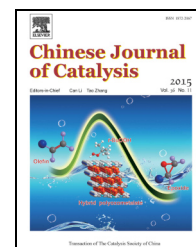


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Article

Carbon monoxide oxidation on copper manganese oxides prepared by selective etching with ammonia



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ABSTRACT

A series of copper manganese oxides were prepared using a selective etching technique with various amounts of ammonia added during the co-precipitation process. The effect of the ammonia etching on the structure and catalytic properties of the copper manganese oxides was investigated using elemental analysis, nitrogen physisorption, X-ray powder diffraction, scanning and transmission electron microscopy, X-ray photoelectron spectroscopy, H₂ temperature-programmed reduction, and O₂ temperature-programmed desorption combined with catalytic oxidation of CO. It was found that ammonia can selectively remove copper species from the copper manganese oxides, which correspondingly generates more defects in these oxides. An oxygen spillover from the manganese to the copper species was observed by H₂ temperature-programmed desorption, indicating that ammonia etching enhanced the mobility of lattice oxygen species in these oxides. The O₂ temperature-programmed desorption measurements further revealed that ammonia etching improved the ability of these oxides to release lattice oxygen. The improvement in redox properties of the copper manganese oxides following ammonia etching was associated with enhanced catalytic performance for CO oxidation.

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1. Introduction

Low-temperature carbon monoxide (CO) oxidation has attracted considerable attention in both academic and industrial fields [1–4]. Supported noble metal catalysts remain the most promising candidates for this reaction because of their distinguished activity and good stability [5–7]; however, the scarcity and high cost of precious metals are driving the search for more economic catalysts [8–13]. Copper manganese oxide (CMO), the major ingredient of hopcalite catalyst, is of great interest because of its low cost and relatively high catalytic activity for CO oxidation [14–17]. In general, the activity of copper manganese mixed oxides originates from the formation

of an amorphous CuMnO_x hybrid, which is produced from the reaction between copper and manganese oxides [18–20].

Many synthesis methods have been developed to improve the efficiency of CMO, including co-precipitation [14], impregnation [21], sol-gel techniques [22], supercritical anti-solvent precipitation [23], and reduction methods [17]. Of these, co-precipitation is considered a convenient way of preparing catalysts with high activity. The preparation conditions have an important influence on the CMO activity. Hutchings and co-workers [14,24] discovered that selection of the correct aging time and use of a low calcination temperature are beneficial for preparing catalysts with high surface area and amorphous structure, which give high CO oxidation reactivity. The

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Cu/Mn ratio is also a crucial parameter which determines the phase composition in the final catalysts. It has been reported that CMO with a Cu/Mn ratio of 0.5 shows the best catalytic activity [24–28].

To date, it has been proved that the catalytic activity can be optimized by adjusting the composition, morphology, or structure of the CMO; however, investigations of their redox properties are rarely reported. In this work, a series of CMO catalysts were synthesized using a selective etching technique. With the aid of ammonia, Cu species can be selectively redissolved during the precipitation process because of the large difference in the stability constants of $[\text{Cu}(\text{NH}_3)_x]^{2+}$ ($\log\beta = 13.1$) [29] and $[\text{Mn}(\text{NH}_3)_x]^{2+}$ ($\log\beta = 1.57$) [30]. The composition and morphology of the final catalysts can therefore be manipulated. This facile pretreatment not only modifies the structure but also enhances the CO oxidation reactivity over CMO catalysts with a Cu/Mn ratio of ~ 0.3 , which is far below the reported optimized ratio of 0.5 [24–28]. Combining the results of various characterization methods, we determined the structural and redox property changes of selectively etched CMO catalysts. The effect of the preparation method on the CO oxidation reactivity is discussed based on these characterization results.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade and used without any further purification. The CMO was prepared by co-precipitation using sodium bicarbonate (NaHCO_3) as the precipitant and copper acetate $[\text{Cu}(\text{OC}_2\text{H}_3)_2]$ and manganese acetate $[\text{Mn}(\text{OC}_2\text{H}_3)_2]$ as the precursors. Typical synthesis procedures are as follows: (1) 18 mmol of NaHCO_3 was dissolved in 22.5 mL of deionized water with an initial pH value of ca. 8; (2) 7.5 mmol of $\text{Cu}(\text{OC}_2\text{H}_3)_2$ and 15.0 mmol of $\text{Mn}(\text{OC}_2\text{H}_3)_2$ were mixed with 22.5 mL of deionized water; (3) the mixed solution was added to the solution containing the precipitant at 25 °C under vigorous stirring; (4) fixed volumes (1 mL) of 0, 5, 10, and 15 mmol of ammonia were rapidly dropped into the above solutions; (5) the suspensions obtained were aged for 30 min under vigorous stirring at 25 °C; (6) the precipitates were finally filtered, washed, and dried in air at 50 °C overnight, followed by calcination at 300 °C for 2 h. The obtained copper manganese oxide catalysts were denoted as CMO- X ($X = 0, 5, 10, \text{ and } 15$), where X corresponds to the amount of added ammonia (mmol).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were measured using a Rigaku D/MAX-2400 diffractometer with a $\text{Cu } K_\alpha$ radiation source (40 kV, 100 mA, $\lambda = 0.154\ 056\ \text{nm}$). The morphologies of the catalysts were characterized using an FEI Quanta 450 scanning electron microscope (SEM) equipped with a cooled energy-dispersive X-ray (EDX) spectrometer from Oxford Instruments for point-resolved elemental analysis. Transmission electron microscope (TEM) images were obtained with an FEI F30 microscope with an accelerating voltage of 300 kV. The

Brunauer-Emmett-Teller (BET) surface area (A_{BET}) was measured by nitrogen sorption at $-196\ ^\circ\text{C}$ using a Micromeritics ASAP 2020 instrument. Before measurement, all samples were degassed under a pressure of 15 Pa at 200 °C for at least 4 h. Elemental analysis was performed by inductively coupled plasma (ICP) atomic emission spectroscopy using an Optima 2000DV instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo VG ESCALAB250 with $\text{Al } K_\alpha$ radiation at 15 kV and 10 mA. The binding energy (BE) of each element was calibrated using a C 1s photoelectron peak at 284.6 eV. Temperature-programmed reduction of hydrogen (H_2 -TPR) was performed on a Micromeritics AutoChem II 2920 apparatus with a thermal conductivity detector (TCD) by passing 8% H_2/Ar (flow rate of 50 mL/min) over 50 mg of sample (40–60 mesh) at a heating rate of 10 °C/min up to 900 °C. Before H_2 -TPR, the samples were pretreated at 200 °C for 1 h under a flow of He gas to ensure a clean catalyst surface. The system was then cooled to ambient temperature under He flow. The amount of hydrogen consumed by each catalyst was calculated from the peak area of the H_2 -TPR profile. Oxygen temperature-programmed desorption (O_2 -TPD) was performed on a Micromeritics AutoChem II 2920 apparatus. A 50-mg sample was pre-treated at 200 °C for 1 h with He, cooled to ambient temperature under He, and finally 5% O_2/He was contacted with the sample for 1 h. Desorption was carried out from ambient temperature to 900 °C at a heating rate of 10 °C/min under He flow (30 mL/min).

2.3. Catalytic tests

The oxidation of CO was tested in a tubular fixed-bed quartz reactor at atmospheric pressure using 200 mg of catalyst (40–60 mesh). The standard composition of the feed gas was 1% CO -20% O_2 -79% N_2 with a space velocity of 20 000 $\text{mL g}^{-1}\ \text{h}^{-1}$. The temperature was ramped at a rate of 1 °C/min from 30 °C to the final temperature. The concentrations of CO were analyzed at the outlet of the reactor by a GC 7890T gas chromatograph (TECHCOMP Limited Company, China) equipped with a TCD.

3. Results and discussion

3.1. Selective etching of copper manganese oxides

Fig. 1 presents the XRD patterns of the CMO- X catalysts. All samples show similar diffraction peaks at $2\theta = 31.4^\circ, 32.3^\circ, 37.1^\circ, 42.1^\circ, \text{ and } 52.7^\circ$, suggesting that the major phases are mixtures of copper manganese hybrid oxides (CuMnO_x , JCPDS No. 41-0182) and manganese oxide (Mn_2O_3 , JCPDS No. 33-0900). The diffraction peak at $2\theta = 24.3^\circ$ indicates the presence of small amounts of manganese carbonate (MnCO_3 , JCPDS No. 44-1472). Because the catalysts were calcined at 300 °C, it is difficult to form complex oxides of CuMnO . The low resolution of the diffraction peaks indicates that the samples are poorly crystallized. These results are consistent with previous reports of amorphous CMOs prepared by co-precipitation [14,15,31–33]. The addition of ammonia hardly affected the

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