Catalysis Communications 82 (2016) 41–45

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Promoting effect of the addition of Ce and Fe on manganese oxide catalyst for 1,2-dichlorobenzene catalytic combustion

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ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 9 April 2016
Accepted 20 April 2016
Available online 22 April 2016

Keywords:
Chlorinated volatile organic compounds
Catalytic combustion
MnO_x
Promoter

ABSTRACT

Mn-based mixed-oxide (MnO_x) catalysts were modified with Fe, Ce, and Ce + Fe, and its catalytic oxidation activity was tested by using 1,2-dichlorobenzene (*o*-DCB) as models of chlorinated volatile organic compounds. Addition of Ce or Ce + Fe into MnO_x promoted their crystals to turn into amorphous powder, enhanced their specific surface area and changed their redox property. The catalytic activity of MnO_x improved remarkably by adding Ce or Ce + Fe indicating Ce plays an important role. Both Mn-Ce and Mn-Ce-Fe catalysts exhibited good stability for catalytic oxidation of *o*-DCB, indicating that the introduction of promoter is an important method to improve the catalytic performance.

1. Introduction

Increasingly stringent targets for permitted levels of atmospheric emission have been imposed by environmental legislation recently. There are increasing concerns over the abatement of chlorinated organic compounds which have been always considered as the most harmful organics because their emission shows direct hazardous effects on human health, as well as result in the depletion of the stratospheric ozone layer, which is bad for our environment [1]. However, in modern society chlorinated compounds are a part and parcel of our civilization which are used to all kinds of industries, as a result, their disposal is an urgent task and also a challenge to mankind for their difficult decomposition. The conventional approach for treatment of high concentration of chlorinated organic compounds is direct thermal combustion. It usually requires temperature higher than 1000 °C and leads to small amounts of more toxic polychlorinated aromatic compounds, such as polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), generally known as dioxins [2,3]. Catalytic oxidation can efficiently eliminate dilute pollutants at much lower temperatures (150–500 °C) than direct incineration with the help of noble metal or transition metal oxide catalysts [4]. It minimizes the energy consumption, recognized as one of the most promising techniques for the abatement of chlorinated organic compounds [2,3,5].

Most reported studies of the catalysts for chlorinated organic compounds catalytic combustion have focused on three types of catalysts based on noble metals [6–10], transition metals [11–19]and zeolites [20–22]. Our group has done a lot of research on structure modification of various catalysts [4,23–26], in which the surface structures or properties of catalysts can be adjusted according to the demand. Furthermore, much effort has been devoted to the research of transition metal oxides, which have been studied extensively as appropriate catalysts for the total combustion of chlorinated organics as their higher thermal stability and lower costs [4,27]. The activity of transition metal oxides is lower than noble metal, therefore how to improve its activity is very important and that is what we try to do. Among the transition metal oxides, manganese oxides (MnO_x) are reported to be one of the most efficient transition metal oxide catalysts for catalytic disposal of pollutants, because they contain various types of labile oxygen and high efficiency in the reaction/oxidation cycles, as well as being environment friendly [28]. It has been widely used in selective catalytic reduction of NO_x [3] and also found in the oxidation of chlorinated aromatics [13]. Although MnO_x catalysts deactivate because of the formation of chlorides at their surface [29], their resistance to the attack by Cl species can be really promoted by the addition of other elements [15,30]. Moreover, the redox capabilities are strongly enhanced when combined with other elements as a promoter [2,31–33]. It's well known that ceria (CeO_2) as a structural promoting component has two stable oxidation states, Ce^{4+} and Ce^{3+}, oxygen could be stored and released via the redox shift between Ce^{4+} and Ce^{3+}. Moreover, it enhances the metal dispersion and participates in stabilization of the support against thermal sintering [3,19]. In addition, Mn-Ce oxide-mixed catalysts have been proved to present high activity in catalytic combustion of chlorobenzene [3,27]. Meanwhile, iron oxide has abundant active sites which are absorbed sites of chlorinated

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http://dx.doi.org/10.1016/j.catcom.2016.04.015
1566-7367/

organics [34]. Khaleel et al. [1] reported that the activity of the Fe_2O_3/TiO_2 catalyst for the oxidative decomposition of chlorobenzene is enhanced by some type of synergic interaction between surface iron oxide and the support TiO_2. Therefore, we believe that the incorporation of Ce and Fe into MnO_x may offer an opportunity to prepare novel catalysts with high performance for the catalytic oxidation of *o*-DCB.

2. Experimental

2.1. Catalysts preparation

MnO_x, Mn-Ce, Mn-Fe, and Mn-Ce-Fe mixed oxide catalysts were prepared by a wet chemical method as following. An amount of 100 mL of distilled water was added to a 250 mL beaker containing $Mn(NO_3)_2$ 50% solution, $Ce(NO_3)_3 \cdot 6H_2O$ and/or $Fe(NO_3)_3 \cdot 9H_2O$, and citric acid (citric acid/total metal = 0.3, Mn/(Ce + Fe) = 6.4, Ce/Fe = 1:1 M ratio) with stirring at room temperature. The mixture was gradually heated to 75 °C and kept at this temperature for about 2 h with stirring, resulting in the formation of a yellowish gel. It was then dried overnight at 105 °C, crushed into fine powder, calcined in air at 500 °C for 4 h. The catalyst was denoted as Mn-M (M = Ce, Fe).

2.2. Characterizations

The phase structure of catalysts were analyzed by X-ray diffraction (XRD) employing a Bruker D8-ADVANCE X-ray diffract meter with Cu Kα radiation (λ = 0.15406 nm). The morphology of catalysts was determined with a scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM was performed with a JEOL JSM-4800 electron microscope. And TEM was performed using a Tecnai G20 instrument. Samples were dispersed in ethanol before being loaded onto lacey carbon copper grid. The specific surface areas of catalysts were measured by Nitrogen adsorption/desorption using a ST08-B gas adsorption system. The samples were dried at 200 °C for 2 h under vacuum prior to the adsorption experiments. The temperature-programmed reduction (H_2-TPR) experiment was carried out with a Gas Chromatograph equipped with thermal conductivity detector (TCD) and silica packed column. Prior to every 50 mg of catalysts were pretreated at 200 °C for 1 h in air. The TPR runs were carried out in a flow of 10 vol% H_2 in argon (30 mL/min) at a linear heating rate of 10 °C/min from 50 to 800 °C. The hydrogen consumption was measured quantitatively by a thermal conductivity detector.

2.3. Catalytic activity tests

The evaluation of catalytic activity of catalysts was carried out in a continuous flow fixed-bed quartz tubular reactor (6 mm i.d., 8 mm o.d.) at atmospheric pressure and in the temperature range of 200–400 °C. Catalyst (0.6 g) was loaded in the quartz reactor with quartz wool packed at both ends of the catalyst bed. The temperature of reaction was measured and controlled by putting a thermocouple in the middle of catalyst bed. The total reactive flow (120 mL/min) through the reactor was composed of air and gaseous 1,2-dichlorobenzene (*o*-DCB) (400–600 ppm, just as 2.625–3.938 g/mL), equivalent to a weight hourly space velocity (WHSV) of 12,000 mL g^{-1} h^{-1}. The feed stream to the reactor was prepared by delivering liquid *o*-DCB with a syringe pump into dry air, which was metered by a mass flow controller. The out and inlet effluent gas was analyzed by gas chromatography with a OV-1 (0.25 mm; 30 m) capillary column and a flame ionization detector (FID) for the quantitative analysis of reactants and products in order to evaluate the *o*-DCB conversion.

3. Results and discussion

3.1. XRD characterization and BET surface areas

The XRD patterns of studied samples are shown in Fig. 1, which indicates that different promoters have great effect on the crystallinity of catalysts. For Mn and Mn-Fe samples, all of the diffraction peaks can be indexed to Mn_2O_3 (PDF 41-1422), indicating that Mn and Mn-Fe samples were well crystallized.

Meanwhile, as for Mn-Ce sample, many diffraction peaks almost disappear, only two small peaks become comparatively broad and weak at 23.9° and 37.1°, indexes of α-Mn_2O_3 crystallization in the form of bixbyite [2,31] and MnO_2 (PDF 31-0820) crystallization in the form of pyrolusite, respectively. However, The XRD pattern of Mn-Ce-Fe after adding Ce and Fe together is quite different to the others. Its diffraction peaks become very broad, almost like steamed bread. It is difficult to identify the crystal structure from this curve due to very poor crystallinity. Compared with pure MnO_x catalyst, the different promoters as Ce and Fe have different effect on the phase structure. It is reasonable to believe that the crystallinity and phase structure of MnO_x don't change obviously after adding Fe, while they change very much when introduced Ce, part of catalyst particles turn into amorphous phase; then Ce and Fe together make Mn-Ce-Fe sample completely change into an amorphous phase.

The specific surface areas for MnO_x catalysts modified with Fe, Ce, and Ce + Fe mixture are summarized in Table 1. The surface area of MnO_x is about 15.1 m^2/g, that of Mn-Fe enhance to 25.4 m^2/g, while the surface area of MnO_x improve very much after adding Ce, like that of Mn-Ce and Mn-Ce-Fe are 90.4 and 100.4 m^2/g, respectively. Among all the studied catalysts, the specific surface area of Mn-Ce-Fe mixed-oxide catalyst is the largest than the others. It implies that Ce plays main role in the enhancement of the specific surface area of the catalyst, and Fe shows the synergistic effect.

3.2. SEM and TEM characterization

Further insights into the influence of the promoters (Ce and Fe) on the morphological properties and the structural features of Mn-based catalysts are investigated by SEM and TEM as shown in Fig. 2. From the SEM images, the pure MnO_x sample is composed of irregular spherical-like particles (0.25 μm) with a large degree of aggregation. Mn-Fe sample also appears surface aggregation to some extent, but the most particles become smaller due to the introduction of Fe. However, the Mn-Ce and Mn-Ce-Fe samples, no special shapes are shown.

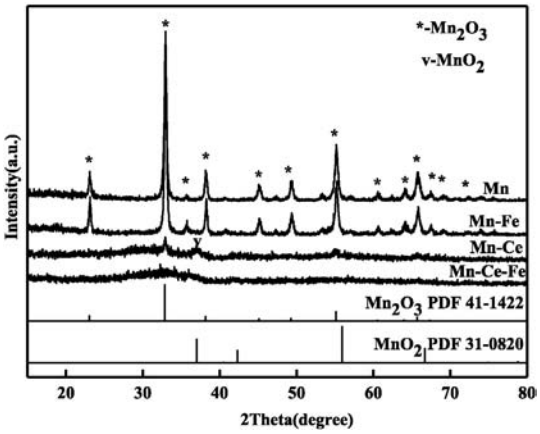

Fig. 1. XRD patterns of MnO_x catalysts with different promoters.