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SYNTHESIS OF COPPER-BASED NANOPARTICLE CATALYSTS BY DIFFERENT METHODS FOR TOTAL OXIDATION OF VOCs

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ABSTRACT

In this paper, the process of preparing 10 wt.% $CuO/\gamma\text{-}Al_2O_3$ catalysts was studied by different methods. The changes in structure and texture of the catalysts were examined by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR) and Brunauer-Emmett-Teller method (BET). The activities of catalysts were investigated by completely oxidized VOCs (toluene and n-butanol) on gas-phase reactions. The results were found that influence of the size of copper nanoparticles enhancing copper dispersion and selectivity of the catalyst prepared by non-thermal plasma (NTP) was superior to those obtained from the impregnation (IMP) and deposition-precipitation (DP). The total oxidation of VOCs to CO_2 and H_2O was achieved above 275 ^{o}C. Compared to the IMP and DP, the NTP method increased the oxidation efficiency by 15-30 %.

Keywords: $CuO/\gamma\text{-}Al_2O_3$, non-thermal plasma, impregnation, deposition precipitation, total oxidation.

1. INTRODUCTION

Volatile organic compounds (VOCs) are important sources of air pollution [1]. The control of their emissions has, therefore, become imperative. Catalytic oxidation of these pollutants has been identified as one of the most efficient ways for removal VOCs. Noble metals such as Pt and Pd supported on alumina and silica are well established as efficient catalysts for complete combustion of VOCs [2, 3], but they are relatively expensive and their resistance to poisoning is low. Transition metal oxides (Cu, Co, Mn) show high activities for eliminating VOCs and for being cheaper than the noble metals [4]. Among them, copper oxides are widely used as combustion catalysts [5-7]. Generally, many factors influence the catalytic activity of copper in VOCs oxidation, such as oxidation state [7], the shape of Cu particles [8, 9], the nature of the support [9]. Some studies have been reported that the activity of copper-based catalysts for VOCs oxidation depends on the preparation methods: Wet-impregnation (IMP) [10], deposition-precipitation (DP) [11] and non-thermal plasma (NTP) [12, 13]. Recently, plasma processing has attracted considerable attention [14, 15]. It has been found that the catalyst prepared by the plasma procedure exhibited a significant rise in activity of the catalyst and a small particle size-distribution is achieved, compared to the conventional methods.

In this work, the effects of preparation methods on the catalyst performance were studied. Furthermore, the catalytic activities of copper-based catalysts supported on γ-Al_2O_3 were investigated for the oxidation of toluene and n-butanol in the gas phase at the atmospheric pressure.

2. MATERIALS AND METHODS

2.1. Catalyst preparation

The 10 wt.% CuO/γ-Al_2O_3 catalysts were prepared by the different methods: (1) IMP (2) DP and (3) NTP. These samples were denoted as Cu-IMP, Cu-DP, and Cu-NTP, respectively.

- IMP method: 5 g of γ-Al_2O_3 (supplied by Sigma-Aldrich, S_{BET} = 180 m^2/g) was first impregnated with a solution of copper (II) chloride (1.33 g of $CuCl_2$/20 ml of deionized water), supplied by Merck. After evaporating under vacuum at 80 °C, the impregnated sample was dried at 110 °C and then heated in air flow for 4 h at 500 °C with a heating rate of 3 $°C.min^{-1}$.

- DP method: 5 g of γ-Al_2O_3 was first added in a solution of copper (II) chloride (1.33 g of $CuCl_2$/50 ml of deionized water) using Na_2CO_3 3M as precipitating agent, which was added dropwise to a solution containing $CuCl_2$, in order to keep pH = 8. The product was isolated by suction filtration and then washed with deionized water. Finally, the sample was dried at 110°C and calcined in air at 500°C for 4 hrs at a heating rate of $3°C.min^{-1}$.

- NTP method: 5 g of γ-Al_2O_3 was first impregnated with a solution of copper (II) chloride (1.33 g of $CuCl_2$/50 ml of deionized water) and dried at 110°C for 24 hrs. The precursor, which was placed in the NTP discharge region using the cylindrical quartz tube located and centered on the holder base plate which consisted of a continuous flow air gas supplying system. The NTP reactor was powered by a homemade high voltage AC generator: 18 kV – 1.5 kHz. A schematic view of the NTP reactor is shown in Figure 1.

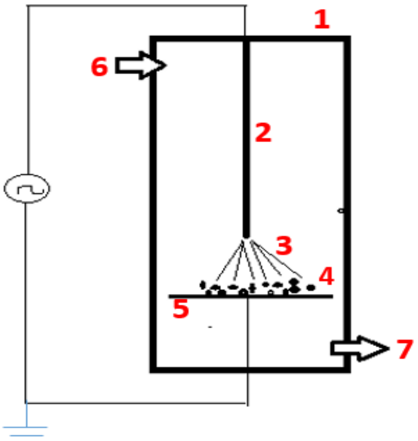

Figure 1. The schematic diagram of the NTP reactor. (1) Quartz tube; (2) Needle electrode; (3) Discharge region; (4) Catalyst; (5) Plate electrode; (6) Feed-gas system; (7) Vacuum system.

2.2. Catalyst characterization

The X-ray diffraction (XRD) measurements were performed on the catalysts with a Siemens D500 diffractometer (Germany). The 2θ range was recorded between 20 and 80° at a rate of 0.02 s^{-1} and a step size of 0.03. The images of transmission electron microscope (TEM) were obtained using a TACHI H-7500 (Japan) at an acceleration voltage of 200 kV. Fourier transform infrared (FT-IR) spectroscopy was measured using an FTIR/NIR spectrometer (USA), the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. The Brunauer-Emmett-Teller specific surface areas were determined by nitrogen adsorption data obtained at -196 °C (Nova-1000e analyzer, USA).

2.3. Catalytic testing

The catalytic activity was performed in a continuous flow fixed-bed reaction in the range of temperature (50-300 °C). The total flow through the catalyst was kept at 6 L/h leading a gas hourly space velocity (GHSV) of about 15000 h^{-1}. The toluene and n-butanol initial concentrations were fixed at 900 ppm and 1000 ppm. The outlet gas was analyzed by gas chromatography HP 6890 (USA) equipped with FID, HP5 column.

3. RESULTS AND DISCUSSION

3.1. The characterization of catalysts

The XRD patterns of catalysts are shown in Fig. 2. The diffraction peaks of γ-Al_2O_3 (2θ = 35.2, 46.1, 67.3, 72.9, PDF No. 79-1558) were assigned. The diffraction peaks of crystalline CuO (2θ= 40, 49.2, 64.3, 72.6, PDF No. 80-1268) are clearly seen, more intense, and narrow for the Cu-NTP sample. This difference is maybe related to the presence of copper particles inside the mesoporous channels of the γ-Al_2O_3. Obviously, the diffraction spots are a little bit blurry in the crystalline phase of copper oxides was observed for the Cu-IMP sample. Moreover, the Cu-DP and Cu-NTP samples have exhibited the intensity of the diffraction peaks of $CuAl_2O_4$ (2θ = 31.2, 74.8, PDF No. 78-1605). According to the literature [7, 9], when the calcination temperature is higher at 700 °C, $CuAl_2O_4$ will be formed by solid-solid interaction between CuO and γ-Al_2O_3. However, this study has shown that $CuAl_2O_4$ phase appears at 500 °C. This could explain the increase of crystallization with the sample on the catalyst surface.

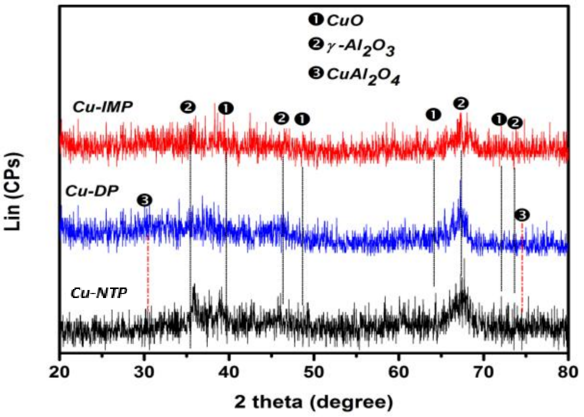

Figure 2. XRD patterns of the catalysts Cu-IMP, Cu-DP and Cu-NTP.

Figure 3 displays the morphology of the catalysts by TEM images. TEM of the Cu-NTP sample (Fig. 3c) shows the high dispersion of copper oxides inside the pores of γ-Al_2O_3. In other word, the copper which has size around 3-6 nm was clearly visible and copper particles were widely distributed in the surface site. In contrast, no copper particle with clear shapes was visible in the Cu-DP sample (Fig. 3b) and especially is with Cu-IMP sample (Fig. 3a). Thus, the results obtained by TEM analysis, which are in line with the XRD results show that the use of NTP method leading to the formation of well-dispersed copper particles [8, 13].

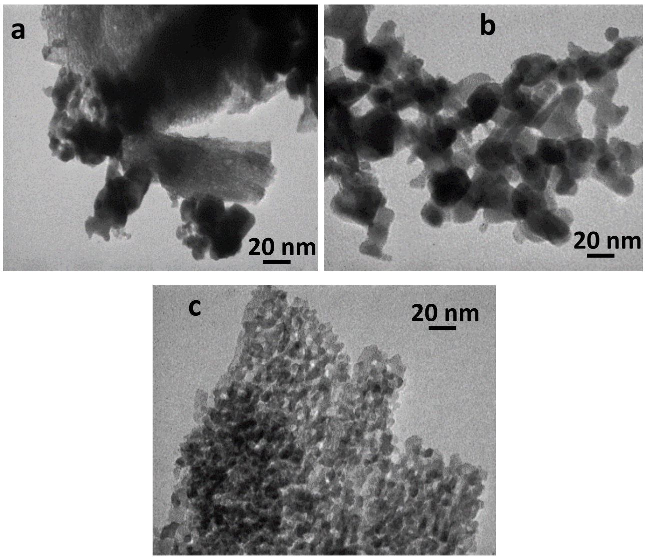

Figure 3. TEM images of the catalysts (a) Cu-IMP, (b) Cu-DP, (c) Cu-NTP (100,000 x).

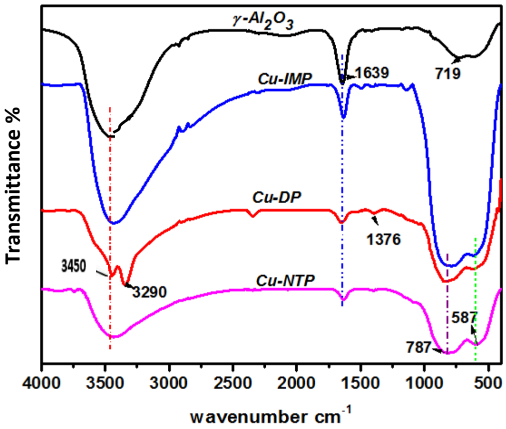

Figure 4. FT-IR spectra of the catalysts Cu-IMP, Cu-DP and Cu-NTP.

FTIR spectra of the samples are shown in Fig. 4. The spectra are given in the range 4000-400 cm^{-1}. According to the results in Fig. 4, the absorption peaks due to Cu-O bonds of the newly formed CuO species were found in the range of 550-800 cm^{-1}, which suggests that Cu was attached to γ-Al_2O_3. The change of the peak shape at 719 cm^{-1} is associated with the Al-O bond vibrations. The band at 3280 cm^{-1} - 3450 cm^{-1} and 1639 cm^{-1} belong to the stretching vibration of the O-H group absorbed on the surface or inside of the γ-Al_2O_3 support structure [18]. Meanwhile, the transmittance peak of Cu-OH group (Cu-DP sample) appears at 1376 cm^{-1} [8]. Nevertheless, the change of peak corresponding to Cu-OH group on CuO/γ-Al_2O_3 is responsible for the different activity for the oxidation of VOCs.

Table 1. The surface areas of γ-Al_2O_3 and three kinds of catalysts.

Sample	**BET area (m^2g^{-1})**
γ-Al_2O_3	180
Cu-IMP	100
Cu-DP	105
Cu-NTP	125

The specific surface area of Al_2O_3 and three kinds of catalyst is shown in Table 1. The synthesis method changes significantly the specific surface area and therefore can affect to the activity for VOCs total oxidation.

3.2. Toluene and n-butanol oxidation over CuO/γ-Al_2O_3 catalyst

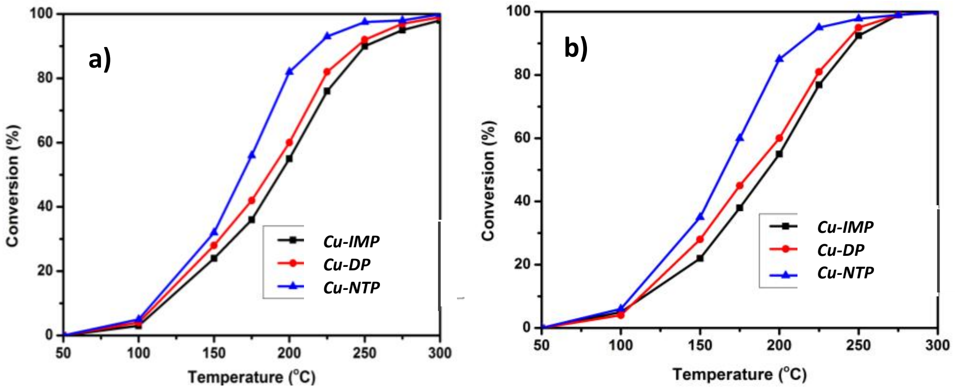

Figure 5. n-butanol (a) and toluene (b) conversion curves of the catalysts Cu-IMP, Cu-DP, and Cu-NTP. Reaction conditions: n-butanol 900 ppm, toluene 1000 ppm, 20 % O_2/N_2, total flow rate 6 L/h, GHSV = 15000 h^{-1}.

Table 2. VOCs conversions over three kinds of catalysts at 200 °C and 275 °C.

Catalyst	**VOCs conversion $^{(*)}$ (%)**			
	n-butanol		toluene	
	200 °C	275 °C	200 °C	275 °C
Cu-IMP	50.0	83.0	55.0	98.1
Cu-DP	52.0	88.0	59.6	99.3
Cu-NTP	80.2	94.1	85.6	100.0

$^{(*)}$ The VOCs conversions were calculated according to the following formula:

$$Conversion\ (\%) = (C_{in}\text{-}C_{out}/C_{in})$$

where C_{in} and C_{out} are molar flow rates of VOCs in the inlet and outlet stream, respectively.

Figure 5 shows the catalytic activity for the n-butanol and toluene oxidation in the gas phase of the three catalysts. The results indicated that $CuO/\gamma\text{-}Al_2O_3$ catalysts present high activity in the reaction of toluene and n-butanol. At 300 °C total conversion is reached. The catalytic activity of Cu-NTP catalyst is the best conversion for toluene oxidation at 275 °C (over 98 %). For n-butanol oxidation, the Cu-NTP catalyst also has the highest activity at 250 °C. In contrast, the Cu-IMP catalyst was found less active compared to the two other catalysts. The following activity was: Cu-NTP > Cu-DP > Cu-IMP, in line with earlier data [16], these results also are suitable with the TEM images (Fig. 3), FTIR spectra (Fig. 4) and BET surface areas (Table 1). Moreover, the achievement of stable catalytic performance is dependent on the nature of support, as well as particle morphology [17].

It can be also seen from Table 2, the catalytic activity of these catalysts at 200 °C and 275 °C show an improvement of the toluene oxidation compared to n-butanol oxidation. It was found 8.5 % than n-butanol oxidation. Further, the Cu-NTP catalyst is about 15.3 % more active than the Cu-DP catalyst. And, the Cu-IMP catalyst was found 3.2 % less active than the Cu-DP. This is an important finding in the understanding of the catalytic preparation using NTP treatment has been improved dispersion, the enhanced catalytic oxidation ability of low-temperature can be achieved with NTP-treated catalysts.

4. CONCLUSIONS

In this research, the 10 wt.% $CuO/\gamma\text{-}Al_2O_3$ catalysts were synthesized by different methods which can change or enhance the properties of the catalysts. The obtained Cu-NTP more increase activity than the corresponding Cu-IMP and Cu-DP catalyst. Highly dispersed Cu-NTP catalyst exhibited excellent catalytic performance in the oxidation of n-butanol and toluene. This catalyst with small particle size can be a promising catalyst for the low-temperature VOCs combustion.

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