



Catalytic oxidation of dichloromethane over Pt/CeO₂–Al₂O₃ catalysts

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ABSTRACT

A series of CeO₂–Al₂O₃ catalysts with different CeO₂ contents were prepared by a co-precipitation method, and supported Pt/CeO₂–Al₂O₃ catalysts were also prepared by an impregnation method. These catalysts were tested for catalytic oxidation of dichloromethane (CH₂Cl₂). It was found that these catalysts were active for the reaction, with a 100% conversion of CH₂Cl₂ obtained at 410 °C over a catalyst with 15% of CeO₂. Various characterization results such as ammonia temperature programmed desorption, hydrogen temperature programmed reduction suggested that the catalytic behaviors were synergistically influenced by surface acidity and redox property of the catalysts. An optimal combination of surface acidity and redox property in the catalyst resulted in a high activity. Moreover, the addition of Pt could further enhance the activity, due to the promotion of surface acidity by the introduction of chlorine species in the catalyst during the preparation using H₂PtCl₆ as the precursor and reducibility of the catalyst probably via the formation of Ce–Pt–O solid solution.

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1. Introduction

Chlorinated volatile organic compounds (CVOCs) are recognized to be hazardous to the environment and public health. These compounds are usually generated from a wide range of industrial processes, including the manufacture of herbicides, plastics and solvents. Dichloromethane (CH₂Cl₂) is a representative CVOCs, which is harmful to the respiratory system and central nervous system of human [1]. Thus, elimination of CVOCs emissions has been receiving much attention in recent decades. Among the technologies, catalytic combustion is regarded as one of the most promising technologies because of its low energy consumption, high efficiency and no associated pollution such as nitrogen oxides (NO_x) since it is operated at relatively low temperatures [2–4].

Catalysts applied in CVOCs combustion could be generally categorized in three groups: transition metal oxides [5], supported noble metals (such as Pt and Pd) [6–8], and zeolites [9,10]. For example, we previously reported that CrO_x/Al₂O₃ catalysts were active for CH₂Cl₂ combustion [11], with a 18% Cr content catalyst having the highest activity. Recently, Gu et al. [12] prepared a CuMnO_x/Zr–Ti–Al catalyst and found that this catalyst was more active than the one without Zr modification, which could be attributed to the higher dispersion of CuMnO entities and the improvement of reducibility after Zr modification. In addition to the oxide catalysts, noble metal catalysts such as Pt and Pd are proven to be more active than the oxides, although these noble metals

may suffer deactivation during the reaction due to the poisoning of chlorine species [13]. Kim et al. reported that Pt–Pd bimetallic catalysts supported on γ-Al₂O₃ were very effective for benzene complete oxidation [14]. Very recently, Maupin et al. [15] studied the dichloromethane oxidation over a Pt/Al₂O₃ catalyst and concluded that the reaction followed a bifunctional mechanism, that is, CH₂Cl₂ disproportionation took place over alumina and oxidation over Pt.

It is well known that for the complete oxidation of CVOCs, the performance of the catalysts correlates to several key factors such as surface acidity and redox properties, as the former is important for chemisorption of CVOc molecules [16] and the latter is important for oxygen activation. In the latter case, CeO₂ appears to be very promising for the promotion of oxygen activation, due to its unique properties such as remarkable redox capability which could significantly ease the activation of oxygen during the reaction [17–23]. Moreover, the presence of CeO₂ as a support could help the dispersion of metals and prevent the sintering of noble metals [18]. Dai et al. [24] compared catalytic oxidation of 1,2-dichloroethane and ethyl acetate over ceria nanocrystals with well-defined crystal planes and found that the ceria nanorods possessed the highest activity due to its smaller crystallite size, more oxygen vacancies, higher OSC and mobility of oxygen than the nanocubes and nano-octahedrons. Abbasi et al. [25] conducted total oxidation of toluene, benzene and xylene over CeO₂ modified Pt/Al₂O₃ catalysts and concluded that the activity was due to the enhanced reducibility after the addition of Pt and CeO₂.

It seems that catalysts with a combination of surface acidity and redox property would be effective for CVOcs combustion. As a typical acidic oxide, Al₂O₃ has been widely used in catalysis, especially

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in the total oxidation of VOCs, as mentioned above [15,25]. Also, the choice of Al_2O_3 instead of other acidic materials such as zeolites lies in its cheap cost and easy synthesis. Moreover, as the CH_2Cl_2 molecule is very stable, the total oxidation of CH_2Cl_2 is challenging. Therefore, in this work, a series of $\text{CeO}_2\text{-Al}_2\text{O}_3$ oxides were synthesized and tested for complete oxidation of dichloromethane as a model reaction. Furthermore, Pt was supported on these oxides in order to promote the catalytic performance. Various characterizations were performed to correlate the catalytic behaviors with the natures of the catalysts.

2. Experimental

2.1. Catalyst preparation

$\text{CeO}_2\text{-Al}_2\text{O}_3$ catalysts were prepared by a co-precipitation method. A detailed process was as follows: an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was mixed with an aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Then an ammonia solution was drop-wise added to the mixture under vigorous stirring. The pH value of the solution was controlled at 8.0 ± 0.5 . The precipitation was aged for 6 h and separated by centrifugation from the mother liquor, washed several times with deionized water and then dried overnight at 120°C . The resulting solid was calcined at 500°C for 4 h with a heating rate of $10^\circ\text{C min}^{-1}$ to obtain the final $\text{CeO}_2\text{-Al}_2\text{O}_3$. The CeO_2 contents were about 5, 15, 27 and 59 wt% in the samples, and these catalysts were denoted as 5CeAlO, 15CeAlO, 27CeAlO and 59CeAlO, respectively. Reference supports Al_2O_3 and CeO_2 were prepared in a similar manner.

Supported Pt catalysts were prepared by an impregnation method. A known amount of platinum precursor ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was impregnated to the support. The solid was dried overnight at 120°C and then it was calcined at 500°C for 4 h to yield the final catalyst. The Pt contents in the catalysts ranged from 0.1 to 3.0 wt%.

2.2. Characterizations

The BET surface areas 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 were recorded with a PANalytical X'Pert PRO MPD powder diffractometer using $\text{Cu K}\alpha$ 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 parameter of CeO_2 was analyzed by full curve fitting using a JADE 6.5 software.

The morphology of the catalysts was observed by a scanning electron microscopy (SEM, Hitachi S-4800), which was operated at 1.0 kV. Detection of Pt particles in the supported catalysts was conducted on a transmission electron microscopy (TEM, JEOL JEM-2100F) operated at 120 kV.

H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) technique was used to measure the reducibility of the catalysts. 25 mg of the catalyst was placed in a quartz reactor, which was heated from 100 to 800°C with a heating rate of $10^\circ\text{C min}^{-1}$ under a mixture of 5% $\text{H}_2\text{-95% N}_2$ (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 acidic properties of the catalysts were studied by ammonia temperature programmed desorption ($\text{NH}_3\text{-TPD}$). 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 . Afterwards, a flow of NH_3 (20 ml min^{-1}) was introduced to the reactor for 15 min, followed by

purging at 80°C for 0.5 h with a N_2 flow (20 ml min^{-1}) to remove the physisorbed NH_3 . Then the sample was heated from 80 to 600°C at a rate of $10^\circ\text{C min}^{-1}$, and the profile was recorded using a gas chromatograph (TECHTEMP GC 7890II) with a TCD detector.

The CH_2Cl_2 chemisorption experiments were carried out a home-made apparatus. 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 30°C . Then a flow of $\text{CH}_2\text{Cl}_2/\text{He}$ mixture (total flow rate = 20 ml min^{-1} , CH_2Cl_2 concentration = 3000 ppm) was introduced to the reactor for 15 min, followed by purging at 30°C for 0.5 h with a He flow (20 ml min^{-1}) to remove the physisorbed CH_2Cl_2 . Then the sample was heated from 30 to 500°C at a rate of $10^\circ\text{C min}^{-1}$, and the profile was recorded using a mass spectrometer (HIDEN, QIC-20) by monitoring $m/e = 97$ (CH_2Cl_2).

Dispersions of Pt in the catalysts were determined by CO chemisorption, which was carried out on a Quantachrome ChemBET-3000 instrument. The sample was placed in a quartz U-tube, and high-purity He (99.999%) was used as the carrier gas. The samples were reduced in a $\text{H}_2\text{-N}_2$ mixture (5 vol% H_2) stream at 300°C for 1 h and cooled down to 30°C in a pure He flow. Then pulses of CO were fed into the stream of carrier gas with a precision analytical syringe.

2.3. Activity test

Catalytic combustion of CH_2Cl_2 was carried out in a conventional fixed-bed reactor (i.d. = 9 mm). 1.0 g of the catalyst in 40–60 mesh was diluted into a volume of 2 ml with quartz sand, and then the mixture 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 dichloromethane and air (moisture containing) was introduced to the catalysts, and the concentration of dichloromethane was 3000 ppm (GHSV = $15,000 \text{ h}^{-1}$). The reaction temperature was raised from R.T. to certain temperature with a heating rate of $10^\circ\text{C min}^{-1}$. After the reaction was held for 1 h at the temperature point, data analysis was conducted. The conversion of CH_2Cl_2 was analyzed by a gas chromatograph (Shimadzu, GC-14C) equipped with a FID detector. The outlet reaction mixture was neutralized by passing through a 0.1 M NaOH solution.

3. Results and discussion

3.1. Characterizations of the catalysts

Table 1 lists the physical properties of the catalysts. It can be seen that the surface areas of the catalysts are similar, except for the pure CeO_2 and 0.2Pt/ CeO_2 samples. For the CeAlO samples, the crystallite sizes of CeO_2 range from 11 to 15 nm, determined by the XRD results using the Scherrer equation. The cell parameters of these CeAlO samples slightly decrease with Ce content in the sample, with the 5CeAlO having a lattice parameter of 0.5415 nm and the 59CeAlO having a lattice parameter of 0.5412 nm (same as that of the pure CeO_2). This is due to the fact that the 5CeAlO sample has a CeO_2 crystallite size of 8.9 nm and that of the 59CeAlO sample is 14.9 nm, which causes a cell expansion because of the smaller CeO_2 particles in the 5CeAlO contain more defect sites than the larger ones. For the Pt containing catalysts, it is found that the addition of Pt in the 15CeAlO support does not change the surface area much, but significantly alters the cell parameter of CeO_2 . Note that the 0.1Pt/15CeAlO has a lattice parameter of 0.5401 nm while the 3.0Pt/59CeAlO has a lattice parameter of 0.5413 nm, which suggests that Pt species may incorporate into the CeO_2 matrix during the synthesis as the ionic radius of Pt^{2+} (0.086 nm) or Pt^{4+} (0.063 nm) is smaller than that of the Ce^{4+} (0.097 nm). Thus, the decreased cell parameter in the low Pt content samples (such as

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