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SnO_x–MnO_x–TiO_2 catalysts with high resistance to chlorine poisoning for low-temperature chlorobenzene oxidation

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In this study, MnO_x–TiO_2 and SnO_x–MnO_x–TiO_2 catalysts were prepared using a homogeneous precipitation method and were investigated for the catalytic combustion of chlorobenzene (CB), which was used as a model compound of chlorinated volatile organic compounds (CVOCs). The catalytic activity tests revealed that both catalysts exhibited an outstanding activity in catalytic degradation of CB, with 90% conversion occurring below 180 °C. A significantly higher stability was observed for the Sn–Mn–Ti catalyst compared with Mn–Ti samples, revealing that the stability of Mn–Ti catalysts for the oxidation of chlorobenzene could be remarkably improved via the introduction of Sn. The obtained catalysts were characterized using X-ray diffraction (XRD), Raman spectroscopy, N_2 physisorption, transmission electron microscopy (TEM), X-ray photoelectron (XPS) and hydrogen temperature-programed reduction (H_2-TPR). Characterization of the catalysts indicated that the enhanced catalytic stability of the SnO_x–MnO_x–TiO_2 catalysts was related to the lower average energy required to desorb Cl species and to the absence of MnO_xCl_y on the active sites during the reaction, which remarkably improved the thermal stability of catalyst. Hence, SnO_x–MnO_x–TiO_2 catalysts are a potential material for the abatement of CVOCs.

1. Introduction

Catalytic combustion is recognized as an effective technology for reducing CVOCs emissions from waste gases because of its high removal efficiency and good selectivity. Among the catalysts employed in the catalytic oxidation of CVOCs, titania-supported vanadium oxide has been successfully applied in industrial processes due to its relatively low cost and high stability. Anatase TiO_2, as the support, has many advantages, such as high specific surface area, excellent dispersing effect for active components, good thermal and anticorrosive properties and so on [1–3]. Nevertheless, the active phase VO_x is not sufficiently desirable (the operating temperature is in the range of 300–450 °C). Moreover, VO_x is highly toxic to humans and animals. Therefore, developing other highly active catalysts as alternatives to vanadium oxide that are not only environmentally friendly but also resistant to catalytic deactivation is of importance.

Manganese oxides, as a type of environmental-friendly material, have attracted continuous attention because of their excellent catalytic performance and widespread applications, such as the catalytic combustion of toluene, benzene and ethyl acetate [4–8]; the selective catalytic reduction of NO_x with NH_3 [9–13]; and CO oxidation or hydrogenation [14–16]. Therefore, manganese oxides have been widely recognized as one of the most efficient transition-metal oxide catalysts for catalytic disposal of pollutants and have great potential as an alternative to VO_x in the abatement of CVOCs [17,18]. However, these oxides are susceptible to catalytic deactivation due to the strong adsorption of dissociative Cl species, which are mainly generated from the combustion processes. For this reason, some researchers have hypothesized that manganese oxides could only be applied in a Cl-free atmosphere [19]. Improving resistance of these catalysts to deactivation will extend the application range of manganese oxides in industry. However, to the best of our knowledge, most researchers have focused more attention on the catalytic performance, with the stability test as a supplementary analysis, and only a few exclusive studies are available with respect to improving the stability of the catalysts.

In this study, we tried to introduce foreign elements to the host MnO_x–TiO_2 catalyst for enhancing its resistance to chlorine poisoning. As far as we know, some elements, such as La, Ce, Ru and Sn, have special effects when added to catalyst as additives. For example, the addition of La can improve the thermal stability of

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catalysts [20]; CeO_2 has been widely investigated due to its high oxygen storage capacity and facile Ce^{4+}/Ce^{3+} redox cycle [21]; the oxides of Ru and Sn are not so susceptible to Cl_2 or HCl and can exist at the atmosphere of Cl_2 or HCl for a relative long time [22]. We introduced the above mentioned elements to MnO_x–TiO_2 catalyst and found that the addition of Sn was effective for our purpose. Subsequently, a series of SnO_x–MnO_x–TiO_2 mixed-oxide catalysts with different Sn content were synthesized using a homogeneous precipitation method to investigate the effect of Sn on the catalytic stability of MnO_x–TiO_2 catalysts for CB combustion. Additionally, a possible reason for the good stability of SnO_x–MnO_x–TiO_2 catalyst was discussed.

2. Experimental

2.1. Catalysts preparation

In this study, SnO_x–MnO_x–TiO_2 catalysts were prepared using a homogeneous precipitation method, as follows: an aqueous solution containing $SnCl_2{\cdot}2H_2O$ (SCRC, 98.0%), $Mn(NO_3)_2$ (50 wt.% solution), $Ti(SO_4)_2$ (SCRC, 96.0%), urea (SCRC, 99.0%) and polyethylene glycol (in the solution, Mn/Ti = 1:3, Sn/(Mn + Ti) = 1:10, molar ratio) was gradually heated to 90 °C and maintained at this temperature for 10 h with vigorous stirring. After filtering and washing several times with ultrapure water, the obtained sample was dried at 110 °C for 12 h and then calcined at 400 °C for 5 h in air. The same method was employed to prepare MnO_x–TiO_2 and TiO_2 catalyst (without the addition of $SnCl_2{\cdot}2H_2O$ or $Mn(NO_3)_2$). The composition of the reaction solution and calcination temperature were the same as those in the aforementioned procedure. The synthesized MnO_x–TiO_2 and SnO_x–MnO_x–TiO_2 catalysts are denoted as Mn–Ti and Sn–Mn–Ti, respectively.

2.2. Characterization

The phase structures of the catalysts were analyzed using an X'Pert PW3050/60 X-ray diffractometer with Cu $K\alpha$ radiation (40 kV and 40 mA). Raman spectra were recorded on a laser confocal Raman miscroscope (DXR, American Thermo Electron) operated at a wavelength of 532 nm. Nitrogen adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 nitrogen-adsorption apparatus. The specific surface areas of samples were measured using the Brunauer–Emmett–Teller (BET) method and the pore volumes and pore size distributions were determined using the Barrett–Joyner–Halenda (BJH) method. TEM images were acquired using a JEOL JEM-2100 microscope. The samples were ground in ethanol using a mortar and mounted onto Cu grids coated with a holey carbon film without any metal coating. X-ray photoelectron spectroscopy with Al $K\alpha$ X-rays radiation ($h\upsilon$ = 1253.6 eV) (XPS: VG Multilab 2000) was used to analyze the surface atomic states of the catalysts. The TPR runs were conducted with a linear heating rate (10 °C/min) in a flow of 10% H_2 in argon at a flow rate of 40 mL/min. The hydrogen consumption was measured quantitatively by a thermal conductivity detector (TCD).

2.3. Catalytic activity test

Catalytic combustion reactions were performed at atmospheric pressure in a continuous flow micro-reactor, which was made of a quartz tube with an 8 mm in inner diameter, with 0.2 g of catalyst packed in the center of the reactor. CB was introduced into the reactor by a carrier gas of N_2 through a saturator maintained at 0 °C, and then it was mixed with N_2 and O_2 in a mixing drum. The feed flow through the reactor was set with a CB concentration of 2500 mg/m^3 and gas hourly space velocity (GHSV) of 20,000 h^{-1}. The reaction temperature was measured and controlled with a thermocouple located at the thermal spot of the reactor. The effluent gases were analyzed at a given temperature using an online gas chromatograph (GC) equipped with a flame ionization detector (FID) for the quantitative analysis of CB.

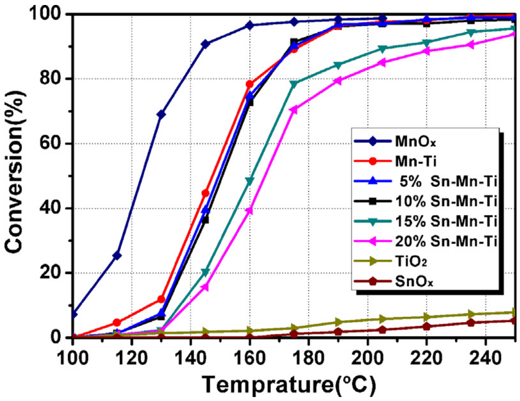

Fig. 1. The activity of TiO_2, MnO_x, SnO_x, Mn–Ti and Sn–Mn–Ti catalysts for CB combustion, gas composition: 2500 mg/m^3 CB, 20% O_2, N_2 balance; GHSV = 20,000 h^{-1}.

3. Results and discussion

3.1. Catalytic activity for CB oxidation

The activities of TiO_2, MnO_x, SnO_x, Mn–Ti and Sn–Mn–Ti are shown in Fig. 1. Compared to the support TiO_2 and additive SnO_x, which exhibit no significant oxidation of CB at temperatures up to 250 °C, the Mn–Ti catalyst exhibits excellent catalytic activity, and the temperatures required for the conversion of 50% and 90% of CB ($T_{50\%}$ and $T_{90\%}$) were 147 °C and 177 °C, respectively. In the case of Sn–Mn–Ti, when the content of Sn was not greater than 10% (Sn/Mn + Ti = 10%, molar ratio), the activity was almost identical to that of the Mn–Ti catalyst, indicating that a small amount of Sn did not affect the activity of Mn–Ti catalyst. With further Sn addition, the activity of the Sn–Mn–Ti catalyst decreased significantly. Although MnO_x performed best for CB combustion, it deactivated quickly during the activity test. The activity tests revealed that Mn is the active component in the catalysts: Sn acts as an additive, and the small amount of Sn minimally affects the activity of the catalyst. Although TiO_2, as a support, exhibits fairly low activity, it plays an important role in the dispersion of Mn or Sn.

3.2. Stability study of catalysts

The stability of catalysts is a very important factor to consider for practical applications. Fig. 2 shows the stabilities of the Mn–Ti and Sn–Mn–Ti catalysts that were continuously reacted for 100 h at different temperatures. As shown in this figure, both catalysts deactivate to some extent at low temperatures (less than 225 °C). The activity of the Mn–Ti catalyst is not stable until 300 °C, whereas for Sn–Mn–Ti, the temperature required for stable activity is 225 °C, which is much lower than that of other manganese-containing catalysts [20,23–27], noble metal catalysts [28] and other catalysts [29]. Moreover, compared with Mn–Ti catalyst, the deactivation rate of Sn–Mn–Ti is slower, and the final stable activity is higher at temperatures below 300 °C. These facts indicate that the addition of Sn can clearly enhance the stability of the Mn–Ti catalyst.

To enhance the catalyst's resistance to chlorine poisoning, we also attempted to introduce some other additives (the rare earth element Ce and La and the noble metal Ru) to the Mn–Ti catalyst. Fig. 3 presents the stabilities of the Mn–Ti and X–Mn–Ti (X = Ce, La, Ru and Sn; X/Mn + Ti = 10%, molar ratio) catalysts for the combustion of CB at 175 °C. As shown, not every additive was capable