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Selective oxidation of *p*-chlorotoluene to *p*-chlorobenzaldehyde over metal-modified OMS-2 molecular sieves

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ABSTRACT

A series of manganese oxide octahedral molecular sieve (OMS-2) doped with Co, V, and Ce (Me) with molar ratio Me/Mn = 0.04 and 0.12 were prepared via a one-step reflux method, and were characterized by XRD, SEM, IR, BET, ICP, XPS, and TG techniques. The OMS-2 materials doped with Me having Me/Mn = x are denoted as Me-M(x). It was found that Ce mainly enters the tunnel structure of OMS-2 instead of K, Co mainly substitutes for Mn in the framework, and V is likely to substitution into both the Mn and K in the cryptomelane tunnel structure. The length of OMS-2 rods decreases with the decline of K^+ mole fraction in the OMS-2 tunnels. Doping V and Ce markedly decreases the crystallization of OMS-2. Ce-M(0.12) shows a specific surface area (142 $m^2\,g^{-1}$) roughly double that of OMS-2 (69 $m^2\,g^{-1}$). All the Me-M(x) materials were tested as catalysts for the oxidation of *p*-chlorotoluene to *p*-chlorobenzaldehyde with molecular oxygen, and it is Ce-M(0.12) that shows the highest catalytic activity. The excellent performance is attributed to the large specific surface area and good mobility of oxygen species of the Ce-M(0.12) material.

1. Introduction

p-Chlorobenzaldehyde (PCB) is an important intermediate for the production of dyes, pharmaceutical drugs, optical brighteners and agricultural chemicals [1]. For industrial PCB production, soluble acetates of transition metals are used as catalysts but some of the processes are expensive and polluting [2]. With the decline of traditional industries and for the protection of environment, efforts were put in to fabricate solid catalysts capable of producing aromatic aldehydes through selective oxidation of aromatic hydrocarbons using molecular oxygen or hydrogen peroxide as oxidant. However, both conversion and selectivity are not satisfactory [3,4].

Cryptomelane-type octahedral manganese oxide molecular sieves (OMS-2) with mixed-valence manganese (Mn^{3+} and Mn^{4+}) and a well-defined 2 × 2 tunnel structure is catalytically efficient for many oxidation processes [5,6]. The stability and charge balance of OMS-2 is maintained by having potassium ions in the OMS-2 tunnels. For further improvement of catalytic activity, OMS-2 is commonly doped with foreign metal ions (e.g. Cu^{2+}, Co^{2+}, Al^{3+}, Fe^{3+}, Ce^{4+}, Zr^{4+} or V^{5+}) using methods such as ball milling, impregnation, reflux, and hydrothermal treatment [7–11]. Depending on the doping strategy, the metal ions can either end up on the surface, in the framework or in the tunnels of OMS-2. Also, with the metal ions incorporated in the framework or tunnel structure of OMS-2, there is the creation of defects and hence increases number of active sites [12,13]. It is known that the doping of OMS-2 with metal ions can result in the generation of materials that are different in nanostructures, but in-depth investigation on the factors affecting the morphology and activity-structure relationship in terms of catalytic performance are lacking [12–14]. Previously, we synthesized a series of OMS-2 materials for the generation of PCB by means of *p*-chlorotoluene (PCT) oxidation [15–17]. It is reckoned that the catalytic performance of OMS-2 is dependent on its preparation method, composition and morphology. To elucidate the activity-structure relationship, we doped OMS-2 with a variety of metal ions, and adopted PCT oxidation for PCB generation as model reaction.

After considering the size, valence, and reducibility of a large number of metal ions, we adopted Co, V and Ce ions (Me) for the doping of OMS-2, with the Me/Mn molar ratio = 0.04 or 0.12. The materials doped with Me having Me/Mn = x are denoted hereinafter as Me-M(x). The results show that the composition, crystallinity, morphology and stability of Me-M(x) are greatly influenced by the valence, amount, and location of the Me ions. It was found that

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Ce-M(0.12) is highly effective for the oxidation of PCT to PCB; while the doping of OMS-2 with Co ions worsens the catalytic performance of OMS-2. Based on the results of characterization and catalytic performance, new insights into the effect of Me doping on the catalytic activity of OMS-2 are acquired.

2. Experimental

2.1. Catalyst preparation

Me-M(x) was synthesized using a reflux method [15]. Typically, a $KMnO_4$ solution (6.5 g in 114 mL of distilled water) was added to a mixture of $MnSO_4 \cdot H_2O$ (9.9 g in 34 mL distilled water) and concentrated HNO_3 (3.4 mL). Then, a designated amount of $Co(NO_3)_2$, NH_4VO_3 or $Ce(NO_3)_3$ was added. The as-resulted material was filtered out, washed, dried and then calcined at 400 °C for 4 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) scanning was conducted on a Brüker D8 Advance diffractometer using Cu Kα radiation. The data were recorded at a scan rate of 0.02° (2θ) s^{-1} in the $10–80^\circ$ range. In the form of KBr thin pellet, the catalyst was studied by Fourier transform infrared (FTIR) spectroscopy (IR Affinity-1 spectrometer). Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 emission scanning microscope with a Schottky Emitter at an accelerating voltage of 5 kV and a beam current of 1 mA. The Brunauer-Emmett-Teller (BET) specific surface areas were measured on a Tristar 3000 instrument whereas element analysis was carried out using ICP-AES (IRIS1000). X-Ray photoelectron spectroscopy (XPS) analysis was conducted over a K-Alpha 1063 (Thermo Fisher Scientific, USA) spectrometer using Al Kα radiation (1486.6 eV). The C 1 s signal of contaminant carbon (BE = 284.6 eV) was taken as a reference for BE calibration. Thermal stability of catalysts was studied by thermogravimetric analysis (TGA, PerkinElmer Diamond TG/DTA instrument) with ca. 10 mg of sample being heated from 30 to 800 °C (ramp rate = 10 °C/min) under a N_2 atmosphere.

2.3. Catalyst evaluation

All experiments were carried out in a three-necked round-bottom flask equipped with a reflux condenser. The detailed procedures for catalyst evaluation were reported elsewhere [18].

3. Results and discussion

3.1. Characterization results

The XRD patterns of OMS-2 and Me-M(x) are shown in Fig. 1. The main diffraction peaks of the three are at $2\theta = 12.7^\circ$, 17.9°, 28.7°, 37.4°, 42°, 50° and 60.2° that are typical of cryptomelane (JCPDS 29-1020). As displayed in Fig. 1, no additional peaks assignable to segregated crystalline phases of Co, V or Ce oxides are observed, suggesting that the Me-M(x) materials are phase pure. There is no obvious change of the OMS-2 pattern with the doping of Co. However, the doping of V or Ce results in marked decrease of peak intensity and broadening of peak width, implying decrease in both grain size and crystallinity of OMS-2 [19]. In addition, the XRD pattern of used (four cycles) Ce-M (0.12) shows no significant difference in comparison with that of the fresh one. It is deduced that there is no change of catalyst structure during the reaction.

Compared with the X-ray diffraction technique, the infrared spectrum method is more sensitive to impurity phase in the structure, and can be used to determine whether there is the presence of impurity atoms in the structure of molecular sieve. The presence of amorphous metal oxide in Me-M (x) can be detected by infrared spectroscopy [20]. As depicted in Fig. 2, the spectrum of OMS-2 shows four bands around 714, 582, 523 and 467 cm^{-1} characteristic of MnO_6 octahedral framework due to Mn-O vibrations [9]. There is only insignificant change of peak intensity in the case of Co doping, but with the doping of V or Ce, the 582 cm^{-1} band slightly increases while the 467 and 714 cm^{-1} band obviously decrease in intensity. The variation in the FTIR spectra indicates that there is entrance of cerium or vanadium into the framework of OMS-2, resulting in the new structure vibration. In addition, the band at ca. 980 cm^{-1} in the V-M(x) case is attributable to vanadium oxide [20,21]. The dominant absorption peak at 1633 cm^{-1} is due to H_2O in the OMS-2 tunnels [22].

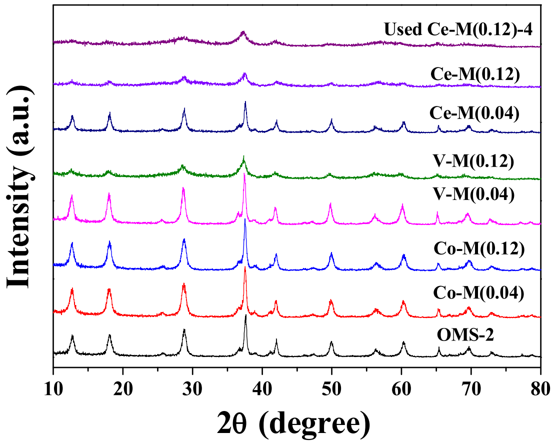

Fig. 1. X-ray diffraction patterns of OMS-2 and Me-M(x).

Fig. 3 shows the representative SEM images of OMS-2 and Me-M(x). The OMS-2 sample has a fibrous rod-like morphology, having a rod length of 1-1.5 μm (Fig. 3g). The surface morphology of OMS-2 remains unchanged after the addition of Co (Figs. 3a and b). However, upon the addition of vanadium or cerium, there is clear change of OMS-2 morphology. For example, the SEM images of V-M(0.04) shows the presence of short rod-like entities around 200 nm in length. With increase of vanadium amount, rods shorter in length are randomly accumulated in the form of bulk assembly. Such a phenomenon is even more obvious with Ce doping: the length of OMS-2 rod-like entities decreases to about 50 nm in the Ce-M(0.04) case, and clusters of the kind are detected (Fig. 3e). With further increase of Ce content, microspheres with relatively flat surface are

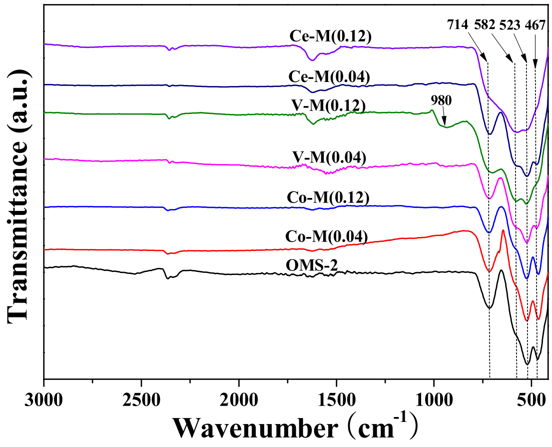

Fig. 2. FT-IR spectra of OMS-2 and Me-M(x).