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The effect of microstructural properties of $CoCr_2O_4$ spinel oxides on catalytic combustion of dichloromethane

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ABSTRACT

It was found that a series of spinel $CoCr_2O_4$ oxides were very active and selective for dichloromethane combustion, and the best performance was obtained on a catalyst calcined at 600 °C (with a areal specific reaction rate of 3.41×10^{-8} mol_{CH2Cl2} s^{-1} m^{-2} at 220 °C). Quantitative analyses revealed that Cr^{3+}/Cr^{6+} cations could partially substitute Co^{3+} cations in the octahedral sites of the spinel oxide at high-temperature calcination and thus to enhanced reducibility and surface acidity of the oxide, which synergistically governed the observed catalytic behaviors. Moreover, it was found that high valent Cr species (Cr^{6+}) played very important role in the reaction, with a much higher turnover frequency (2.2×10^{-3} s^{-1}) than that of the Cr^{3+} (0.56×10^{-3} s^{-1}).

1. Introduction

Chlorinated volatile organic compounds (CVOCs) are generated from various industrial processes such as the manufacture of herbicides, plastics and solvents. Dichloromethane (CH_2Cl_2) is a representative CVOCs, which is harmful to the respiratory system and central nervous system of human [1]. Catalytic combustion is an effective way for the abatement of CVOCs because of its advantages over thermal destruction such as lower operating temperature and higher destructive efficiency [2]. Highly efficient catalyst systems are the core of catalytic combustion of CVOCs, which mainly include supported noble metals (such as Pt and Pd) [3–6], transition metal oxides such as supported Cr-containing materials [7–17] and perovskite-type oxides [18–20], zeolites [21–25].

Cr-containing oxides are very effective for CVOCs oxidation. For example, CrO_x supported on TiO_2 was more active for the oxidation of 1,2-dichlorobenzene compared to other TiO_2-supported oxides (e.g. V_2O_5, MoO_3, Fe_2O_3, and Co_3O_4) [12]. CrO_x supported on active carbon was also active for deep oxidation of CH_2Cl_2 due to the presence of highly dispersed Cr^{6+} species on the catalyst surface [14]. However, the main disadvantages of the Cr-containing catalysts are that they usually deactivate due to the loss of active CrO_x species during the reaction, and the possible formation of toxic chromium oxychloride at low temperature [21], which could limit their potential applications.

Alternatively, structured oxides with Cr species confined in a robust matrix may overcome the disadvantages of the supported Cr catalysts. Therefore, spinel type cobalt chromite oxide ($CoCr_2O_4$) has attracted much attention in catalysis, particularly for CVOCs oxidation. For example, it was reported that the spinel type $CoCr_2O_4$ showed superior performance to other supported Cr catalysts such as CrO_x/Al_2O_3 and CrO_x/MCM-41 in total oxidation of trichloroethylene due to the presence of abundant surface Cr^{3+} species in the $CoCr_2O_4$ oxide [26]. However, quantitative analysis of the effect of microstructures on the physical/chemical properties and consequently catalytic behaviors of the spinel oxides has been rarely investigated, rendering it difficult to obtain a better understanding of this system. Therefore, in this work, detailed characterizations of the microstructures of the $CoCr_2O_4$ spinel oxide was conducted and their significant influences on the observed catalytic behaviors for CH_2Cl_2 combustion has been discussed in a quantitative manner.

2. Experimental

2.1. Catalyst preparation

The $CoCr_2O_4$ catalysts were prepared with a co-precipitation method. 50 mmol of $Co(NO_3)_3 \cdot 6H_2O$ (99.0%) and 50 mmol of $Cr(NO_3)_3 \cdot 9H_2O$ (99.0%) were dissolved in 100 ml distilled water.

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The mixture was added drop-wise to an aqueous solution containing 200 mmol of NH_4HCO_3 kept at 75 °C. After the precipitation was completed, the suspension was filtered and washed with distilled water and ethanol for 3 times, then the solid was dried at 100 °C overnight. The solid was divided to four parts, followed by calcination in static air at different temperatures (400–700 °C) for 4 h. The obtained catalysts were designated as $CoCr_2O_4$-*x*, with *x* referring to calcination temperature. Also, reference pure Co_3O_4 and Cr_2O_3 oxides were prepared by calcination of $Co(NO_3)_3 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ at 600 °C for 4 h, respectively.

2.2. Characterizations

Surface areas of the catalysts were measured by N_2 adsorption at 77 K on a Quantachrome Autosorb-1 apparatus after pretreatment at 120 °C for 6 h in vacuum. The contents of Co and Cr in the catalysts were determined by X-ray fluorescence (XRF) analysis (ARL ADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer). X-ray diffraction (XRD) patterns were recorded with a PANalytical XíPert PRO MPD powder diffractometer using Cu Kα radiation, operated at 40 kV and 40 mA. Crystallite sizes and lattice parameters of the catalysts were analyzed using a JADE 6.5 software. High resolution transmission electron microscopy (HRTEM) was performed on a JEM-2100F microscopy operated at 200 kV.

Reducibility of the catalyst was measured by hydrogen temperature-programmed reduction (H_2-TPR). 25 mg of the catalyst was placed in a quartz reactor and pretreated in a O_2 flow (20 ml min^{-1}) at 300 °C for 1 h, then it was cooled down to 50 °C. The sample was heated from 50 to 900 °C with a 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), and the H_2 consumption was calibrated by the reduction of a known CuO powder sample.

The surface acidity of the catalyst was measured by ammonia temperature programmed desorption (NH_3-TPD). 50 mg of the catalyst was pretreated in a flow of N_2 at 300 °C for 0.5 h, and then was cooled down to 40 °C. Afterwards, a NH_3 flow (20 ml min^{-1}) was introduced to the sample for 15 min, followed by purging at 80 °C for 0.5 h with a N_2 flow. Then the sample was heated from 40 to 600 °C at a rate of 10 °C min^{-1}, and the profile was recorded using a gas chromatograph with a TCD detector.

The oxidation states of the samples were analyzed by X-ray photoelectron spectra on an ESCALAB 250Xi instrument with a Al Kα X-ray source (1486.6 eV). The binding energy (BE) of C1s core level at 284.8 eV was taken as the internal standard.

Temperature-programmed surface reaction (TPSR) 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 air (20 ml min^{-1}) at 300 °C for 0.5 h, and then was cooled down to 50 °C. A flow of CH_2Cl_2/air mixture (20 ml min^{-1}, 3000 ppm CH_2Cl_2) was introduced to the reactor and the sample was heated from 50 to 400 °C at a rate of 10 °C min^{-1}. And m/e signals of 70, 44, 18, 36.5, 50.5 and 30 were monitored, corresponding to Cl_2, CO_2, H_2O, HCl, CH_3Cl and HCHO, respectively. Also, the effluent gas was first passed through a $CaCl_2$ filter to remove H_2O, in order to prevent the possible damage of the MS.

The CH_2Cl_2 chemisorption experiments were measured by break-through curves. 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 200 °C. Then a flow of CH_2Cl_2/He mixture (total flow rate = 20 ml min^{-1}, CH_2Cl_2 concentration = 3000 ppm) was introduced to the reactor. Meanwhile, the outlet CH_2Cl_2 signal was monitored by a MS (Qic-20 Benchtop, HidenAnalytical) with a m/e = 97 (CH_2Cl_2). The amount of chemisorbed CH_2Cl_2 could be calculated based on the profile. Dead volume of the apparatus was also subtracted by running a blank test with the same volume of quartz sand.

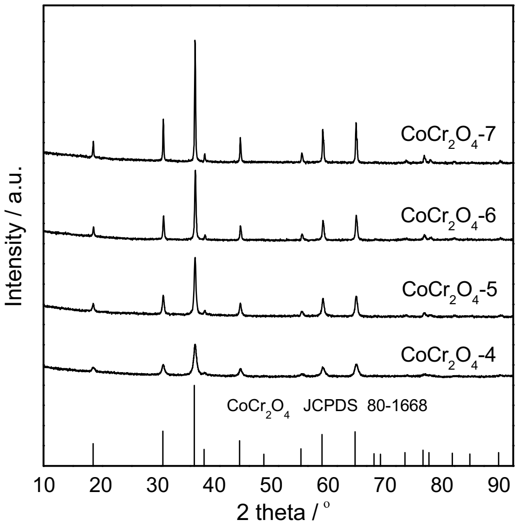

Fig. 1. XRD patterns of various catalysts.

2.3. Activity test

Catalytic test was performed in a fixed-bed reactor (i.d. = 9 mm), loaded with 1.0 g catalyst in 40–60 mesh diluted to 2 ml with quartz sand. The CH_2Cl_2 was introduced to the reactor via passing moisture-containing air through a quartz beaker containing liquid CH_2Cl_2 kept at 0 °C. The reaction conditions were as follows: Concentration of CH_2Cl_2 was 3000 ppm; water vapor concentration was 12,000 ppm; total flow rate was 500 ml min^{-1}; space velocity was 15000 h^{-1}. 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 aqueous solution.

Conversion of CH_2Cl_2 was calculated as follows:

$$X_{CH_2Cl_2} = \frac{[CH_2Cl_2]_{in}\text{vol.\%} - [CH_2Cl_2]_{out}\text{vol.\%}}{[CH_2Cl_2]_{in}\text{vol.\%}}$$

where $[CH_2Cl_2]_{in}$ and $[CH_2Cl_2]_{out}$ were the CH_2Cl_2 concentrations in the inlet and outlet gas (vol.%), respectively.

The kinetic study was performed on the same reactor for catalytic test. The CH_2Cl_2 conversion was less than 15% to ensure a differential reaction mode and the reaction conditions were the same as in the catalytic test. Also, the absence of mass transport resistances and hear transfer was guaranteed by evaluation with Weisz-Prater criterion and Mears' criterion, respectively [27].

3. Results

3.1. Catalyst characterizations

Table 1 shows that the surface area of the catalyst gradually declines due to the sintering of crystallites under high temperature. The actual contents of Co and Cr in the catalysts are 24.2 and 40.6 wt.%, respectively, which corresponds to a Co/Cr molar ratio of 0.52.

The XRD patterns of the catalysts (Fig. 1) perfectly match the standard diffractions of spinel $CoCr_2O_4$ (JCPDS 80-1668). No diffractions of CoO_x or CrO_x could be detected, indicating that either the absence of such species or highly dispersed CoO_x or CrO_x in the catalysts. The $CoCr_2O_4$-4 has a crystallite size of 14.8 nm (Table 1), which is much lower than that of the $CoCr_2O_4$-7 (41.3 nm).