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Catalytic removal of perchloroethylene (PCE) over supported chromium oxide catalysts

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Abstract

The oxidation of perchloroethylene (PCE) was investigated over chromium oxide catalysts supported on SiO_2, SiO_2–Al_2O_3, activated carbon, mordenite type zeolites, MgO, TiO_2 and Al_2O_3. Supported chromium oxide catalysts were more active than any other metal oxide catalysts including noble metal examined in the present study. PCE removal activity of chromium oxide catalysts mainly depended on the type of supports and the content of metal loaded on the catalyst surface. TiO_2 and Al_2O_3 containing high surface areas were effective for the high performance of PCE removal, since the formation of well dispersed Cr(VI) active reaction sites for the present reaction system, was enhanced even for the high Cr loading on the catalyst surface. CrO_x catalysts supported on TiO_2 and Al_2O_3 also exhibited stable PCE removal activity at a low feed concentration of PCE of 30 ppm up to 100 h at 350°C. However, significant catalyst deactivation was observed at high PCE concentration of 10 000 ppm. CrO_x/TiO_2 revealed stronger water tolerance than CrO_x/Al_2O_3 due to the surface hydrophobicity. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chromium oxide catalyst; Chlorinated hydrocarbons; Perchloroethylene (PCE); CVOCs; Complete oxidation

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1. Introduction

Chlorinated volatile organic compounds (CVOCs) are widely used in the chemical industry, including such processes as dry cleaning and degreasing operations, as an organic solvent; however, their emissions are detrimental to human health when they are included in an exhaust stream. The current technology for the complete oxidation of chlorinated hydrocarbons is thermal incineration which requires extremely high temperatures of about 1000°C. The process also produces highly toxic byproducts including nitrogen oxides, phosgene and dioxins by incomplete combustion [1].

However, the catalytic removal of chlorinated hydrocarbons is an energy-efficient method, since the process is carried out at relatively low temperatures compared to thermal incineration. There have been numerous studies on the catalytic oxidation of CVOCs over supported metal and metal oxide catalysts. The deactivation and volatilization of metal catalysts by the products of the decomposition reaction including Cl_2 and HCl are recognized as a drawback to the catalytic removal of CVOCs [2].

On the other hand, transition metal oxide catalysts have been reported to be very active and resistant to

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catalyst deactivation by HCl and Cl_2 poisoning. Spivey [3] reviewed transition metal oxide catalysts such as V, Cr, Mn, Fe, Co and Ni, which are active for the complete oxidation of VOCs. Among these catalysts, supported chromium oxide catalysts have been generally known as one of the most promising catalysts for the complete oxidation of CVOCs by the previous studies [3–12]. Chromium oxide catalysts supported on Al_2O_3 [3–7], porous carbon [8], pillared clay [9], zeolites [10,11] and SnO_2 [12] were reported to be effective for the removal of CVOCs. These studies indicate that the chromium oxide is a major active catalytic reaction site and the catalyst support simply enhances the dispersion of chromia on the catalyst surface. Recently, Cr_2O_3/Al_2O_3 based commercial catalysts were investigated for the removal of CVOCs and their stability when there is water vapor in the feed gas stream [4,6]. Although a variety of supported chromium oxides were suggested as an effective catalyst for the removal of CVOCs, no direct comparison of the activity can be achieved due to the variation of the content of Cr on the catalyst surface and the reaction conditions. Furthermore, there has been little systematic study of the effect of Cr loading, the supports and the reaction conditions on the high performance of CVOCs removal.

In the present study, the effects of the supports on the activity of CrO_x based catalysts containing a variety of Cr loading were examined in a fixed bed flow reactor for the removal of perchloroethylene (PCE) as a standard compound of CVOCs. The catalyst was characterized by XRD and XPS to elucidate the role of the Cr content and the supports for the formation of active CrO_x species and the high performance of PCE removal. Furthermore, the water tolerance and catalytic stability of chromia catalysts were also investigated with respect to the feed concentration of H_2O and PCE.

2. Experimental

2.1. Catalyst preparation

The supported CrO_x, VO_x, Pt and Pd catalysts were prepared by the incipient wetness impregnation method with aqueous solution of chromium nitrate [$Cr(NO_3)_3 \cdot 9H_2O$], ammonium metavanadate [NH_4VO_3], hydrogen hexachloroplatinate [H_2PtCl_6–xH_2O] and palladium chloride [$PdCl_2$], all from Aldrich Chemical. The supports employed in the present study include SiO_2–Al_2O_3, SiO_2, activated carbon, MgO, HM, NZA, TiO_2 and Al_2O_3. BET surface areas of the supports are listed in Table 1. After the impregnation of metal precursors on the supports, the catalysts were subsequently dried at 110°C for 12 h, and calcined in air at 450°C for 5 h. Note that CrO_x/activated carbon was calcined in air at 350°C for 5 h to avoid the oxidation of carbon. After calcination, supported Pt and Pd catalysts were reduced in H_2 atmosphere at 450°C for 5 h. Copper ion-exchanged hydrogen mordenite (CuHM) and copper ion-exchanged natural zeolite (CuNZA) catalysts were prepared by the typical ion exchanging procedures. Details of the preparation of CuHM and CuNZA have been described elsewhere [13]. All samples were reported as weight percent of Cr, V, Pt, Pd and Cu in the catalyst sample.

Table 1
BET surface areas of the catalyst supports employed in the present study

Catalyst supports	Surface area (m^2/g)	Supplier
$TiO_2$250	250	Hombikat UV-100
$TiO_2$58	58	Degussa P-25
$TiO_2$17	17	Shinyo Chemical
$Al_2O_3$290	290	Aldrich Chemical
$Al_2O_3$155	155	Aldrich Chemical
$Al_2O_3$25	25	Aldrich Chemical
SiO_2–Al_2O_3	560	JRC-SAL-2
SiO_2	300	Aldrich Chemical
Activated carbon	850	Aldrich Chemical
MgO	10	Yakuri Pure Chemical
HM	449	PQ
CuNZA	210	Mined from Youngil, Korea

2.2. Reactor system

The oxidation of PCE was carried out in a fixed-bed continuous-flow reactor system. The reactor is a 6 mm o.d. Pyrex glass tube operated in the mode of down flow. A reactant mainly containing air with 30 ppm of PCE was fed into the reactor containing 60/80 mesh size catalyst at the flow rate of 600 ml/min, equivalent to the reactor space velocity of 30 000 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 H.P. 5890 gas chromatography (GC) with TCD and FID detectors. The conversion of PCE was calculated based upon the difference between inlet and outlet concentrations of PCE. 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.

2.3. *Catalyst characterization*

X-ray powder diffraction patterns of the catalyst prepared in the present study were observed by an M18XHF (MAC Science) diffractometer employing Cu Kα radiation ($\lambda = 1.5405$ Å). The specific surface areas were determined by BET apparatus from Micromeritics (ASAP 2010C). XPS data 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 using the Cr $2p_{3/2}$ envelope. In order to minimize the photoreduction of chromium oxide species on the catalyst surface during XPS experiments, all the catalyst samples were analyzed within a short period of time less than 20 min [14].

3. Results and discussion

3.1. *Effect of Cr loading and support*

Fig. 1 shows PCE removal activity of transition and noble metal supported on $TiO_2$17 and Cu ion-exchanged zeolite catalysts. Chromium oxide catalysts showed the highest PCE removal activity among the catalysts employed in the present study including Pt, Pd, and $VO_x/TiO_2$17, CuHM and CuNZA. The results are in agreement with the previous study exhibiting that supported chromium oxide catalysts are more active than noble and the other transition metal oxide catalysts [15]. For chromium oxide catalysts, $CrO_x/TiO_2$17 was more active than $CrO_x/Al_2O_3$290 when both catalysts contained 1 wt.% chromium oxides.

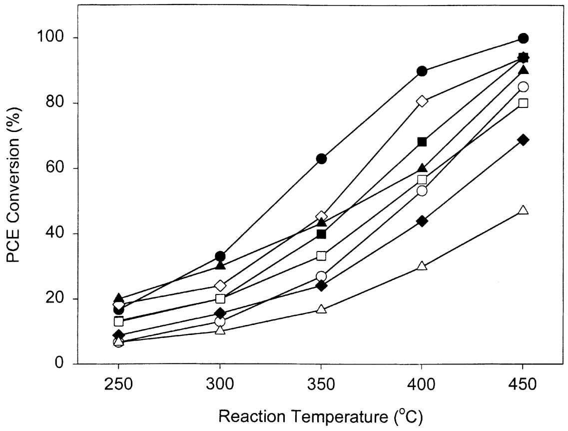

Fig. 1. PCE removal activity of 1 wt.% $CrO_x/TiO_2$17 (●) $CrO_x/Al_2O_3$290 (○), $Pt/TiO_2$17 (◇), $Pd/TiO_2$17 (◆), $VO_x/TiO_2$17 (□), Pd(0.5 wt.%)-Pt(0.03 wt.%)/$TiO_2$17 (■) and 2.3 wt.% CuHM (▲) and CuNZA (△) catalysts.

To examine the effect of Cr loading and the type of the support for the PCE removal activity, 5 wt.% chromium oxide catalysts supported on SiO_2–Al_2O_3, HM, $Al_2O_3$290, $TiO_2$17 and MgO were investigated as shown in Fig. 2. The results reveal that the activity of 5 wt.% chromium oxide catalysts totally depends on the type of the supports and the activity is in the order of HM $\sim$ SiO_2–Al_2O_3 $>$ $Al_2O_3$290 $>$ $TiO_2$17 $>$

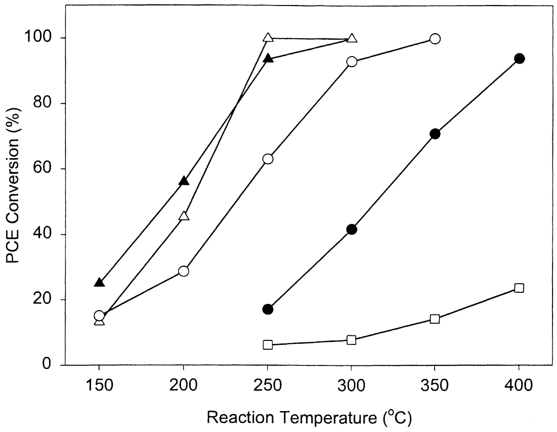

Fig. 2. PCE removal activity of 5 wt.% CrO_x catalysts supported on SiO_2–Al_2O_3 (▲), HM (△), $Al_2O_3$290 (○), $TiO_2$17 (●) and MgO (□).

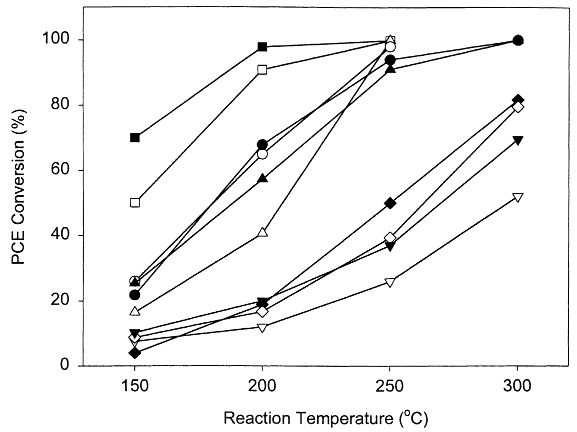

Fig. 3. PCE removal activity of 12.5 wt.% CrO_x catalysts supported on $TiO_2$250 (■), $Al_2O_3$290 (□), $Al_2O_3$155 (●), SiO_2–Al_2O_3 (○), $TiO_2$58 (▲), HM (△), SiO_2 (◆), $Al_2O_3$25 (◇), $TiO_2$17 (▼) and activated carbon (▽).

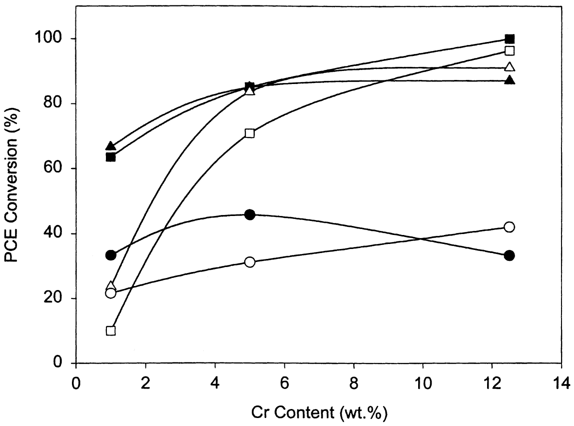

Fig. 4. PCE removal activity of CrO_x catalysts supported on $TiO_2$250 (■), $TiO_2$58 (▲), $TiO_2$17 (●), $Al_2O_3$290 (□), $Al_2O_3$155 (△) and $Al_2O_3$25 (○) containing a variety of Cr content at 300°C; SV = 60 000 h^{-1}.

MgO. $CrO_x/Al_2O_3$290 showed higher activity than $CrO_x/TiO_2$17 as opposed to the catalyst containing 1 wt.% of CrO_x. Fig. 3 shows PCE removal activity of 12.5 wt.% CrO_x supported catalysts. The high surface area of TiO_2 and Al_2O_3 supports reveal the highest oxidation activity among the catalysts examined in the present study. It indicates that the activity is critically dependent on the type and the surface area of the supports. The CrO_x catalysts supported on HM, SiO_2, SiO_2–Al_2O_3 and activated carbon exhibited relatively low PCE removal activity although their surface areas are rather high. The activity of 12.5 wt.% CrO_x on HM and SiO_2–Al_2O_3 was slightly improved when the Cr content increased from 5 to 12.5 wt.%, which differed from the activity examined for $TiO_2$250 and $Al_2O_3$290.

The relationship between Cr loading and PCE conversion over CrO_x supported on TiO_2 and Al_2O_3 containing a variety of surface area is clearly shown in Fig. 4. The activity proportionally increased with respect to the Cr loading for $TiO_2$250 and $Al_2O_3$290. However, for $TiO_2$58 and $Al_2O_3$155, PCE conversion improved as the content of Cr increased to 5 wt.%, but further increase of Cr loading did not enhance the activity. In addition, any significant improvement of PCE removal activity of CrO_x supported on $TiO_2$17 and $Al_2O_3$25 is hardly observed with respect to the content of Cr on the catalyst surface. These results suggest that Cr loading, type and surface area of supports may directly influence the formation of the active reaction sites, chromium oxide on the catalyst surface.

3.2. Characteristics of CrO_x on the catalyst surface

Fig. 5 shows the XPS spectra of 5 wt.% chromium oxide-supported catalysts to examine the state of CrO_x on the catalyst surface. The XPS spectra of Cr $2p_{3/2}$ for the supported chromium oxide catalysts reveal two main peaks at ∼579.2 eV for Cr(VI) and ∼576.5 eV for Cr(III) [14]. For SiO_2–Al_2O_3, $Al_2O_3$290 and MgO supports, Cr(VI) is the main component on the catalyst surface. However, Cr(III) is dominant on the surface of $TiO_2$17. It is generally known that Cr(VI) is the active reaction site on the catalyst surface for the complete oxidation of CVOCs [8,9]. The XPS results are in good agreement with the results of PCE removal activity when the catalysts contain 5 wt.% of CrO_x shown in Fig. 2. CrO_x/MgO catalyst, however, revealed much lower PCE removal activity, although the formation of Cr(VI) species is significant on the catalyst surface, probably due to the low surface acidity of MgO [16]. It was previously examined that the catalyst surface acidity is another important criterion for the high performance of CVOCs removal catalyst [10,17].

The XRD patterns of 12.5 wt.% CrO_x supported catalysts can be examined in Fig. 6. The results

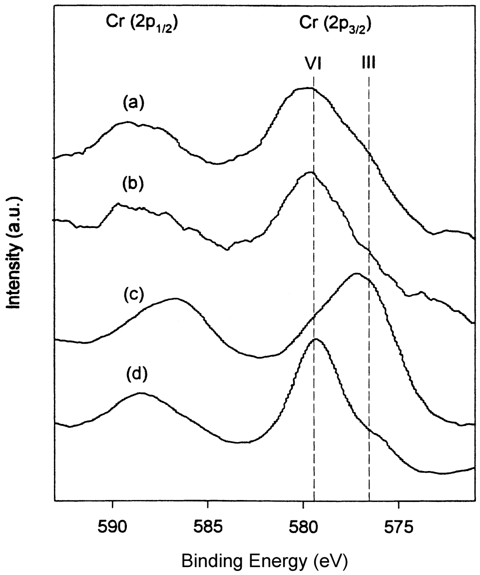

Fig. 5. XPS spectra of 5 wt.% CrO_x catalysts supported on SiO_2–Al_2O_3 (a), $Al_2O_3$290 (b), $TiO_2$17 (c) and MgO (d).

for CrO_x/$TiO_2$250 and CrO_x/$Al_2O_3$290 only show the peaks of anatase type TiO_2 and γ-Al_2O_3. This indicates that chromium oxides are well dispersed on $TiO_2$250 and $Al_2O_3$290 supports. For CrO_x supported on activated carbon, SiO_2, SiO_2–Al_2O_3, $TiO_2$17, $TiO_2$58, $Al_2O_3$25 and $Al_2O_3$155, the crystalline α-Cr_2O_3 peaks are observed. The intensities of α-Cr_2O_3 peaks, probably revealing the extent of crystallinity of chromium oxide on the catalyst surface, are strong for the catalysts exhibiting low PCE removal activity as discussed.

The results from XRD were quite consistent with XPS studies of 12.5 wt.% CrO_x catalysts as shown in Fig. 7. The XPS patterns indicate that $TiO_2$250 and $Al_2O_3$290 supports are mainly containing Cr(VI) on the catalyst surface. However, the other supports such as activated carbon, SiO_2–Al_2O_3, $TiO_2$17, $TiO_2$58, $Al_2O_3$25 and $Al_2O_3$155 are forming dominantly Cr(III) species on the catalyst surface, mainly attributed to the formation of α-Cr_2O_3. These results reveal that the state of CrO_x on the catalyst surface is critical for the high performance of PCE removal activity. Poorly dispersed α-Cr_2O_3 is not effective for the oxidation of PCE. The formation of Cr(VI) and α-Cr_2O_3 mainly depends on the content of Cr loading and the surface area of the supports accommodating CrO_x. The 12.5 wt.% CrO_x supported on $TiO_2$250 and $Al_2O_3$290 mainly contains Cr(VI) on the catalyst surface as characterized by XRD and XPS. It is well recognized that the surface of TiO_2 and Al_2O_3 containing sufficient OH groups strongly interacts with metal oxides such as chromium oxide and vanadium oxide. This leads to the high dispersion of metal oxide on the catalyst surface [18]. Again, Cr content and surface areas of supports are also critical for the formation of highly dispersed CrO_x catalysts.

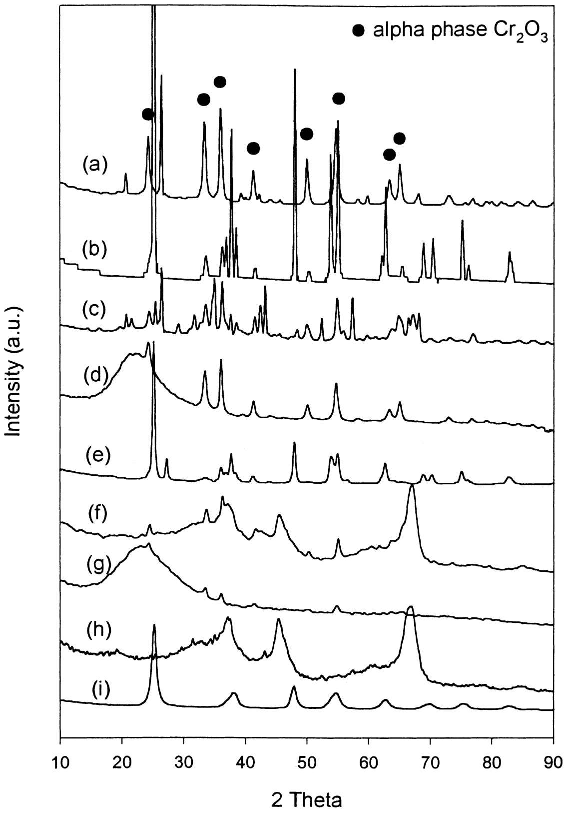

Fig. 6. X-ray diffraction patterns of 12.5 wt.% CrO_x catalysts supported on activated carbon (a), $TiO_2$17 (b), $Al_2O_3$25 (c), SiO_2 (d), $TiO_2$58 (e), $Al_2O_3$155 (f), SiO_2–Al_2O_3 (g), $Al_2O_3$290 (h) and $TiO_2$250 (i).

There may be a trade-off between the content of Cr and the surface area of the supports for the formation of Cr(VI) and Cr(III) on the surface of the support. The transformation of Cr(VI) into crystalline α-Cr_2O_3 can occur on the catalyst surface with respect to the content of Cr. It is quite clear that the content of Cr

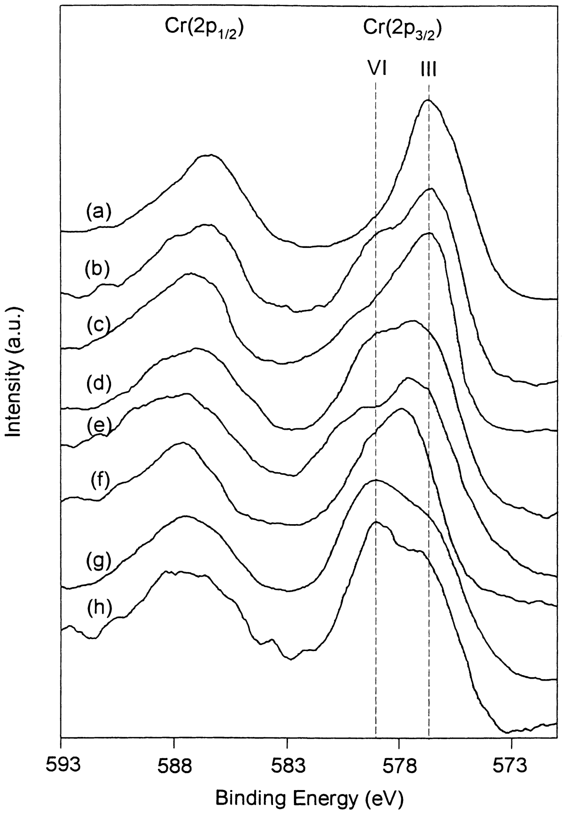

Fig. 7. XPS spectra of 12.5 wt.% CrO_x catalysts supported on activated carbon (a), $TiO_2$17 (b), $Al_2O_3$25 (c), $TiO_2$58 (d), $Al_2O_3$155 (e), SiO_2–Al_2O_3 (f), $Al_2O_3$290 (g) and $TiO_2$250 (h).

significantly alters the PCE removal activity as shown in Fig. 4. An increase of Cr loading did not proportionally enhance the PCE removal activity for low surface area of TiO_2 and Al_2O_3, since they can be easily saturated at a relatively low Cr content and form a poorly dispersed α-Cr_2O_3 on the catalyst surface. This is evident for $TiO_2$250 and $Al_2O_3$290 as observed in Fig. 4. The 12.5 wt.% CrO_x supported on TiO_2 and Al_2O_3 containing a variety of the surface area clearly reveals the dependence of the surface area of the supports for the formation of Cr(VI) on the high performance of PCE removal as shown in Figs. 4–6.

However, the CrO_x supported on activated carbon, SiO_2 and SiO_2–Al_2O_3 are exhibiting relatively low activity for the oxidation of PCE although they contain rather high surface area. It may be due to the fact that they contain low density of OH groups on their surface compared to TiO_2 and Al_2O_3. Weckhuysen et al. [19] observed that the formation of crystalline α-Cr_2O_3 increases as the silica content of the support increases due to the lower density of OH group on the surface of high silicious supports. Note that the high PCE removal activity of 5 wt.% CrO_x/SiO_2–Al_2O_3 is probably due to the difference of the surface area and the surface acidity of the supports. In addition, the degree of polymerization of Cr(VI) on the catalyst surface cannot be excluded to elucidate the high performance of PCE removal as extensively discussed in the previous study [20]. The trend of PCE removal activity over 1 and 5 wt.% CrO_x supported catalysts shown in Fig. 4 can also be understood by the degree of polymerization of CrO_x on the catalyst surface.

3.3. *Effect of feed concentration of water and PCE*

The effect of water vapor on the catalytic activity of 12.5 wt.% CrO_x supported on $TiO_2$250 and $Al_2O_3$290 has been examined in Fig. 8 for the complete oxidation of PCE. It is generally understood that the presence of water vapor in the feed gas stream alters the removal activity of CVOCs in the catalytic reactor due to the competitive adsorption of water and reactants on the active reaction sites on the catalyst surface [10]. However, the low concentration of water vapor may improve the CVOCs' removal activity in some cases by providing the source of hydrogen to dissociate Cl_2 from CVOCs producing HCl during the course of reaction [8]. Water vapor can also improve the deactivation of CrO_x catalyst by accelerating the reverse Deacon reaction [1].

As shown in Figs. 8, 10–30% of PCE conversion was reduced for $CrO_x/TiO_2$250 and $CrO_x/Al_2O_3$290 catalysts with respect to the concentrations of water vapor existing in the feed gas stream. PCE removal activity of both catalysts decreased with increasing water concentrations. However, the degree of loss of PCE removal activity of $CrO_x/TiO_2$250 catalyst was much milder than $CrO_x/Al_2O_3$290, probably due to the difference of the surface hydrophobicity between $TiO_2$250 and $Al_2O_3$290 [8]. Furthermore, the deactivated catalysts were quite stable without further activity loss within the operating time examined in the present study and completely recovered their initial activity by the elimination of the feed of water vapor to

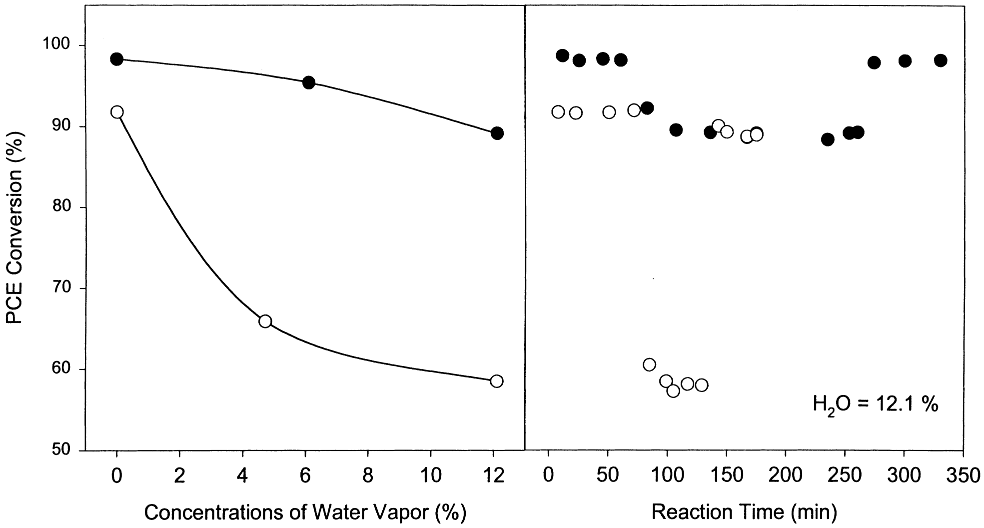

Fig. 8. Effect of water vapor on the catalytic activities of 12.5 wt.% CrO_x catalysts supported on $TiO_2$250 (●, SV = 150 000 h^{-1}) and $Al_2O_3$290 (○, SV = 100 000 h^{-1}) at 300°C.

the reaction system. This indicates that the activity loss of the catalysts due to water vapor is fully reversible. It also confirms that the deactivation is mainly due to the competitive adsorption of water and reactants on the active reaction sites on the catalyst surface.

Fig. 9 shows the stability of 12.5 wt.% CrO_x catalysts supported on $Al_2O_3$290 and $TiO_2$250 when the feed concentration of PCE increases from 30 to 10 000 ppm. It is generally known that the chromium oxide catalysts are unstable for the oxidation of

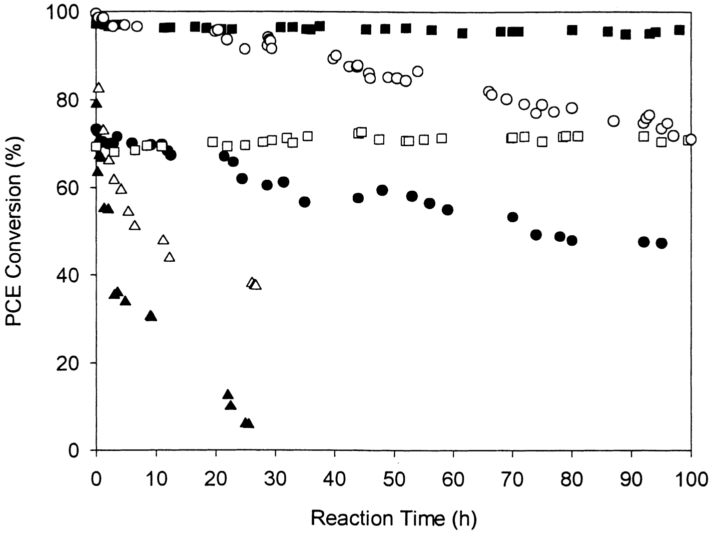

Fig. 9. Effect of the concentrations of PCE on the catalytic activities of 12.5 wt.% CrO_x catalysts supported on $TiO_2$250 (30 ppm, SV = 200 000 h^{-1}, ■ ; 1000 ppm, SV = 100 000 h^{-1}, ●; 10 000 ppm, SV = 100 000 h^{-1}, ▲) and $Al_2O_3$290 (30 ppm, SV = 150 000 h^{-1}, □; 1000 ppm, SV = 60 000 h^{-1}, ○; 10 000 ppm, SV = 60 000 h^{-1}, △) at 350°C.

CVOCs, especially at the high concentrations of CVOCs, mainly due to the volatilization of chromium oxide by the formation of CrO_2Cl_2 during the course of the reaction.

The activity of both CrO_x catalysts on $TiO_2$250 and $Al_2O_3$290 is stable at the low PCE feed concentration of 30 ppm up to 100 h at 350°C as observed in Fig. 9. However, the activity severely decreased with respect to the reaction on-stream time when the PCE feed concentration increased to 1000 and 10 000 ppm in the feed gas stream. The rate of the catalyst deactivation significantly depended on the feed concentrations of PCE. However, the deactivated catalysts were easily regenerated and their initial activity was nearly restored after treatment under air at 400°C for 1 h. The reversibility of the PCE removal oxidation for CrO_x catalysts observed in the present reaction systems implies that the catalyst deactivation is not mainly attributed to the volatilization of the chromium compound on the catalyst surface as previously suggested [1]. Instead, it may be due to another deactivation mechanism such as coking, poisoning by Cl_2 and the phase transformation of chromium oxide [8]. Indeed, most of the Cr was still existing on the surface of the deactivated catalyst as confirmed by elementary analysis. It has been also observed that the catalyst deactivation of CrO_x supported on TiO_2 and Al_2O_3 can be controlled by a common operating strategy of a deactivating reactor such as the increase of the reactor space time and the reaction temperature.

4. Conclusions

The content of Cr and the types of supports were critical for the high performance of PCE removal. The high surface area of TiO_2 and Al_2O_3 supports was especially efficient for the formation of Cr(VI) on the catalyst surface, which is the active reaction site for the complete oxidation of PCE. The relatively low PCE removal activity of CrO_x supported on SiO_2, activated carbon and SiO_2–Al_2O_3 containing high surface areas is mainly attributed to the formation of α-Cr_2O_3 on the catalyst surface as examined by XRD and XPS. The density of OH groups on the surface of the supports also plays an important role in the formation of the active reaction sites, Cr(VI). The stronger water tolerance of TiO_2 compared to Al_2O_3 is probably due to the surface hydrophobicity of TiO_2. The effect of the feed concentration of PCE was significant on the deactivation of CrO_x supported on TiO_2 and Al_2O_3 catalysts. However, it can be improved by the feed of water vapor to the reactor system and the control of the reactor space time and the reaction temperature.

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