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Enhanced catalytic performance by oxygen vacancy and active interface originated from facile reduction of OMS-2

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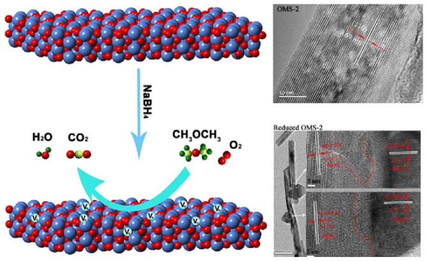
GRAPHICAL ABSTRACT

We report a facile $NaBH_4$ reduction method to enhance the catalytic activity of OMS-2. The moderate reduction treatment can create oxygen vacancies and active interface on the OMS-2 structure. The reduced OMS-2 exhibit substantially enhanced catalytic combustion performance for dimethyl ether.



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ABSTRACT

Manganese oxide octahedral molecular sieves (OMS-2) is a kind of excellent redox catalysts, a key challenge still remains to further increase their catalytic performance. Herein, we report a facile reduction method to enhance the catalytic activity of OMS-2 by producing more oxygen vacancy and creating an active interface between the main phase MnO_2 and the minor phase Mn_3O_4. Compared to the pristine OMS-2, the OMS-2 catalyst reduced in a relatively short time exhibits superior performance for dimethyl ether combustion with a starting-off temperature of 163 °C and a complete combustion temperature of 230 °C. Such enhanced activity can be ascribed to the higher reducibility, the more oxygen vacancy, and the active heterogeneous interface. These findings open up a new way to design highly efficient catalysts, especially the metal oxides-based catalysts, for redox reactions.

1. Introduction

With rich morphologies and crystal structures, manganese oxides have emerged as prospective material finding wide applications in such areas as catalysis [1], energy storage and conversion (supercapacitor and Li-air batteries) [2,3], biological application [4,5], metal and organics detection [6,7]. Manganese oxide octahedral molecular sieves (OMS-2), which belong to α type of MnO_2, has drawn worldwide interest because of their highly porous structure and excellent redox activity [1,8]. Therefore, the OMS-2 materials have been reported as outstanding catalyst for a number of reaction, including catalytic oxidation, combustion, hydrogenation, and amination, *etc* [8–19].

To enhance the performance of the OMS-2 catalyst, many strategies have been suggested. (1) Doping with transition metal or noble metal ions. This is the most common way to modify the redox activity of OMS-2, and further to increase its catalytic properties. Up to now, a number

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of metals ions were used such as Fe, Co, Ni, Cu, Ce, Zr, Ag, Pd, Au, Nb, V, Ti [9–13,19–26]; (2) Morphology-controlling. The shape of MnO_2 have potential influence on the catalytic activity. Through the selection of synthesis method and parameters, the morphology of OMS-2 can be controlled to be nanorod, nanowire, nanofiber, or 3D nanoflower [27]. With the morphology change, the crystal size could be tuned, and mesoporous OMS-2 were obtained resulting in an enhancement in reducibility and catalytic performance [28]; (3) Adjusting surface defects or oxygen vacancy. The defect nature and the concentration of oxygen species are one of the important influencing factors for the activity, especially for the catalytic redox reaction [29]. The reported literatures can be simply classified into two types. The first one is the manipulation of the synthetic parameters. For example, Li [30] et al. designed OMS-2 with different oxygen vacancies by changing the reaction temperature, and the catalyst demonstrated a giant oxygen vacancy effect in the catalytic combustion of benzene. We reported the sonochemical synthesis of OMS-2 under ultrasonic irradiation, and the prepared OMS-2 possessed more surface defects, higher oxygen mobility, and superior catalytic combustion of dimethyl ether (DME) [31]. The second approach can be named as the post-treatment of the OMS-2. For instance, by means of acid-treated process, the oxygen vacancy could be improved, and so did the catalytic activity [32]. Recently, it is reported that the electrochemical performance of MnO_2 could be improved by oxygen vacancy. The hydrogenation treatment of MnO_2 resulted in the oxygen-deficient MnO_2, which showed higher electrochemical performance than the pristine one [33]. The hydrogenation treatment is an effective strategy to enhance the activity (electrochemical, photocatalytic) of metal oxide (MO), and several works have been reported such as WO_3 [34,35], V_2O_5 [36], ZnO [37], TiO_2 [38–40], Co_3O_4 [41]. The starting point of the hydrogenation treatment of metal oxide is the facile reduction of MO by hydrogen. We could substitute the hydrogen to other reducing agent, for example ethylene glycol [42] and $NaBH_4$. The Co_3O_4 treated by $NaBH_4$ showed substantially increasing oxygen vacancies and electrocatalytic activity [43]. The adjusting of oxygen vacancy provides an effective means to promote the electrochemical and catalytic activity of MO. Therefore, this method should also be suitable for increasing the catalytic performance of OMS-2.

Inspired by the above studies, herein, we first synthesized OMS-2 catalyst, then use a facile solution reduction method to partially reduce OMS-2 catalyst by $NaBH_4$. We explored the influence of reduction time on the crystal structure, morphology, and the oxygen vacancy. To study the effect of the reduction treatment on OMS-2, we applied the OMS-2 catalysts in the catalytic combustion of dimethyl ether (DME), and discussed the structure-performance relationship. DME is regarded as a new kind of energy because of such merits of high cetane number, low-cost and emission of pollutant. DME can be used as alternative clean fuel, a replacement for liquefied petroleum gas, for diesel engines (bus, power plant) and household cooking [44,45]. Via catalytic combustion, the efficiency of DME combustion can be enhanced and the discharge of CO and hydrocarbons could be decreased [46]. Based on the results, we find that the reduction treatment produce two kinds of effects: the first one is to increase the defects and oxygen vacancy, and the second is to create a second phase, forming active interface of between OMS-2 and Mn_3O_4. Under the co-action of oxygen vacancy and active interface, the treated OMS-2 catalyst showed the excellent activity for DME combustion.

2. Experimental

All of the chemical reagents were purchased from Guangzhou Chemical Reagent Factory, and used as received without further purification.

2.1. Catalysts preparation

Preparation of OMS-2. The OMS-2 were prepared as reported previously [47]. A solution of 0.4 M of $KMnO_4$, 1.7 M of $MnSO_4$ and 6.0 M solution of HNO_3 were mixed and reacted under reflux at 98–100 °C for 24 h. The molar ratio between MnO_4^- and Mn^{2+} is fixed as 0.76. After the reaction, the sample was washed with deionized water thoroughly, and then dried at 60 °C overnight.

Reduction of OMS-2. The prepared OMS-2 (2.0 g) was added into 1 mol/L $NaBH_4$ solution (200 mL), then stirred for different time (for 0.25 h, 0.5 h, 1 h, 2 h; The sample was denoted as *n*h-OMS-2, where *n* stands for the reduction time). Then, the slurry was immediately filtered, washed by deionized water and ethanol repeatly, and dried at low temperature to get the final product.

2.2. Materials characterization

The crystal phase of the catalyst was determined by X-ray diffractometer (MSAL-XDII, 40 kV, 20 mA, Cu Kα radiation) at a scan rate of 3°/min. The Raman spectra were performed with a dispersive Horiva Jobin Yvon LabRam HR800 Microscope, using a 24 mW He-Ne green laser (633 nm). The morphology of the catalyst was observed by field emission scanning electron microscopy (FESEM, Hitachi SU8020) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G20). The Brunauer-Emmett-Telle (BET) surface areas and N_2 adsorption-desorption isotherms were tested on a Micromeritics ASAP 2020 Analyzer under liquid nitrogen (−196 °C). Temperature programmed reduction of hydrogen (H_2-TPR) was conducted on a chemisorption analyzer (Micromeritics AutoChem 2920). About 30 mg of sample was loaded in a U-shaped tube, and pretreated at 150 °C under Ar atmosphere for 1 h, then cooled to 50 °C. The catalyst was then heated to 600 °C (10 °C/min) in a flowing mixture of hydrogen and Ar (50 ml/min, 5 vol% H_2/Ar), and the reduction signal was detected by TCD detector. The chemical states were collected from X-ray photoelectron spectroscopy (XPS) analysis (VG MultiLab 2000) with an Mg Kα X-ray source. The spectra are calibrated using the carbon peak. The K and Mn bulk molar ratio were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PROFILE SPEC).

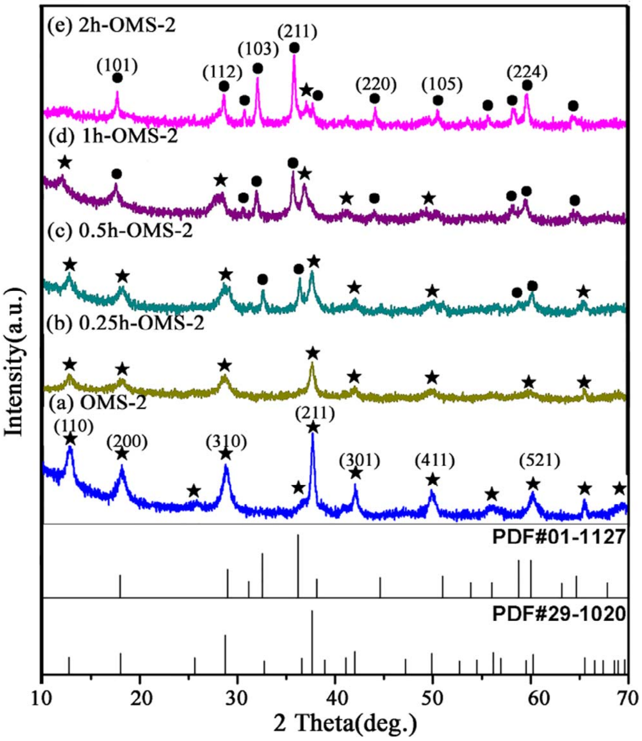

Fig. 1. XRD patterns of the OMS-2 catalysts.