크롬 촉매를 이용한 트리클로로에틸렌의 산화분해반응

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Oxidative Decomposition of Trichloroethylene over Cr-containing Catalysts

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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 organic compounds [1]. Kim and Ihm [2,3] have reported the high activity of supported chromium catalysts and spinel-type chromites for the decomposition of trichloroethylene (TCE). But these catalysts showed significant drop of their activity in the first few hours. This deactivation was more pronounced for the reactions at low temperatures. Causes of this deactivation were discussed by temperature programmed oxidation experiments.

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℃ for 5 hrs. CrO_x/γ-Al_2O_3 samples were prepared by incipient wetness impregnation of γ-Al_2O_3 (Aldrich) using the corresponding nitrate salts as precursors. Physical properties and XRD analysis of catalysts are summarized in Table 1.

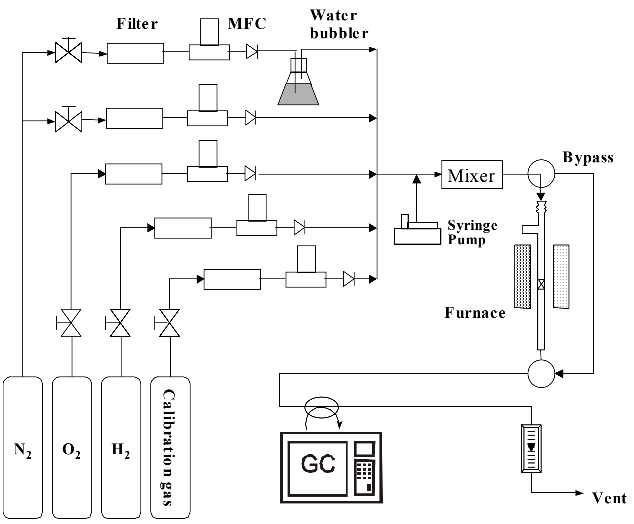

Fig. 1. Schematic diagram of reaction apparatus

The activity of the catalysts in oxidative decomposition of TCE was measured in a fixed bed apparatus (Fig. 1) at the temperatures between 280℃ and 340℃. The reaction feed mixture contained 800 ppm of TCE and 10000 ppm of H_2O with balance air. The weight hourly space velocity (WHSV) was 78 l/g-cat·hr.

Table 1. Physical properties of prepared catalysts

Catalyst	Loading amount [wt%]	Surface area [m^2/g]	Pore volume [cm^3/g]	Avg. Pore dia. [Å]	Bulk Structure (XRD)
$CoCr_2O_4$	-	53	0.14	150	Spinel
CrO_x/Al_2O_3	9	203	0.39	58	γ-Alumina

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℃ for 1 h, and cooled down to 200℃. The sample was flushed with He for 15 min, TCE (1%) was introduced at 200℃ for 30 min. After the additional cooling down to 100℃, the TPO was performed from 100 to 600℃ in a stream of O_2(10%)/He (100 ml/min at 5℃/min).

Results and discussion

Both of $CoCr_2O_4$ and alumina supported catalysts showed obvious deactivation during the first few hours of the reaction while the selectivity between CO and CO_2 remained almost constant (Fig. 2). This trend of the deactivation was more significant at the lower temperature as shown in Fig. 2. A distinct color change from brown to blue after the reaction at 300℃ for supported catalysts and a reduction of surface chromate species (Cr(VI)) by the interactions with trichloroethylene was reported in the previous work of Kim and Ihm [4]. It was concluded that the initial deactivation of supported chromium oxide catalysts were caused by the dissociative adsorption of TCE on the active sites, which could not be easily re-oxidized at the temperatures below 300℃. The first step in catalytic oxidation of TCE seemed to be fast but forms less reactive intermediates, which are oxidized at much slower rates than the original compound.

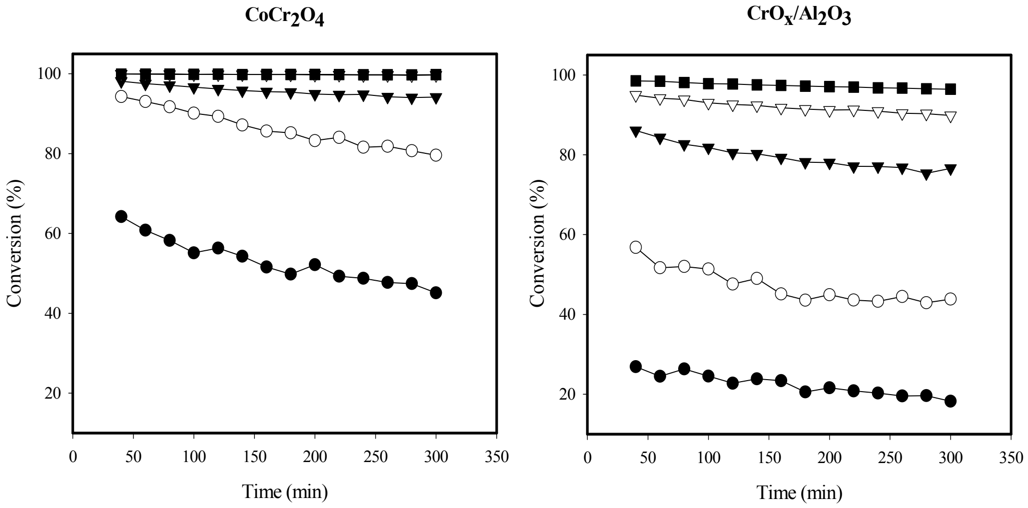

Fig. 2. Catalytic activity and CO/CO_2 ratio of Cr-containing catalysts for the decomposition of TCE with time-on-stream.
(800 ppm TCE; WHSV: 78 l/g-cat·hr)
● : 280°C ; ○ : 300°C ; ▼ : 320°C ; ▽ : 330°C ; ■ : 340°C

Fig. 3 is the results of temperature programmed oxidation of $CoCr_2O_4$ and CrO_x/Al_2O_3 after the adsorption of TCE at 200℃ following the signal of CO and CO_2 evolution. 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/Al_2O_3 and $CoCr_2O_4$. It should be pointed out that temperature higher than 300℃ is to be required for the complete desorption of carbon oxides in all cases. Similar results were reported by Grzybowska et al. [5] in their work on the temperature programmed experiments of chromium oxides for the oxidation of hydrocarbons. These desorption peaks around 300℃ could be another supporting evidence of the previous assumption [4] that the active sites with reduced species could not be rapidly re-oxidized or hydrolyzed to regenerate active species at low temperatures such as 300℃.

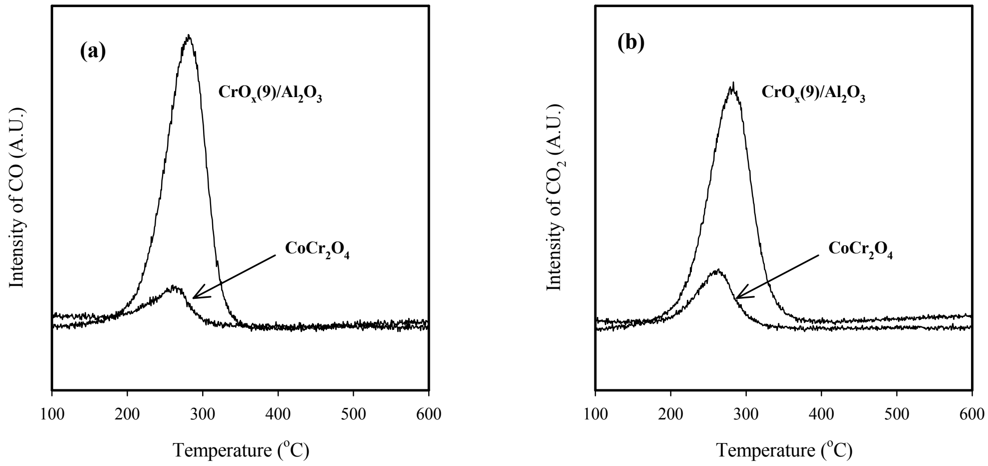

Fig. 3. TPO spectra of $CoCr_2O_4$ and $Cr(9\%)/Al_2O_3$ after the adsorption of TCE at 200°C; (a) : evolution of CO, (b) : evolution of CO_2

It was expected that the initial deactivation would not be observed if the reaction had been carried out at higher temperatures beyond 300℃. Slight decrease of activity was, however, observed during the catalytic oxidation of TCE over CrO_x/Al_2O_3 when the experiments was carried out at 320℃ and 330℃ as shown in Fig. 3. This high temperature deactivation (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 for the cases of carbon oxides as shown in Fig. 4. It should be noted that the difference in the desorption peak temperatures between carbon dioxides and HCl was more significant in the case of supported chromium catalysts

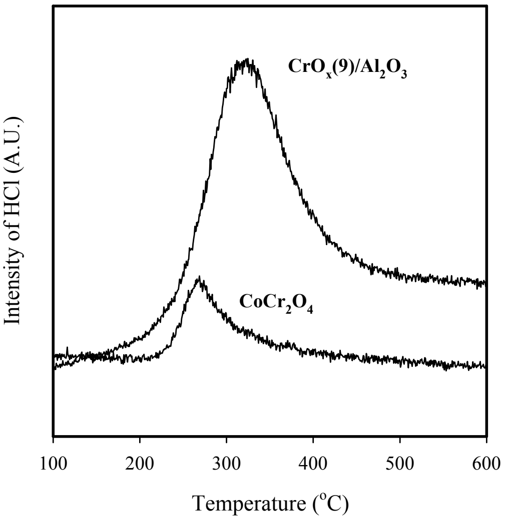

Fig. 4. Evolution of HCl during the TPO of $CoCr_2O_4$ and CrO_x/Al_2O_3 after the adsorption of TCE at 200°C.

than in the case of $CoCr_2O_4$ whose desorption of HCl was almost completed at 330℃.

Acknowledgement

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References

[1] R.A. Keller and J.A. Dyer, Chem. Eng., January 100-105(1998)
[2] Dae-Chul Kim and Son-Ki Ihm, J. Chem. Eng. Japan, 43(2), 143-147 (2001)
[3] Dae-Chul Kim and Son-Ki Ihm, Environ. Sci. Tech., 35, 222-226 (2001)
[4] Dae-Chul Kim and Son-Ki Ihm, Annual Conference of KICHE, Hanyang Univ., April, 2000, Ansan, Korea
[5] B. Grzybowska, J. Sloczynski, R. Grabowski, L. Keromnes, K. Wcislo, T. Bobinska, Applied Catalysis A: General 209, 279-289 (2001)