dalian University of Technology, Dalian 116024, Liaoning, China²Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian 116024, Liaoning, China³Department of Chemistry, Center for Surface Analysis and Research, Hong Kong Baptist University, Kowloon Tong 999077, Hong Kong, China

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: copper oxide clusters; stability; surface interaction; carbon monoxide; propene; nitric oxide; catalytic abatement

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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 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 $2\theta = 35.44^\circ$ 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.

Table 1 Crystallite sizes of ceria (cubic) and copper oxide

Sample	Crystallite size of CeO ₂ ^a (nm)	Crystallite size of CuO ^b (nm)		
		7 wt%	15 wt%	20 wt%
CuA	—	22 (—)	23	24
CuC	12 (63)	18 (32)	19	20
CuCA	13 (17)	25 (—)	27	27

^aCalculated from the CeO₂ (111) crystallographic plane. ^bCalculated from the CuO (111) crystallographic plane. Values in parentheses are the corresponding crystallite sizes of the aged samples.

Fig. 1. XRD patterns of CuA (a), CuC (b), and CuCA (c) catalysts with different CuO loadings.

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 (≥ 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.

The TPR characterization showed that the catalyst with the lowest metal oxide loading had a single reduction peak centered at 222 °C (Fig. 3(a)). At CuO loadings of 7 wt% and 10 wt%, the CuA samples showed two peaks: one in the region of 190–200 °C and the other at 230 °C. Over the 15 wt% and 20 wt% CuA catalysts, two overlapping peaks were also observed in the higher temperature region, at 235 and 250 °C for the former and at 242 and 255 °C for the latter. Because the γ -Al₂O₃ support showed no pronounced peaks during the TPR experiment (data not shown), the H₂

Fig. 2. UV-Vis DR spectra of CuA (a), CuC (b), and CuCA (c) catalysts with different CuO loadings.

consumption peaks were attributed to the reduction of the Cu species. Moreover, the H_2/Cu ratio calculated based on the H_2 -TPR profiles were close to 1 for the CuA samples. Therefore, considering that the UV-Vis DR result suggested the existence of isolated Cu^{2+} ions on $\gamma-Al_2O_3$ at 3 wt% CuO loading (Fig. 2(a)), we attributed the peak at 222 °C to the reduction of well-dispersed Cu^{2+} . The peaks at 199 and 192 °C observed over 7%CuA and 10%CuA, respectively, suggested the presence of CuO species that were reduced more readily than the isolated Cu^{2+} entities (reduced at 222 °C). Larsson et al. [17] suggested that these reduction peaks can be attributed to well dispersed copper aluminate species that were different from bulk $CuAl_2O_4$. Wan et al. [6] considered that they were due to the occupancy of Cu^{2+} species at sites

Fig. 3. TPR profiles of CuA (a), CuC (b), and CuCA (c) catalysts with different CuO loadings.

of different coordinate environments on the surface of $\gamma-Al_2O_3$ such as symmetric hexacoordinate and asymmetric pentacoordinate. They believed that the copper species located at the former were more facily reduced than those located at the latter. In addition, Martinez-Arias et al. [9] suggested, based on electron paramagnetic resonance (EPR) and CO-TPR results, that CuO clusters could be more easily reduced than isolated Cu^{2+} . Since the broad band at around 450 nm observed over 7%CuA and 10%CuA in the UV-Vis DR investigation (Fig. 2(a)) can be related to the formation of highly dispersed $(Cu-O-Cu)^{2+}$ clusters on $\gamma-Al_2O_3$, we tentatively assigned the 199 and 192 °C peaks to the reduction of CuO clusters. With the further increase of CuO loading to 15 wt% and 20 wt%, the 199 and 192 °C peaks

vanished, suggesting that highly dispersed CuO clusters cannot exist at such high CuO loadings. Based on the XRD (Fig. 1(a)) and UV-Vis (Fig. 2(a)) characterizations, we attributed the reduction peaks at or above 230 °C to the reduction of large CuO particles and/or bulk CuO.

In the case of the ceria supported catalysts, the XRD patterns obtained for different CuO concentrations are shown in Fig. 1(b). The appearance of bulk CuO was seen except for the catalyst with 3 wt% CuO. The crystallite size also increased with the loading (Table 1). The UV-Vis DR spectra of these catalysts are shown in Fig. 2(b). Besides the bands at 210–270 nm and 600–800 nm, there was another absorption band at 310 nm. According to Velu et al. [18] and Turco et al. [19], bands at 300–350 nm can be assigned to charge transfer involving Cu²⁺-O-Cu²⁺ cluster-like species that were not detectable by XRD. It was noted that unlike the CuA catalysts, all the CuC catalysts showed the 310 nm band, indicating that CeO₂ promoted the formation of CuO clusters regardless of CuO loading (from 3 to 20 wt%). Similarly to the case of the CuA catalysts, an absorption edge at 740–800 nm was also observed over the CuC catalysts when the CuO loading was at or above 7 wt%. The results indicated the formation of bulk CuO, in agreement with the XRD results (Fig. 1(b)). Over the CuC catalysts with CuO loading ranging from 3 wt% to 20 wt%, two H₂ reduction peaks were detected (Fig. 3(b)). With increased loading, the peak at 147 °C did not change in position while the larger peak shifted from 174 to 191 °C. The increase in intensity of the small peak was less pronounced than that of the large peak. Similar TPR profiles had been reported elsewhere over CeO₂-supported CuO. Hu et al. [20] assigned the peaks to the two-step reduction of highly dispersed Cu²⁺: first to Cu⁺ and then to Cu⁰. Because the UV-Vis DR result of the 3%CuC catalyst (Fig. 2(b)) demonstrated the existence of Cu²⁺-O-Cu²⁺ clusters, we assigned the 147 °C peak to the reduction of CuO clusters. Accordingly, the 174 °C peak can be attributed to the reduction of CuO particles with a larger size, in agreement with the suggestions by Zheng et al. [21] and Rao et al. [22]. Actually, the calculated H₂/Cu ratio was slightly higher than 1 for all the CuC samples, indicating that the reduction process involved surface oxygen species of the CeO₂ support. Moreover, an increase in CuO loading resulted in an intensity increase and position shift of this peak. The results suggested the aggregation of CuO particles and the formation of bulk CuO. Nonetheless, it was apparent that the CuO clusters observed at 3 wt% loading still existed. The results are in agreement with the UV-Vis DR (Fig. 2(b)) and XRD (Fig. 1(b)) results.

The XRD results for the CuCA catalysts with different CuO loadings (Fig. 1(c)) were similar to the CuA and CuC catalysts. At or above 7 wt% CuO loading, bulk CuO peaks

were pronounced, and the crystallite size was increased as shown in Table 1. Moreover, based on the strong diffraction peaks of CeO₂ detected over CuCA, it was ascertained that there were CeO₂ crystallites on the 10%CeO₂/γ-Al₂O₃ binary support. It was more interesting that the UV-Vis results (Fig. 2(c)) gave similar spectra to the CuC catalysts. All the CuCA catalysts showed band at 300 nm, which was attributed to CuO clusters, regardless of the loading. On the other hand, the TPR profiles of the CuCA catalysts had features that resembled those of CuA and CuC (Fig. 3(c)). In the 130 to 200 °C region, the features resembled those of CuC while in the 200 to 280 °C region, the features resembled those of CuA. According to Fernández-García et al. [23], the TEM results of the Cu/CeO₂/Al₂O₃ catalyst suggested the preferential nucleation of CuO on regions that were rich with CeO₂. As illustrated above, the CuCA catalysts showed strong XRD signals of CeO₂ (Fig. 1(c)) as well as the strong absorption band of CuO clusters at 300 nm (Fig. 2(c)). We thus associate the peaks at 156 and 170 °C, respectively, to the reduction of CuO clusters and large CuO particles on CeO₂, and the peaks located in the 200 to 280 °C region to CuO species on γ-Al₂O₃. With an increase in CuO loading, the peaks at 156 and 170 °C remained unchanged in position, similar to that observed over CuC (Fig. 3(b)).

2.2 Investigation on thermal aging resistance

After thermal aging (950 °C for 4 h), the XRD patterns of CuO observed over 7%CuA were not detected (Fig. 4). It is plausible to consider that during the aging process, there was the formation of CuAl₂O₄ due to Cu²⁺ incorporation into tetrahedral vacancies. Its generation was supported by the pronounced adsorption in the UV-Vis DR spectra (Fig. 5). According to Chen et al. [15], bulk-like CuAl₂O₄ shows absorption at 400–500 nm, and that was the case with the 7%CuA-a sample. By considering that the temperature

Fig. 4. XRD patterns of fresh and aged (broken line) CuA, CuC, and CuCA catalysts.

Fig. 5. UV-Vis DR spectra of fresh and aged (broken line) CuA, CuC and CuCA catalysts.

adopted for aging was much higher than that for fresh catalyst calcining, this suggestion is reasonable. However, we detected no XRD peaks over CuA-a that could be related to CuAl_2O_4 crystallites, which was plausibly because the CuAl_2O_4 were dispersed copper aluminate species. In addition, the absorption band at 235 nm observed with 7%CuA was shifted to 240 nm after thermal aging. This was probably due to some slight aggregation of CuO entities. In the TPR investigation (Fig. 6), the 199 °C peak detected over 7%CuA was significantly decreased in intensity after aging. This indicated the sintering of CuO species, which was consistent with the UV-Vis DR results. Moreover, a new reduction peak at 282 °C was detected over CuA-a, which could be attributed to the reduction of CuO from CuAl_2O_4 .

Fig. 6. TPR profiles of fresh and aged (broken line) CuA, CuC, and CuCA catalysts.

After aging, all the XRD peaks of CuC-a were sharpened as shown in Fig. 4. This showed the occurrence of CeO_2 sintering and CuO aggregation during the thermal process. From the inset in the pattern, the increase in intensity of CuO was more pronounced. The changes of crystallite sizes

of ceria (cubic) and copper oxide during the aging process are also shown in Table 1. Upon thermal aging of 7%CuC at 950 °C, the crystallite size of CeO_2 and CuO changed from 12 to 63 nm and from 18 to 32 nm, respectively. There was also a significant change in absorbance: the band at 310 nm observed over 7%CuC was shifted to 350 nm after aging (Fig. 5). This showed that there was a dramatically increase of CuO particle size. The change in the TPR profile was even more drastic: over 7%CuC, reduction occurred at 147 and 176 °C; over CuC-a, it occurred at 300 and 310 °C, which was a shift of nearly 150 °C (Fig. 6). It is clear that after aging, the catalyst became more difficult to reduce, and that was accompanied by the aggregation of CuO particles and the disappearance of copper oxide clusters.

As for the 7%CuCA catalyst, the XRD peaks of Al_2O_3 and CeO_2 sharpened while those of CuO disappeared after thermal aging (Fig. 4). From Table 1, one can see that the change in particle size of CeO_2 from 13 to 17 nm by aging is insignificant. The UV-Vis DR spectrum of CuCA-a showed absorption bands at 250 and 300 nm, and compared with those of 7%CuCA (Fig. 5) there was no significant shift in this position. In addition, there was a new adsorption band at 400–500 nm, which was similar to that observed over CuA-a, which demonstrated the existence of CuAl_2O_4 . The TPR profiles of Fig. 6 suggested the formation of CuAl_2O_4 (reduction peak of CuO at 282 °C) and the disappearance of larger CuO particles that had existed on CeO_2 (reduction peak at 170 °C). It should be noted that CuO clusters (reduction peak at 156 °C) still existed despite the high aging temperature. Furthermore, the disappearance of the 232 °C peak detected over 7%CuCA and the generation of the 210 °C peak over CuCA-a were detected. The results suggested that due to high temperature aging, there was strengthened CuO/ Al_2O_3 interaction and occupancy of the surface tetrahedral vacancy sites on $\gamma\text{-Al}_2\text{O}_3$ [7]. With CuAl_2O_4 formation, the remaining copper oxide species (reduced at 210 °C) had less interaction with the support.

2.3 Catalytic activity

The catalytic performance of freshly calcined 7%CuA, 7%CuC, and 7%CuCA catalysts are shown in Fig. 7. 7%CuCA was superior to 7%CuA in CO, NO, and C_3H_6 conversion. The result indicated that the presence of CeO_2 on $\gamma\text{-Al}_2\text{O}_3$ enhanced the oxidation activity of CuO. On the other hand, 7%CuCA was superior to 7%CuC for NO conversion (in the 200–350 °C range only), but was inferior to CuC for CO and C_3H_6 conversion. Nonetheless, the fresh and aged CuO catalysts showed a similar decline in the conversion of the three pollutants. However, the CuCA-a catalyst retained a superior performance, which was similar to that of 7%CuCA. The aging effect was most detrimental

Fig. 7. Catalytic performance of fresh and aged (broken line) CuA, CuC, and CuCA catalysts. Gas composition: 0.1% NO, 1% CO, 0.1% C₃H₆, 0.9% O₂, N₂ balance, GHSV = 50000 h⁻¹.

on the CuC-a catalyst, and the CuC-a catalyst was the least effective in eliminating NO in the low temperature region (100–400 °C). Overall, in terms of the simultaneous removal of NO, CO, and C₃H₆ as well as stability of activity against thermal aging, the 7%CuCA catalyst was the best among the catalysts.

2.4 Relation between copper oxide clusters and catalytic performance

In the cases of the freshly calcined CuA catalysts, the TPR and UV-vis DR investigations revealed that CuO ex-

isted as isolated Cu²⁺ and in the form of clusters at or below 10 wt% CuO loading. At higher CuO loadings, both the XRD signals and UV-Vis DR peaks of bulk CuO appeared and there was the disappearance of the CuO clusters as confirmed in the TPR studies. The results clearly demonstrated that with increased CuO loading, CuO on γ -Al₂O₃ changed from isolated Cu²⁺ to CuO clusters and then aggregated into bulk CuO. For the CuC catalysts with 3 wt% CuO loading, the XRD results showed no signal of CuO crystallites, and the UV-Vis DR and TPR results indicated that the copper species was in the form of Cu²⁺ clusters. At higher CuO loading, there was formation of bulk CuO as shown by the XRD, UV-Vis DR, and TPR results. However, considering that the low temperature reduction peak at 147 °C in the TPR profiles did not change in position regardless of the increase in CuO loading, we deduced that there were always some CuO clusters on the surface of CeO₂. Over the CuCA catalysts, we observed results similar to those of CuC. We found the existence of CuO clusters regardless of the increase in CuO loading. In other words, there was the coexistence of CuO clusters and larger CuO particles, which were dispersed on the surface of CeO₂, and the aggregation of copper species seemed to occur on γ -Al₂O₃.

By comparing the states of the copper species on CuA, CuC, and CuCA, one can deduce: (i) γ -Al₂O₃ can disperse active copper components but cannot stabilize them due to the relatively weak interaction between CuO and γ -Al₂O₃, and with increasing CuO loading, there was aggregation of small particles and formation of bulk CuO, and (ii) dispersed copper oxide species can be stabilized on CeO₂ due to strong interaction of CuO with CeO₂, and CuO clusters can stably exist on the CuC and CuCA catalysts even when there was aggregation of copper oxide species on the surface of the catalysts.

As to the thermal stability of the CuO clusters, the CuA-a characterization results suggested the conversion of CuO crystallites to bulk-like CuAl₂O₄ species during thermal aging at 950 °C. Moreover, the UV-Vis DR and TPR results demonstrated the aggregation of copper species on γ -Al₂O₃ after aging. It is apparent that CuC-a was significantly different from CuC as indicated by the XRD, UV-Vis DR, and TPR results due to the severe sintering of CeO₂. In particular, the TPR results indicated severe aggregation of copper species and the complete disappearance of CuO clusters. There was, however, UV-Vis DR and TPR evidence for the presence of CuO clusters on CuCA-a. Despite the high temperature and the formation of CuAl₂O₄, some CuO clusters survived the aging treatment.

With the correlation of the existence of CuO clusters and catalytic behavior, the significance of CuO species stability on catalytic performance is more significant. Based on the TPR results, one knows that the CuC and CuCA catalysts

were easily reduced because of the stable CuO clusters generated by the strong CuO/CeO₂ interaction. Due to this, they showed catalytic activity better than that of CuA, especially for CO and C₃H₆ oxidation. Nonetheless, compared with CuCA, CuC was less able to retain CuO clusters during a thermal treatment. As a result of CeO₂ sintering and the disappearance of CuO clusters, CuC-a had poor activity. On the other hand, γ -Al₂O₃ in CuCA stabilized the CeO₂ particles during the thermal process. The detection of CuO clusters on CuCA-a was strong evidence that γ -Al₂O₃ stabilized CeO₂ against sintering. It is because of the presence of CuO clusters on CuCA-a that had a satisfactory activity.

In summary, γ -Al₂O₃ can disperse but cannot stabilize CuO species while the promotion of γ -Al₂O₃ with CeO₂ can result in CuO being stabilized, which remained in the form of clusters. Under severe thermal condition such as aging at 950 °C, CeO₂ alone cannot stabilize CuO clusters but the co-existence of both CeO₂ and γ -Al₂O₃ resulted in some CuO clusters remaining. We attribute the good and stable performance of 7%CuCA to the high dispersion and thermal stability of the CuO clusters. Among the catalysts investigated in this study, 7%CuCA performed the best, and the highly dispersed CuO species are believed to be active in the removal of CO, NO, and C₃H₆.

3 Conclusions

Due to the relatively weak interaction between CuO and γ -Al₂O₃, CuO is well dispersed on γ -Al₂O₃ below 3 wt% loading. With increased CuO loading above 3 wt%, γ -Al₂O₃ fails to maintain CuO as a well dispersed species and CuO existed as clusters and then gradually as bulk particles. On the other hand, due to the strong interaction between CuO and CeO₂, there were always some CuO clusters on the CuO/CeO₂ catalysts regardless of how high the CuO loading was. However, after thermal aging treatment at 950 °C for 4 h, CuO clusters dispersed on CeO₂ were severely sintered due to the poor thermal stability of the support. Accordingly, by pre-dispersing CeO₂ on γ -Al₂O₃ followed by dispersing CuO on CeO₂, CuO clusters were stabilized due to the better aging resistance of γ -Al₂O₃. Consequently, as compared with CuO/ γ -Al₂O₃ and CuO/CeO₂, a CuO/CeO₂/ γ -Al₂O₃ catalyst gave better catalytic performances and thermal aging properties. Therefore, stabilized CuO clusters are important as the active species for the re-

moval of CO, NO, and C₃H₆.

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