

The Role of Monolayer Dispersed Copper Oxide for Benzene Catalytic Combustion over Cu/Al₂O₃ Catalyst

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Abstract: The surface dispersion behavior of a series of Cu/ γ -Al₂O₃ catalysts calcined at 300, 450 and 600 °C were investigated. The dispersion status of copper species obtained from surface and bulk characterization, studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR), has been correlated with benzene oxidation activity of the catalysts. The results indicated that copper oxide present in a monolayer dispersed state below the dispersion loading threshold, which could be reduced at lower temperature. The remarkable increase of activity was observed over Cu/ γ -Al₂O₃ catalyst when higher copper loading was imputed even total copper amount was less than threshold. Further increase of copper loading (higher than threshold) resulted in comparatively lower activity. The monolayer dispersed phase was thermodynamically unstable. Dispersion threshold increased with increasing calcination temperature because copper ions diffused into the support, which led to lower catalytic activity for benzene oxidation.

Key words: monolayer dispersion; CuO; benzene catalytic combustion

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Catalytic combustion is one of the most effective and promising methods of controlling the emission of volatile organic compounds (VOCs), since catalytic incineration can proceed at lower temperature and can oxidize dilute pollutions totally^[1-12]. The catalysts used for abatement of VOC emissions are mainly divided into two categories: supported noble metals and transition metal oxides. In recent years, many efforts have been devoted towards the design of catalysts based on transition metal oxides for the replacement for noble metal catalysts because of their potential advantages of lower cost, higher loading, higher thermal stability and greater resistibility to poison^[2-16]. Many different transition metal oxides are known to be active for the combustion of VOCs, e. g., V₂O₅, CuO, Co₃O₄, MnO₂, Fe₂O₃ and Cr₂O₃^[11-16]. Among the metal oxides, copper oxide is often employed as a catalyst for its high ac-

tivity and selectivity for VOC oxidation. Actually, Rajesh and Ozkan's study^[15] found that CuO/Al₂O₃ was even more active than Pt/Al₂O₃ for the complete oxidation of ethanol. Wang^[17] and Kim^[18] reported that copper based catalyst was the most active one among the metals based catalysts for the combustion of aromatic hydrocarbons.

The dispersion state of the active phases has been recognized to be important in supported copper oxides catalysts. Strong relationship between dispersion state and catalytic activity has been observed. Severino and Laine^[19] reported that maximum CO conversion was achieved with copper catalyst supported on alumina (100 m²/g) with a loading ratio close to 4%. They proposed that the activity of the highly dispersed Cu species was greater than that of bulk CuO. Park and Ledford^[20] studied the methane combustion over a se-

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ries of Cu/Al₂O₃ catalysts, they suggested that the active phase for CH₄ oxidation with O₂ was the superficial phase formed by isolated or highly dispersed Cu, which was formed at low metal loadings. However, there is limited information about the relationship between the highly dispersed Cu species and the combustion of aromatic hydrocarbons available.

It is well known that copper is present as a well dispersed surface phase under low loading conditions ($< 8 - 10\%$ Cu on 200 m²/g γ -Al₂O₃ support)^[21]. Xie and Tang^[22] proposed a principle of spontaneous monolayer dispersion of oxides and salts onto surfaces of supports, This theory suggests that copper oxides can disperse spontaneously onto γ -Al₂O₃ surfaces to form a monolayer, The highest dispersion capacity is called dispersion threshold, The monolayer dispersion threshold of CuO on γ -Al₂O₃ is 4.1 mg CuO /100 m² of γ -Al₂O₃ surface. However, the exact nature of the monolayer dispersion phase of CuO is not clearly understood for working catalyst. Whether the monolayer dispersion phase is a thermodynamically stable form or not is waiting further studying.

The present study aims at elucidating the effect of the calcination temperature on well dispersed surface phase and the relationship between dispersion state and catalytic activity of benzene oxidation. In this paper, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) have been used to determine the chemical state and dispersion of copper species supported on γ -Al₂O₃. The information derived from these techniques is correlated with benzene oxidation activity in order to develop a more complete understanding of Cu/Al₂O₃ catalysts. Benzene is selected as probe molecule because it is a main component of VOC present in different industries, such as petrochemical, paint and coating industries and steel manufacture and controlling its emission in the atmosphere is becoming relevant.

1 Experimental

1.1 Preparation of catalysts

CuO/Al₂O₃ catalysts were prepared by impregnation method with copper nitrate aqueous solution with

the desired concentrations. The support was γ -Al₂O₃ with 40 – 60 meshes and its BET surface area is 204 m²/g. The alumina was calcined in air at 500 °C for 24 h prior to impregnation. Then the copper was deposited on γ -Al₂O₃ in a calculated amount. The samples were dried at 110 °C for 4 h and followed calcined for 8 h at 300, 450, 700 °C in the air, respectively. The loading amount of CuO is expressed as wt. % CuO in γ -Al₂O₃, ranges from 2.0 to 24.0% to γ -Al₂O₃. The catalysts are denoted as CuO-T-(x%)/Al₂O₃, where T is the calcinations temperature.

1.2 Characterization of catalysts

Powder XRD analysis was performed to identified the main species in the catalysts on a Rigaku D/MAX-RB X-ray diffractometer with a Cu K α target operated at 50 kV and 40 mA, with a scanning speed of 0.5° min⁻¹ and a scanning angle (2 θ) range of 10 – 90°. The peak intensity ratio between the diffraction peak of CuO (2 θ at 35.5) and that of γ -Al₂O₃ (2 θ at 45.8) was used to represent the relative crystalline content of CuO in sample. Then, the dispersion threshold was calculated on this ratio.

Chemical states of the species on the catalyst surface were investigated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 210 electron spectrometer (Mg K α radiation; $h\nu = 1253.6$ eV). XPS data were calibrated using the binding energy of C1s (284.60 eV) as the standard.

H₂-TPR of the catalyst was performed at atmospheric pressure in a conventional flow system built in laboratory at a linearly programmed rate of 13 °C/min from 50 °C to 830 °C (5% H₂ in an Ar stream with a flow rate of 40 mL/min). 50 mg sample was used for each run. The amount of the consumed H₂ was determined by a thermo-conductivity detector (TCD).

1.3 Catalytic activity of benzene oxidation

The catalytic tests were carried out at atmospheric pressure in a fixed-bed flow reactor. A tubular quartz reactor with 10 mm diameter was placed inside an electrical furnace and the reaction temperature was measured by a type K thermocouple located near the catalyst bed in a protective tube. The exit line of the reactor was heated to prevent any condensation. The tests were

performed using 0.2 mL of catalyst. The reactant gas mixture (air containing 4.1 g/m³ of benzene) was prepared by passing air through a saturator containing benzene which was kept at 20 °C. The reactant mixture was fed into reactor with a flow rate of 36 L/h and the space velocity (GHSV) for the reaction was maintained at 18 000 h⁻¹. The feed and the reaction products were analyzed by on-line gas chromatograph equipped with a flame ionization detector (FID). The benzene was analyzed with a Paraplot Q capillary column. The catalytic activity was evaluated in the temperature range between 150 and 500 °C, in terms of apparent benzene conversion calculated as $([\text{benzene}]_{\text{in}} - [\text{benzene}]_{\text{out}}) / [\text{benzene}]_{\text{in}}$. At each reaction temperature, the conversions were analyzed along time-on stream (TOS) for 1 h. It should be noted that the only product detected under the present experimental conditions was CO₂.

2 Results and Discussion

2.1 XRD

The XRD patterns of different CuO/ γ -Al₂O₃ catalysts calcined at 600 °C are shown in Fig. 1. The crys-

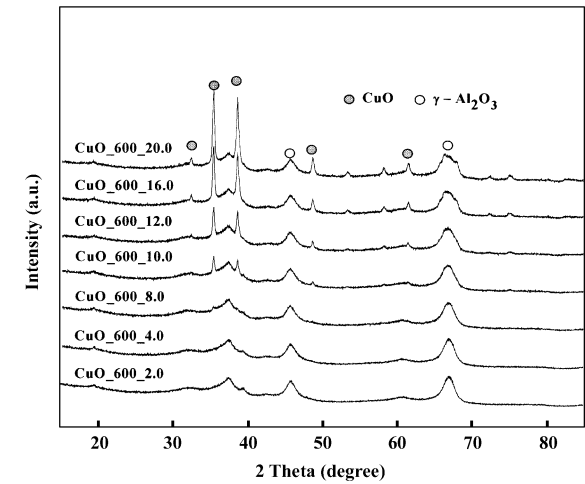


Fig. 1 XRD patterns of samples with different CuO loading calcined at 600 °C

talline phases were determined in comparison with IC-DD file. No CuO characteristic line was observed in the samples when CuO loading was less than 8%. This indicates CuO species on the alumina surface was highly dispersed. For the samples with higher Cu loadings (> 8%), the characteristic of CuO is present, which

suggests that when CuO content exceeds a certain value, the surplus CuO exists as CuO crystallite. Further increasing CuO content, the clear increase of intensity of XRD line for CuO is observed. The intensities of the CuO diffraction lines increased linearly with increasing CuO loading from 10.0 to 20.0% as shown in Fig. 2. From the plot one can see a threshold at 8.1%, corresponding to the dispersion capacity.

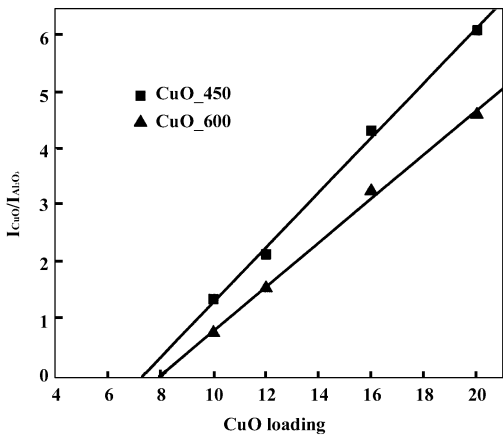


Fig. 2 Relative intensity of CuO diffraction as a function of copper loading on γ -Al₂O₃

It is well known that the structure of CuO/ γ -Al₂O₃ catalysts depends on the metal loading. For low copper loadings, copper is present as a well dispersed surface phase which cannot be detected by XRD. At a critical metal loading, the support becomes saturated and further addition of metal results in segregation of a separate metal oxide phase and crystallite growth, the critical metal loading is called dispersion capacity of the support. The work by Friedman et al.^[23] showed that the support capacity of several γ -Al₂O₃ for copper surface phase is approximately 4% Cu/100 m²/g support. Strohmeier et al.^[21] also reported that 9 ~ 10% copper (for 195 m²/g γ -Al₂O₃) is the maximum copper loading that can be accommodated as a surface phase. Xie and co-workers^[22] have found that many oxides and salts can disperse spontaneously as a monolayer on the surface of supports and suggested that the support capacity of γ -Al₂O₃ for copper surface phase was approximately 4% at the 100 m²/g support.

However, it is interesting to point out that the surface dispersion threshold of CuO on γ -Al₂O₃ seems to dependent on the calcination temperature. According to

our results, the CuO threshold for the sample calcined at 600 °C is 8.1% , while that for the sample calcined at 450 °C is 7.3% , and the slopes of the two straight lines are apparently different. Since the higher calcinations temperature of support corresponds to lower surface area, it is reasonable the threshold for the 450 °C calcined sample is larger than that of 600 °C calcined sample, but our results contrast with this analysis. Hence, variation in surface area cannot account for the

change in the dispersion capacity observed here. Combining the formation of CuAl₂O₄ at high calcination temperatures (>700 °C)^[18], it is presumable that the diffusion of copper ions into the support is closely related to the change in the threshold.

2.2 XPS

The XPS data in terms of binding energies and satellite/main peak ratios are listed in Table 1 for CuO / Al₂O₃ samples calcined at 300 and 600 °C , re-

Table 1 XPS results for 4.0% , 8.0% and 16.0% CuO/ γ -Al₂O₃ samples

Catalysts	Binding energy of Cu2p _{3/2} (eV)	satellite intensity	I _{Cu2p_{3/2}} /I _{Al2p}
Cu_300_4	934.8	0.49	1.55
Cu_600_4	935.0	0.54	1.29
Cu_300_8	934.7	0.48	1.47
Cu_600_8	934.9	0.49	1.17
Cu_300_16	934.5	0.46	1.40
Cu_600_16	934.6	0.45	1.16

spectively. More detail Cu_{2p} spectra of the 8% CuO/ γ -Al₂O₃ calcined at 300 and 600 °C are shown in Fig. 3.

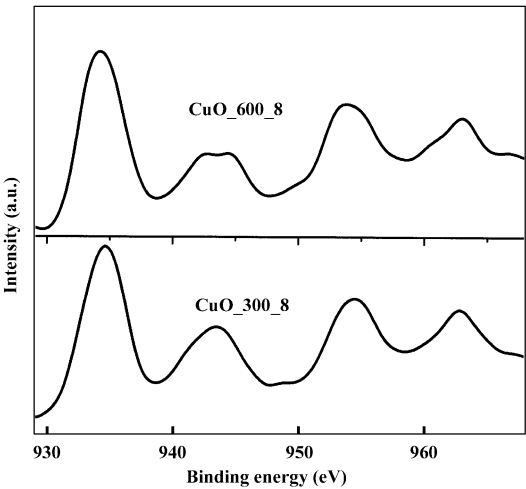


Fig. 3 Cu_{2p} XPS spectra of 8.0% CuO calcinated at 300 and 600 °C

The spectra are fitted with two peaks for the Cu 2p_{3/2} , Cu 2p_{1/2} and two satellite peaks. Cu 2p_{3/2} peaks at 934.7 are attributed to Cu²⁺ species characterized by the shake up features at high binding energy , because

the shake-up satellite peaks are not seen for Cu⁺ compounds or Cu⁰ species. And the catalysts calcined at 300 and 600 °C show different bandshapes of Cu 2p_{3/2} satellite peak. The other catalysts exhibit the similar results. Previous study shows that the reference CuO and CuAl₂O₄ possess the XPS Cu 2p_{3/2} binding energies at 934.1 and 935.0 eV , respectively^[21]. The Cu 2p_{3/2} binding energies for catalysts calcined at either 300 or 600 °C are similar to that of CuAl₂O₄ and higher than the value measured for CuO. The satellite/main peak ratio measured for the CuO/ γ -Al₂O₃ catalysts is similar to that measured for CuO (0.45^[21]) and lower than the value for CuAl₂O₄ (0.71^[15]). The apparent discrepancy has been reported by previous researchers^[21, 23]. This suggested that the copper surface species are chemically different from bulk CuO and CuAl₂O₄.

In fact, CuO/Al₂O₃ catalysts have been thoroughly studied by many authors using many physical methods. According to the literature^[21-28], the surface

copper species supported on γ -Al₂O₃ can be classified into three types: (a) Isolated Cu²⁺ ions can strongly interact with the support even to form the surface spinel. Diffuse reflectance spectroscopy results have shown that cupric ions in the surface spinel predominantly occupy tetragonally distorted octahedral sites (> 90%) with only a small fraction located in tetrahedral sites^[21]. (b) Weak magnetic associates consist of several or many Cu²⁺ ions and these Cu²⁺ ions have close contact with each other. They can also be considered to form chain or two-dimensional clusters. (c) Large three-dimensional clusters and bulk CuO phase have characters and properties identical to those of pure CuO powder. Below the surface dispersion threshold loading, copper is present as a well dispersed surface phase which cannot be detected by XRD, some authors call them monolayer dispersion phase, The surface copper species belong to (a) and (b). Since their structure and coordination environment are different from bulk CuO and CuAl₂O₄, they possess the different binding energy.

The Cu 2p_{3/2}/Al2p intensity ratios for catalysts calcined at 300 and 600 °C are listed in Table 1. It is important to note that the Cu/Al intensity ratios are lower for catalysts calcined at 600 °C than for those calcined at 300 °C. This effect is related to the extent of metal-support interaction, as the calcination temperature is increased, a greater percentage of copper ions diffuse into the γ -Al₂O₃ lattice. This effect has been demonstrated previously^[23], if more copper ions diffuse into the support, the Cu/Al intensity ratios should become lower. However, the absence of its X-ray diffraction pattern indicates that the diffusion is confined to the surface or perhaps a few subsurface layers.

2.3 TPR

To further elucidate the nature of copper species in these catalysts, the TPR experiment was performed. The reduction profile provides information on the dispersion of Cu species over γ -Al₂O₃ and the interaction between copper ions and the support. Fig. 4 shows the H₂-TPR profiles of CuO/ γ -Al₂O₃ catalysts calcined at 300 °C. It can be seen that there are two H₂-TPR peaks, namely, α 1 (240 - 270 °C) and α 2 (270 -

280 °C). Combined with XRD results, that TPR peak

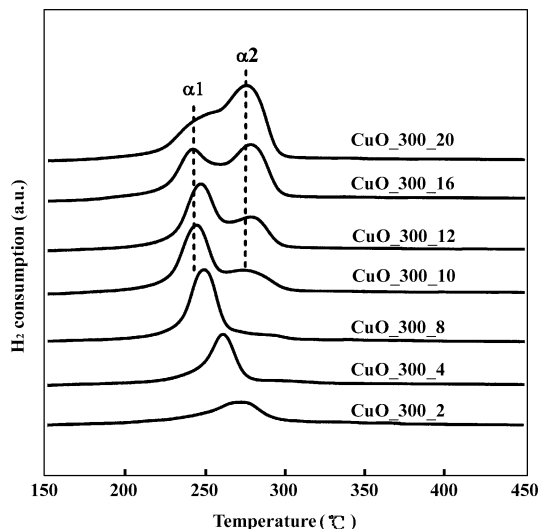


Fig. 4 TPR profiles for CuO/ γ -Al₂O₃ catalysts calcined at 300 °C

α 1 can be attributed to reduction of highly dispersed CuO species, peak α 2 is attributed to the reduction of bulk CuO species. Increasing the CuO loading results in the increase of peak α 1 intensity and shift to lower temperature; it seems to have a saturated phenomenon occurring at 8% CuO for peak α 1, which is consistent with the monolayer capacity obtained by XRD. As the CuO loading is increased to 8% Cu, the peak shifts to lower temperatures, this suggests that the existence of different copper species in the monolayer dispersed phase. In the sample CuO_300_2, the Cu is present as isolated Cu ions (a) that strongly interact with the support, and reduction requires a higher temperature of 270 °C. This is in good agreement with the conclusion of other authors obtained from the ESR results^[23, 29]. Approached to the dispersion threshold, the reduction peak is shifted toward lower temperatures (240 °C), it is presumable that there are mainly chain or two-dimensional clusters (b) on the support.

When the CuO loading is above 8.0%, peak α 2 is observed. Further increasing CuO loading, the changes of peak α 1 are not evident, but peaks α 2 has increased obviously due to the increase in crystallinity of CuO with an increase in Cu loading, as evidenced from XRD results. When the copper loading is higher than 16% the α 2 peak area is larger than that of α 1 peak and the α 1 peak becomes a shoulder. In addi-

tion, overlap of $\alpha 1$ and $\alpha 2$ peaks becomes very serious when copper loading is larger than 10%. The serious overlap of $\alpha 1$ and $\alpha 2$ peaks implies that the reducibility of these two types of copper oxide species gradually approaches to the same.

For the samples calcined at 450 and 600 $^{\circ}\text{C}$, we observed that basically same phenomenon with that of the samples calcined at 300 $^{\circ}\text{C}$, but $\alpha 1$ peak area of H_2 consumptions of highly dispersed CuO decreases gradually with increasing of calcinations temperature (see Fig. 5). The results indicate that the monolayer

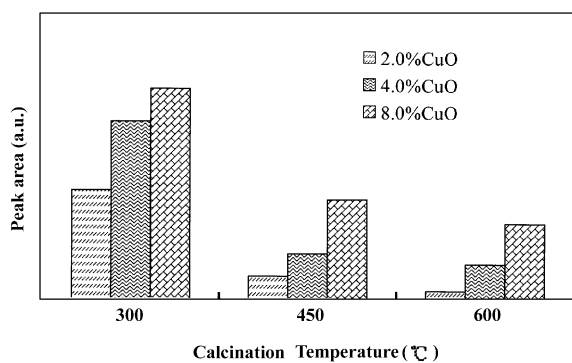


Fig. 5 TPR Peak area of different CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts calcined at 300, 450, 600 $^{\circ}\text{C}$ respectively

dispersed phase is thermodynamically unstable, with increasing calcination temperature, the uppermost surface layer has been depleted due to increased diffusion of copper ions into the support. Hence, the catalytic activity should decrease for catalysts prepared at the higher calcination temperature (relative to those prepared at 300 $^{\circ}\text{C}$).

To sum up the above discussion, the characteristic results for CuO/ $\gamma\text{-Al}_2\text{O}_3$ can be interpreted on the basis of interaction between the dispersed Cu oxide and the alumina support. When CuO is supported on alumina, formation of a “surface monolayer dispersion species” and diffusion into the support may occur concurrently. These two processes are affected by the amount of metal loading and calcination temperature. The monolayer dispersed CuO is the main species when CuO loading is less than threshold, and large crystallized CuO exists when CuO loading is larger than threshold. As the calcination temperature is increased, the monolayer dispersion threshold increased because a greater percentage of copper ions diffusing into the $\gamma\text{-}$

Al_2O_3 lattice. This effect has been verified by XPS and TPR results.

2.4 The catalytic activity for benzene oxidation

To find out the relation between surface Cu species and the activity for benzene oxidation, the catalytic experiments were carried out under similar conditions employed for all the samples. Fig. 6 shows the

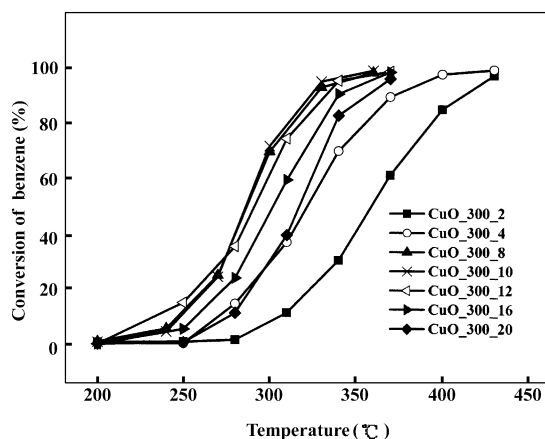


Fig. 6 Catalytic activities of CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts with different CuO loading calcined at 300 $^{\circ}\text{C}$ activity of CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts calcined at 300 $^{\circ}\text{C}$ with various CuO loadings for benzene oxidation. Fig. 7

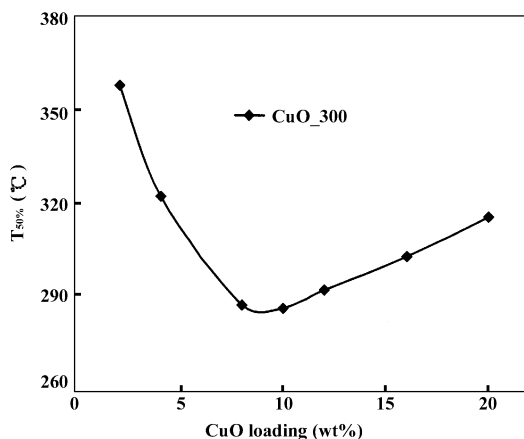


Fig. 7 $T_{50\%}$ of CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts with different CuO loading calcined at 300 $^{\circ}\text{C}$

presents the evolution of $T_{50\%}$ (temperature for 50% of conversion into CO_2) as a function of the CuO content for the series of CuO_300. It is found that the conversion curves are displaced to lower temperatures with increasing CuO loading, indicating that the activity of these catalysts increases with CuO concentration below 8%. Above 8% Cu, there is a shift of the conversion curve to higher temperatures, indicating a significant

decrease of the catalytic activity. These results clearly show the existence of an optimum copper loading when $\gamma\text{-Al}_2\text{O}_3$ is used as the support. This optimum is close to 8% Cu, value similar to the Cu loading at which bulk CuO species starting formation. As discussed previously, at low Cu loadings and before reaching the surface dispersion threshold, which in our catalysts occurs at CuO loadings 8%, monolayer dispersed species are formed on the surface, and this explains why the activity of the catalysts increases in a certain range of loadings. As the copper loading increases further, the bulk CuO species is formed, and these species interact with the monolayer dispersed Cu species, probably blocking them, causing the decreased activity.

Although it is clear that the activity of the monolayer dispersed species is greater than that of the bulk CuO species, it is important to point out an aspect that the monolayer dispersed species is thermodynamically unstable. Below the monolayer dispersion threshold (8%), as the calcination temperature increasing from 300 to 600 °C, the catalytic activity of CuO/ $\gamma\text{-Al}_2\text{O}_3$ decreases gradually at same loading, as demonstrated in Fig.8. The results are agreement with the TPR

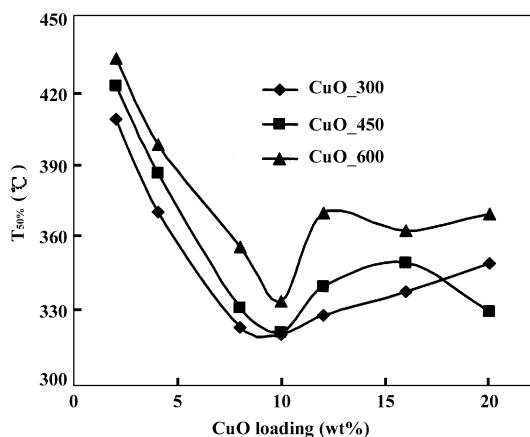


Fig. 8 Catalytic activities of CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts with different CuO loading calcinated at different temperature data. As the calcination temperature is increased, a greater percentage of surface copper ions diffuse into the $\gamma\text{-Al}_2\text{O}_3$ lattice, the catalytic activity of Cu catalyst for benzene oxidation decreases gradually.

3 Conclusions

The combined use of several techniques to investi-

gate the effect of Cu loading, calcination temperature on the structure and catalytic activity of CuO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts for benzene oxidation lead to the following conclusions. When the CuO loading is lower than the threshold amount, copper oxide mainly exists as a monolayer dispersed copper surface phase. These species exhibit much higher activity for benzene catalytic combustion than the larger crystalline CuO oxide, the maximum activity basically coincides with the monolayer dispersion threshold. The dispersion threshold increases with increasing calcination temperature because copper ions diffuse into the support, and the catalytic activity of monolayer dispersed species for benzene oxidation decrease consequently.

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单层分散 CuO_x 对甲苯催化燃烧作用的研究

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摘 要: 考察了一系列在不同温度下制备的 Cu/ γ -Al₂O₃ 催化剂对苯催化燃烧的性能, 并利用 X-射线粉末衍射 (XRD)、X-射线光电子能谱 (XPS)、程序升温还原 (TPR) 对催化剂进行了表征. 结果表明: 低于单层分散的 CuO 具有可在低温还原的特性. 在低于单层分散阈值的范围内, 随着 CuO 负载量的增加催化剂活性加. 超过单层分散阈值, 催化剂活性反而下降. 单层分散的 CuO 物种是非稳态的. 随着焙烧温度的增加, 分散阈值也会发生增加, 这可能是 Cu 物种扩散至载体晶相引起的, 在这种中情况下, 催化剂活性下降.

关 键 词: 单层分散; CuO; 苯催化燃烧