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Comparative study for low-temperature catalytic oxidation of *o*-xylene over doped OMS-2 catalysts: Role of Ag and Cu

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ABSTRACT

Ag or Cu doped manganese oxide octahedral molecular sieve (OMS-2) was prepared through the one-step reduction of KMnO_4 , Tollens' reagent, or Fehling' reagent with propionaldehyde. The influences of the dopants on the structure, redox ability and catalytic performance of OMS-2 were investigated. The results indicate that Ag-OMS-2 and Cu-OMS-2 exhibited relatively higher catalytic activity for *o*-xylene oxidation at higher ($>185^\circ\text{C}$) and lower temperatures ($\leq 185^\circ\text{C}$), respectively. This can be illustrated as follows. The doped Ag increased the content of surface absorbed oxygen and inhibited the adsorption of CO_2 . The doped Cu increased the content of lattice oxygen and the surface area of OMS-2, but increased its adsorption capacity toward CO_2 . In situ DRIFT study demonstrates that the oxidation of low molecular weight carboxylates (the stable intermediates in the oxidation of *o*-xylene) is the rate-determining step, which is closely related with the active oxygen species. The doped Ag increased the content of electrophilic oxygen (O_2^- , O^- or O_2^{2-}) and promoted the transformation of O_2 into nucleophilic oxygen (O^{2-}), which facilitated the oxidation of benzene ring and small molecule carboxylate, respectively.

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1. Introduction

Benzene, toluene and xylene (BTX) are classified as priority environmental pollutants, and the development of effective treatment technologies for their removal is highly desired [1–3]. Catalytic combustion is considered to be a promising method due to its low cost and high efficiency. Up to now, a variety of catalysts have been applied in the catalytic combustion of BTX, and the design of effective low-temperature catalysts has received increased attention in recent years [4–14].

Cryptomelane-type manganese oxide octahedral molecular sieve (OMS-2) has long been used as a highly active, low cost, and environmental friendly catalyst for the removal of volatile organic compounds (VOCs). It has a porous structure and contains mixed-valent Mn species, which facilitate the adsorption and activation of oxygen. Especially, it has a hydrophobic property that increases its stability against H_2O [15]. It is generally believed that the incorporation of transition metals or noble metals into the channels or in the structure of OMS-2 can promote its catalytic performance. Hence various metal doped or modified OMS-2 materials have been synthesized [16–24]. Recent researches reported that both Cu and

Ag are effective dopants. As for Cu, it could be loaded on the surface, incorporated into the framework, or entered into the tunnel of OMS, which are dependent on the preparation methods [25–28]. Yang et al. found that the catalytic performance of Cu-OMS was associated with the location of doped Cu. $\text{CuO}/\text{Cu}^{2+}$ incorporated into the framework or enters into the tunnel structure of OMS promoted the textural properties and the amount of surface labile oxygen, thus improving the adsorption and destruction performance for VOCs. By contrast, CuO attached on the external surface of OMS had the opposite effect [29]. As for Ag, its doping often leads to the formation of oxygen vacancies or distortion effects, which may increase the amount of highly reactive surface oxygen species [30]. Özacar et al. reported that the superior performance of Ag-OMS-2 catalysts in the low-temperature CO oxidation was due to their unique morphologies and the stable presence of highly dispersed Ag/Ag^+ species [31]. Huang et al. found that single-atom Ag supported on Hollandite-type manganese oxide showed high activation ability to both lattice oxygen and molecule oxygen, which resulted in excellent activity in the HCHO oxidation at low temperatures [32]. It can be seen that Ag/Cu doped OMS-2 catalysts show potential application in the removal of VOCs. The development of new methods for the synthesis of highly efficient Ag/Cu doped OMS-2 catalysts and further understanding of their catalytic mechanism are desired.

In this work, Ag-OMS-2 and Cu-OMS-2 were prepared by a novel one-step reduction method. KMnO_4 , Tollens' or Fehling' reagent

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were reduced by propionaldehyde at the same time to produce OMS-2, Ag, or Cu₂O. The influences of Cu and Ag on the structure and redox properties of OMS-2 were studied by different characterization techniques, and the catalytic activities of the materials for *o*-xylene oxidation were evaluated. In addition, the role of oxygen species in the catalysts and the possible mechanism for the oxidation of *o*-xylene were discussed.

2. Experimental

2.1. Catalyst preparation

All the chemicals were of analytical grade and used as received without further purification, and deionized water was used throughout. Preparation of Tollens' reagent: 0.4 mmol of AgNO₃ was dissolved in 3.5 mL of deionized water, and then ammonia (25 wt.%) was slowly added under stirring until the solution became clear. Preparation of Fehling' reagent A: 0.2 mol L⁻¹ potassium sodium tartrate (C₄H₄O₆KNa) solution was mixed with an equal volume of 0.2 mol L⁻¹ KOH solution. Fehling' reagent B was 0.05 mol L⁻¹ Cu(NO₃)₂ solution. Ag-OMS-2 and Cu-OMS-2 were prepared by a one-step reduction method. For Ag-OMS-2: 1.8 mL of propionaldehyde was slowly added to 50 mL of 0.02 mol L⁻¹ KMnO₄ solution. Subsequently, 120 mL of Tollens' reagent was successively dropped into the above system. The mixture was vigorously stirred in a water bath at 35 °C for 24 h. The product was washed several times with deionized water and absolute alcohol to remove any possible residual reactants, dried at 110 °C for 12 h, and then calcined in air at 400 °C for 6 h. For Cu-OMS-2: 0.5 mL of propionaldehyde was slowly added to 30 mL of Fehling's reagent (Fehling's reagent A:B = 1:2) to form a suspension. Subsequently, 50 mL of 0.02 mol L⁻¹ KMnO₄ solution and 1.5 mL of propionaldehyde were successively dropped into the above suspension in 10 min. The following steps were same as those in Ag-OMS-2. We examined the catalytic performance of Ag-OMS-2 and Cu-OMS-2 with different compositions, and found the optimized molar ratio Ag:Mn and Cu:Mn was 0.02 and 0.025, respectively.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried out in a Bruker D8-Advance using Cu K α radiation at 40 kV and 40 mA. The morphology was observed on a Hitachi S-4800 scanning electron microscope (SEM). The chemical composition was analyzed with an energy dispersive spectrometer (EDS, EDAX PV9900). Nitrogen adsorption-desorption isotherms were obtained at -196 °C using a Quantachrome NOVA 4000e instrument. Brunauer-Emmett-Teller (BET) method was used to calculate the surface area. The pore diameter distributions were calculated from desorption branches using the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Shimadzu ESCA-3400 spectrometer (Mg K α radiation). The average oxidation state (AOS) of manganese was determined by a potentiometric titration method. The thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA7 thermogravimetric analyzer at a heating rate of 5 °C min⁻¹.

Temperature-programmed reduction by hydrogen (H₂-TPR) was carried out on a PCA-1200 multifunction adsorption apparatus equipped with a TCD detector. 0.04 g of the sample was pretreated at 300 °C under Ar flow (40 mL min⁻¹) for 1 h to remove the adsorbed carbonates and hydrates, and cooled to room temperature. The sample was then contacted with a H₂:Ar mixture (10 vol.% H₂) at a flow rate of 30 mL min⁻¹ and heated at a rate of 10 °C min⁻¹ from room temperature to 600 °C.

Temperature-programmed desorption of O₂ (O₂-TPD) experiments were conducted on the same apparatus. 0.04 g of the catalyst was pretreated at 300 °C under Ar flow (40 mL min⁻¹) for 1 h to eliminate contaminants. After that, the catalyst was cooled down to 50 °C, and was oxidized in pure O₂ flow (40 mL min⁻¹) for 30 min. Then, the catalyst was cooled down to 30 °C under oxidative atmosphere and was flushed with Ar for 30 min. Desorption experiment was carried out under Ar (40 mL min⁻¹) by increasing the temperature up to 900 °C. The TPD spectra were recorded at a ramp rate of 10 °C min⁻¹.

Temperature-programmed desorption of CO₂ (CO₂-TPD) was also conducted on the same apparatus. 0.04 g of the catalyst was pretreated at 300 °C under Ar flow (40 mL min⁻¹) for 1 h, and was then cooled down to 30 °C. CO₂ was subsequently introduced into the flow system for 30 min. The TPD spectra were recorded at a ramp rate of 10 °C min⁻¹ from 30 °C to 500 °C under a He flow.

Thermal programmed reduction and thermal-programed re-oxidation tests (TPR-TPO) were carried out using the same apparatus. Before the TPR analysis, the samples were pretreated at 300 °C in Ar at a flow rate of 40 mL min⁻¹ for 1 h. TPR was performed by heating the pretreated samples at a rate of 10 °C min⁻¹ to 600 °C in 10 vol.% H₂/Ar at a flow rate of 30 mL min⁻¹. After the TPR analysis, the sample was treated in Ar at 25 °C for 0.5 h. Then TPO analysis was performed by heating the sample at a rate of 10 °C min⁻¹ to 300 °C (avoiding the decomposition of O₂ in the sample) in 5 vol.% O₂/He at a flow rate of 30 mL min⁻¹.

2.3. Catalytic activity evaluation

Catalytic tests were performed in a 4 mm i.d. quartz tubular reactor. 0.5 g of catalyst supported by quartz wool was placed in the center of the reactor. Simulated air (20 vol.% O₂, 80 vol.% N₂) containing 500 ppm of *o*-xylene was continuously passed through the catalyst bed at a flow rate of 50 mL min⁻¹ (W/F = 0.60 g s mL⁻¹), corresponding to a GHSV of 6000 h⁻¹. Here, W/F is defined as a ratio of catalyst weight to gas flow rate. CO₂ was the only detectable C-containing product, which initially passed through the TDX-01 stainless steel packed column, and then converted to methane in a reformer furnace. The reactant and product were analyzed with an on-line gas chromatograph equipped with two flame ionization detectors (FID) in series. The yield of CO₂ (Y_{CO2}) was calculated according to the following formula:

$$Y_{CO_2} = 100 \times CO_{2out} / ^8O - xylene_{in}$$

In situ diffuse reflectance Fourier transformation infrared (in-situ DRIFTS) measurements were conducted on a Tensor-II FTIR equipped with a smart collector and a MCT/A detector cooled by liquid nitrogen. The sample was mixed with a KBr/catalyst weight ratio of 9:1, and then the mixture was finely ground and placed in a ceramic crucible. Prior to the experiment, pure KBr was pre-heated in a flow of nitrogen at 300 °C for 1 h, then cooled to the desired temperature and was recorded as the background value. The spectra were recorded with a resolution of 4 cm⁻¹ and with an accumulation of 100 scans.

3. Results and discussion

3.1. Structural and textural properties of the catalysts

The XRD patterns of the prepared catalysts are shown in Fig. 1. All the diffraction peaks can be indexed to the typical manganese oxide octahedral molecular sieve (OMS-2) crystal phase (JCDPS 44-0141, tetragonal, I4/m, a = b = 0.978 nm, c = 0.286 nm) [32]. However, the peak intensities of OMS-2 decreased obviously after doping Cu or Ag, suggesting that Ag and Cu might be incorpo-

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