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The nature of low temperature deactivation of $CoCr_2O_4$ and $CrO_x/\gamma\text{-}Al_2O_3$ catalysts for the oxidative decomposition of trichloroethylene

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Abstract

The $CoCr_2O_4$ and $CrO_x/\gamma\text{-}Al_2O_3$ catalysts were used for the oxidative decomposition of trichloroethylene (TCE). Both catalysts showed an initial deactivation at low temperatures around 280 °C, mainly due to the dissociative adsorption of reactant TCE. This was confirmed by the temperature programmed oxidation of TCE where the carbon oxides were formed up to a temperature below 300 °C. Possible changes in the oxidation state of chromium species were observed with XANES and ESR. During the oxidation reaction at low temperatures, the Cr(VI) species were reduced to Cr(III) species, which seemed to be coupled with TCE adsorption. At higher temperatures, however, the Cr(VI) species appeared again and the catalytic activity was completely recovered.

Keywords: Spinel-type oxides; Cobalt chromite; VOC; TCE; Dissociative adsorption

1. Introduction

Catalyst deactivation has been identified as one of the most serious problems associated with the commercial application of catalysts for the decomposition of chlorinated volatile organic compounds (CVOC) [1]. Even though the higher resistance to poisoning of transition metal oxides in comparison with the noble metal catalysts are believed mainly due to their higher active surface area, the nature of deactivation in metal oxides has yet to be elucidated.

Several factors have been considered as the origins of this deactivation with transition metal oxide catalysts. It was suggested that chlorine (Cl_2), produced by the Deacon reaction during CVOC oxidation can cause chlorination and hence deactivation of the transition metal oxide catalysts as in the case of noble metals. Therefore, catalysts that are less efficient for the Deacon reaction would be more suitable for chlorocarbon oxidation. Addition of water to the reactants has also been found to inhibit the Deacon reaction and thus improve the catalyst stability by preventing direct chlorination [2]. Another mechanism of the deactivation is the poisoning by coke deposition [3–6]. For the oxidation of trichloroethylene (TCE) over acidic zeolite catalysts, it was found that there was a large amount of coke deposit [4]. Imamura et al. [6] reported that the oxidative decomposition of 1,2-dichloroethane on zeolite Y resulted in the deposits of carbonaceous compounds which seemed to deactivate zeolite Y.

Kim and Ihm [7,8] reported that the supported chromium and spinel-type chromites catalysts showed

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good activities for the decomposition of TCE. Even though the Cr(VI) species are believed to be active in $CrO_x/\gamma\text{-}Al_2O_3$ catalysts [9,10], the active sites of $CoCr_2O_4$ catalyst should be further elucidated. Both catalysts, however, showed significant drop of their activity during the first few hours. This deactivation was more pronounced for the reactions at low temperatures. Causes of this deactivation were discussed through temperature programmed oxidation experiments. The effect of reaction temperatures on the low temperature deactivation was discussed in view of the change in the oxidation state of supported chromium species.

2. Experimental

Mixed oxides of Cr and Co were prepared by coprecipitation at pH 8. The precipitation was accomplished by adding dropwise the co-solution of metal nitrates with desired proportions of ammonium hydroxide at room temperature under continuous stirring. The filtered precipitate was dried and calcined at 600 °C for 5 h to prepare the spinel-type $CoCr_2O_4$ catalyst [8]. $CrO_x/\gamma\text{-}Al_2O_3$ samples with 9 wt.% of Cr were prepared by incipient wetness impregnation of $\gamma\text{-}Al_2O_3$ (Aldrich) using the corresponding nitrate salts as precursors. Physical properties and XRD analysis of catalysts are summarized in Table 1.

The surface area was measured by the nitrogen BET method with a Micromeritics ASAP 2000. The crystal structures of catalysts were confirmed by powder X-ray diffraction pattern using Cu Kα radiation. The X-ray absorption spectroscopy measurement was carried out above Cr K-edge at room temperature using Beamline 3C1 at Pohang Light Source. The ESR spectra were recorded on a Bruker EMX 1113 spectrometer operating at a cavity resonance frequency of 9.76 GHz. The curves of the first derivative were obtained and their relative intensities were compared by the graphical integration. Also DPPH was used as reference to calibrate the *g*-value. All spectra were obtained at room temperature.

The activity of the catalysts in oxidative decomposition of TCE was measured in a fixed bed apparatus at the temperatures between 280 and 340 °C. The reaction feed mixture contained 800 ppm of TCE and 10,000 ppm of H_2O with balance air. The weight hourly space velocity (WHSV) was 78 l/g-cat h.

The TPO experiments were carried out in a microreactor coupled to a quadrupole mass spectrometer (Balzers QMS422). A 0.5 g of a sample was pretreated in a stream of O_2 (10%)/He at 500 °C for 1 h, and cooled down to 200 °C. The sample was flushed with He for 15 min, and TCE (1%) was introduced at 200 °C for 30 min. After the additional cooling down to 100 °C, the TPO was performed from 100 to 600 °C in a stream of O_2 (10%)/He (100 ml/min at 5 °C/min).

3. Results and discussion

Both $CoCr_2O_4$ and $CrO_x/\gamma\text{-}Al_2O_3$ catalysts showed obvious deactivation during the first few hours of the reaction especially at lower temperatures (Fig. 1). It was observed that there was no significant deactivation at higher temperatures, which was confirmed through stable catalytic activity at a lower conversion which was achieved with higher space velocity. A distinct color change from brown to blue after the reaction at 300 °C for supported catalysts suggested that there should be some change in the catalyst structure. It can be seen that $CoCr_2O_4$ showed higher activity as reported previously by the authors [8]. The CO_2 selectivity was found to remain almost constant.

The oxidation state of chromium species has been considered as one of the most important properties for determining their catalytic activity. The Cr(VI) species has been considered as active centers of supported CrO_x catalysts [9,10], while the nature of

Table 1
Physical properties of prepared catalysts

Catalyst	Chromium content (wt.%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	Bulk structure (XRD)
$CoCr_2O_4$	46	53	0.14	150	Spinel
CrO_x/Al_2O_3	9	203	0.39	58	γ-Alumina

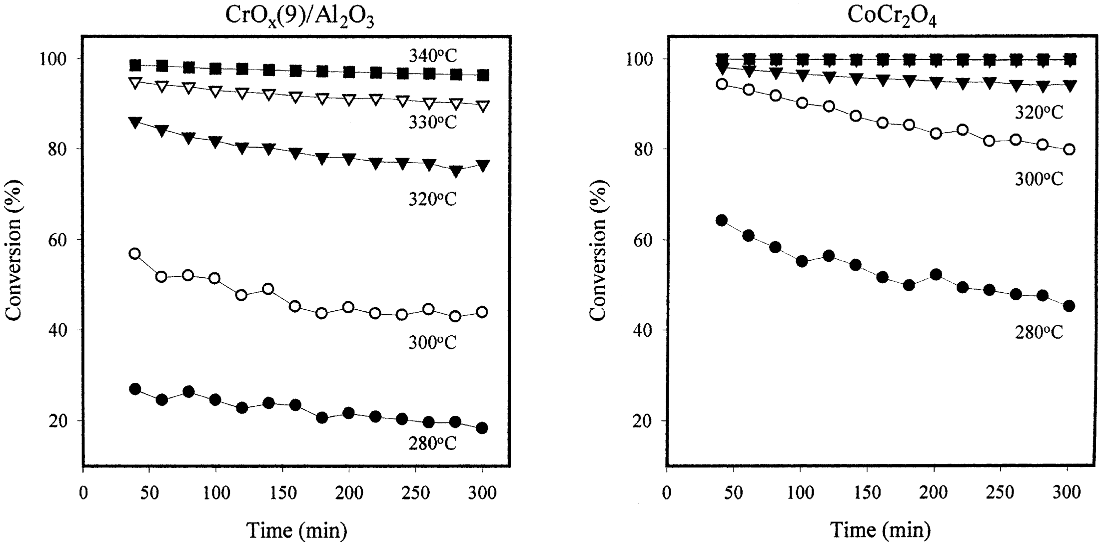

Fig. 1. Catalytic activity of Cr-containing catalysts for the decomposition of TCE with time-on-stream (800 ppm TCE; 10,000 ppm H_2O; WHSV: 78 l/g-cat h).

active species of $CoCr_2O_4$ should be further elucidated even though the presence of Cr(III)–Cr(VI) pair sites may explain its reactivity [8]. The change of oxidation state of Cr-containing catalyst was followed by XANES and ESR.

Fig. 2 shows the X-ray absorption near edge spectra of Cr-containing reference materials. K-edge Cr spectrum of Na_2CrO_4 having Cr(VI) shows the obvious pre-edge peak at approximately 5992 eV, which is absent for Cr metal foil and Cr_2O_3 whose oxidation states of chromium are 0 and +3, respectively. The pre-edge 1s → 3d transition is strictly electric-dipole forbidden for Cr_2O_3, which contains symmetrical CrO_6 octahedra with an inversion center. Lowering the symmetry to T_d or less, as occurs in $Na_2Cr_2O_7$ and CrO_3, allows stronger 3d–4p(metal) and 3d(metal)–2p(ligand) orbital mixing to occur, relaxing the selection rule [11].

X-ray absorption near edge spectra of CrO_x/γ-Al_2O_3 were obtained before and after the reaction at 280 and 340 °C (Fig. 3). The pre-edge peak representing Cr(VI) species disappeared almost completely after the reaction at 280 °C, but it appeared during the reaction at 340 °C. This implies that the geometrical structure of chromium was changed from tetrahedral shape to the highly symmetrical structure such as octahedral Cr(III) during the reaction at 280 °C.

Formation of Cr(III) was also observed from the room temperature electron spin resonance spectra

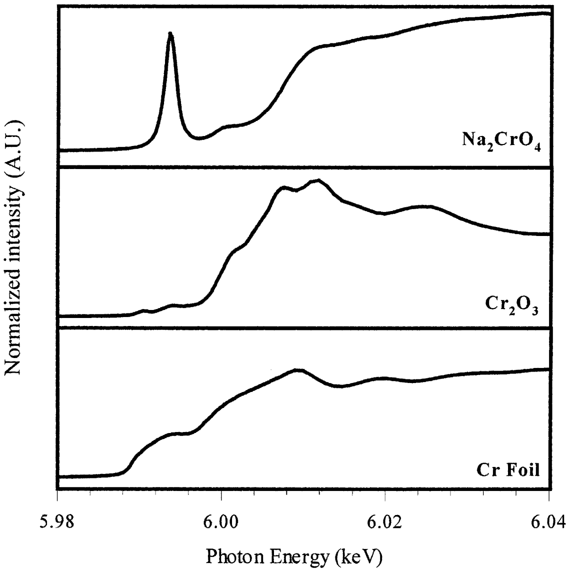

Fig. 2. X-ray absorption near edge spectra of Cr-containing reference materials.

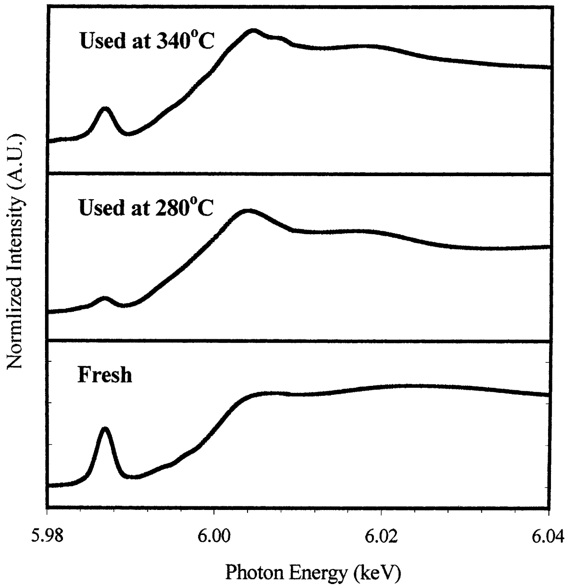

Fig. 3. X-ray absorption near edge spectra of $CrO_x(9)/Al_2O_3$ catalysts.

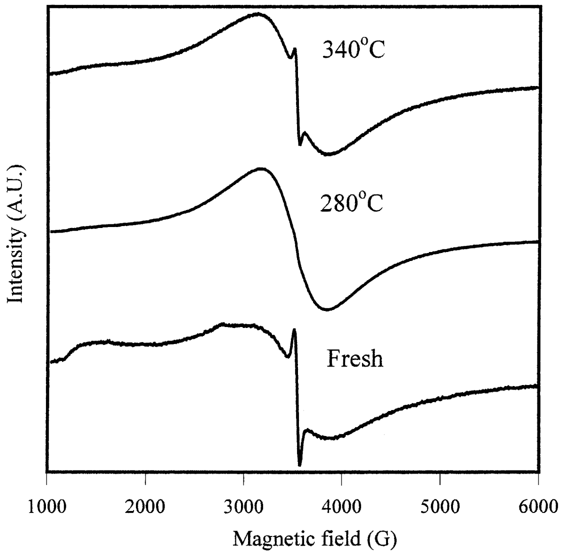

Fig. 4. Electron spin resonance spectra of $CrO_x(9)/Al_2O_3$ catalysts at 25 °C.

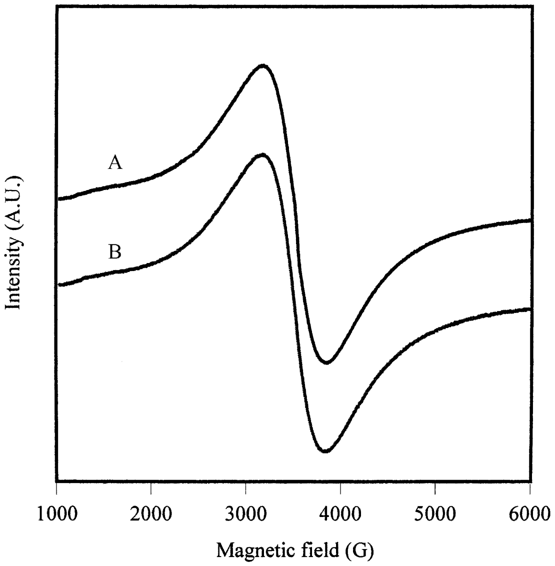

Fig. 5. Electron spin resonance spectra of $CrO_x(9)/Al_2O_3$ at 25 °C: (A) after 80 h reaction at 280 °C; (B) after CO chemisorption at 280 °C.

of CrO_x/γ-Al_2O_3 as shown in Fig. 4. Fresh catalysts showed the γ phase signal representing high oxidation state chromium. After the reactions at 280 °C, the spectra showed only the β phase signal indicating the formation of reduced species. Catalysts used at 340 °C maintained their γ phase signal, which was consistent with the temperature effect in the XANES analysis of Fig. 3. Fig. 5 shows the room temperature electron spin resonance spectra of CrO_x/Al_2O_3, comparing the catalysts used for 80 h at 280 °C and the fresh catalysts with CO chemisorbed at 280 °C. The spectra observed from the two catalysts were almost the same, and this suggested that the chemisorption of reducing molecule would be one of the possible mechanisms for the structural change.

Even if there was no observable difference in the spectroscopic data of $CoCr_2O_4$ whose dominant surface Cr species is Cr(III), similar change is expected to take place on the surface $CoCr_2O_4$. For $CoCr_2O_4$ catalysts, the dominant surface chromium species are Cr(III) (about 66%) while their surface Cr(VI) species are very stable under reducing environments [8]. Our speculation, however, is that there should be similar redox couples of Cr(III)/Cr(VI) due to different reaction temperature in TCE oxidation.

Fig. 6 is the TPO results of $CoCr_2O_4$ and CrO_x/γ-Al_2O_3 after the oxidation of TCE at 280 and 340 °C. Catalysts used at 280 °C showed a desorption peak

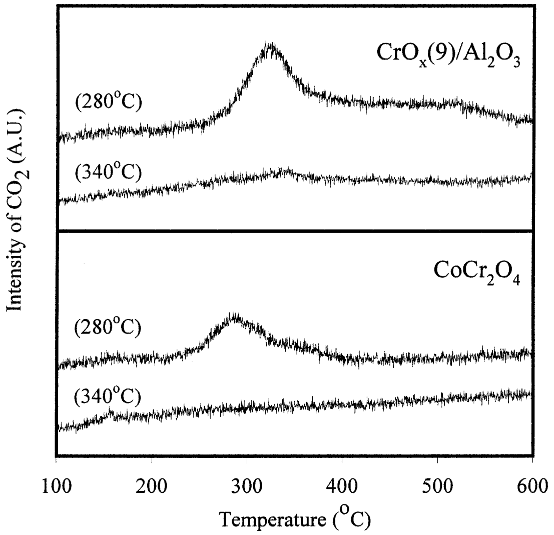

Fig. 6. CO_2 evolution during temperature programmed oxidation of TCE over the $CoCr_2O_4$ and CrO_x/Al_2O_3 catalysts used for the reaction at 280 and 340 °C, respectively.

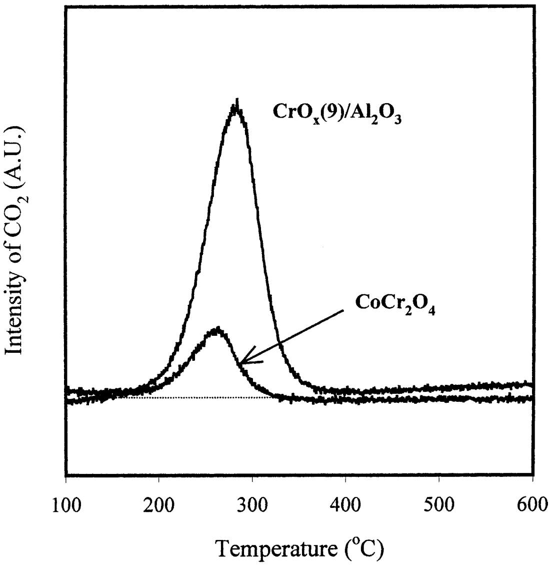

Fig. 7. Evolution of CO_2 during the TPO of the $CoCr_2O_4$ and CrO_x/Al_2O_3 catalysts after the adsorption of TCE at 200 °C.

at 300 °C while the catalysts used at 340 °C showed no desorption peak. To explain the initial deactivation (decrease of catalytic activity exhibited during the first few hours after the reaction started), it was assumed that the initial deactivation of chromium oxide catalysts were caused by the dissociative adsorption of TCE on the active sites, which could not be easily re-oxidized or hydrolyzed at the temperatures below 300 °C. The first step in catalytic oxidation of TCE seemed to be fast but to form less reactive intermediates, which were oxidized at much slower rates than TCE.

Fig. 7 is the results of temperature programmed oxidation of $CoCr_2O_4$ and $CrO_x/\gamma\text{-}Al_2O_3$ after the adsorption of TCE at 200 °C following the signal of carbon oxides. The almost same spectra were obtained from the results of CO and CO_2 even if there was a large difference in the desorption amount of carbon oxides between $CrO_x/\gamma\text{-}Al_2O_3$ and $CoCr_2O_4$. This difference in the amount of desorbed carbon oxides must be mainly due to the large adsorptive capacity of alumina support in $CrO_x/\gamma\text{-}Al_2O_3$ for TCE. It should be pointed out that temperature higher than 300 °C is to be required for the complete desorption of carbon oxides in all cases. Similar results were reported by Grzybowska et al. [12] in their work on the temperature programmed experiments of chromium oxides for the oxidation of hydrocarbons. These desorption peak around 300 °C could be another supporting evidence of the previous assumption that the active sites with reduced Cr(III) species could not be rapidly re-oxidized or hydrolyzed to make active species at low temperatures below 300 °C.

It was expected that the initial deactivation would not be observed if the reaction experiments were carried out at higher temperatures beyond 300 °C. Slight decrease of activity was, however, observed during the catalytic oxidation of TCE when the experiments were carried out at 320 and 330 °C as shown in Fig. 1. This deactivation at higher temperature (slight decrease of catalytic activity exhibited during the first few hours after the reaction started) was ascribed to the adsorption of HCl on the surface of catalyst. The complete desorption of HCl required higher temperature than that of carbon oxides as indicated by the long tail in their spectra in Fig. 8. It should be noted that the difference in the desorption peak temperatures between carbon oxides and HCl was more significant in the case of supported chromium catalysts than in the case of $CoCr_2O_4$ whose desorption of HCl could be completed until up to a higher temperatures far beyond 400 °C.

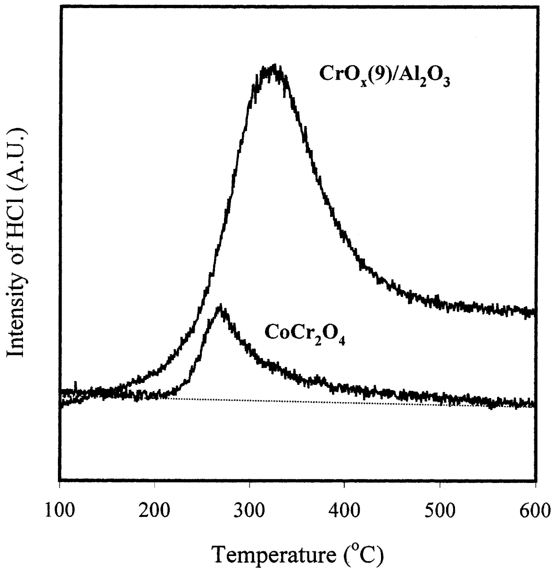

Fig. 8. Evolution of HCl during the TPO of the $CoCr_2O_4$ and CrO_x/Al_2O_3 catalysts after the adsorption of TCE at 200 °C.

4. Conclusion

Both $CoCr_2O_4$ and alumina supported catalysts experienced significant deactivation during the first few hours with distinct color change from brown to blue after the reaction at 280 °C. Spectroscopic investigation revealed that the active Cr(VI) species of the catalysts were reduced at 280 °C. The initial deactivation of supported chromium oxide catalysts were caused by the dissociative adsorption of reactants on the active sites, which could not be regenerated easily at lower temperatures around 280 °C. The reduced Cr(III) species seemed to be coupled with dissociative adsorption of TCE.

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