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Enhanced activity for catalytic oxidation of 1,2-dichloroethane over Al-substituted $LaMnO_3$ perovskite catalysts

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ABSTRACT

A series of Al-substituted $La_{1-x}Al_xMnO_3$ ($x = 0 - 0.3$) catalysts were prepared using a sol–gel method and tested for 1,2-dichloroethane oxidation in order to investigate the effects of Al-doping and thermal treatment on the catalyst structures and catalytic behaviors. It was found that both Al-doping and thermal treatment had great influence on the activities of the catalysts, and the highest activity was obtained on a $La_{0.8}Al_{0.2}MnO_3$ catalyst calcined at 700 °C, with a T_{50} of 295 °C. The enhanced activity could be attributed to synergetic effects of its high surface area, high reducibility and surface acidity, as evidenced by various characterizations such as H_2 temperature-programmed reduction and NH_3 temperature-programmed desorption. However, comparisons of the areal specific reaction rates revealed that the catalysts calcined at 900 °C had much higher rates than the ones calcined at 500 and 700 °C, suggesting that structural properties of the catalysts exerted much stronger influence on the catalytic performance than the surface area. It was also evidenced that the reducibility of the catalyst had a dominant role in determining the intrinsic activity, which was closely related to the presence of high valent Mn^{4+} species in the catalyst as induced by the introduction of Al in the catalyst.

1. Introduction

The abatement of chlorinated volatile organic compounds (CVOCs) such as dichloromethane (DCM), 1,2-dichloroethane (DCE) and trichloroethylene (TCE) has been received much attention because they are recognized as major pollutants which are hazardous to the environment and public health. With many advantages such as low energy consumption and high efficiency, catalytic oxidation (combustion) of CVOCs is regarded as a promising technology for CVOCs elimination [1].

Highly efficient catalyst systems are decisive in order to obtain good performance for CVOCs combustion. Catalysts for CVOCs oxidation mainly include noble metals [2–5], transition metal oxides [6,7], and zeolites [8–10]. Although noble metals such as Pt, Pd are effective catalysts for CVOCs combustion, their high cost and easy deactivation by Cl poisoning limit the practical applications, while zeolite catalysts are less active at low temperature region. Among the transition metal oxides, perovskite-type oxides seem to be potential catalysts because of their low costs, widely resources, good thermal stability and relatively high catalytic activities for the complete oxidation of hydrocarbons [11–16]. The most commonly employed perovskite-type oxides are the compounds containing rare earth or alkaline earth metals (i.e. La, Pr, Ce, Ba) in the A-site and transition metals (i.e. Co, Ni, Fe, Mn and Cr) in the B-site [12–21]. In order to further improve the activity, modification of the perovskite-type oxide is necessary. One approach is the synthesis of perovskite-type oxides with high surface areas because the main obstacle that limits the application of such oxides is the low surface area. Sui et al. [22] prepared $LaMnO_3$ samples with citrate and sol–gel combustion methods, and they found that the $LaMnO_3$ prepared by the citrate method had a higher surface area than that prepared by the combustion method, which accounted for its enhanced activity for butane total oxidation. Liu et al. [23] prepared 3-demonsional ordered macroporous (3DOM) $LaMnO_3$ with high surface areas (37–39 $m^2 g^{-1}$) by a surfactant-assisted method and tested for the oxidation of toluene. They attributed the enhanced activity on the 3DOM $LaMnO_3$ than that on the bulk $LaMnO_3$ to its large surface area, good low-temperature reducibility and unique nanovoid-containing 3DOM structure of the materials. Besides, partial substitution of other cations with similar oxidation state and ionic radius in the A- or B-site could promote the catalyst activity because of the modified redox properties and oxygen defects of the catalysts after doping. For example, Zhang et al. [24] studied A-site substituted $LaMnO_3$ catalysts with Sr, Mg and Ce for

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vinyl chloride oxidation, and they found that the Ce-substituted $La_{0.8}Ce_{0.2}MnO_3$ had the highest activity, which was due to its high surface area and low-temperature reducibility. The same group [25] also prepared B-site modified $LaB_{0.2}Mn_{0.8}O_3$ (B = Co, Ni, Fe) perovskite-type oxides for vinyl chloride oxidation. They found that the substituted $LaB_{0.2}Mn_{0.8}O_3$ samples showed higher catalytic activities than the pure $LaMnO_3$, and they concluded that the catalytic activity was greatly related to the low-temperature reducibility of the B site and the amount of adsorbed oxygen species and vacancies on the catalyst surface.

The above-mentioned findings suggest that the redox properties of the catalysts are crucial for CVOCs oxidation. Another important aspect should be considered is the surface acidity, because the surface acidic sites are centers for chemisorption of CVOC molecules [26]. High surface acidity is usually beneficial to the promotion of CVOCs oxidation activity, which has been confirmed on Ce–Zr mixed oxides for DCE and TCE oxidation [27], and on CeO_2 modified USY zeolite for DCE oxidation [10]. As a typical acidic support, Al_2O_3 has been widely applied in CVOCs oxidation [5]. In our previous work [4], a series of CeO_2-doped $Pt/CeO_2–Al_2O_3$ catalysts were tested for DCM oxidation and it was concluded that high surface acidity in the catalyst was helpful for DCM decomposition.

Therefore, in this work, various Al-substituted $LaMnO_3$ catalysts were synthesized. Effects of Al content in the catalyst and calcination temperature on the catalyst properties and their catalytic behaviors were investigated.

2. Experimental

2.1. Catalyst preparation

Perovskite-type oxides $La_{1-x}Al_xMnO_3$ catalysts were prepared by a sol–gel method [28]. The detailed process was as follows: $La(NO_3)_3$ was prepared by dissolving quantity of high purity La_2O_3 in moderate concentrated nitric acid, then the solution was mixed by aqueous solutions of $Mn(NO_3)_2$ (50 wt.%) and $Al(NO_3)_3$. Citric acid with twice molar amount of metal ions (Al + La + Mn) was added to the above solution and the mixture was heated to 90 °C to produce a viscous gel, which was then dried at 200 °C for 2 h. The final product was calcined at different temperatures (500, 700 and 900 °C) for 4 h with a heating rate of 10 °C min^{-1}. The samples were designated as $La_{1-x}Al_xMnO$-5, $La_{1-x}Al_xMnO$-7 and $La_{1-x}Al_xMnO$-9, where x refers to the molar ratio of Al/(Al + La) in the samples, and the number refers to the calcination temperature.

2.2. Characterizations

Specific surface areas (SSA) of the catalysts were measured by N_2 adsorption at liquid-nitrogen temperature (77 K) using a surface area analyzer (Quantachrome Autosorb-1). The catalysts were pretreatment at 120 °C for 6 h in vacuum.

X-ray diffraction (XRD) patterns of the samples were collected with a PANalytical X'Pert PRO MPD power diffractometer using Cu $K\alpha$ radiation. The working voltage was 40 kV and the working current was 40 mA. The patterns were collected in a 2θ range from 10 to 90°, with a scanning speed of 0.15° s^{-1}. Cell parameters and crystallite sizes of the samples were analyzed using the JADE 6.5 software.

The morphologies of the catalysts were observed by a scanning electron microscopy (SEM, Hitachi S-4800) operated at 5.0 kV.

H_2 temperature-programmed reduction (H_2-TPR) technique was used to measure the redox properties of the catalysts. 50 mg of the catalyst was placed in a quartz reactor, which was heated from 100 to 900 °C with a heating rate of 10 °C min^{-1} under a mixture of 5% H_2—95% N_2 (20 ml min^{-1}). The amount of H_2 consumption was determined by a gas chromatograph with a thermal conductivity detector (TCD), which was calibrated by the quantitative reduction of a known amount of CuO powder.

The acidity of the catalyst was studied by ammonia temperature-programmed desorption (NH_3-TPD). 50 mg of the catalyst was pretreated in a flow of N_2 (20 ml min^{-1}) at 300 °C for 0.5 h, and then was cooled down to 50 °C. After that, a flow of NH_3 (20 ml min^{-1}) was introduced to the reactor for 30 min, followed by purging at for 1 h with a N_2 flow (20 ml min^{-1}) to remove the physisorbed NH_3. Then the sample was heated from 50 to 900 °C at a rate of 10 °C min^{-1}, and the profile was recorded using a gas chromatograph (TECHTEMP GC 7890II) with a TCD detector.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250Xi analyzer. Mn 2p and O 1s binding energies (BEs) were recorded using Al $K\alpha$ ($h\nu$ = 1486.6 eV) as the excitation source, and a passing energy of 20 eV. The C 1s signal at 284.6 eV was taken as a reference for BE calibration.

Temperature-programmed surface reaction was conducted on a home-made reactor connected with a mass spectrometer (MS, Qic-20 Benchtop, HidenAnalytical). 50 mg of the catalyst was pretreated in a flow of O_2 (20 ml min^{-1}) at 300 °C for 0.5 h, and then was cooled down to 30 °C. Then a flow of DCE/O_2 mixture (1000 ppm DCE, total flow rate = 20 ml min^{-1}) was introduced to the reactor and the sample was heated from 30 to 500 °C at a rate of 10 °C min^{-1}. And m/e signals of 28, 44, 18, 36, 70, 50, 62, 64, 43 and 29 were monitored, corresponding to CO, CO_2, H_2O, HCl, Cl_2, CH_3Cl, DCE, CH_3CH_2Cl, CH_3COOH and HCHO, respectively.

2.3. Catalytic testing

Catalytic oxidation of DCE was carried out in a tubular fixed-bed reactor (i.d. = 9 mm) at atmospheric pressure. Typically, 1.5 g of catalyst (1.5 ml in volume, 40–60 mesh) was loaded in the reactor. A thermal couple was placed in the middle of the catalyst bed to monitor the reaction temperature. A gaseous mixture of DCE (1000 ppm) in moisture-containing air was introduced to the reactor, with a total gas flow of 500 ml min^{-1} (space velocity = 20,000 h^{-1}). After the reaction was stabilized for 1.5 h at certain temperature, product analysis was conducted using a gas chromatograph (Shimadzu, GC-14C) equipped with a flame ionization detector (FID). Because of the limitation of test conditions, only chlorohydrocarbon products were detected.

3. Results and discussion

3.1. Structural properties

Calcination temperature exerts significant influences on the catalyst structural properties such as surface area, phase composition and crystallite size. Table 1 summarizes surface areas of the $La_{1-x}Al_xMnO$ samples calcined at different temperatures. The samples calcined at 500 °C possess surface areas of 20.9–43.6 $m^2\,g^{-1}$, which are slightly lower than the corresponding samples calcined at 700 °C (22.2–47.3 $m^2\,g^{-1}$), but are much higher than those calcined at 900 °C (4.6–8.1 $m^2\,g^{-1}$). The lowered surface areas of the $La_{1-x}Al_xMnO$-9 samples are due to the sintering of crystallites during the high temperature calcination. In addition, for the samples with different Al contents, the surface areas first increase with Al content and then decline, with the highest surface area obtained on the $La_{0.8}Al_{0.2}MnO$ catalysts ($La_{0.8}Al_{0.2}MnO$-5 and $La_{0.8}Al_{0.2}MnO$-7).

Fig. 1a shows the XRD patterns of the $La_{1-x}Al_xMnO$ samples calcined at 500, 700 and 900 °C. For the samples calcined at 500 °C, amorphous structures are detected, and no crystalline perovskite structure is formed. When the samples are calcined at 700 and