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Promoting effect of unreducible metal doping on OMS-2 catalysts for gas-phase selective oxidation of ethanol

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ABSTRACT

Various unreducible-metal cations can be successfully doped into the tunnel of manganese octahedral molecular sieve (OMS-2) by using "one-pot" refluxing method to tune the acid-base and redox properties. The resulting M-OMS-2 materials were used as efficient catalysts for gas-phase aerobic oxidation of ethanol to acetaldehyde. The activity of the M-OMS-2 catalysts was demonstrated to be proportional to the surface basicity. Na-OMS-2 exhibited the highest catalytic activity at 200 °C, which is higher than and comparable to the previously reported preferred Fe-OMS-2 and Ag-OMS-2 catalysts, respectively. The beneficial effect of Na^+-doping is related to the enhancement of surface oxygen vacancies, basicity and reducibility, which also result in better catalytic stability. Kinetic studies indicate that reaction rates depend weakly on the concentration of O_2 and ethanol. Ethanol O—H and α-C—H bond cleavages are both kinetically-relevant, with the latter being the more difficult step. O_2 is the most efficient oxidant and is thought to be activated at oxygen vacancies of Mn^{2+}/Mn^{3+} species to form superoxide-type O_2^- and lattice-oxygen-type O^{2-} species, which act as dual active sites for the rate-controlling ethanol activation steps.

1. Introduction

Selective oxidation of ethanol to acetaldehyde (AC) has drawn much attention in both academic and industrial areas, as bioethanol is becoming more abundant and its use as a renewable feedstock for bulk chemicals production is increasingly competitive [1]. The commercial production of AC tends to use fossil ethylene and homogeneous $PdCl_2$-$CuCl_2$ catalyst in HCl solution (the Wacker process) [2], suffering from high cost and serious environmental problems conflicting the goals of green chemistry. Thus, it would be highly desirable to develop more sustainable AC production process that uses bioethanol and heterogeneous catalysts under solvent-free conditions [3].

From a practical viewpoint, gas-phase ethanol oxidation is more attractive than liquid-phase ethanol oxidation, because higher AC selectivity and yield can be achieved by the gas-phase oxidation and acetic acid is the main product in the liquid-phase oxidation [3,4]. Although much of the earlier effort focused on supported noble metal catalysts [5–9], transition-metal (such as V, Mn, Co, Cu and Mo) oxides are promising catalysts given their low cost of production and easy regeneration [3]. Among various transition-metal catalysts, Cu-based catalysts showed superior performance in non-oxidative dehydrogenation of ethanol to AC [10–12], but the higher reaction temperature (> 250 °C) required by the endothermic reaction may cause deactivation by metal sintering and coking. Although V-based catalysts showed high activity in aerobic oxidation of ethanol below 250 °C [13–15], the toxicity of these catalysts limited their practical application. The other transition-metal oxide catalysts showed moderate to high activity in aerobic oxidation of ethanol, but the maximum AC yield was usually below 50% with space–time-yield (STY) less than 2 $g_{aldehyde}\ g_{cat}^{-1}\ h^{-1}$ [3]. Therefore, the development of more efficient transition-metal oxide catalysts that can selectively convert ethanol and achieve high AC yield at lower temperature remains a challenge.

Manganese-oxide-based catalysts have been demonstrated to be effective catalysts for low-temperature aerobic oxidation of ethanol [16–25]. However, most of these catalysts were used for catalytic combustion of ethanol with a large excess of oxygen [17–25]. Cryptomelane (KMn_8O_{16})-like octahedral molecular sieve materials (OMS-2) have shown promise for the selective oxidation

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of ethanol to AC [16], mainly due to their open tunnel structure, mixed valence (Mn^{4+}, Mn^{3+}) framework, mild surface acidity-basicity, high mobility of lattice oxygen, and ion-exchange ability [26,27]. Suib and his group screened various transition-metal-doped TM-OMS-2 (TM = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) catalysts for ethanol oxidation at 300 °C, and found that Fe-OMS-2 showed the highest conversion (72%) and AC selectivity (79%) [16]. Shen and his group reported that Ag-OMS-2 nanofibers showed an ethanol conversion of 75% with 95% AC selectivity at 230 °C for 200 h time-on-stream [6]. Despite these interesting results, it is highly desired to further enhance the activity and selectivity of OMS-2 catalysts and reduce the cost by using non-noble metal instead of silver.

Since selective alcohol dehydrogenation is crucial for the aerobic oxidation of alcohol to aldehyde, it would be helpful to use solid base catalyst to improve the dehydrogenation ability [28,29]. Obviously, if the OMS-2 catalysts also possess substantial basicity, there would be great opportunity to enhance the activity for ethanol oxidation. To tune the basicity of OMS-2, a feasible strategy involves the ion-exchange of K^+ in the tunnel of OMS-2 structure with alkali metal and alkaline-earth metal cations [30,31]. However, to the best of our knowledge, there is no reports on the selective catalytic oxidation of ethanol over basic OMS-2 catalysts. Intrigued by our previous findings on the promotional effect of metal-doping on the basicity and catalytic activity for alcohol activation [32–34], and by the tunable composition of OMS-2, we prepared a series of unreducible-metal-doped M-OMS-2 (M = Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Al^{3+}, La^{3+}) and the reference K-OMS-2 and Fe-OMS-2 catalysts by "one-pot" refluxing method and evaluated them in the gas-phase ethanol oxidation. The aim of present work is to clarify the influence of the metal-doping on the acid-base and redox properties of M-OMS-2 catalysts and on the catalytic performance in aerobic ethanol oxidation. The results firmly demonstrate that the unreducible-metal-doping can be more efficient than the transition-metal doping, with Na-OMS-2 showing the highest catalytic activity and good catalytic stability. The promotional effect of Na^+-doping is related to the enhancement of surface oxygen vacancies, basicity and reducibility. Further kinetic studies provide insight into the role of O_2 and the activation of O_2 and ethanol over Na-OMS-2 catalyst.

2. Experimental

2.1. Materials

Various metal salts with AR grade ($KMnO_4$, $MnSO_4 \cdot H_2O$, LiCl, $NaNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$), nitric acid (HNO_3, 65%), hydrochloric acid (HCl, 37%), ethanol (>99.8%) and acetaldehyde (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. $La(NO_3)_3 \cdot 6H_2O$ (99.9%) was purchased from Adamas Reagent Co., Ltd. CH_3CH_2OD (99 atom% D) and CD_3CD_2OD (99.5 atom% D) were purchased from Sigma-Aldrich. All chemicals were used as received.

2.2. Catalyst preparation

K-OMS-2 sample was prepared by using refluxing method for the oxidation of Mn^{2+} by $KMnO_4$ [35]. Typically, an aqueous solution (100 mL) of $KMnO_4$ (5.89 g) was added to an aqueous solution (30 mL) of $MnSO_4 \cdot H_2O$ (8.8 g) and concentrated HNO_3 (3 mL). The resulting mixture was refluxed at 100 °C for 24 h. The sample was then filtered, washed with deionized water, dried at 110 °C overnight, and calcined at 400 °C for 4 h. All metal-doped M-OMS-2 (M = Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Al^{3+}, La^{3+}, Fe^{3+}) samples were prepared intrinsically using the same procedure for the non-doped K-OMS-2. The dopant source with M/(Mn + M) molar ratio of 3 mol% was initially added to the acidic $MnSO_4 \cdot H_2O$ solution, followed by the above procedure.

2.3. Catalyst characterization

X-ray diffraction (XRD) was performed on an Empyrean apparatus using Cu K_α radiation (40 kV and 30 mA). Nitrogen physisorption was done on a Tristar 3000 automated gas adsorption system. Scanning electron microscopy (SEM) images were taken using a FEI Nova NanoSEM 450 microscope. Transmission electron microscopy (TEM) images were obtained by using a FEI Tecnai G2 F30 electron microscope. The metal content was determined by ICP-OES on a Thermal Scientific iCAP7000 spectrometer after dissolving the sample in concentrated hydrochloric acid. Raman spectra were recorded on a Horiba JobinYvon LabRAM HR800 Raman spectrometer using an excitation of 532 nm laser light. X-ray photoelectron spectroscopic (XPS) measurements were conducted on an AXIS-ULTRA DLD-600W spectrometer with Al Kα irradiation and the binding energies were calibrated by using the C 1s peak of contaminant carbon at 284.5 eV as an internal standard.

Temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) experiments were performed on Micrometrics AutoChem 2920II instrument. For TPR, typically, 20 mg of the sample was loaded in a U-shape quartz tube and pretreated in argon at 400 °C for 1 h. After cooling to room temperature in flowing Ar, the sample was reduced in 10% H_2/Ar at a flow rate of 10 mL/min, while it was heated from room temperature up to 600 °C at a ramp rate of 10 °C/min. The outlet gas was detected by the thermal conductivity detector (TCD). The H_2 consumption was calculated from the peak areas. The acidic and basic properties of M-OMS-2 samples were studied with the TPD of NH_3 and CO_2, respectively. The sample (50 mg) was loaded in a U-shape quartz tube and pretreated in argon at 400 °C for 2 h to exclude the interference of O_2 release during TPD. Then the sample was cooled to 100 °C and saturated with NH_3 or CO_2 gas in a flow (30 mL/min) of 0.3% NH_3/Ar or 10% CO_2/Ar, respectively, for 1 h. After that, the sample was flushed with argon at 100 °C for 1 h to remove the physical adsorbed NH_3 or CO_2 and then heated in argon from 100 to 400 °C at ramp rate of 10 °C/min. The evolution of NH_3 or CO_2 was monitored by the TCD. The total amount of desorbed NH_3 or CO_2 was calculated from peak areas using a calibration coefficient.

2.4. Catalytic tests

Ethanol oxidation was carried out in a fixed-bed plug flow reactor system at atmospheric pressure. Typically, M-OMS-2 (0.06 g, 150–180 μm) catalyst diluted with α-Al_2O_3 (0.6 g, 180–250 μm) was loaded into a quartz reactor with an internal diameter of 8 mm and a thermal couple inside the catalyst bed. Prior to reaction, the catalyst was treated with O_2 at 400 °C for 2 h. Ethanol was charged through a micro-pump and vaporized with a mixture gas of O_2 and N_2, resulting in 2.5 mL/min of ethanol and a molar ratio of ethanol/O_2/N_2 = 1/1/38 in the gas phase. The preheated gas mixture was then passed through the catalyst bed with a gas hourly space velocity (GHSV) of about 100,000 mL $g_{cat}^{-1}\,h^{-1}$. The reaction products were analyzed online by using GC (Fuli GC 9070II) equipped with a 30 m RB-InnoWax capillary column and a TDX-01 packed column. In all cases, the carbon balances closed at 100 ± 2%. To exclude the presence of diffusional limitations, experiments performed were replicated with other particles sizes and working with the double of the catalyst weight. The results obtained suggested the absence of both external and internal mass transfer effects. Blank experiments were also performed to verify the absence of catalytic activity in the conditions used in this