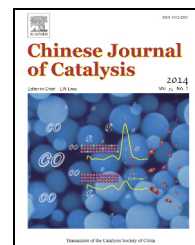


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Article

The effect of doping transition metal oxides on copper manganese oxides for the catalytic oxidation of CO

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ABSTRACT

A series of copper manganese oxides doped with transition metal oxides were prepared by co-precipitation using copper acetate and manganese acetate as precursors, ammonium bicarbonate as precipitant, and metal nitrates as dopants. The catalysts were characterized by N₂ adsorption-desorption, X-ray powder diffraction, temperature-programmed reduction, and in situ diffuse reflectance infrared Fourier transform spectroscopy. The results showed that doping transition metal oxides into copper manganese oxides can modify the CO adsorption ability of the catalyst and thus affect the catalytic oxidation of CO.

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1. Introduction

Catalytic oxidation of CO is one of the most effective methods of CO removal at low temperatures and has received considerable attention because of its many applications in industry and environmental fields. These include personal respiratory protective devices, CO₂ laser gas generation, proton exchange membrane fuel cells, and automobile emission controls [1–6]. Compared with noble metal catalysts, non-noble metal oxide catalysts have the advantages of high availability and low cost. Among them, hopcalite based on manganese-copper mixed oxide, a well-known catalyst for CO oxidation, has attracted attention because of its low price and relatively high catalytic activity. However, it has poor low-temperature catalytic activity and moisture resistance [7–9].

More recently, many attempts have been made to improve

the catalytic activity of copper manganese oxides for CO oxidation, in particular by optimizing the preparation technologies and the improvement of preparation methods [7–20]. Among these methods, doping a transition metal oxide into the copper manganese oxide catalysts could tune the oxygen mobility and the reduction ability of the catalysts, thus improving the catalytic activity. It was found that after doping a small amount of CeO₂ into copper manganese oxide, a highly dispersed CeO₂ phase could prevent sintering and aggregating of the catalyst. In addition, the reducibility was enhanced, the particle size was decreased, and the formation of the active sites for the oxidation of CO was improved significantly. Therefore, the activity of this rare earth-promoted catalyst was enhanced remarkably [7]. It was also reported that copper manganese oxide catalysts, prepared by co-precipitation, had improved O²⁻ availability in the lattice and an enhanced surface area. By adding low levels

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(~1.0 wt%) of Co, these materials can display much higher activity for CO oxidation compared with the current commercial copper manganese oxide catalysts at ambient conditions [8].

In our previous work [20], the combination effect of precipitant and precursor in the preparation has been studied. The precipitant shows the greatest influence on the crystalline phases of the catalyst while the precursor shows a greater effect on the number of catalytic active sites, both of which are directly related to the CO oxidation activity. In the present study, to further improve the catalytic activity of copper manganese oxide, we have prepared copper manganese oxide catalysts via co-precipitation by doping with transition metal oxides with (FeO_x or CeO₂) or without (ZnO) oxygen storage capacity. This study focuses on the influences of doping different transition metal oxide on CO adsorption and the resulting performance of the copper manganese oxide catalysts.

2. Experimental

2.1. Catalyst preparation

All chemicals used in this study were of analytical grade and used without further purification. The copper manganese oxide catalysts were prepared by co-precipitation using NH₄HCO₃ as the precipitant, the acetates of the copper and manganese as the precursors, and Fe(NO₃)₃, Ce(NO₃)₃, and Zn(NO₃)₂ as dopant. The typical procedure to synthesize the catalysts was as follows. A precipitant (30 mmol) was dissolved in deionized water (30 mL) with an initial pH value of *ca.* 8. The precursors (7.5 mmol) were mixed with deionized water (30 mL) with a 1/2 molar ratio of copper to manganese species. The mixed precursor solution was then added to the precipitant solution at 298 K with vigorous stirring. The resultant suspensions were aged for 30 min with continued vigorous stirring at 25 °C. Finally the precipitate was filtered, washed with deionized water and anhydrous alcohol, dried in air at 50 °C for 24 h, and then calcination at 300 °C for 2 h (denoted as CuMO_x-M, M = Fe, Zn, Ce) to obtain the final catalysts. The content of the doping transition metal oxide was fixed at 5 wt%. For comparison, the pure copper oxide and manganese oxide catalysts were prepared separately using the acetate as the precursor and NaOH as the precipitant, and keeping the other synthesis and after-treatment conditions the same as the copper manganese oxides. The corresponding samples were named CuO and MnO_x, respectively.

2.2. Catalyst characterization

X-ray diffraction patterns (XRD) were obtained with a Rigaku D/MAX-2400 diffractometer using Cu K_α radiation (40 kV, 100 mA, λ = 1.54056 Å). The textural characterizations of the samples were performed by nitrogen sorption at -196 °C using a Micromeritics Instrument Corporation Tristar 3000 device. Approximately 200 mg of the samples were heated to 200 °C under vacuum for 4 h to remove all adsorbed species. The surface area (*S*_{BET}) and pore size distribution were calcu-

lated using the BET method and BJH method, respectively. The total pore volume (*V*_{total}) was estimated from the amount adsorbed at a relative pressure of 0.99. The micropore volume was determined using the *t*-plot method. The morphologies of the catalysts were characterized with a FEI Quanta 450 instrument microscope equipped with a cooled energy-dispersive X-ray (EDX) spectrometer from Oxford Instruments for point-resolved elemental analysis. Hydrogen temperature programmed reduction (H₂-TPR) was performed by passing 8% H₂/Ar (50 mL/min) over a 20 mg sample (40–60 mesh size) at a heating rate of 10 °C/min to 900 °C. Before H₂-TPR, the samples were pretreated with Ar at 200 °C for 1 h. The system was then cooled to ambient temperature under Ar. The amount of hydrogen consumed (H₂ cons.) by each catalyst was calculated from the peak area of the H₂-TPR profile. In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) were recorded using a Nicolet 6700 FT-IR spectrometer at a resolution of 4 cm⁻¹ from 4000 to 640 cm⁻¹. Self-supporting disks were prepared from the sample powders and treated directly in the IR cell. The catalysts were connected to a vacuum-adsorption apparatus with a residual pressure below 10⁻³ Pa. Prior to CO adsorption (5 vol% CO and N₂ in balance), the catalysts were evacuated for 30 min at 200 °C. After flushing with pure He for 10 min, the CO spectrum was collected again.

2.3. Catalytic test

The activity of the copper manganese oxide catalysts for CO oxidation was measured in a quartz tubular fixed-bed flow reactor at atmospheric pressure using 200 mg of catalyst (40–60 mesh). The standard composition of the feed gas was 1% CO, 20% O₂, and 79% N₂ with a space velocity (SV) of 20000 mL/(h·g_{cat}). The temperature was ramped to the final temperature at a rate of 1 °C/min. The concentrations of CO were analyzed at the outlet of the reactor by a Techcomp GC 7890T gas chromatograph equipped with a thermal conductivity detector. Temperatures for 100% conversion of CO (*T*_{100%}) and 50% conversion of CO (*T*_{50%}) were used to evaluate the activity of the catalysts. Long-term stability test of the CuMnO_x-Fe sample was conducted under atmosphere 30 °C, and SV = 20000 mL/(h·g_{cat}).

3. Results and discussion

3.1. Structure analyses of copper manganese oxides

XRD analysis was used to determine the final phase of the copper manganese oxide catalysts doped with different metal oxides after heat treatment at 300 °C in static air for 2 h (Fig. 1). It can be seen that the main crystal phase composition of the catalysts are Mn₂O₃, CuO, and Cu_{0.139}Mn_{0.861}O₂ with lower crystallinity. The crystal phase composition of the catalysts did not change significantly by doping with transition metal oxides, indicating that this addition does not significantly alter the bulk composition of the catalyst. Moreover, the characteristic diffraction peaks of the doped transition metal or any derivative did not appear due to low doping contents (below 5 wt%) or

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