

Bifunctional Pd/Cr₂O₃–ZrO₂ Catalyst for the Oxidation of Volatile Organic Compounds

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ABSTRACT: This study focuses on developing a catalyst for the removal of volatile organic compounds (VOCs) accompanied chlorinated volatile organic compounds (CVOCs). By a combination of deposition–precipitation and impregnation methods, a Pd/Cr₂O₃–ZrO₂ catalyst was prepared and tested for catalytic oxidation of dichloromethane, ethyl acetate, and toluene. It was found that the Pd/Cr₂O₃–ZrO₂ catalyst are very active for the catalytic oxidation of all these three different organics, due to the bifunctional catalysis of Pd and Cr. By comparing the catalytic performance of Cr₂O₃–ZrO₂, Pd/ZrO₂, and Pd/Cr₂O₃–ZrO₂ catalysts, it suggested that the Cr species are more active for dichloromethane and ethyl acetate oxidation, while the Pd species play a very important role in toluene oxidation.

INTRODUCTION

Volatile organic compounds (VOCs) are mainly generated from industrial processes and transportation activities, including a wide range of compounds such as oxygenates, aromatic and chlorinated volatile organic compounds (CVOCs).¹ VOCs are hazardous to the environment and human health and their emission is restricted by increasing stringent regulations.² Catalytic oxidation is regarded as one of the most promising techniques for the abatement of VOCs.³ Generally, supported noble metals catalysts such as Pd and Pt^{4–8} as well as transition-metal oxides catalysts such as Mn and Cu^{9,10} are employed for the catalytic oxidation of VOCs. Noble metal catalysts usually show good activity for the catalytic oxidation of hydrocarbons. However, these catalysts with only a single-component suffer severe deactivation in the presence of chlorine, and thus are less active for the oxidation of chlorinated organics.^{11–13} On the other hand, transition metal oxides such as chromium-based catalysts are effective for the catalytic oxidation of oxygenated compounds and especially chlorinated hydrocarbon,^{14–17} while they are inactive for the oxidation of hydrocarbons oxidations.¹⁸ Regarding the fact that the compounds emitted from chemical processes usually contain a mixture of VOCs and CVOCs, effective catalyst system for the oxidation of both VOCs and CVOCs is much desirable. Unfortunately, such system is rarely reported in literature. Therefore, in this paper, a bifunctional Pd/Cr₂O₃–ZrO₂ catalyst was synthesized and tested for oxidation of toluene, ethyl acetate, and dichloromethane as the model VOCs and CVOCs, and the correlation between the catalyst characteristics and the catalytic behavior was discussed.

EXPERIMENTAL SECTION

Catalyst Preparation. The Cr₂O₃–ZrO₂ support was prepared by a deposition–precipitation method. In a typical preparation, an aqueous solution of Cr(NO₃)₃·9H₂O was mixed with ZrO₂ powder (phase composition, SBET = 30 m² g^{−1}). Then an aqueous solution of (NH₄)₂CO₃ (1 M) was dropwise

added to the mixture under vigorous stirring. The pH value of the suspension was controlled at 8.0 ± 0.5. The resulting precipitation slurry was aged for 2 h and separated by centrifugation from the mother liquor, washed several times with deionized water and then dried overnight at 120 °C. Supported Pd catalysts were prepared by impregnating the ZrO₂ or Cr₂O₃–ZrO₂ support with an aqueous solution of H₂PdCl₄, and the nominal Pd content in the catalyst was 0.5 wt %. The excess solution was removed by mild evaporation and the sample was dried overnight at 120 °C. Finally, the dried sample were calcined at 600 °C for 4 h with a heating rate of 10 °C min^{−1}. The resulting catalysts Cr₂O₃–ZrO₂, Pd/ZrO₂, and Pd/Cr₂O₃–ZrO₂ were denoted as CrZr, Pd/Zr, and Pd/CrZr, respectively. The Cr content in the catalyst was 21 wt %, as determined by X-ray fluorescence (XRF) analysis.

Characterizations. X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert PRO MPD powder diffractometer using Cu Kα 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 80°, with a scanning rate of 0.33° min^{−1}.

Specific surface areas (S_{BET}) of the catalysts were calculated from a multipoint Braunauer–Emmett–Teller (BET) analysis of the nitrogen adsorption and desorption isotherms at 77 K recorded on an Autosorb-1 apparatus.

Elemental compositions of the catalysts were determined by X-ray fluorescence (XRF) analysis, in an ARL ADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer. The results were analyzed using UniQuant nonstandard sample quantitative analysis software.

The reduction properties of the catalysts were measured by H₂ temperature-programmed reduction (H₂-TPR). A 25 mg portion of catalyst was placed in a quartz reactor and heated from 50

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to 600 °C with a heating rate of 10 °C min⁻¹, in a gas mixture (5% H₂ in N₂, 30 mL min⁻¹). The amount of H₂ consumption was determined by a gas chromatograph with a TCD detector, calibrated by the reduction of a known amount of CuO powder.

The acidic properties of the catalysts were studied by ammonia temperature programmed desorption (NH₃-TPD), on a home-made apparatus. A 50 mg portion of the catalyst was placed in a tubular quartz reactor and pretreated in a flow of N₂ (20 mL min⁻¹) at 550 °C for 0.5 h, and then cooled down to room temperature. After that, a flow of NH₃ (20 mL min⁻¹) was introduced to the reactor for 15 min, followed by purging at 100 °C for 1 h with a N₂ flow (20 mL min⁻¹) to remove the physisorbed NH₃. Then the sample was heated from 100 to 600 °C at a rate of 20 °C min⁻¹. The signal was continuously monitored by a TECHTEMP GC 7890 II gas chromatograph equipped with a thermal conductivity detector (TCD).

Catalytic Testing. Catalytic oxidation reaction was carried out in a quartz tubular fixed-bed reactor (i.d. = 9 mm). A 2.5 g portion of the catalyst (20–40 mesh) was used for the reaction. For the oxidation of a single component, a gas mixture of the reactant and

air with a total flow rate of 0.03 m³ h⁻¹ was introduced to the catalyst. The concentration of dichloromethane was 3000 ppm (GHSV = 20 000 h⁻¹), and that of toluene and ethyl acetate were 1000 and 1500 ppm, respectively. For the oxidation of multi-components, the concentration of dichloromethane was one-third of the single VOCs (1000 ppm), that of toluene and ethyl acetate were 330 and 500 ppm, respectively, and the GHSV was 20 000 h⁻¹. The products were analyzed by a GC (GC-14C, Shimadzu) equipped with a flame ionization detector (FID).

RESULTS AND DISCUSSION

Figure 1 shows the catalytic oxidation of single component VOC over the CrZr, Pd/Zr, and Pd/CrZr catalysts. For the oxidation of dichloromethane and ethyl acetate, the Cr-containing catalyst (CrZr) is more active than the Pd/Zr catalyst. For example, the conversions of dichloromethane over CrZr and Pd/Zr catalysts at 330 °C are 79 and 7%, and that of ethyl acetate at 210 °C are 40 and 13%, respectively. For the oxidation of toluene, the Pd/Zr catalyst is more active than the CrZr catalyst, the conversion of toluene at 210 °C over the two catalysts are 81 and 7%, respectively. The dual-component Pd/CrZr catalyst exhibits the highest activity for catalytic oxidation of these three VOCs. It could be concluded that the Cr species are more active for the dichloromethane and ethyl acetate oxidation, and the Pd species in the catalyst play a very important role in catalytic oxidation of toluene. Moreover, the Pd/CrZr catalyst remarkably promotes the oxidations of the three different VOCs, implying that it possesses a bifunctional property to the catalytic oxidations of both VOCs and CVOCs.

Generally, catalytic oxidation of chlorinated and oxygenated VOCs usually leads to the formation of byproducts. In this work, for the oxidations of ethyl acetate and dichloromethane over the CrZr catalyst, the main byproducts are ethanol and CO, respectively. However, for the oxidations over the Pd/Zr and Pd/CrZr catalysts, the reaction products are only CO₂, probably because the byproducts could be easily further oxidized to CO₂ in the presence of Pd. Figure 2 shows the oxidation of dichloromethane and ethyl acetate over the CrZr catalyst. It can be seen that for both reactants, with increasing reaction temperature, the reactant conversion and selectivity to CO₂ increase, accompanied by a decline in the selectivity to CO or ethanol.

To further investigate the bifunctionality of the Pd/CrZr catalyst, the catalytic activities for the single VOC and the mixture are compared, and the results are shown in Figure 3. For the oxidation of toluene and ethyl acetate, the required

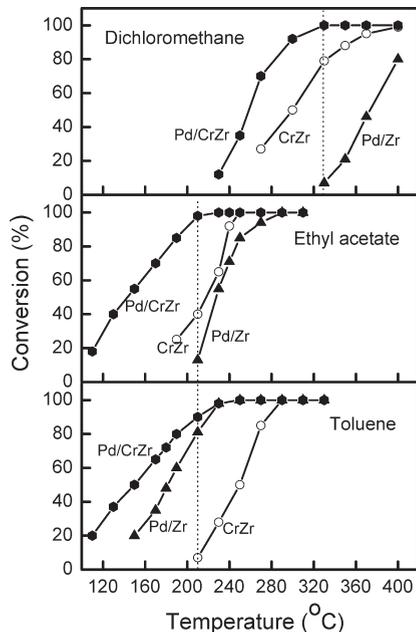


Figure 1. Catalytic oxidation of VOCs over CrZr, Pd/Zr, and Pd/CrZr catalysts.

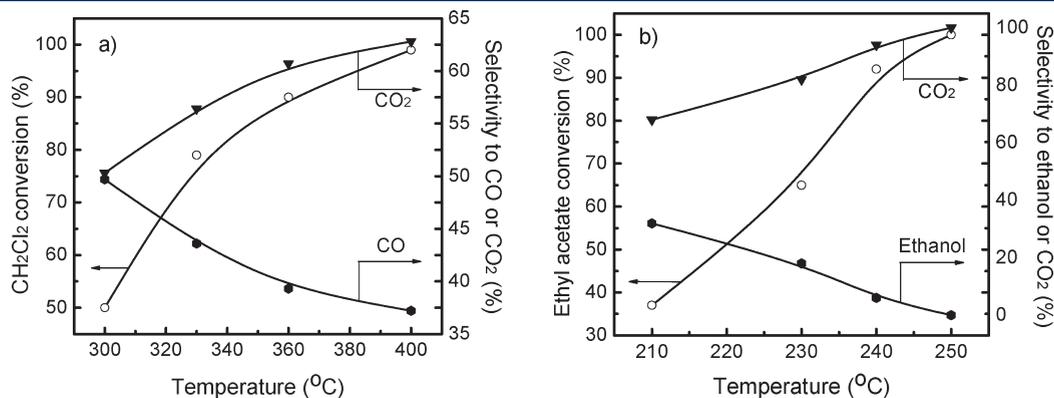


Figure 2. Catalytic oxidation of (a) dichloromethane and (b) ethyl acetate over CrZr catalyst.

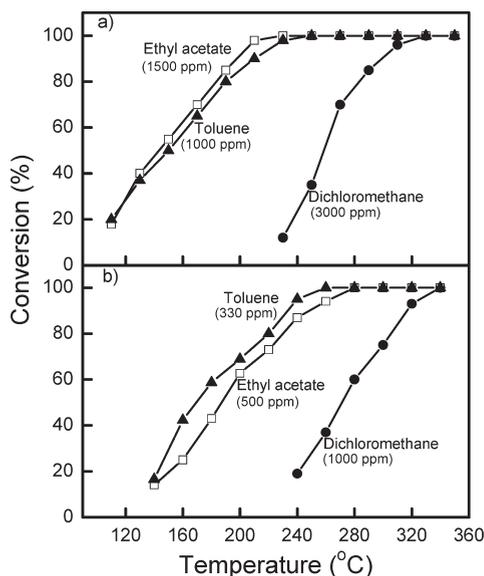


Figure 3. Catalytic oxidation of VOCs over Pd/CrZr catalyst, (a) single reactant, (b) mixture reactant.

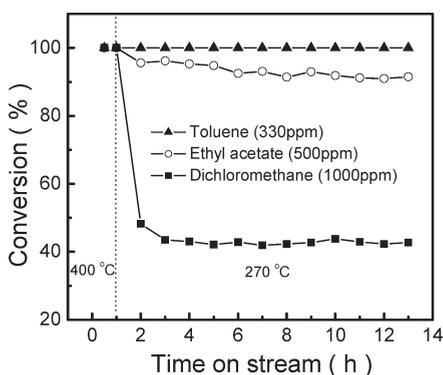


Figure 4. Catalytic oxidation of VOCs mixture over Pd/CrZr catalyst with time on stream at 270 °C, GHSV = 20 000 h⁻¹.

reaction temperatures for the mixture are obviously higher than that for the single reactant. However, for the dichloromethane oxidation, the required reaction temperature is only slightly higher than that for the single one. This implies that the oxidation of toluene and ethyl acetate in the mixture are remarkably inhibited while that of dichloromethane is hardly affected. Similar results were also reported by Wang *et al.*¹⁹ This makes the Pd/CrZr catalyst very promising for VOCs oxidation, because dichloromethane is the most difficult to be oxidized; once it is completely oxidized, the removal of toluene and ethyl acetate could be readily accomplished.

Figure 4 shows the stability of the Pd/CrZr catalyst for oxidation of toluene, ethyl acetate, and dichloromethane mixture. The reaction temperature was kept at 400 °C for 1 h under reaction conditions, and then declined to 270 °C, in order to stabilize the catalyst. It can be seen that full conversion of each reactant is obtained at 400 °C, and during the 12 h continuous reaction at 270 °C, the conversions of the three reactants have no obvious changes, implying a good stability of this catalyst.

Figure 5 shows the XRD patterns of the CrZr, Pd/Zr, and Pd/CrZr catalysts. For the pure ZrO₂ and Pd/Zr, only diffraction

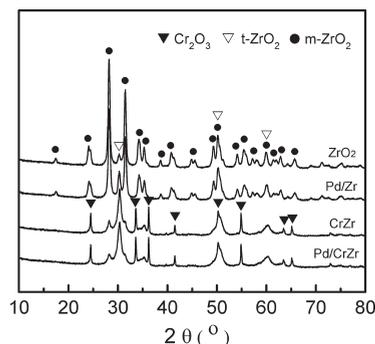


Figure 5. XRD patterns of CrZr, Pd/Zr, and Pd/CrZr catalysts.

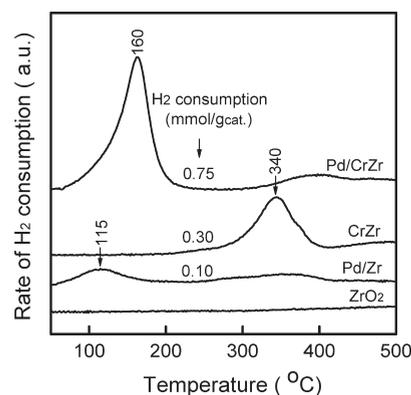


Figure 6. H₂-TPR profiles of CrZr, Pd/Zr and Pd/CrZr catalysts.

peaks due to monoclinic and tetragonal ZrO₂ phase are observed. The absence of the diffraction lines of Pd species implies that the Pd species in the Pd/Zr catalyst are highly dispersed. However, when Cr is added to the catalysts, diffraction peaks due to crystalline Cr₂O₃ appear, together with enhanced diffraction peaks of tetragonal ZrO₂ and weakened peaks of monoclinic ZrO₂ phase. It indicates that the addition of Cr inhibits the transformation of tetragonal ZrO₂ to monoclinic phase and favors the formation of tetragonal ZrO₂.

Figure 6 shows the H₂-TPR profiles of CrZr, Pd/Zr, and Pd/CrZr catalysts, along with the amount of H₂ consumptions calibrated by the quantitative reduction of CuO also given. For the ZrO₂ support, no reduction peak is observed from 50 to 500 °C. For the Pd/Zr catalyst, the profile is featured by a main reduction peak at 115 °C, which is related to the easily reducible PdO.⁴ When Cr species are added to ZrO₂, the CrZr catalyst exhibits a peak at 340 °C, which is assigned to the reduction of high oxidation state Cr species to crystalline Cr₂O₃, as Cr₂O₃ could not be reduced in the temperature range of 50–500 °C.^{20,21} For Pd/CrZr catalyst, an intensive peak at about 160 °C is observed, which could be assigned to the reduction of PdO and CrOx species. Compared with the CrZr catalyst, the reduction of the Cr species in the Pd/CrZr catalyst shifts to lower temperature because of the effect of H-spillover on Pd catalysts,²² and the reductions of PdO and CrOx are overlapped. Moreover, the peak area of Pd/CrZr catalyst increases dramatically, and the amount of H₂ consumption (0.75 mmol/g_{cat.}) is much larger than the total H₂ consumption (0.40 mmol/g_{cat.}) of the Cr/Zr and Pd/Zr catalysts, which may be attributed to the presence of Pd species that probably favors the formation of the high oxidation state Cr species in the catalyst. This

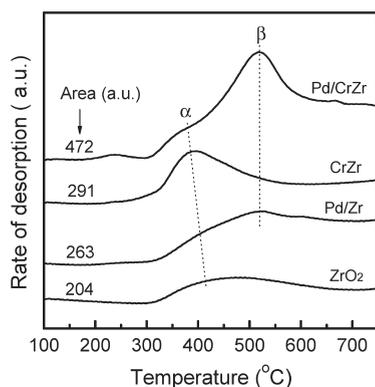


Figure 7. NH_3 -TPD profiles of CrZr, Pd/Zr and Pd/CrZr catalysts.

might be one of the reasons that the activity of Pd/CrZr catalyst is higher than that of CrZr and Pd/Zr catalysts.

Figure 7 shows the NH_3 -TPD profiles of the CrZr, Pd/Zr, and Pd/CrZr catalysts, along with peak areas also given. For all catalysts, there are NH_3 desorption peaks (α) at about 400 °C. However, desorption peaks (β) at higher temperatures (about 520 °C) are observed only for Pd/Zr and Pd/CrZr catalysts. This indicates that the introduction of Pd precursor (H_2PdCl_4) enhances the acid strength of the catalyst. Moreover, it is found that for the Pd/CrZr catalyst, the peak area of NH_3 desorption is much larger than that for the Pd/Zr catalyst, implying that there are more surface acidic sites in the Pd/CrZr catalyst. These results indicate that the Pd/CrZr catalyst possesses the strongest acid strength and the highest amount of surface acidic sites, which are favorable for the adsorption and disassociation of dichloromethane²³ and this could be related to the higher catalytic activity.

Based on the H_2 -TPR and NH_3 -TPD results, it can be concluded that the Pd/CrZr catalyst possesses the highest reducibility and acidity, which may lead to the highest activity of the catalyst.

CONCLUSIONS

It is found that the bifunctional Pd/Cr₂O₃–ZrO₂ catalyst is very active for the catalytic oxidation of both VOCs (ethyl acetate and toluene) and CVOCs (dichloromethane). More importantly, the catalyst is quite stable during the reaction. The Cr species are more active for the dichloromethane and ethyl acetate oxidation, and the Pd species play a very important role in toluene. The H_2 -TPR and NH_3 -TPD results show that the Pd/Cr₂O₃–ZrO₂ catalyst has higher reducibility and acidity, which may be favorable for the enhanced reactivity.

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