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Removal of Cl adsorbed on Mn–Ce–La solid solution catalysts during CVOC combustion ☆

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ABSTRACT

Mn–Ce–La oxide-mixed catalysts prepared by the method of complexation followed by calcination at 750 °C were tested in the catalytic combustion of chlorobenzene (CB) taken as a model of chlorinated aromatics. XRD analyses show that Mn and La enter CeO_2 matrix with a fluorite-like structure to form solid solution. The catalysts with high ratio of Mn/Mn + Ce + La exhibit high activity for CB combustion, due to high oxygen mobility. For all Mn–Ce–La catalysts, deactivation due to Cl adsorption is observed at different temperatures, depending on composition. At 330 °C or higher temperature, the removal of Cl species from the surface in the forms of Cl_2 (produced through Deacon reaction) and HCl (produced through hydrolysis of Cl) occurs and the activity of catalysts for CB combustion becomes thus stable. Either the addition of water or the increase in gaseous oxygen concentration can promote the removal of Cl species, and thus to increase the activity for CB combustion. High stable activity of Mn–Ce–La catalysts can be related to the combination of good oxidation and Deacon reaction performances.

1. Introduction

Aryl chlorides are hazardous pollutants that are considered among the most harmful organic contaminants due to their acute toxicity and strong bioaccumulation potential [1], and therefore, the safe disposal of aryl chloride pollutants has acquired great importance with the ever increasing concern for environmental protections [2]. Among various available detoxification techniques, catalytic combustion is an interesting one which can be efficiently performed. As reported, most catalysts used in the catalytic combustion of aryl chlorides were noble metals, zeolites and transition metals [3–5]. Transitional metal oxides, for example, V-based oxide catalysts (especially V_2O_5/TiO_2 catalysts) which were used widely in combustion of chlorobenzene (CB), presented high activity and stability [6–8]. Many efforts were paid for exploring the application of manganese oxides in catalytic combustion of CB [9,10], mainly owing to manganese oxides being environmentally friendly materials [11]. As reported in the previous work, highly active catalysts of Mn–Ce–O for CB combustion can be composed of MnO_x and MnCeO solid solution with fluorite-like structure. The separation of Mn species from the solid solution was observed at 650 °C or higher, leading to the deactivation of Mn–Ce–O catalysts [12]. With incorporation of La, separation of Mn species can be effectively inhibited. However, deactivation of these Mn based catalysts was observed below ca. 300 °C. It was reported that the deactivation of catalysts based on CeO_x was probably caused by the adsorption of Cl species formed during the reaction on active sites [13]. The adsorption strength of Cl species was critical to CB combustion, because the adsorbed Cl species can decrease the oxygen mobility of catalysts [9]. However, the investigation on Mn–Ce–La–O catalysts with the respect to deactivation process and activity recovery has not still been enough. Therefore, to study the deactivation of Mn–Ce–La–O catalysts is significant to understand the process of CB catalytic combustion on transitional metal oxides catalysts. In this work, Mn–Ce–La oxide-mixed catalysts prepared by the method of complexation and calcination at 750 °C were tested in the catalytic combustion of CB, as a model of chlorinated aromatics. The deactivation of Mn–Ce–La–O catalysts was investigated with various CB concentrations, oxygen concentrations in gas phase, the addition of water in the feeding stream and other assistant experiments.

2. Experimental

2.1. Catalysts preparation

Mn-based catalysts doped with La and Ce were prepared by complextion method: an aqueous solution containing $Mn(NO_3)_2$

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(SCRC, 50.0%), $Ce(NO_3)_3·6H_2O$ (SCRC, 99.0%), $La(NO_3)_3·6H_2O$ (SCRC, 99.0%), citric acid (SCRC, 99.0%) (citric acid:(Mn/1.5 + Ce + La) = 0.3) was gradually heated to 80 °C and kept at this temperature for 7 h while stirring, so that a yellowish sticky suspension was finally formed. The suspension was then dried at 110 °C for 12 h, followed by calcination at 750 °C for 5 h in air. The synthesized catalyst was denoted as Mn(0.86)–CeLa, where 0.86 represents the molar ratio for Mn/(Mn + Ce + La) and the atomic ratio of Ce to La is 1. Changing the molar ratio of Mn/(Mn + Ce + La) (X), a series of Mn(X)–CeLa catalysts can be obtained. The same method was employed in preparation of CeO_2, Mn(X)–La (X = Mn/(Mn + La)) and CeLa catalysts which were used as control samples with which Mn(X)–CeLa catalysts are compared. The used Mn(0.86)–CeLa catalyst in CB combustion at different temperature for 1 h was noted as U-T_1, where T_1 represented the reaction temperature; the treated U-T_1 by air for 12 h was noted as U-T_1-TT_2, where T_2 represents the treatment temperature.

2.2. Catalyst characterization

The powder X-ray diffraction patterns (XRD) of samples were recorded on a Rigaku D/Max-rC powder diffractometer using Cu Kα radiation (40 kV and 100 mA). The diffractograms were recorded within the 2θ range from 10° to 80° with a 2θ step size of 0.01° and a step time of 10 s.

The nitrogen adsorption and desorption isotherms were measured at −196 °C on an ASAP 2400 system in static measurement mode. The samples were outgassed at 160 °C for 4 h before the measurement. The specific surface area was calculated using the BET model.

Coke formation on the catalyst was evaluated with thermogravimetric analysis (TGA) using a PerkinElmer Pyris Diamond TG/TGA Setaram instrument. The fresh and used Mn(X)–CeLa samples were heated up to 800 °C from room temperature (heating rate of 10 °C min^{-1}) in a N_2/O_2 stream.

The XPS measurements were made on a VG ESCALAB MK II spectrometer by using Mg Kα (1253.6 eV) radiation as the excitation source. Charging of samples was corrected by setting the binding energy of adventitious carbon (C1s) at 284.6 eV. The powder sample, pressed into self-supporting disks, was loaded in a sub-chamber and then evacuated for 4 h, prior to the measurements at 25 °C.

H_2-temperature programmed reduction (H_2-TPR) was investigated by heating Mn(X)–CeLa samples (150 mg) in H_2 (5 vol.%)/Ar flow (30 ml min^{-1}) at a heating rate of 10 °C min^{-1} from 20 to 750 °C. The hydrogen consumption was monitored by thermo-conductivity detector (TCD). Before H_2-TPR analysis, the samples were heated for 60 min in Ar flow at 500 °C, and then treated in O_2 at room temperature for 30 min.

2.3. Catalytic activity measurement

Catalytic combustion reaction was carried out at atmospheric pressure in a continuous flow micro-reactor made of a quartz tube with inner diameter of 4 mm. 200 mg of catalyst as the reaction bed was packed. The feeding flow rate to the reactor was set at 50 cm^3 min^{-1} and the gas hourly space velocity (GHSV) was maintained at 15,000 h^{-1}. Feed stream to the reactor was prepared by delivering liquid CB with a syringe pump into dry air, which was metered by a mass flow controller controlling CB concentration in the feed stream at 1000 ppm. The injection part was electrically heated to ensure complete evaporation of CB. The temperature of the reactor was measured with a thermocouple located just at the exit of the micro-reactor. The effluent gases were analyzed on-line by two gas chromatographs (GC), one equipped with FID for the quantitative analysis of the organic chlorinated reactant, and the other, with TCD for the quantitative analysis of CO_2 and CO. The concentrations of Cl_2 and HCl were analyzed by the effluent stream bubbling through a 0.0125 N NaOH solution, and chlorine concentration was then determined by the titration with ferrous ammonium sulfate (FAS) using N,N-diethyl-p-phenylenediamine (DPD) as indicator [14]. The concentration of chloride ions in the bubbled solution was determined by using a chloride ion selective electrode [15].

3. Results and discussions

3.1. Characterization of catalysts

Wide angle XRD patterns of catalysts are shown in Fig. 1. For pure MnO_x sample, there appear five intense and sharp peaks at 32.9°, 38.13°, 49.56°, 55.17° and 65.77°, the indices of incipient α-Mn_2O_3 crystallization in the form of bixbyite (JCPDS #24-0508) [16]. And pure CeO_2 in the form of cerianite with a fluorite-like structure exhibits diffraction peaks at 28.7°, 33.3°, 47.5°, 56.5° and 59.2° (JCPDS #43-1002). With the incorporation of Ce and La by both atom ratios of Ce/Mn and La/Mn as 0.08 (Mn(0.86)–CeLa), the reflection from crystal α-Mn_2O_3 almost disappears. Moreover, slightly asymmetry shape of reflection of lower intensity from cerianite confirms the weakening degree of the crystallinity of cerianite in Mn(0.86)–CeLa sample. The Bragg angle of cerianite shifting slightly to high value indicates that Mn^{3+} or Mn^{4+} species enters the fluorite-like lattice, leading to the formation of $MnCeO_x$ solid solution [17]. The increase in the ratios of both Ce/Mn and La/Mn makes the reflection from cerianite become strong with the shift of Bragg angle of cerianite to low values, due to the entrance of La into CeO_2 matrix. It is noted that the average particle size of ceria, calculated from the peak at 28.6° of ⟨1 1 1⟩ crystal plane, is inversely proportional to the surface area (see Table 1), indicating main contribution of the matrix to surface area. As known, the fluorite structure of ceria is retained up to an ionic fraction of about 0.7 in manganese [18] and of 0.6 in lanthana [19]. Within the entire range of compositions, most of Mn and La species exist in the phase of fluorite structure where ceria is the solvent, except for the catalysts with La/Mn ratio higher than 1.1, such as Mn(0.39)–CeLa (La/Mn + Ce + La = 0.305) and Mn(0.27)–CeLa (La/Mn + Ce + La = 0.365), where weak reflection from $LaMnO_3$ in the form of perovskite structure appears at 40.12°, 46.71° and 58.07° (JCPDS #54-1275). Moreover, the lattice parameters of cerianite for these

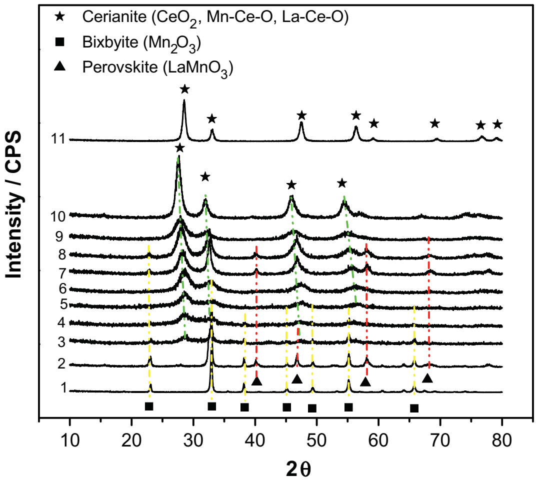

Fig. 1. XRD patterns of Mn–CeLa mixed oxide catalysts with different ratios of Mn/Mn + Ce + La; 1 – MnO_x, 2 – Mn(0.86)–La, 3 – Mn(0.86)CeLa, 4 – Mn(0.78)–CeLa, 5 – Mn(0.69)–CeLa, 6 – Mn(0.5)–CeLa, 7 – Mn(0.39)–CeLa, 8 – Mn(0.27)–CeLa, 9 – Mn(0.14)–CeLa, 10 – CeLa and 11 – CeO_2.