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A pilot plant study for catalytic decomposition of PCDDs/PCDFs over supported chromium oxide catalysts

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Abstract

Chromium oxide catalysts supported on TiO_2 and Al_2O_3 were examined in a fixed-bed flow reactor system for the removal of PCE (perchloroethylene), a simulant of 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin), and in a pilot plant employing actual flue gas from a sintering plant for the removal of PCDDs/PCDFs (poly-chlorinated dibenzo-dioxin/poly-chlorinated dibenzo-furan). The 12.5 wt.% chromium oxides supported on TiO_2 and Al_2O_3 revealed excellent stability and performance of PCE removal in the feed gas stream containing water vapor. In a pilot plant study, the catalysts washcoated on the honeycomb reactor revealed 93–95% of PCDDs/PCDFs removal activity over CrO_x/Al_2O_3-HC20 (CrO_x/Al_2O_3 catalyst washcoated on 20 cell-honeycomb), and more than 99% of the decomposition activity over CrO_x/TiO_2-HC20 (CrO_x/TiO_2 catalyst washcoated on 20 cell-honeycomb) at 325 °C and 5000 h^{-1} of reactor space velocity without the de novo synthesis of PCDDs/PCDFs. In particular, CrO_x/TiO_2-HC20 showed 94% of PCDDs/PCDFs decomposition activity even at 280 °C reaction temperature. The catalyst also exhibited significant NO removal activity. The chromium oxide seems to be a promising catalyst for the removal of PCDDs/PCDFs and NO_x contained in the flue gas. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PCDDs/PCDFs; Dioxin; CVOCs; Catalytic decomposition; Chromium oxide catalyst; Nitric oxide

1. Introduction

Much attention has been focused on the emissions of PCDDs/PCDFs (poly-chlorinated dibenzo-dioxin/poly-chlorinated dibenzo-furan) from waste incineration facilities due to fears of their high toxicity and on the stringent emission limit, 0.1 ng TEQ (toxic equivalency factor)/N m^3. For the control of PCDDs/PCDFs emission, primary measures such as the design and operation of the incinerator to minimize the formation of PCDDs/PCDFs cannot achieve this emission limit. Therefore, secondary measures, including adsorption by carbon or the catalytic oxidation of PCDDs/PCDFs into CO_2, H_2O and HCl, should be employed to meet the regulation. Recently, it has been reported that the SCR process for the catalytic removal of NO_x is also very effective for decomposing PCDDs/PCDFs at reaction temperatures which ranged from 250 to 350 °C [1–4]. Hagenmaier et al. [1] observed that NH_3-SCR type catalyst, especially V_2O_5–WO_3/TiO_2, revealed removal efficiency of PCDDs/PCDFs at a level less than 0.1 ng TEQ/N m^3 and proved the stability of the SCR catalyst by the catalyst deactivation during the pilot plant study at a municipal waste combustor. In addition, Pt-supported honeycomb catalysts were also employed to remove 85–95% of PCDDs at reaction temperatures of 300–450 °C and reactor space velocities of 5400 h^{-1} [5]. Toshihiko et al. [6] reported the catalytic decomposition of exhaust gases containing dioxins over the catalyst containing Pt, Pd and Ir.

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In the earlier study, the chromium oxide catalyst seems to be very effective for the complete oxidation of chlorinated hydrocarbons [7,8]. It has also been confirmed that the PCE (perchloroethylene) removal activity of the chromium oxide catalysts supported on TiO_2 and Al_2O_3 is stable for more than 100 h of the operating time when the feed concentration of PCE is 30 ppm at 350 °C. In the present study, the removal activity of PCDDs/PCDFs was investigated over chromium oxide catalysts washcoated on honeycomb reactor in a pilot plant handling 1000 N m^3/h of actual gas from a sintering plant based on the catalytic activity on the decomposition of PCE. The removal efficiency of NO_x over the present chromium oxide catalytic system was also examined for the simultaneous decomposition of dioxins and NO_x.

2. Experimental

2.1. Preparation of catalyst and honeycomb reactor

Chromium oxide catalysts supported on TiO_2 (Degussa P25) and Al_2O_3 (Aldrich) were prepared by wet impregnation method with aqueous solution of chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$, Aldrich Chemical). After the impregnation of CrO_x on the supports, the catalysts were subsequently dried at 110 °C for 12 h and calcined in air at 450 °C for 5 h.

The honeycomb reactors containing 20 cpsi (cell/in.^{2}) employed in the present study were prepared by washcoating aluminum and titanium oxide with silica binder on the cordierite honeycomb with the dimensions of $150 \times 150 \times 100$ mm^3. Aluminum or titanium oxide powder was washcoated on the channels of the cordierite honeycomb. The washcoated honeycomb was blown with compressed air to remove excess slurry on the wall of honeycomb and then dried at 110 °C for 3 h. The amount of catalyst washcoated on the surface of the honeycomb, varying 10–15% based on the weight of the honeycomb, can be controlled by repeating these procedures. The washcoated honeycomb was calcined at 400 °C for 3 h. The alumina or titania washcoated honeycomb was then dipped into the chromium solution for the impregnation of chromium oxide on the surface of the honeycomb. The same procedures for dipping and drying were repeated to obtain the desired amount of chromium oxide on the surface of the alumina or titania washcoated honeycomb. The chromium oxide impregnated honeycomb was then calcined at 450 °C for 3 h before the pilot plant test.

2.2. Reactor system

The oxidation of PCE was carried out in a fixed-bed continuous-flow reactor system. A reactant mainly containing air with 30 ppm of PCE was fed into the reactor containing 60/80 mesh size catalyst at a flow rate of 600 ml/min, equivalent to a reactor space velocity of 60,000 h^{-1}. The reaction temperatures were varied from 150 to 450 °C under atmospheric pressure. The feed and product streams of the reactor were analyzed by on-line HP 5890A gas chromatography (GC) with TCD and FID detectors. The products, such as HCl and Cl_2, were not analyzed due to the low concentration in the product stream. However, it has been confirmed that more than 90% of PCE was converted to CO and CO_2 by carbon balance. The details of the reaction system were described in the earlier study [8].

The CrO_x/TiO_2 and CrO_x/Al_2O_3 catalysts washcoated on honeycomb reactor have been examined to remove PCDDs/PCDFs contained in the flue gas from the sintering plant. The details of the pilot plant were well described elsewhere in [9]. The flue gas was introduced into the pilot plant at about 130 °C by a blower from the side stream of the main duct of the sintering plant. The flue gas, which is produced from the sintering process of iron ore, normally contains N_2 of 70%, O_2 of 13%, CO_2 of 5%, H_2O of 11%, CO of 1%, SO_x of 150 ppm, NO_x of 170 ppm and particulate of about 50 mg/N m^3 [9]. The pilot plant was normally operated at a feed gas flow rate in the range of 300–700 N m^3/h and 200–400 °C. The reactor consists of a dummy honeycomb support layer and a catalytic reactor layer with dimensions of $600 \times 600 \times 100$ mm^3, respectively. An NH_3 cylinder supplied the NH_3 required for the NO_x removal. The quantitative and qualitative analysis of PCDDs/PCDFs have been made by Micromass HRGC/MS (AutoSpec-*Ultima*). The concentration of NO_x was measured by the on-line chemiluminescence-type NO_x analyzer (TEI 42C). The reactor space velocity was defined as the ratio of the gas flow rate to the volume of honeycomb reactor.

2.3. Catalyst characterization

XPS data for the chemical state of CrO_x on the catalyst surface were obtained by KRATOS Analytical XSAM 800 cpi ESCA equipped with a Mg anode (Mg Kα radiation, 1253.6 eV) and spherical analyzer operating at 15 kV and 15 mA. Binding energies of the catalyst samples were referenced to the C 1s line (284.6 eV) of the carbon overlayer. The oxidation state of chromium on the catalyst surface was determined by nonlinear least-squares curve fitting by using the Cr $2p_{3/2}$ envelope. Temperature-programmed desorption of H_2O was carried out for the hydrophobicity of the catalyst surface by using 50 mg of the catalysts heated at 10 °C/min in the flow of helium with 40 ml/min. The catalysts were pre-treated with oxygen at 500 °C for 0.5 h, and then water vapor was adsorbed on the catalyst surface at 50 °C for 1 h. A thermal conductivity detector (HP 5890 GC) was employed to monitor desorption of water during the temperature ramping.

3. Results and discussion

3.1. Decomposition of PCE over CrO_x/Al_2O_3 and CrO_x/TiO_2 catalysts

The decomposition activity of PCE over CrO_x/TiO_2 and CrO_x/Al_2O_3 catalysts containing a variety of Cr content with respect to reaction temperature is shown in Fig. 1. The activity of both catalysts enhanced with increasing Cr content from 1 to 12.5 wt.% at the reaction temperatures covered in the present study. In particular, the PCE decomposition activity of CrO_x/Al_2O_3 catalyst strongly depends on the contents of Cr on the catalyst surface compared to that of CrO_x/TiO_2. 12.5 wt.% CrO_x/Al_2O_3 catalyst showed higher activity than 12.5 wt.% CrO_x/TiO_2, mainly due to the distinction of surface area of the catalysts that could directly affect the formation of active reaction species of Cr(VI) on the catalyst surface [8]. Further increase of Cr on the surface of Al_2O_3 and TiO_2 did not enhance the decomposition activity, indicating that about 12.5 wt.% Cr content may be an optimum for the present catalytic system.

For the identification of CrO_x phase on the surfaces of 12.5 wt.% CrO_x/Al_2O_3 and CrO_x/TiO_2 catalysts, XPS spectra were obtained as shown in Fig. 2. The spectra of Cr $2p_{3/2}$ exhibited two main peaks at ∼579.2 eV for Cr(VI) and ∼576.5 eV for Cr(III) indicating that both catalysts mainly contain Cr(VI) and Cr(III) on the catalyst surface [8,10]. The shape of XPS spectra reveals that CrO_x/Al_2O_3 contains a relatively higher amount of Cr(VI) than CrO_x/TiO_2, which may be an indication of the high performance of CrO_x/Al_2O_3. Fig. 3 simply shows the water tolerance of 12.5 wt.% CrO_x/Al_2O_3 and CrO_x/TiO_2 cata-

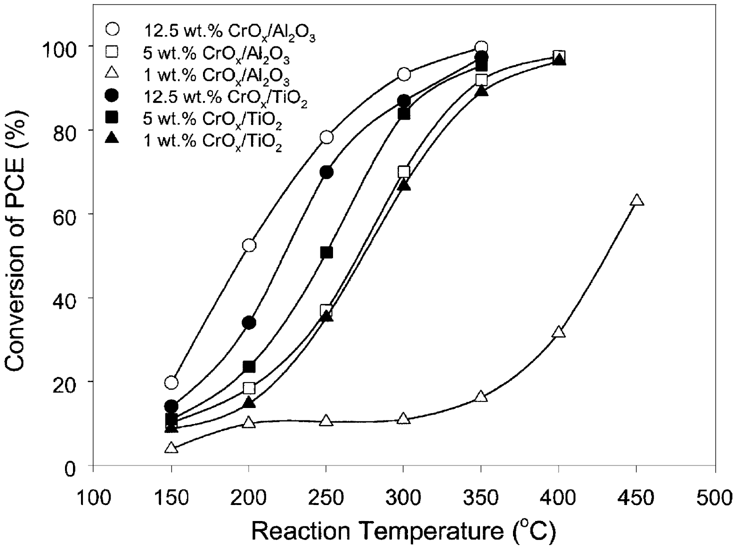

Fig. 1. PCE removal activity of CrO_x catalysts supported on Al_2O_3 and TiO_2.

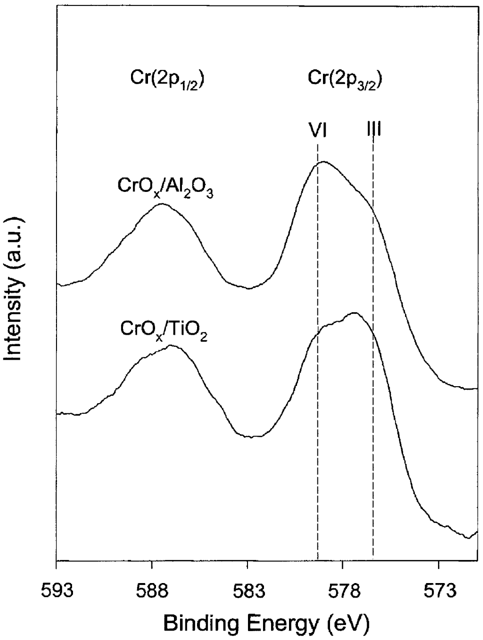

Fig. 2. Cr 2p XPS spectra of 12.5 wt.% CrO_x catalysts supported on Al_2O_3 and TiO_2.

lysts in the presence of 440 ppm of PCE and 5% of H_2O at 350 °C. It has been reported that the presence of water vapor in the feed gas stream deteriorates the removal activity of CVOCs due to the competitive adsorption of water and reactants on the surface of the catalyst [9,11]. On the other hand, the water vapor can even improve the stability of CrO_x catalyst by promoting reverse Deacon reaction and facilitating desorption of Cl from the catalyst surface during the decomposition of CVOCs [12,13]. Fig. 3 also reveals that the removal activity of CrO_x/TiO_2 is higher than that of CrO_x/Al_2O_3 in the presence of water vapor, strongly implying that the initial loss of activity by water was significant for CrO_x/Al_2O_3 catalyst. Both catalysts, however, show stable activity in the presence of 440 ppm of PCE with 5% of H_2O up to 25 h of operating time.

In order to distinguish the water tolerance of the catalysts, H_2O-TPD has been employed for the hydrophobicity of the present catalytic system. The H_2O-TPD patterns clearly reveal that the CrO_x/TiO_2 is far more hydrophobic than CrO_x/Al_2O_3, confirming that the significant activity loss of CrO_x/Al_2O_3 by H_2O is mainly due to the competitive adsorption of PCE and water on the catalyst surface.

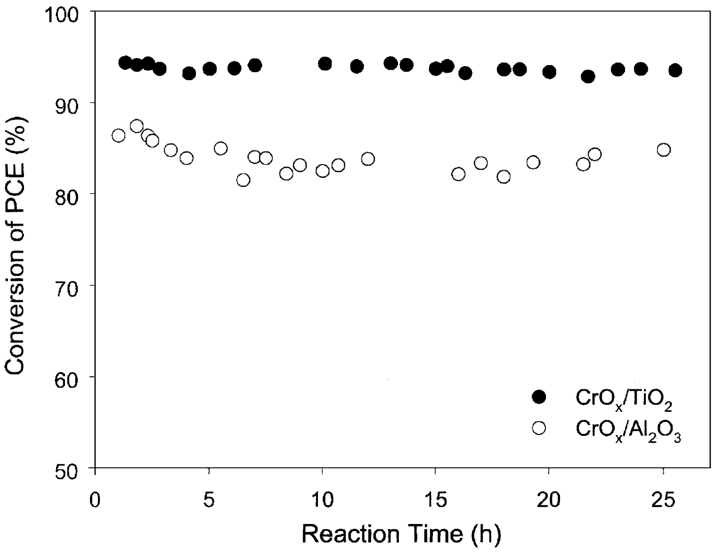

Fig. 3. Water tolerance of 12.5 wt.% CrO_x catalysts supported on Al_2O_3 and TiO_2 for the removal of PCE in the presence of 5% H_2O and 440 ppm PCE at 350 °C.

Based upon the experimental results examined in the present study, CrO_x-based catalyst, especially CrO_x/TiO_2, can be regarded as a promising catalyst for the decomposition of PCDDs/PCDDFs, and a pilot plant study for the decomposition of PCDDs/PCDDFs over CrO_x/TiO_2 and CrO_x/Al_2O_3 catalysts has been conducted.

3.2. Decomposition of PCDDs/PCDF$_S$ over CrO_x/Al_2O_3 catalyst

The decomposition activity of PCDDs/PCDFs including 17 isomers revealing significant toxicity based on TEQ (2,3,7,8-TCDD = 1) has been examined over 12.5 wt.% CrO_x/Al_2O_3 and CrO_x/TiO_2 catalyst washcoated on 20 cell-honeycomb (CrO_x/Al_2O_3-HC20 and CrO_x/TiO_2-HC20) at a reactor space velocity of 5000 h^{-1} and a reaction temperature of 325 °C as shown in Figs. 4 and 5. The total removal efficiency of PCDDs/PCDFs over CrO_x/Al_2O_3-HC20 was 95%. This high activity may indicate that no de novo synthesis occurred during the course of the present catalytic system.

The effect of reaction temperature, reactor space velocity and reaction time on the decomposition of PCDDs/PCDFs over CrO_x/Al_2O_3-HC20 catalyst has been also observed. When the reaction temperature increased to 380 °C, the decomposition activity of CrO_x/Al_2O_3-HC20 slightly improved to 98%. During 413 h of the reaction on-stream time at 5000 h^{-1} and 380 °C, the decomposition activity decreased from initial activity of 98–91%. Further decrease of the activity, however, was not observed up to 500 h of reaction time. The PCDDS/PCDFs decomposition activity of CrO_x/Al_2O_3-HC20 decreased from 91 to 82% and 91 to 89%, respectively, when the reaction temperature and the reactor space velocity were varied from 380 to 280 °C and 5000 to 8000 h^{-1}, respectively.

Fig. 5 shows the catalytic decomposition activity of PCDDs/PCDFS over 12.5 wt.% CrO_x/TiO_2 catalyst washcoated on honeycomb-20 cell (CrO_x/TiO_2-HC20) at the identical condition examined for 12.5 wt.% CrO_x/Al_2O_3. The total decomposition activity of PCDDs/PCDFs over CrO_x/TiO_2-HC20 is 99%, which is higher than that over CrO_x/Al_2O_3-HC20. This is also in good agreement with the results on the decomposition of PCE [14]. The catalyst also exhibited 94% of PCDDs/PCDFs decomposition activity at a reaction temperature as low as 280 °C. When the reactor space velocity increased from 3000 to 5000 h^{-1}, the overall decomposition activity did not change significantly. It, however, apparently decreased when the reactor space velocity changed to 8000 h^{-1}.

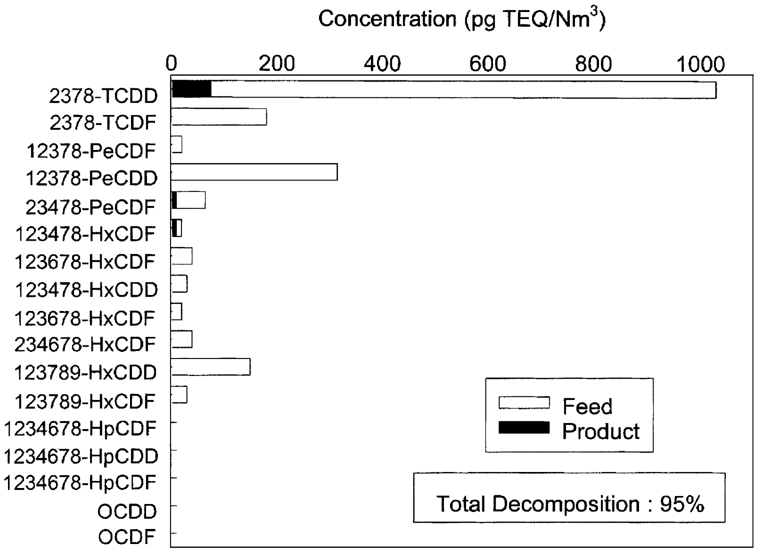

Fig. 4. Decomposition activity of PCDDs/PCDFs over CrO_x/Al_2O_3-HC20 at 5000 h^{-1} and 325 °C.

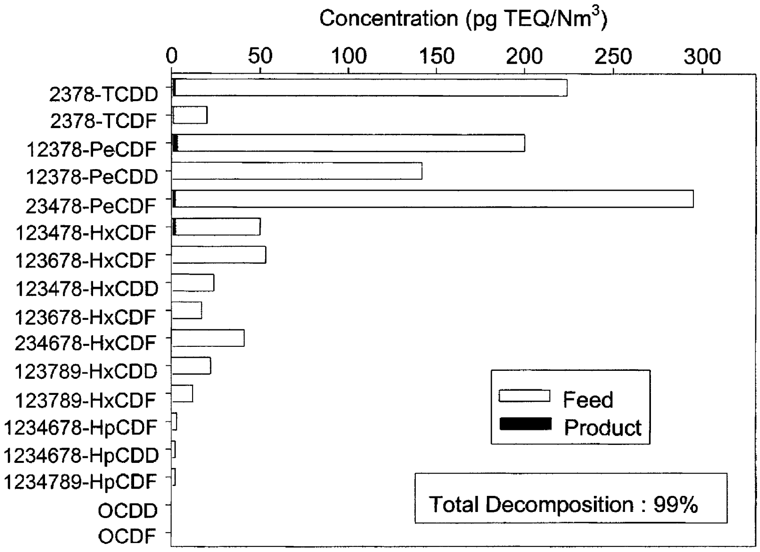

Fig. 5. Decomposition activity of PCDDs/PCDFs over CrO_x/TiO_2-HC20 at 5000 h^{-1} and 325 °C.

3.3. SCR reaction of NO by NH_3

The dioxin abatement catalytic reactor is commonly installed along with SCR reactor for $deNO_x$ [15]. For the simultaneous removal of PCDDs/PCDFs and NO_x in the present reactor system, it is necessary to examine the effect of NH_3 feed into the reactor for the decomposition of PCDDs/PCDFs. The decomposition activity of PCDDs/PCDFs over CrO_x/Al_2O_3-HC20 in the presence of 200 ppm of NH_3 was 93% in terms of total conversion at 325 °C as shown in Fig. 6. This indicates that the feed of NH_3 into the catalytic reactor

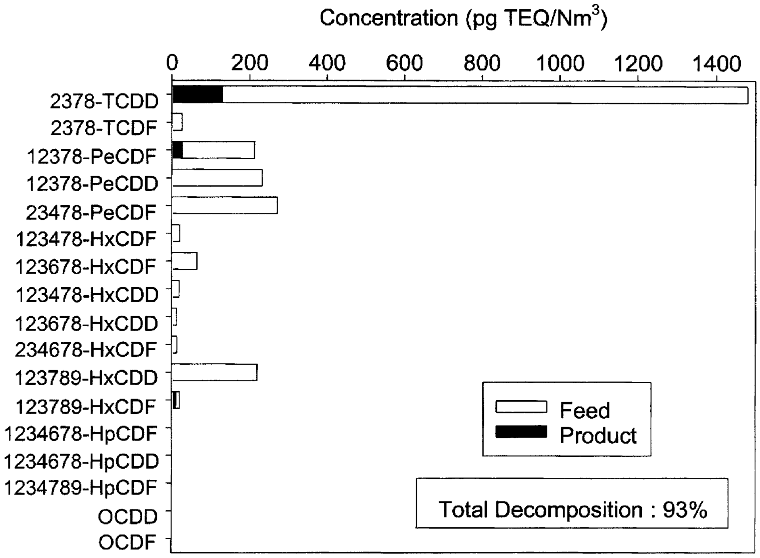

Fig. 6. Effect of NH_3 feed on the decomposition of PCDDs/PCDFs over CrO_x/TiO_2-HC20 at 5000 h^{-1} and 325 °C.

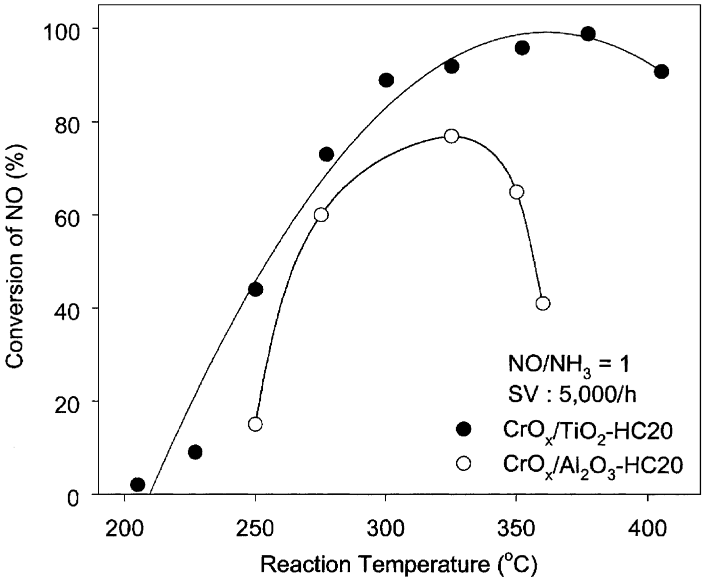

Fig. 7. NO removal activity of CrO_x/Al_2O_3-HC20 and CrO_x/TiO_2-HC20.

basically does not alter the dioxin removal activity as also observed by Ok et al. [2], and the simultaneous removal of PCDDs/PCDFs and NO_x over the present catalytic reaction system is promising.

Fig. 7 shows the NO removal activity over CrO_x catalysts at a reactor space velocity of $5000\,h^{-1}$. CrO_x/Al_2O_3-HC20 exhibited 76% of NO conversion at 325 °C. The removal activity, however, decreased significantly at high reaction temperatures due to the oxidation of NH_3 [16]. However, CrO_x/TiO_2-HC20 revealed high performance of NO conversion more than 90% at 300–400 °C. This confirms that chromium oxide, especially CrO_x/TiO_2, is an effective and promising catalytic system for the removal of PCDDs/PCDFs and NO_x as well.

4. Conclusions

The active reaction site of CrO_x supported on Al_2O_3 and TiO_2 is Cr(VI) on the catalyst surface for the removal of PCE and PCDDs/PCDFs. With water in the feed gas stream, both catalytic systems showed stable removal activity, although the initial loss of activity was observed for CrO_x/Al_2O_3 catalyst. In addition, CrO_x/TiO_2 revealed high removal activity compared to CrO_x/Al_2O_3 in wet conditions mainly due to the hydrophobicity of the surface of CrO_x/TiO_2 catalyst. In a pilot plant study, the catalysts washcoated on the honeycomb reactor revealed 93–95% of the total decomposition of PCDDs/PCDFs for CrO_x/Al_2O_3-HC20, and higher than 99% for CrO_x/TiO_2-HC20 at 325 °C and $5000\,h^{-1}$ without de novo synthesis of dioxin compounds. In particular, CrO_x/TiO_2-HC20 showed 94% of PCDDs/PCDFs decomposition activity even at 280 °C of reaction temperature. The catalyst also exhibited significant NO removal activity. The chromium oxide catalyst developed in the present study appears to be a promising catalyst for the decomposition of PCDDs/PCDFs and NO_x as well.

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