TiO₂ NTS-SUPPORTED COPPER OXIDE WITH IMPROVED CATALYTIC PERFORMANCE FOR LOW-TEMPERATURE CO OXIDATION VIA CERIUM OXIDE MODIFICATION

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ABSTRACT

High catalytic activity for CO oxidation can be obtained on TiO₂ nanotubes (NTs) -supported copper oxide (CuO/TiO₂ NTs). But the relatively low thermal stability limits its practical application. Via cerium oxide modification, catalysts with enhanced catalytic activity and higher thermal stability can be obtained. The prepared materials are characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), and temperature-programmed reduction (TPR). Catalytic performance for low-temperature CO oxidation is studied by using a microreactor-GC system. Obtained results indicate that CuO/TiO₂ NTs exhibit higher thermal stability and higher catalytic activity for CO oxidation after cerium oxide is added.

Keywords: TiO₂ NTs-supported copper oxide; cerium oxide modification; thermal stability; catalytic activity; CO oxidation

1. INTRODUCTION

As a common heterogeneous catalyst, copper-based catalysts have a variety of applications in the field of CO oxidation^{1,2}, steam reforming and methanol dehydrogenation³, reduction of nitrogen oxides^{4,5} and various of volatile organic compounds (VOCs)⁶⁻⁸. Compared to pure copper or copper oxide catalyst, the supported ones usually have higher catalytic activity because the copper species can be highly dispersed on the support^{1,9}. Recently, tubular supports have attracted considerable attention due to their unique structure and high surface area. It has been reported that high catalytic activity can be obtained when the copper species were dispersed on nanotube supports^{2,10}. However, the utility of tubular support is limited by the complicated fabrication process and high cost. In 1998, Kasuga et al. developed a simple hydrothermal method to turn TiO₂ powders into tubular structure in 10 mol·L⁻¹ NaOH solution¹¹. From then, the investigation and modification of this kind of NTs have attracted growing interest¹²⁻¹⁴. By using the formed hydrogen titanate NTs as support, we have prepared CuO/TiO₂ NTs via impregnation method. It is observed that the support structure play a key role on the catalytic activity of the supported CuO catalysts. Compared with the catalyst prepared from common powder support, CuO particles in CuO/TiO₂ NTs can be highly dispersed on the NTs with large surface area, and results in higher catalytic performance for CO oxidation¹⁵. However, the structure of hydrogen titanate NTs has been discovered to be relatively unstable¹⁴. The calcination process can induce the change of their crystalline form and results in the morphology destroy, which will result in the decrease of their surface area. It has been reported that surface area and active sites govern the activity of copper oxide-based catalysts¹. So the stabilization of the tubular structure is important for the CuO/TiO₂ NTs. To improve the structural stability of TiO₂, adding other atoms to titania is proven to be an effective method. It has been reported that CeO₂ can stabilize the active phase in a fine dispersed state and improve the thermal resistance of the supported catalyst¹⁶.

In this paper, CeO₂ is added in CuO/TiO₂ NTs as modification component to improve the catalytic performance of CuO/TiO₂ NTs for CO oxidation. The influence of calcination temperature and CeO₂ content on the structure and catalytic performance of CuO/TiO₂ NTs is also discussed.

2. EXPERIMENTAL

2.1 Materials

All the reagents are analytical grade and used without further purification.

2.2 Catalyst Preparation

Hydrogen titanate NTs are synthesized according to the published procedure¹¹. CuO and CeO₂ modified TiO₂ NTs (CuO-CeO₂/TiO₂ NTs) are prepared by impregnation method¹⁵. In a typical synthesis, the NTs are dispersed in water (1g NTs/100mL H₂O) and then appropriate quantity of Cu(NO₃)₂·3H₂O and Ce(NO₃)₃·6H₂O powder are added. After water is removed

completely at 100 °C under stirring, the impregnated samples are calcined at different temperatures for 2 h to obtain CuO-CeO₂/TiO₂ NTs. CuO/TiO₂ NTs are prepared by a similar process. The information of the prepared samples is shown in Table 1 and Table 2.

Cu(NO₃)₂·3H₂O and Ce(NO₃)₃·6H₂O powder are calcined at 200 °C and 300 °C for 2 h to obtain pure CuO and CeO₂, respectively.

2.3 Characterization

The samples are characterized with transmission electron microscopy (TEM, Philips T20ST), X-ray diffraction (XRD, Rigaku D/Max-2200 X-ray diffractometer with Cu K α radiation), nitrogen adsorption (BET, JW-K, at liquid N₂ temperature), and temperature-programmed chemisorption instrument (Micromeritics, U. S. A).

2.4 Catalytic Activity Test

Catalytic activities of all samples are tested using a fixed bed microreactor (7 mm i.d.) under atmospheric pressure using 100 mg catalyst powder. Reaction gas mixture consisting of 1% CO balanced with air is passed through the catalyst bed at a total flow rate of 33.6 mL/min. The reactant and product composition are analyzed on-line with a GC-508A gas chromatograph equipped with a thermal conductivity detector (TCD). The catalyst bed is heated at different temperatures. Then the corresponding CO conversion ratios are monitored. The CO conversion ratios increase with the raise of catalyst bed's temperature. When 100% CO conversion is obtained, the temperature of catalyst bed is marked as T_L (light-off temperature for CO conversion).

3. RESULTS AND DISCUSSION

3.1 Microstructural Characterization of the Catalysts

Figure 1 depicts XRD patterns of hydrogen titanate NTs, CuO and CuO/TiO₂ NTs (calcined at 200 °C) with different Cu/Ti atomic ratios. The hydrogen titanate NTs are mainly composed of titanate phase H₂TiO₅·H₂O (JCPDS 47-0124). In the CuO pattern, the diffraction peaks at 2 θ = 32.4°, 35.4°, 38.8°, 48.5°, 53.1°, 58.3°, 61.5°, 66.2° and 68.9° are designated as reflections of CuO (1 1 0), overlapping reflections of (0 0 2) and (-1 1 1), overlapping reflections of (1 1 1) and (2 0 0), (-2 0 2), (0 2 0), (2 0 2), (-1 1 3), (-3 1 1) and (2 2 0) (JCPDS 5-661). For CuO/TiO₂ NTs, the diffractions that are attributable to anatase TiO₂ crystal are clearly detectable (JCPDS 21-1272). It seems that the hydrogen titanate in the tubular support has turned into anatase TiO₂ after the calcination process. When Cu/Ti atomic ratios (Cu/Ti = 1:20, 1:15, 1:12.5, 1:10) are relatively low, no obvious CuO peak is found in the samples. That should be attributed to the high distribution of CuO particles. When Cu/Ti = 1:5, a weak CuO peak appears at 2 θ = 35.4°. The intensity of this peak increases with the raise of Cu/Ti atomic ratio. From Table 1, it can be observed that the size of CuO particles supported on the NTs increases with the raise of CuO content. When Cu/Ti = 1:2 and 1:1, another new CuO peak appears at 2 θ = 58.3°.

Figure 1. XRD patterns of hydrogen titanate NTs (a), CuO (b) and CuO/TiO₂NTs with different Cu/Ti atomic ratios (c) 1:20; (d) 1:15; (e) 1:12.5; (f) 1:10; (g) 1:5; (h) 1:2; (i) 1:1.

Figure 2. XRD patterns of CeO₂ (a), CuO/TiO₂NTs (Cu/Ti=1:10) (b), CuO-CeO₂/TiO₂NTs with different Cu/Ce/Ti atomic ratios (c) 1:1:10; (d) 1:2:10; (e) 1:3:10; (f) 1:4:10; (g) 1:5:10; (h) 1:10:10.

After CeO₂ is added in CuO/TiO₂ NTs, obvious difference can be seen from the XRD patterns. Figure 2 shows the XRD patterns of CuO/TiO₂NTs (Cu/Ti=1:10), CeO₂ and CuO-CeO₂/TiO₂ NTs with different Cu/Ce/Ti atomic ratios. They are all calcined at 300 °C. In the CeO₂ pattern, the diffraction peaks at $2\theta = 28.7^\circ, 33.3^\circ, 47.8^\circ, 56.8^\circ, 59.6^\circ$ and 69.6° are designated as reflections of CeO₂ (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), and (4 0 0) (JCPDS 81-0792). Compared with the XRD pattern of CuO/TiO₂ NTs, new CeO₂ peaks appear at $2\theta = 29^\circ$ and 33° in CuO-CeO₂/TiO₂ NTs. CeO₂ peaks at $2\theta = 47.8^\circ$ and 56.8° are overlapped by the (2 0 0) and (2 1 1) reflection peaks of TiO₂, and results in the two broad peaks. Above mentioned new peaks indicates that the CeO₂ particles have been supported on the NTs. Furthermore, the peak intensity of anatase TiO₂ is relatively low after CeO₂ is added. With the increase of Cu/Ce atomic ratios, the line broadening of CeO₂ diffraction peaks can be observed in Figure 2. That indicates the increase of CeO₂ particle size, as shown in Table 2. Similar to the XRD curves of CuO/TiO₂ NTs, no obvious CuO peak is found, which should be attributed to the high distribution of CuO particles. From Figure 3, it can be observed that the intensity of CuO-CeO₂/TiO₂ NTs' diffraction peaks increases with the raise of calcination temperature, indicating the increase of particle size. That also can be revealed by the data of CeO₂ particle sizes in Table 2.

Figure 3. XRD patterns of CuO-CeO₂/TiO₂NTs (Cu/Ce/Ti=1:2:10) calcined at (a) 200 °C, (b) 300 °C, (c) 400 °C

Figure 4. The TEM images of CuO/TiO₂NTs calcined at 300 °C

A deep insight into the structure of the supported catalyst can be obtained by TEM observations. Figure 4 and Figure 5 shows the TEM images of CuO/TiO₂NTs and CuO-CeO₂/TiO₂NTs calcined at 300 °C, respectively. Compared with CuO/TiO₂NTs, CuO-CeO₂/TiO₂NTs shows better tubular structure. It seems that CuO-CeO₂/TiO₂NTs have better thermal stability. NTs mixed with nanoparticles can be observed in CuO/TiO₂NTs, and the NTs have length less than 100 nm. In Figure 4B, the average length of the NTs is about 50 nm. Compared with pure hydrogen titanate NTs¹⁷, the tubular structure of CuO/TiO₂NTs is seriously damaged after the calcination process at 300 °C. As indicated in the XRD patterns, the hydrogen titanate NTs have been transformed to anatase TiO₂, which results in the destruction of tubular structure. In our previous work, we have observed that the hydrogen titanate NTs can keep their tubular structure well after the calcination treatment at 300 °C¹⁸. It has been reported that the presence of copper oxide can accelerate the sintering of TiO₂ support^{19,20}. For the supported catalyst, the support structure and stability has important influence on the performance and reuse of the catalysts. So the stability of the tubular support of CuO/TiO₂NTs needs to be improved.

Figure 5. The TEM images of CuO-CeO₂/TiO₂NTs calcined at 300 °C

After CeO₂ is added in CuO/TiO₂ NTs, better thermal stability can be obtained, as shown in Figure 5. From this figure, it can be observed that CuO-CeO₂/TiO₂NTs show fine tubular structure and large length. Most of the NTs

have length more than 100 nm. At higher magnification (Figure 5B), it can be seen that the NTs have multilayer structure and diameter of about 10 nm. The supported particles should be composed of CuO and CeO₂. It seems that the CeO₂ modification can improve the stability of CuO/TiO₂NTs obviously.

From the TEM images of CuO/TiO₂NTs and CuO-CeO₂/TiO₂NTs, better tubular structure can be observed in CuO-CeO₂/TiO₂NTs. Surface area is an evident parameter for the tubular catalysts. So the surface areas of CuO/TiO₂NTs (Cu/Ti = 1:10) and CuO-CeO₂/TiO₂NTs (Cu/Ce/Ti = 1:2:10) calcined at 300 °C are measured. They are 164.7 and 145.4 m²/g, respectively. The specific surface of CuO-CeO₂/TiO₂NTs is lower than that of CuO/TiO₂NTs'. That should be mainly attributed to the lower NTs content in the CuO-CeO₂/TiO₂NTs.

In order to investigate the reducibility of the catalysts, temperature-programmed reduction (TPR) experiments are performed. The TPR profiles of CuO/TiO₂NTs (Cu/Ti = 1:10) and CuO-CeO₂/TiO₂NTs (Cu/Ce/Ti = 1:2:10) are shown in Figure 6. In the profile of CuO/TiO₂NTs, two individual peaks are centered at 163 and 178 °C, which are assigned to the stepwise reduction of surface dispersed CuO species, i.e., Cu²⁺→Cu⁺ and Cu⁺→Cu⁰, respectively^{21,22}. For CuO-CeO₂/TiO₂NTs, the two peaks are centered at 167 and 192 °C, which are a little larger than that of the CuO/TiO₂NTs'. That should be attributed to the hydrogen spill-over effect²², which is caused by the relatively low content of copper species in CuO-CeO₂/TiO₂NTs. The existence of Cu⁺ has been proved to have positive influence on the catalytic activity of the copper oxide-based catalysts²³. High catalytic performance can be anticipated on the CuO/TiO₂NTs and CuO-CeO₂/TiO₂NTs. Moreover, a broad peak appears between 350 and 600 °C. It should be attributed to the reduction of the surface capping oxygen of CeO₂²⁴. From the TPR patterns, the reduction peaks of CuO/TiO₂NTs are centered at relatively low temperature. It seems that higher catalytic performance can be obtained on CuO/TiO₂NTs.

Figure 6. The TPR profiles of CuO/TiO₂NTs (Cu/Ti = 1:10) and CuO-CeO₂/TiO₂NTs (Cu/Ce/Ti = 1:2:10)

Table 1. Information and catalytic performance of CuO/TiO₂NTs for CO oxidation.

Cu/Ti	1:20	1:15	1:12.5	1:12.5	1:10	1:5	1:2	1:1
CuO content (wt. %)	4.8	6.7	7.4	7.4	9.1	17	33	50
CuO size (nm) ^a	— ^b	—	—	—	—	—	13.0	15.9
Tc(°C)	200	200	200	300	200	200	200	200
T _L (°C)	142	124	90	114	86	82	88	86

^aFrom line broadening of CuO (2 0 0) peak

^bNo obvious CuO peak can be used to calculate the CuO size

Tc: calcination temperature T_L: light-off temperature for CO conversion

Table 2. Information and catalytic performance of CuO-CeO₂/TiO₂NTs for CO oxidation.

Cu/Ce/Ti	1:1:10	1:2:10	1:2:10	1:2:10	1:3:10	1:4:10	1:5:10	1:10:10
CuO content (wt. %)	7.6	6.5	6.5	6.5	5.7	5.1	4.6	3.1
CeO ₂ content (wt. %)	16.4	28.1	28.1	28.1	36.9	43.9	49.4	66.2
CeO ₂ size (nm) ^a	6.7	6.5	7.1	7.9	7.5	8.2	9.1	10.0
Tc(°C)	300	200	300	400	300	300	300	300
T _L (°C)	80	85	75	90	85	83	85	82

^aFrom line broadening of CeO₂ (1 1 1) peak

Tc: calcination temperature T_L: light-off temperature for CO conversion

3.2 Catalytic Activities of the Tubular Catalysts

For CuO/TiO₂NTs, the CuO content and calcination temperature both have obvious influence on their catalytic activity for CO oxidation. Table 1 shows the relation between the preparation parameters and catalytic activity of CuO/TiO₂NTs. From Table 1, it can be observed that the light-off temperature decreases with the increase of Cu/Ti atomic ratio when Cu/Ti atomic ratios are lower than 1:12.5. When the Cu/Ti atomic ratios are between 1:12.5 and 1:1, no obvious difference is detected for the catalytic activity of the CuO/TiO₂NTs. It seems that the active centers increase with the raise of CuO content when the Cu/Ti atomic ratio is relatively low ($\leq 1:12.5$). However, excess CuO will not form more active centers due to the invariable surface area of the TiO₂ NTs.

So the light-off temperature of the CuO/TiO₂NTs does not increase obviously when Cu/Ti atomic ratios are between 1:12.5 and 1:1, and excess CuO has no obvious influence on the supported CuO catalysts²⁵.

Except for the Cu/Ti atomic ratio, calcination temperature is also an important preparation parameter for CuO/TiO₂NTs with high catalytic activity. From Table 1, it can be seen that the light-off temperature of CuO/TiO₂NTs (Cu/Ti = 1:12.5) calcined at 300 °C (T_L = 114 °C) is 24 °C higher than that of sample calcined at 200 °C (T_L = 90 °C). It seems that high calcination temperature will cause aggregation of the CuO particles and tubular support, which results in the decrease of active centers and low catalytic activity. As

discussed above and reported in our previous work¹⁵, the surface area of the support have obvious influence on the catalytic activity of this CuO/TiO₂NTs catalyst. From the TEM images, the structure damage of the CuO/TiO₂NTs also can be observed at some area. So the unstable structure of this CuO/TiO₂NTs catalyst results in the reduced activity at high calcinations temperature. That would hinder their utility as thermal catalysts.

Table 2 shows the information and catalytic performance for the CuO-CeO₂/TiO₂NTs. From Table 1 and Table 2, it can be seen that the light-off temperatures of CuO/TiO₂NTs (Cu/Ti = 1:10) and CuO-CeO₂/TiO₂NTs (Cu/Ce/Ti = 1:2:10), which are both calcined at 200 °C, are 86 °C and 85 °C, respectively. But the T₁ of CuO-CeO₂/TiO₂NTs is changed to 75 °C when they are calcined at 300 °C. That should be attributed to that the Ce(NO₃)₃·6H₂O has not been completely decomposed to CeO₂ when the catalysts are calcined at 200 °C.

Compared with CuO/TiO₂NTs, the light-off temperature of CuO-CeO₂/TiO₂NTs does not change obviously with the increased calcination temperature, which indicates the stabilization of CeO₂ in this tubular catalyst. Among the three samples (Cu/Ce = 1:2, calcination temperature are 200, 300, and 400 °C, respectively), the one calcined at 300 °C shows the best catalytic activity. So 300 °C is selected as the calcination temperature for CuO-CeO₂/TiO₂NTs with different Cu/Ce/Ti atomic ratios. From Table 2, it can be seen that the addition of CeO₂ also can improve their catalytic activity slightly. Except for the synergistic interaction between CuO and CeO₂, the structure stabilization of the tubular support and better dispersion of CuO particles induced by the CeO₂ modification are also responsible for the high activity. The influence of CeO₂ content on the catalytic activity is also investigated. Among different Cu/Ce atomic ratios, 1:2 should be the best ratio.

From above data, it can be observed that CeO₂ modification not only can improve the catalytic activity of CuO/TiO₂NTs, but also can improve their thermal stability. As catalysts for CO oxidation, thermal stability is vital for catalysts' lifetime and their reuse. So CuO-CeO₂/TiO₂NTs are prior to CuO/TiO₂NTs in thermal catalytic reaction.

To monitor the stability of CuO-CeO₂/TiO₂NTs, the catalytic activities of a catalyst with Cu/Ce/Ti= 1:1:10 calcined at 300 °C for CO oxidation as a function of reaction time are measured. After 100% CO conversion is obtained on them, the CO conversion is measured every half an hour under the same experiment condition (T = T₁). Activities of the catalyst do not decay over 10 h in the present study, which indicates high stability of the prepared catalysts.

In conclusion, relatively low structure stability of CuO/TiO₂NTs restricts their practical utility as CO oxidation catalyst. CeO₂ modification can enhance the catalytic performance of CuO/TiO₂NTs, which would be a favor for the practical applications of tubular supported CuO catalysts for CO oxidation.

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