

Preparation of α -MnO₂ nanowires and its application in low temperature CO oxidation

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Abstract— α -MnO₂ nanowires were synthesized through a simple hydrothermal route and employed as support to obtain CuO/ α -MnO₂ catalysts in low temperature CO oxidation. The prepared samples were characterized by X-ray diffraction (XRD), N₂ adsorption (BET), temperature programmed reduction (TPR), thermal gravimetric/differential thermal analysis (TGA/DTA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The results showed that the prepared samples have nanowire morphology with a size about 30-40 nm in diameter. The obtained results revealed a remarkably high activity for the prepared catalysts in low temperature CO oxidation.

Key words: α -MnO₂, Nanowire, CO Oxidation, Catalysis

INTRODUCTION

Carbon monoxide is a harmful atmospheric pollutant produced by incomplete combustion of fossil fuels. The conversion of CO to CO₂ is one of the most important catalytic reactions about environmental and industrial applications. For example, the ability to remove byproduct such as CO in fuel cell systems through the water-gas shift (WGS) reaction at low temperatures and at fast reaction rates would aid in the development of lower cost fuel alternatives [1]. The production of high purity streams through preferential oxidation of CO (PROX) has recently garnered much attention for low temperature CO oxidation catalysts [2]. Other applications for low temperature CO oxidation catalysts could consist of indoor air purification, the removal of CO from closed cycle CO₂ lasers [3] and low temperature hydrocarbon combustion. The costs of noble metals do not make them economically feasible to be used for practical applications, so this has led to searches for other catalysts which are cheaper and more abundant. Transition mixed metal oxides are attractive alternatives. Among transition metal mixed oxides of interest for low temperature CO oxidation, MnO_x-based mixed oxide catalysts exhibit great potential [4]. Deposition of both oxides on supports and each other can produce new catalysts with higher activities in regard to the systems with one type of oxide due to interaction between two components [5]. Moreover, the above-mentioned, catalytic oxidation over materials with different morphologies is an interesting topic that has been developed in recent years. For instance, supports with nanowire and nanorod morphologies have been synthesized and used in CO oxidation reaction [6,7]. Catalytic performance depends on the morphology and hence crystal planes and crystal phase to a large extent. A CO oxidation rate on CuO nanoplatelets was found to be over six-times higher than nanoparticles and about three-times higher than that on nanobelts. It is due to more reducibility and catalytic activity of CuO nanoplatelets with respect

to nanoparticles and nanobelts. The CuO nanoplatelets with (011) planes released oxygen from the surface lattice more easily [8]. In addition, crystal planes, crystal phase of nanocatalyst has also been found to affect the catalytic activity of supported catalysts [7]. It has been proved that α -MnO₂ nanowires are more active than β -MnO₂ in CO oxidation reaction [9]. To our knowledge, α -MnO₂ nanowires have not been employed as catalyst support in this reaction. The purpose of this study is to investigate the potential of α -MnO₂ nanowires as support for CuO catalysts in low temperature CO oxidation. We synthesized α -MnO₂ nanowires through a simple hydrothermal route and employed as support for CuO catalysts in low temperature CO oxidation, and parameters affecting catalytic performance were investigated.

EXPERIMENTAL

1. Catalyst Preparation

α -MnO₂ nanowires were synthesized via a simple hydrothermal method. In a typical synthesis, 16.85 mmol KMnO₄ and 22.60 mmol MnSO₄·H₂O were dissolved in 120 ml deionized water under vigorous stirring. After 20 min, the prepared mixture was transferred into a 125 ml Teflon-lined stainless steel autoclave followed by heating at 140 °C for 12 h. The precipitate was washed several times with distilled water and dried at 80 °C. The prepared powders were impregnated by Cu(NO₃)₂·3H₂O solution to obtain 10%, 15% and 20 wt% of CuO/ α -MnO₂ catalysts. The impregnated samples were dried at 80 °C and calcined at different temperatures in air atmosphere.

2. Catalyst Characterization

X-ray diffraction patterns were obtained from an X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu-K α monochromatized radiation source and an Ni filter. The surface areas (BET) were determined by nitrogen adsorption at -196 °C using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method. Thermo-

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gravimetric (TG) and differential thermal analysis (DTA) was performed in a Netzsch STA 409 system in a static air atmosphere at a heating rate of 10 °C/min. Temperature programmed reduction (TPR) analysis was conducted for evaluating the reduction properties of prepared catalysts. In the TPR measurement, about 50 mg of samples was loaded and subjected to a heat treatment (10 °C/min) in a gas flow (30 ml/min) containing a mixture of H₂ : Ar (10 : 90). Prior to TPR experiment, the samples were pretreated under an inert atmosphere (Ar) at 200 °C for 1 h and then cooled to room temperature. The amount of H₂ uptake during the sample reduction was measured with a thermal conductivity detector (TCD). The morphology of samples was characterized by scanning electron microscopy (SEM, VEGA@TESCAN), and transmission electron microscopy (TEM) was performed with JEOL JEM-2100UHR, operated at 200 kV.

3. Catalyst Activity Tests

Catalytic activity tests for CO oxidation reaction were performed in a continuous-flow fixed-bed quartz reactor at ambient pressure. The reactor was charged with 100 mg of the prepared catalyst sieved to 35-70 mesh. Prior to reaction, the catalyst was pretreated at 300 °C for 2 h in 20% O₂ balanced with He. After pretreating, activity tests were performed with the mixed feed gas consisting of 4% CO, 20% O₂, 10% N₂ and 68% He as carrier gas with the gas hourly space velocity (GHSV) of 60,000 ml/g·h. The reactor effluent was analyzed by gas chromatograph (Varian 3400) with a thermal conductivity detector (TCD) and a molecular sieve 5A column.

RESULTS AND DISCUSSION

1. Structural Properties

X-ray diffraction was used to investigate the crystal structure of prepared catalysts. Crystal structure investigation, calcination effect was also evaluated by XRD. Fig. 1(a) shows the XRD patterns of catalysts. For pure MnO₂ it can be observed clearly that all diffraction peaks can be exclusively indexed as the tetragonal α -MnO₂ (JCPDS 44-0141) and no other impurities were observed. As shown in Fig. 1(a), with increasing in CuO loading two peaks marked by (•) related to (111) and $\bar{1}\bar{1}1$ planes of CuO in monoclinic phase (JCPDS 05-0661) appeared. On the other hand, with increasing in CuO content, intensities of the peaks corresponding to CuO increased, indicating an increase in CuO crystallite size. CuO average crystallite size was calculated from the half-width of main diffraction peaks by using Scherrer's formula. Also, the theoretical particle size with assuming spherical shape for sample particles was calculated from the following equation (Eq. (1)), and the results are presented in Table 1.

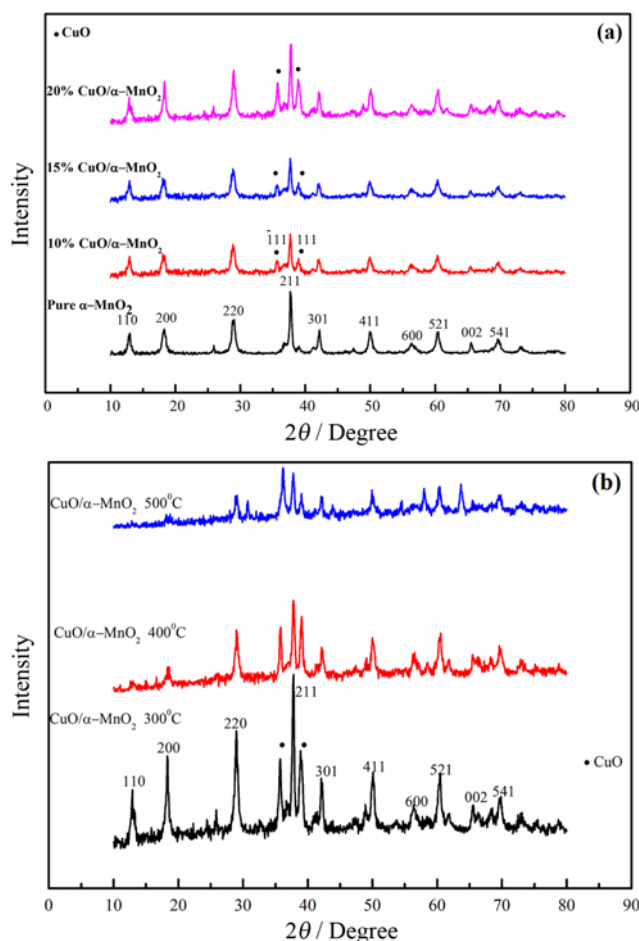


Fig. 1. (a) XRD patterns of pure α -MnO₂ and prepared catalysts with different CuO loadings calcined at 300 °C and (b) XRD patterns of catalysts calcined at different temperatures.

$$D_{BET} = 6000 / (\rho \times s) \quad (1)$$

Fig. 2 shows the SEM and TEM images of catalysts. As can be seen, prepared samples have nanowire morphology with a size about 30-40 nm in diameter. Fig. 2(a) and 2(b) show the SEM of α -MnO₂ nanowires before and after impregnation, respectively. According to Fig. 2(b), the morphology of the nanowires did not change after impregnation. Fig. 2(d) and 2(c) show TEM images of pure and impregnated nanowires. Fig. 2(c) shows TEM image of impregnated nanowires. As can be seen, no change in morphology was observed. Fig. 2(d) shows HRTEM of pure α -MnO₂, which indi-

Table 1. Structural properties of prepared catalysts

Catalysts	BET surface area (m ² /g)	Average pore volume (cm ³ /g)	Average pore size (nm)	CuO average crystallite size (nm)	D _{BET} (nm)
Pure α -MnO ₂	31.34	0.114	26.04	-	-
10% CuO/ α -MnO ₂ calcined at 300 °C	27.63	0.099	25.74	7.77	33.35
15% CuO/ α -MnO ₂ calcined at 300 °C	25.88	0.092	28.25	7.77	33.35
20% CuO/ α -MnO ₂ calcined at 300 °C	22.03	0.065	23.97	9.76	41.84
20% CuO/ α -MnO ₂ calcined at 400 °C	16.26	0.070	27.52	11.08	56.68
20% CuO/ α -MnO ₂ calcined at 500 °C	1.30	0.005	24.48	11.10	709.22

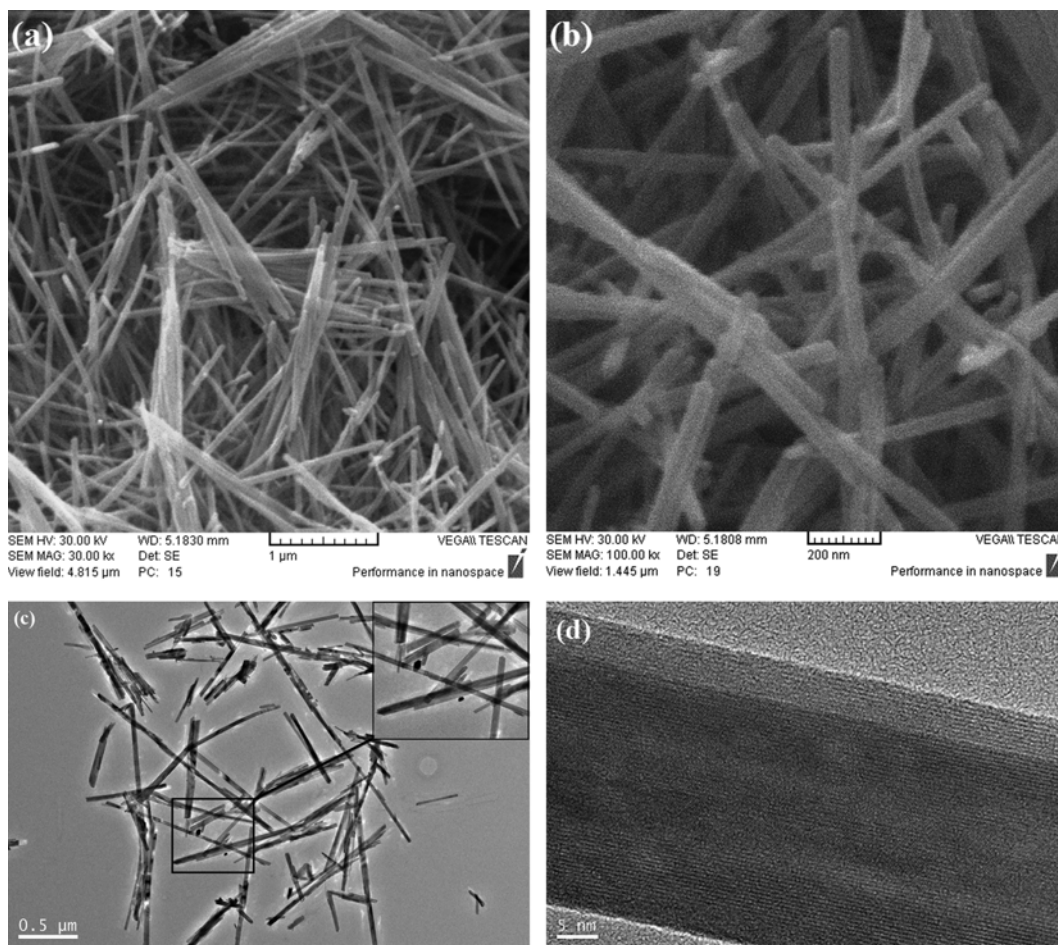


Fig. 2. SEM ((a) and (b)) and TEM ((c) and (d)) images of α - MnO_2 nanowires after and before impregnation.

cates crystal structure of pure α - MnO_2 .

The structural properties of catalysts are presented in Table 1. The results show that increasing in CuO content decreased the specific surface area and average pore volume, due to pore blocking of catalyst support. Pore size distribution of different samples and N_2 adsorption/desorption isotherms of calcined catalysts at 300 °C are shown in Fig. 3(a) and 3(b), respectively. All materials show type IV isotherms which are typical of mesoporous materials. Pore size distribution is broader at higher temperatures. In addition, increasing in calcination temperature decreased the surface area and average pore volume. The sample calcined at 500 °C showed the lowest surface area and the biggest particle size (Table 1).

DTA and TGA thermograms of CuO/ α - MnO_2 are shown in Fig. 4(a) and 4(b). The TGA analysis of CuO/ α - MnO_2 shows a sharp mass loss from 50–150 °C, which is related to evaporation of the surface adsorbed water from materials. The second weight loss at around 200–260 °C is due to evaporation of surface hydroxyl group and the decomposition of residual nitrates from base material. The mass loss at 580–610 °C is due to phase transition of CuO/ α - MnO_2 catalyst. Because a small endothermic peak can be observed in this area in the DTA thermogram, it can be assigned to phase transition and CuMn_2O_4 formation. Because of small amount of CuMn_2O_4 , its related endothermic peak has low intensity.

Fig. 4(c) presents the TPR profiles of α - MnO_2 nanowires and

20% CuO/ α - MnO_2 catalyst calcined at 300, 400 and 500 °C. Fig. 4c-(a) shows the TPR profile of α - MnO_2 nanowires with two major peaks with a maximum centered at 337 and 408 °C, respectively. The first peak at 337 °C is attributed to the reduction of MnO_2 to Mn_3O_4 , whereas the second peak at 408 °C can be attributed to the reduction of Mn_3O_4 to MnO [10]. Addition of CuO to the α - MnO_2 nanowires changed the reduction behavior of α - MnO_2 nanowires as the reduction of nanowires shifted to higher temperatures. In other words, reducibility of nanowires was decreased with addition of CuO (Fig. 4c-(b)). In Fig. 4c-(b), a wide reduction peak with a shoulder at 540 °C probably is related to the reduction of MnO_2 to MnO without formation of Mn_3O_4 as intermediate. It was suggested that copper has greater reducibility in mixed compounds than manganese [11]. Therefore, the reduction peak at 314 °C is related to reduction of CuO to Cu. Fig. 4c-(c) shows the TPR profile of CuO/ α - MnO_2 calcined at 500 °C. In this case TPR curves were shifted to higher temperatures and the two reduction peaks became closer together. It might be due to stronger interaction between CuO and α - MnO_2 nanowires at higher temperatures.

2. Catalytic Performance

Fig. 5(a) shows the effect of CuO loading on the catalytic performance of prepared catalysts. The obtained results indicate that with increasing CuO content up to 20 wt%, the conversion of CO occurred at lower temperatures and the best efficiency was obtained

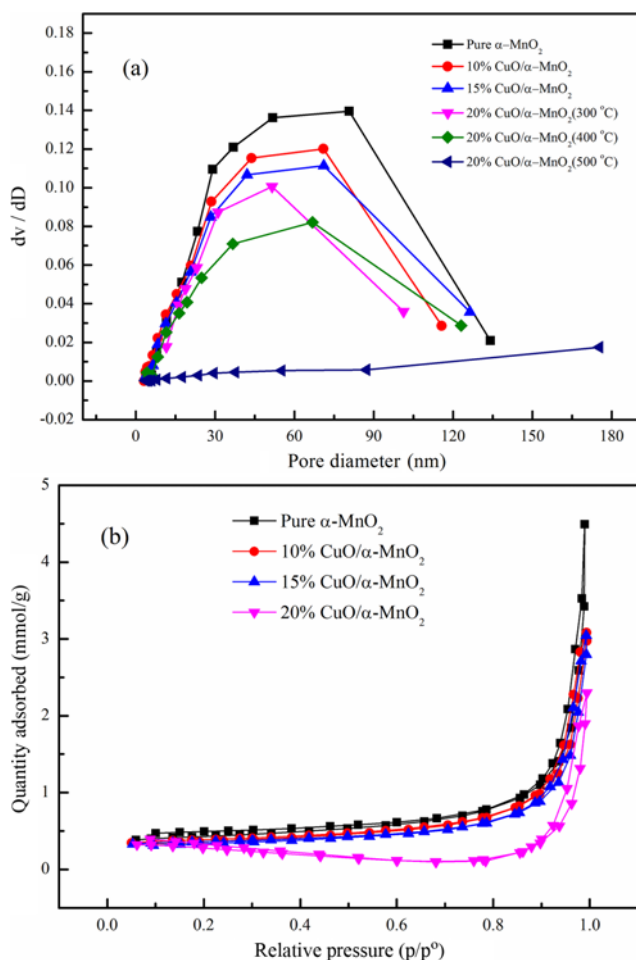


Fig. 3. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of different catalysts.

at this loading. The lowest catalytic activity was observed for pure MnO₂. Catalytic activity is improved by increasing in CuO loading. Such activity is not only due to surface area. As can be seen in Table 1, with increasing CuO loading, the surface area is being decreased, whereas the catalytic activity increases. So, in this case, one can conclude that the activity is not only related to the surface area. According to the literature [12], in these types of catalysts CO oxidation occurs at MnO₂/CuO interfaces. Actually, these interface places are the active sites for this reaction. Hence, the concentration of active sites increases with increasing copper oxide loading, which in turn leads to enhanced activity in higher CuO loadings. At these places, oxygen transfer between the two metal oxides occurs. This type of MnO₂-CuO structure interaction led to formation of the Mn₃O₄ phase. This indicated that there are existed a synergistic mechanism between the manganese and copper oxides [13]. The proposed mechanism in this case is as follows:

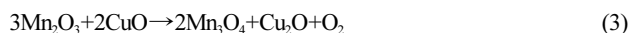


Fig. 5(b) shows the effect of calcination temperature on the catalytic activity. It is seen that calcination at higher temperature decreased

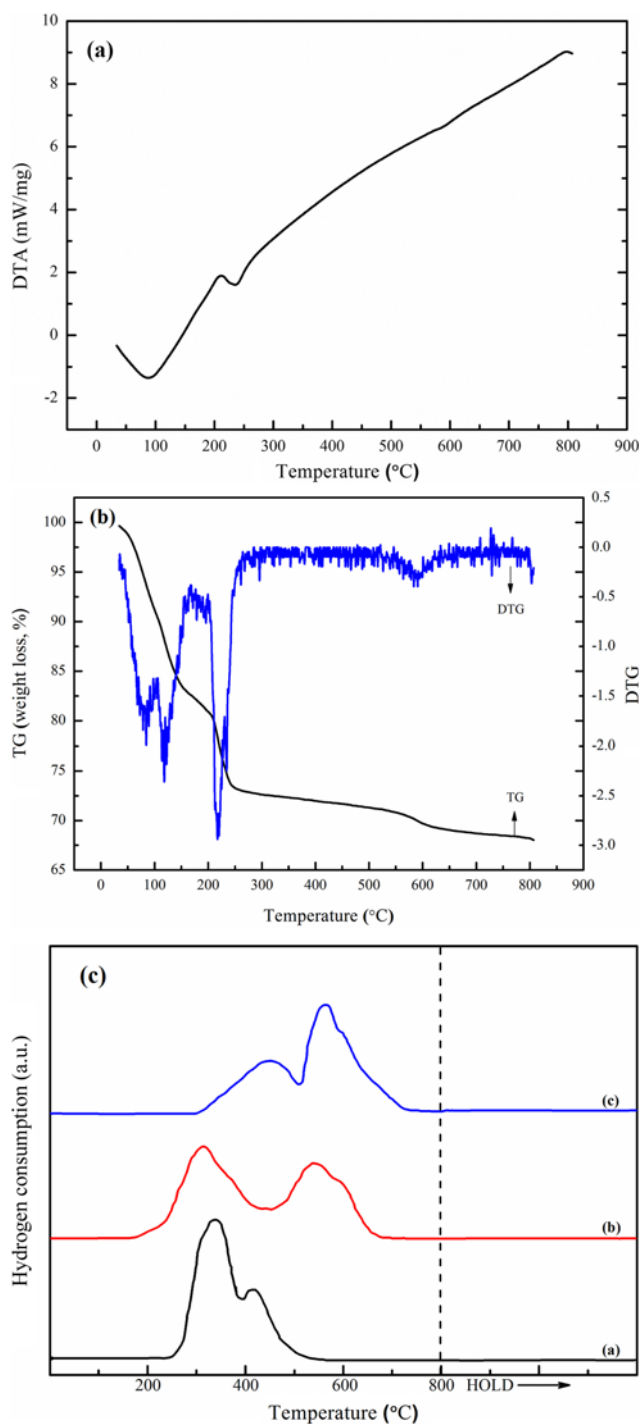


Fig. 4. (a) DTA and (b) TGA profile of CuO/ α -MnO₂ and (c) H₂-TPR profiles of (c-a) Pure α -MnO₂ nanowires (c-b) CuO/ α -MnO₂ calcined at 300 °C (c-c) CuO/ α -MnO₂ calcined at 500 °C.

the catalytic activity. The lowest catalytic activity was observed for the sample calcined at 500 °C. The lower catalytic activity for the samples calcined at higher temperatures could be related to sintering of active sites. When the calcination temperature was increased to 500 °C, surface area was decreased dramatically to 1.29 m²/g.

Generally, calcination at higher temperatures is always accompanied by an increase in the mean particle diameter and decrease in

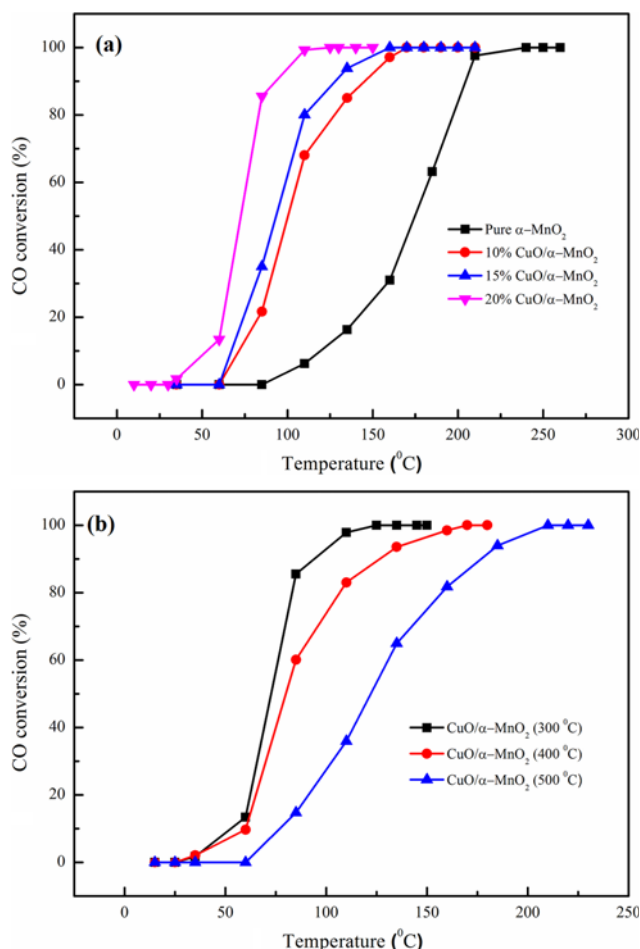


Fig. 5. (a) CO conversion in terms of temperature for pure α - MnO_2 and CuO/ α - MnO_2 catalysts with different CuO loadings and (b) Effect of calcination temperature on catalytic conversion.

the specific surface area due to blocking of the pores [14]. In addition to decreasing the surface area, higher temperatures decrease the active component, which ultimately results in decreasing of active interface sites. Surface decreasing is mainly because of penetration of the dispersed CuO into the pores of the support. On the other hand, a catalyst loses its activity at higher temperature where crystallization of CuMn_2O_4 takes place [15]. Effect of calcination temperature could be observed in XRD patterns. Fig. 1(b) shows the XRD patterns of 20% CuO/ α - MnO_2 catalyst calcined at different temperatures. At higher temperatures peak intensities diminished. Peak intensities at 300 °C were maximum but when temperature increased to 400 and 500 °C, peak intensities decreased, and it is due to the formation of CuMn_2O_4 . But because of its low content, it can't be seen in XRD patterns.

CONCLUSIONS

α - MnO_2 nanowires (30–40 nm in diameter) were synthesized through a simple hydrothermal route. The prepared nanowires were employed as catalyst support for Cu catalysts in low temperature CO oxidation. The results revealed that calcination at high temperature was accompanied by an increase in the mean particle diameter and decrease in the specific surface area; the sample calcined at 500 °C showed the lowest surface area. Increasing the CuO content decreased the specific surface area and average pore volume, due to pore blocking of catalyst support. In addition, increasing Cu content improved the activity of catalyst, and the catalyst with 20 wt% of CuO showed the highest catalytic activity.

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