

Effects of Carrier on CuO/TiO₂ and CuO/Ti_{0.5}Zr_{0.5}O₂ Catalysts in the NO+CO Reaction

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Abstract: Using TiO₂ and Ti_{0.5}Zr_{0.5}O₂ as carriers, the CuO/TiO₂ and CuO/Ti_{0.5}Zr_{0.5}O₂ catalysts were prepared by the impregnation method with Cu(NO₃)₂ as active component. The catalytic activities in NO+CO reaction were investigated using a microreactor-GC system, and structure and reducibility of catalysts were characterized by means of physical adsorption, TPR, XRD, NO-TPD technologies. It was found that the activity of CuO/Ti_{0.5}Zr_{0.5}O₂ catalyst was higher than that of CuO/TiO₂, probably due to the large specific surface area of Ti_{0.5}Zr_{0.5}O₂ that played an important role in NO+CO reaction.

Keywords: Ti_{0.5}Zr_{0.5}O₂ solid solution, supported CuO catalysts, NO+CO reaction.

As important catalyst carriers, TiO₂ and ZrO₂ have attracted much attention in recent years¹⁻³. But they have small specific surface area and poor thermal stability. The specific surface area of TiO₂-ZrO₂ is three- and five-fold bigger than that of TiO₂ and ZrO₂ alone, respectively. Thermal stability, surface acidity and alkalescence of TiO₂-ZrO₂ solid solution are also better than those of the singles, which are extensively used as catalyst carriers for NO removal recently. Haneda *et al.*⁴ reported that addition of Ag greatly improved NO reduction activity in NO+C₃H₆+O₂ reaction. Das *et al.*⁵ prepared a series of TiO₂-ZrO₂ with different molar ratio of Ti:Zr (from 0 to 1) and found that the optimal Zr concentration was 60 mol% and ZrTiO₄ phase was formed in the samples calcined at 700 °C. Mariscal *et al.*⁶ have studied the effect of pre-reduction and surface acidity on Pt/TiO₂-ZrO₂ activities. However, there has been little information in the literature on the application of CuO/TiO₂-ZrO₂ catalyst in the NO+CO reaction.

In this study, CuO/TiO₂ and CuO/Ti_{0.5}Zr_{0.5}O₂ catalysts were prepared by impregnating the TiO₂ and Ti_{0.5}Zr_{0.5}O₂ carrier with aqueous solutions containing required amount of Cu(NO₃)₂. The activities of catalysts were determined under the steady state in a fixed-bed quartz reactor, and the catalyst reducibility and characteristics were investigated using the methods of physical adsorption, TPR, XRD and NO-TPD.

Figure 1 illustrates the adsorption-desorption isotherms and pore size distribution of Ti_{0.5}Zr_{0.5}O₂. Its total pore volume and average aperture were 0.356 mL/g and 5.89 nm, respectively. The pore size distributions of Ti_{0.5}Zr_{0.5}O₂ were mainly as micro-pores and

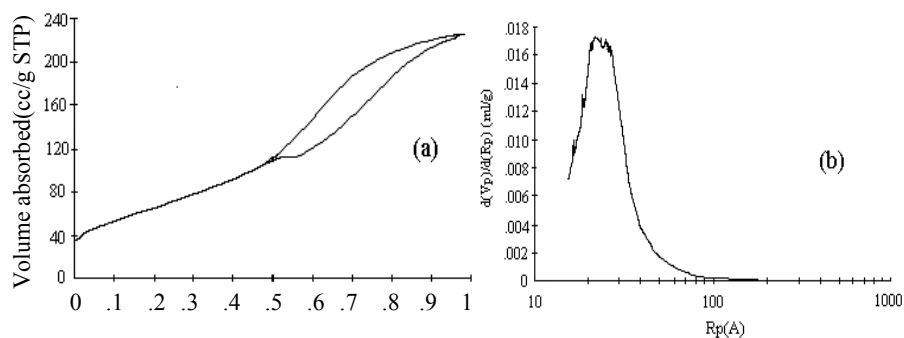
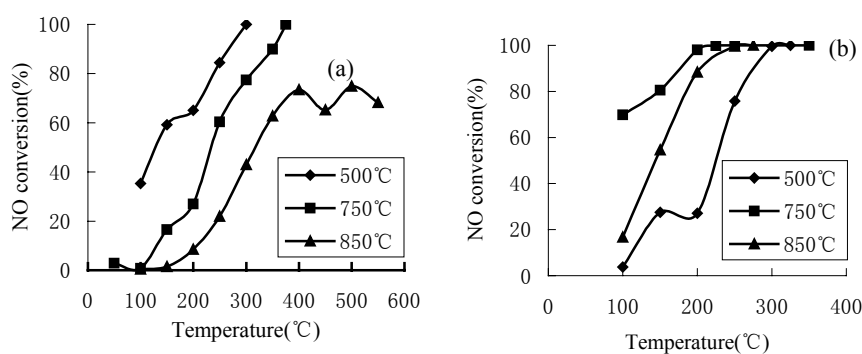
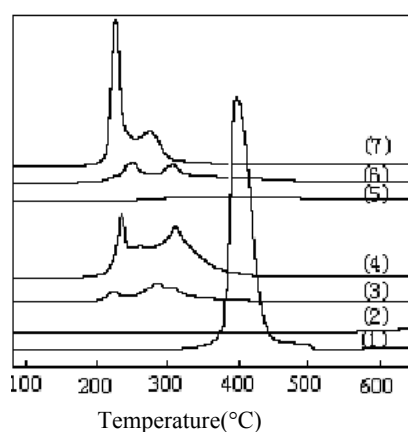
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meso-pores, and the isotherms were the type IV of BDDT classification. The specific surface area of $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ was $242 \text{ m}^2\text{g}^{-1}$ after calcined at 450°C for 2 h, while the specific surface area of TiO_2 was $65 \text{ m}^2\text{g}^{-1}$.

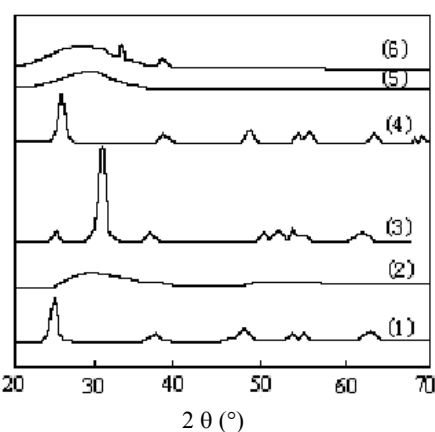
Figure 2 shows the relationship between calcination temperature and NO conversion by 6%CuO/ TiO_2 and 6%CuO/ $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ pretreated in H_2 atmosphere. It can be seen that NO conversion efficiency of 6%CuO/ TiO_2 decreased with the increase of calcination temperature. The reaction temperature of 99% NO conversion was 300°C after the catalyst was calcined at 500°C . The catalytic activity decreased slightly after calcination at 750°C and 99% NO conversion was obtained at reaction temperature of 375°C , but marked decrease in activity occurred after calcination at 850°C . In contrast, 6%CuO/ $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst had the highest activity in NO+CO reaction after calcination at 750°C with 99% NO conversion at reaction temperature of 225°C , followed by calcination at 850°C with 99% NO conversion at reaction temperature of 250°C . The results indicated that CuO/ $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalysts retained good thermal stability, and its activities were higher than those of CuO/ TiO_2 under conditions of the same CuO loading.

The TPR analysis (**Figure 3**) showed no visible peaks (curves 2 and 5) of TiO_2 and $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ within the range of experimental temperature, indicating that (TiO_2 and $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$) reduction of were very difficult. After CuO was loaded, the TiO_2 and $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ reducibility increased markedly. For CuO/ TiO_2 catalyst, there were three reduction peaks (α peak at 220°C , β peak at 290°C and γ peak at 310°C) at 6%CuO loading. When the CuO loading was increased to 18%, α peak and γ peak became sharp and the area of peaks largely increased. We assumed that the α peak was the high dispersed copper oxide, the β peak was copper oxide, and the γ peak was the crystalline copper oxide. When $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ was used as carrier, there were two reduction peaks (α and β) at 250°C and 315°C on 6%CuO/ $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst, but the peaks shifted towards lower temperatures and a third un conspicuous peak was observed at 18%CuO loading. In contrast, the area of α peak of CuO/ $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ was larger than that of CuO/ TiO_2 at the same CuO loading. For pure CuO, a large and sharp peak was observed at about 392°C . The findings indicated that there were interactions between CuO and TiO_2 or $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$, which shifted the CuO reduction peak from 392°C to $220\sim 250^\circ\text{C}$, and $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ dramatically increased CuO dispersion which was related with the specific area of carrier. Combined with the data of activity, we considered that the high dispersion of CuO caused the high activity of CuO/ $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$.

The XRD patterns of various samples are shown in **Figure 4**. After calcined at 500°C for 2 h, anatase phase characteristic diffraction peak of TiO_2 was detected at $2\theta=25.2^\circ$, 37.0° and 48.1° , but rutile phase did not formed. When 6%CuO was supported on TiO_2 , TiO_2 still existed in the form of anatase. While $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution was amorphous after calcination at 500°C , crystalline ZrTiO_4 appeared XRD pattern at $2\theta=24.7^\circ$ and 30.6° after calcination at 650°C , the XRD pattern moved to $2\theta 30.6^\circ$. When the 6%CuO of load, no CuO crystal diffraction peak was observed, probably due to the large specific surface area of $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ causing the dispersion of CuO. Two CuO diffraction peaks were detected ($2\theta=35.5^\circ$ and 38.7°) at 18%CuO loading, and $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_2$ was still amorphous. This was consistent with the TPR profiles (**Figure 3**).

Figure 1 Adsorption-desorption isotherm (a) and pore size distribution (b) of Ti_{0.5}Zr_{0.5}O₂

Figure 2 Effect of calcination temperature on NO conversion of 6%CuO/TiO₂ (a) and 6%CuO/Ti_{0.5}Zr_{0.5}O₂ (b) pretreated in H₂ atmosphere for NO+CO reaction

Figure 3 TPR profiles of various samples calcined at 500°C for 2 h


- (1) CuO (2) TiO₂ (3) 6%CuO/TiO₂
 (4) 18%CuO/TiO₂ (5) Ti_{0.5}Zr_{0.5}O₂
 (6) 6%CuO/Ti_{0.5}Zr_{0.5}O₂
 (7) 18%CuO/Ti_{0.5}Zr_{0.5}O₂

Figure 4 XRD patterns of various samples


- (1) TiO₂(500°C) (2) Ti_{0.5}Zr_{0.5}O₂(500°C)
 (3) Ti_{0.5}Zr_{0.5}O₂(650°C) (4) 6%CuO/TiO₂(500°C)
 (5) 6%CuO/Ti_{0.5}Zr_{0.5}O₂(500°C)
 (6) 18%CuO/Ti_{0.5}Zr_{0.5}O₂(500°C)

Figure 5 NO-TPD spectra of 6%CuO/TiO₂ (a) and 6%CuO/Ti_{0.5}Zr_{0.5}O₂ (b) with different calcinations temperature pretreated in H₂ atmosphere

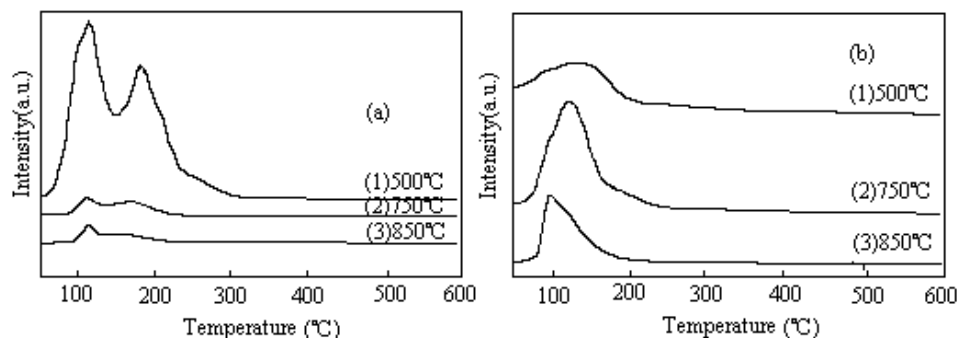


Figure 5 shows that curves of desorptional NO in the NO-TPD process of 6%CuO/TiO₂ and 6%CuO/Ti_{0.5}Zr_{0.5}O₂ which were pretreated in H₂ atmosphere. It can be seen that the NO desorption processes of 6%CuO/TiO₂ (500 °C) and 6%CuO/Ti_{0.5}Zr_{0.5}O₂ (750 °C) had three desorption peaks at 120, 180, 250 °C and 100, 130, 190 °C, respectively. In contrast, other catalysts had only two adsorption peaks. The highest catalytic activity of 6%CuO/Ti_{0.5}Zr_{0.5}O₂ (750 °C) was owing to its low NO desorption temperature and multiple desorption centers.

In summary, the large specific surface area of Ti_{0.5}Zr_{0.5}O₂ enhanced the dispersion of CuO, and therefore CuO/Ti_{0.5}Zr_{0.5}O₂ had higher catalytic activity than CuO/TiO₂.

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