Journal of Catalysis 316 (2014) 57–66

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on manganese oxide catalysts

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ARTICLE INFO

Article history:
Received 25 January 2014
Revised 1 May 2014
Accepted 3 May 2014
Available online 2 June 2014

Keywords:
Biomass
5-Hydroxymethylfurfural
2,5-Diformylfuran
Aerobic oxidation
Manganese oxide
Reaction mechanism

ABSTRACT

A cryptomelane-type manganese oxide octahedral molecular sieve with a (2 × 2, 4.6 Å × 4.6 Å) tunnel size (OMS-2) efficiently catalyzed aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) with a high yield of 97.2% at 383 K and 0.5 MPa O_2 in N,N-dimethylformamide. OMS-2 was superior to other MnO_2 catalysts with different morphologies, including OMS-1, OMS-6, and OMS-7 with various tunnel sizes, amorphous MnO_2 and birnessite-type MnO_2, apparently due to its (2 × 2) tunnel structure and consequently high reducibility and oxidizability. Kinetic and isotopic studies on OMS-2 showed near half-order dependence of the activities on HMF and O_2 concentrations and marked kinetic isotope effects for deuterated HMF at its methylene group. These results, together with the similar initial rates under aerobic and anaerobic conditions, suggest that HMF oxidation to DFF on OMS-2 proceeds via a redox mechanism involving kinetically-relevant steps of C–H bond cleavage in adsorbed alcoholate intermediate, derived from quasi-equilibrated dissociation of HMF, using lattice oxygen and reoxidation of Mn^{3+} to Mn^{4+} by dissociative chemisorption of O_2.

1. Introduction

5-Hydroxymethylfurfural (HMF) is an important platform molecule, which can be synthesized readily from cellulose-derived sugars or directly from cellulose [1–4] and applied to produce many value-added chemicals via different catalytic reactions [5]. One of the noteworthy examples is selective oxidation of HMF to 2,5-diformylfuran (DFF), a versatile chemical intermediate for the synthesis of pharmaceuticals [6,7], functional polymers [8–10], and other important products [5].

It is known that the presence of the more reactive α,β-unsaturated aldehyde group in HMF leads to the challenge in the aerobic oxidation of HMF to DFF with a high yield [11]. In this regard, various catalysts have been explored to date for the aerobic oxidation of HMF to DFF [11–18]. Quantitative DFF yields can be achieved by homogeneous catalysts [11,12], but they encounter difficulties, such as separation between catalysts and products. On the other hand, heterogeneous catalysts generally suffer low activity or low DFF selectivity [13–18] or require use of noble metals [19–22]. For example, an 85% DFF yield is obtained on VO_x/TiO_2 [13], but a high catalyst/substrate ratio (2:1 wt/wt) is required. Supported Ru-based catalysts [20–22], such as $Ru(OH)_x$/HT, Ru/C, and $RuCl_3/Al_2O_3$, can afford good DFF yields (92–97%), but the Ru catalysts are expensive. Therefore, it is highly desirable to develop more practical and efficient catalysts for the synthesis of DFF.

Recently, a cryptomelane-type manganese oxide octahedral molecular sieve ($KMn_8O_{16}\cdot nH_2O$; OMS-2), which possesses a 2 × 2 hollandite structure with one-dimensional pores [23] and also high efficacy in many oxidation reactions [24–26], has been reported to be a cheap and efficient catalyst for the HMF oxidation to DFF [27]. Similar catalytic performance was achieved by Yadav and Sharma on an OMS-2 supported Ag catalyst [28]. However, in these preliminary reports, the key fundamental issues including the relationship between the structure of OMS-2 and its performance and the reaction mechanism remain unclear, which are unequivocally important for further improving the catalyst efficiency in the DFF synthesis. Herein, we present a detailed study on the HMF oxidation to DFF on OMS-2 and other MnO_2 catalysts with different morphologies. Their structures and redox properties are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectra (XPS), H_2-temperature-programmed reduction (H_2-TPR), and O_2-temperature-programmed oxidation (O_2-TPO) and correlated with their HMF oxidation activities. Reaction kinetic

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http://dx.doi.org/10.1016/j.jcat.2014.05.003
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and isotopic studies are also carried out to elucidate the reaction mechanism for the HMF oxidation on OMS-2.

2. Experimental

2.1. Catalyst preparation

OMS-2 was prepared by a reflux route [23]. Briefly, 30 mL aqueous solution of $KMnO_4$ (2.2 g) was added dropwise to a solution of $MnSO_4 \cdot H_2O$ (3.0 g) in water (10 mL) and a concentrated HNO_3 solution (1.0 mL) under magnetic stirring. The resulting slurry was refluxed at 383 K for 24 h. Afterward, the obtained dark brown precipitates were filtered and washed with deionized water until the filtrate was neutral, which were then dried at 383 K overnight.

For comparison, other MnO_2 catalysts including amorphous MnO_2 (AMO), birnessite-type MnO_2 (Na-OL-1), OMS-7, γ-MnO_2, OMS-6, and OMS-1 were also prepared according to the methods reported in the literature [29–31]. Mn_2O_3 and Mn_3O_4 were prepared by calcination of OMS-2 in a N_2 flow at 873 and 1173 K, respectively. MnO was obtained by calcination of $MnCO_3$ at 873 K in a 20% H_2/N_2 flow. CrO_3, V_2O_5, and MoO_3 were purchased (AR, Sinopharm Chemical) and used directly.

2.2. Catalyst characterization

BET surface areas of the catalysts were obtained by nitrogen physisorption at 78.3 K. The measurement was taken on a Micromeritics ASAP 2010 analyzer after the samples were treated at 423 K under dynamic vacuum conditions to desorb the possible adsorbates (e.g., H_2O and CO_2).

The Mn contents in the reaction filtrate were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Profile Spec, Leeman Labs).

XRD patterns of the as-prepared catalysts were taken on a Rigaku D/Max-2000 diffractometer in the 2θ range of 10–80° using a Cu Kα radiation source ($\lambda = 1.5406$ Å) at a scanning rate of 4°/min. The measurement was taken at 40 kV and 100 mA.

TEM images were obtained on a Philips Tecnai F30 FEG-TEM operated at 300 kV. Before the measurement, the catalyst powders were treated ultrasonically in ethanol for 30 min and then deposited on carbon-coated Cu grids.

XPS analyses were performed on an AXIS Ultra (Kratos, UK) spectrometer using an Al anode (Al Kα, $h\nu = 1486.6$ eV). The measuring chamber was operated at $\sim 5 \times 10^{-9}$ Torr. The binding energies were calibrated by referring to the C_{1s} line at 284.6 eV.

H_2-TPR experiments were carried out on a TP-5000 (Tianjin Xianquan) flow unit. Typically, 20 mg samples were placed in a quartz cell and then heated in a 5% H_2/N_2 flow (30 mL/min). The temperature ramped from 298 to 923 K at a rate of 10 K/min. The consumption of H_2 was calibrated by the reduction in pure CuO powder. The initial reduction rates for the MnO_2 catalysts, denoted as $R_{red,497K}$, were estimated by the reduction rates at 497 K, corresponding to the temperature at which 5% of the lattice oxygen atoms of OMS-2 were reduced by H_2.

O_2-TPO experiments were performed on a TP-5080 (Tianjin Xianquan) flow unit in a way similar to the H_2-TPR measurement. Before the O_2-TPO, the samples were reduced in a 5% H_2/N_2 flow (30 mL/min) for 1 h at 497 K, a low temperature to avoid destroying the tunnel structures of the OMS materials. After the samples were cooled to 298 K, they were heated in a 5% O_2/He flow (20 mL/min) from 298 to 723 K at a rate of 10 K/min. The consumption of O_2 was calibrated by the oxidation of Cu powder. The initial oxidation rates for the MnO_2 catalysts, denoted as $R_{oxi,383K}$, were estimated by the oxidation rates at 383 K, the reaction temperature typically used for HMF oxidation in this work.

2.3. HMF oxidation reactions

HMF oxidation reactions were carried out in a Teflon-lined stainless steel autoclave (50 mL). Typically, 1 mmol HMF (98%, Alfa Aesar) and 50 mg catalysts were introduced to 10 mL DMF (J.T. Baker, $\leqslant$0.02% H_2O) in the autoclave and were stirred at ca. 700 rpm. The reactants and products were analyzed by HPLC (Shimadzu LC-20A) using a UV detector and an Alltech OA-1000 organic acid column (0.005 M H_2SO_4 mobile phase, 0.7 mL/min flow rate, and 353 K oven temperature). HMF reaction activities were reported as molar HMF conversion rates per gram (or m^2) of catalysts per hour (i.e., mmol HMF/(g_{cat} h) or mmol HMF/(m^2_{cat} h)) and selectivities on a carbon basis. For catalyst recycling tests, if not specially stated, the retrieved catalysts were washed thoroughly with deionized water and then dried in vacuum oven before being recycled.

2.4. Kinetic isotope effects and oxygen isotope exchange

Kinetic isotope effects on the HMF oxidation were examined using α-deuterated HMF ($CHO{-}C_4H_2O{-}CH_2OD$) and β-deuterated HMF ($CHO{-}C_4H_2O{-}CD_2OH$), i.e. HMF molecules deuterated at the hydroxyl (–OH) and methylene ($-CH_2-$) groups, respectively, for comparison with undeuterated HMF. The deuterated HMF molecules were prepared according to our previous report [21].

Oxygen isotope exchange reactions between $^{16}O_2$ and $^{18}O_2$ were carried out under the same reaction conditions described above for the HMF oxidation, using a mixture of 0.25 MPa $^{18}O_2$ (97% isotopic purity, GAISI) and 0.25 MPa $^{16}O_2$. The oxygen isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ were measured by mass spectrometry (Hiden HPR20).

3. Results and discussion

3.1. Characterization of MnO_2 catalysts

Fig. 1 shows the XRD patterns for the MnO_2 catalysts. AMO only shows a broad peak at $2\theta = 37.2°$. The peaks of Na-OL-1 at $2\theta = 12.5$ and 25.0° are characteristic features of birnessite materials with layered structures (JCPDS 43-1456), corresponding to the (001) and (002) crystal phases, respectively [32,33]. The patterns of

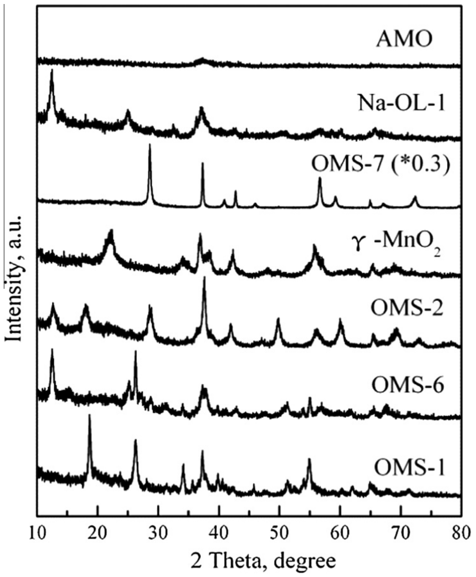

Fig. 1. XRD patterns for MnO_2 catalysts with different morphologies.