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Remarkable promotion effect of trace sulfation on OMS-2 nanorod catalysts for the catalytic combustion of ethanol

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ABSTRACT

OMS-2 nanorod catalysts were synthesized by a hydrothermal redox reaction method using MnSO_4 (OMS-2- SO_4) and $\text{Mn}(\text{CH}_3\text{COO})_2$ (OMS-2-AC) as precursors. SO_4^{2-} -doped OMS-2-AC catalysts with different SO_4^{2-} concentrations were prepared next by adding $(\text{NH}_4)_2\text{SO}_4$ solution into OMS-2-AC samples to investigate the effect of the anion SO_4^{2-} on the OMS-2-AC catalyst. All catalysts were then tested for the catalytic oxidation of ethanol. The OMS-2- SO_4 catalyst synthesized demonstrated much better activity than OMS-2-AC. The SO_4^{2-} doping greatly influenced the activity of the OMS-2-AC catalyst, with a dramatic promotion of activity for suitable concentration of SO_4^{2-} ($\text{SO}_4/\text{catalyst} = 0.5\% \text{ W/W}$). The samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), NH_3 -TPD and H_2 -TPR techniques. The results showed that the presence of a suitable amount of SO_4^{2-} species in the OMS-2-AC catalyst could decrease the Mn–O bond strength and also enhance the lattice oxygen and acid site concentrations, which then effectively promoted the catalytic activity of OMS-2-AC toward ethanol oxidation. Thus it was confirmed that the better catalytic performance of OMS-2- SO_4 compared to OMS-2-AC is due to the presence of some residual SO_4^{2-} species in OMS-2- SO_4 samples.

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Introduction

Volatile organic compounds (VOCs) are major organic pollutants in the atmosphere and are very harmful to human health (Jacobson, 2007). Industrial pollution and vehicle emissions are the main sources of VOCs. Ethanol is a widely used solvent and an important fuel supplement for vehicles, and has been recognized as one of the major contributors to VOC pollution (Poulopoulos et al., 2001). Therefore, it is of great importance to develop an effective method for ethanol elimination. Catalytic oxidation is considered to be the most effective technology for this purpose, because VOCs can be oxidized to CO_2 over certain catalysts at much lower temperatures than

in thermal oxidation. There are two main types of conventional catalysts used for ethanol oxidation reactions: noble metals (Avgouropoulos et al., 2006; Mitsui et al., 2008; Tang et al., 2005) and metal oxides (Idriss and Seebauer, 2000; Li et al., 2011; Ye et al., 2006; Trawczyński et al., 2005; Luo et al., 2000). Taking account of economic factors and catalytic properties, recent studies on catalytic oxidation of ethanol have been more focused on metal oxide-based catalysts.

Manganese oxides, especially OMS (octahedral molecular sieve) oxides, have many intrinsic advantages as oxidation catalysts, since OMS oxides have a variety of 3D structures (such as OL-1, OMS-1, OMS-2, etc.), and Mn atoms are present in various oxidation states (Mn^{4+} , Mn^{3+} , Mn^{2+}) in these

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structures (Suib, 2008; Wang et al., 2012). The OMS-2 structure comprises a peculiar sharing of 2×2 $[\text{MnO}_6]$ octahedral chains that form one-dimensional tunnel structure with a pore size of $0.46 \text{ nm} \times 0.46 \text{ nm}$. OMS-2 catalysts have been found to be particularly effective in ethyl acetate (Gandhe et al., 2007), benzyl alcohol (Makwana et al., 2002) and benzene (Luo et al., 2000) oxidation compared with other OMS materials. A great deal of research has been carried out to improve the catalytic activity of OMS-2 by various means, such as using different preparation methods (Malingier et al., 2006), incorporation of metal cations into the OMS-2 tunnel (Chen et al., 2002) and using different precursors (Wang and Li, 2010). Alkali metal cations and NH_4^+ cations have been used as the templates to synthesize 2×2 tunnel structures (A-OMS-2; A = Li, Na, K Rb, or NH_4^+). It was found that the nature of the cations affects the crystallinity, microstructure, and properties of these materials such as the surface area, thermal stability, and chemical composition (Liu et al., 2003). Hou et al. (2014) recently reported that increasing the K^+ concentration could greatly enhance the lattice oxygen activity of OMS-2 nanorod catalysts, thus significantly increasing the catalytic activity for benzene oxidation. The precursor of OMS-2 was also found to have a big influence on the activity. Wang and Li (2010) observed that OMS-2(S), prepared using MnSO_4 as precursor, exhibited better catalytic performance in ethanol oxidation than OMS-2(AC), with $\text{Mn}(\text{CH}_3\text{COO})_2$ as precursor, and they attributed this to the weaker Mn–O bond in OMS-2(S), resulting in more lattice defects and labile lattice oxygen. However, they did not discuss the factor in OMS-2(S) that induces this weaker Mn–O bond.

It is known that SO_4^{2-} treatment of catalysts can change the catalytic behavior significantly in some cases. It has been reported that the addition of SO_4^{2-} enhanced the activity of MoO_x and VO_x/TiO_2 for the reduction of NO with NH_3 or H_2 . Wang et al. (2011) recently also found that the sulfation of Zr–Co hydroxides induced higher activity in Pd/ZC catalysts for CH_4 -SCR of NOx. The positive effect of SO_4^{2-} on the activity was mainly ascribed to the change in acidity on the catalyst surface. It is also well known that the acidic properties of mixed oxide catalysts play an important role in the catalytic oxidation of hydrocarbons, and strong acidity could generally facilitate the breaking of carbon-carbon bonds and promote CO_2 production (Rajesh and Ozkan, 1993). Therefore, we proposed that the anion SO_4^{2-} may also have a great influence on OMS-2 activity, and that the better performance of OMS-2(S) for ethanol oxidation compared to OMS-2(AC) is possibly related to the presence of SO_4^{2-} species.

Herein, OMS-2 catalysts were first synthesized by a hydrothermal method using MnSO_4 and $\text{Mn}(\text{CH}_3\text{COO})_2$ as the precursors. The OMS- SO_4 catalyst (MnSO_4 precursor) exhibited better catalytic performance than the OMS-2-AC catalyst ($\text{Mn}(\text{CH}_3\text{COO})_2$ precursor). We next prepared SO_4^{2-} -doped OMS-2-AC catalysts with different SO_4^{2-} concentrations to investigate the effect of the anion SO_4^{2-} on the OMS-2-AC catalyst for ethanol oxidation. It was demonstrated that a suitable SO_4^{2-} concentration could dramatically promote the activity of the OMS-2-AC catalyst. In addition, the samples were characterized by several methods, and the mechanism of the promoting effect of sulfation on the OMS-2 catalyst was also elucidated. Based on the obtained results, we confirmed

that the better catalytic performance of OMS-2- SO_4 compared to OMS-2-AC is due to the presence of some residual SO_4^{2-} species in the OMS-2- SO_4 sample.

1. Experimental

1.1. Catalyst preparation

OMS-2 catalysts were prepared by a hydrothermal method that mainly depends on self-redox between Mn^{7+} (KMnO_4) and Mn^{2+} ($2 \text{ MnO}_4^- (\text{aq}) + 3 \text{ Mn}^{2+} (\text{aq}) \rightarrow 5 \text{ MnO}_x (\text{s})$). $\text{Mn}(\text{CH}_3\text{COO})_2$ and MnSO_4 were used as precursors to provide the Mn^{2+} source. The KMnO_4 solution was added into a Mn^{2+} solution ($\text{Mn}(\text{CH}_3\text{COO})_2$ or MnSO_4) at a $\text{MnO}_4^-/\text{Mn}^{2+}$ molar ratio of 0.78, then 2 mL nitric acid was added to adjust the pH value. The mixed solution was stirred for 1 hr and then placed in a Teflon liner and sealed in a stainless-steel vessel, and a hydrothermal treatment was performed at 100°C for 24 hr. The product was separated by filtration, washed several times with deionized water and dried at 100°C overnight. All the samples were calcined at 400°C in air for 2 hr. The as-prepared catalysts are designated as OMS-2-AC and OMS-2- SO_4 , respectively.

In order to assess the influence of sulfation species on activity, SO_4^{2-} -doped OMS-2 was next obtained by adding a $(\text{NH}_4)_2\text{SO}_4$ solution into OMS-2-AC samples. 3.0 g OMS-2-AC catalyst was mixed with 30 mL distilled water in a beaker, then 12.4, 20.6, 41.2, or 82.4 mg of $(\text{NH}_4)_2\text{SO}_4$ was added into the solution under vigorous magnetic stirring for 1 hr, and dried at 100°C overnight. All the samples were calcined at 400°C in air for 2 hr. The results of inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima-2000DV, PerkinElmer Co, Waltham, Massachusetts, USA) measurements (determined by elemental analysis of S) showed that the SO_4^{2-} loading was 0.3, 0.5, 1.0, and 2.0 wt.%, respectively, and the catalysts are hereinafter designated as 0.3%, 0.5%, 1.0%, and 2.0% SO_4 -OMS-AC.

1.2. Material characterizations

The samples were characterized structurally by X-ray diffraction (XRD, X'Pert Pro, PANalytical Co, Almelo, Holland), using a Bruker D8 Advance Diffractometer with a monochromatic Cu K α source operated at 40 kV and 40 mA. The diffraction patterns were taken at room temperature in the range of $10 < 2\theta < 90^\circ$. For phase identification purposes, the JCPDS database of reference compounds was used. Surface area and pore volume were measured using a Quadrasorb system (Autosorb-IQ-1MP, Quantachrome Co, Boynton Beach, Florida, USA) at liquid nitrogen temperature (77 K). Transmission electron microscopy (TEM, JEM-2011LaB6, JEOL Ltd., Tokyo, Japan) images were obtained with a JEOL JEM-2011LaB6 at an accelerating voltage of 200 kV. The samples were ultrasonically suspended in ethanol and deposited on a copper grid covered with a thin layer of holey carbon. The field-emission scanning electron microscopy (FE-SEM, S-3000N, Hitachi Ltd., Tokyo, Japan) images were taken using a SU-8020 scanning electron microscope. The samples for FE-SEM measurements were prepared by depositing the powder on graphite tape.

ICP-OES (inductively coupled plasma optical emission spectroscopy, Prodigy XP, Leeman LABS, Hudson, New Hampshire,

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