Catalysis Today 175 (2011) 598–602

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Characterization of CrO_x/Al_2O_3 catalysts for dichloromethane oxidation

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ARTICLE INFO

Article history:
Received 9 October 2010
Received in revised form 28 February 2011
Accepted 12 April 2011
Available online 11 May 2011

Keywords:
CrO_x/Al_2O_3 catalysts
Catalytic oxidation
Dichloromethane

ABSTRACT

Chlorinated volatile organic compounds (CVOCs) are hazardous and potent environmental pollutants. Catalytic combustion has been regarded as one of the most promising technologies to eliminate CVOCs emissions. CH_2Cl_2 is difficult to be oxidized among CVOCs. A catalyst with high activity for CVOCs oxidation is desirable. In this paper, CrO_x/Al_2O_3 catalysts with different Cr contents were prepared using a deposition–precipitation method and tested for CH_2Cl_2 oxidation. The highest activity was obtained over the catalyst with 18% Cr content, with a complete oxidation of CH_2Cl_2 at 350 °C. Characterization results indicated that both high oxidation state Cr species (Cr(VI) species) and crystalline Cr_2O_3 existed in the CrO_x/Al_2O_3 catalysts, and the average valence of Cr species in the catalysts decreased with Cr content. It was found that the reaction rate for CH_2Cl_2 oxidation increased with increasing average valence of Cr, which indicated that high oxidation state Cr species were probably the active phase for the reaction.

1. Introduction

Chlorinated volatile organic compounds (CVOCs), such as dichloromethane (DCM), 1,2-dichloroethane (DCE), trichloroethylene (TCE) and chlorobenzene (CB), are hazardous and potent environmental pollutants. The amount of CVOCs released into the environment from industrial sources is increasing and needs to be regulated [1,2]. Technologies to eliminate CVOCs emissions are currently receiving increased attention. Catalytic combustion has been regarded as one of the most promising technologies because of its low energy consumption, high efficiency and no associated pollution such as nitrogen oxides (NO_x) since it is operated at low temperatures [3–5] (compared to thermal oxidation). A catalyst with high activity and thermal stability for CVOCs oxidation is desirable. Catalysts in reported studies for CVOCs catalytic oxidation are categorized in three groups: supported noble metals Pt, Pd [6], or transition metal oxides [7] and zeolites [8].

Noble metals are very active catalysts for CVOCs deep oxidation reactions [9]. Miranda et al. [10] reported the performance of 0.5% Ru/Al_2O_3 for the deep oxidation of trichloroethylene, both high activity and selectivity for total combustion are obtained. Although very active, application of noble metal catalysts is restricted due to the high cost and the formation of volatile metal oxychlorides [11]. Moreover, noble metal catalysts are known to be poisoned by HCl or Cl_2. Transition metal oxides can resist the deactivation caused by chlorine poisoning [12]. Chromium oxides are well known catalysts for total oxidation of CVOCs among transition metal oxides [13]. Yim et al. [14] investigated the oxidation of perchloroethylene (PCE) over supported chromium oxide catalysts. The results indicated that catalysts supported on TiO_2 and Al_2O_3 exhibited high activity and thermal stability because of their high surface areas. Moreover, supported chromium oxide catalysts are crucial in the synthesis of hydro fluorocarbons (HFCs) and other oxygen depleting substance (ODS) substitutes [15]. Dichloromethane is very stable and difficult to be oxidized in all the chlorinated organic compounds. In this work, catalytic oxidation of dichloromethane was selected as a model reaction to evaluate the catalytic properties of CrO_x/Al_2O_3 catalysts. Furthermore, the effects of Cr valence and surface acidity of the catalysts on the oxidation reaction were investigated.

2. Experimental

2.1. Catalysts preparation

The CrO_x/Al_2O_3 catalysts were prepared by a deposition–precipitation method. A detailed process was as follows: an aqueous solution of $Cr(NO_3)_3 \cdot 9H_2O$ was mixed with a Al_2O_3 powder. Then an aqueous solution of $(NH_4)_2CO_3$ (1 mol/L) was drop-wise added to the mixture under vigorous stirring. The pH value of the suspension was controlled at 8.0 ± 0.5. Then 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. Finally, all the dried materials were calcined at 600 °C for 4 h with a heating rate of 10 °C/min. The Cr content was about 5.0, 9.3, 18 and 33 wt% in the catalysts, determined by X-ray fluorescence (XRF) analysis. These catalysts were denoted as 5CrAlO, 9.3CrAlO,

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doi:10.1016/j.cattod.2011.04.025

18CrAlO and 33CrAlO, respectively, with the number representing the Cr content.

2.2. Characterizations

X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert PRO MPD powder diffractiometer 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 speed of $0.57^\circ\ s^{-1}$.

Raman spectra were recorded on a Renishaw RM1000 with a confocal microprobe Raman system using an excitation wavelength of 514 nm.

H_2 temperature-programmed reduction (H_2-TPR) was used to measure the reducibility of the catalysts. 25 mg of catalyst was placed in a quartz reactor, which was heated from 100 to 700 °C with a heating rate of 10 °C/min under a mixture of 5%H_2–95%N_2 (30 mL/min). The amount of H_2 consumption was determined by a gas chromatograph with a thermal conductivity detector (TCD), which was calibrated by the quantitative reduction of a known amount of CuO powder.

The acidic properties of the catalysts were studied by ammonia temperature programmed desorption (NH_3-TPD). For the experiment, 100 mg of the catalyst was pretreated in a flow of N_2 (20 mL/min) at 550 °C for 0.5 h, and then was cooled down to room temperature. Afterwards, a flow of NH_3 (20 mL/min) was introduced into the reactor for 15 min, followed by purging at 80 °C for 1 h with a N_2 flow (20 mL/min) to remove the physisorbed NH_3. Then the sample was heated from 80 to 600 °C at a rate of 20 °C/min, and the NH_3-TPD profile was recorded using a gas chromatograph (TECHTEMP GC 7890 II) with a TCD detector.

The Fourier transform infrared spectroscopy (FTIR) of the CH_2Cl_2 adsorption were performed on a NEXUS 670 Fourier transform infrared spectroscopy at room temperature, with a resolution of $4\ cm^{-1}$ and an accumulation of 32 scans. Before adsorption, the sample was dried in a vacuum oven for 1 h at 100 °C to remove water. Then the sample was exposed in gaseous CH_2Cl_2 for 30 min at room temperature. The sample was heated in a vacuum oven at 100 °C for 1 h to remove physisorbed CH_2Cl_2, then it was cooled down to room temperature for IR measurement.

2.3. Activity test

Catalytic oxidation reaction was carried out in a conventional fixed-bed reactor (i.d. = 9 mm). 2.5 g of the catalysts in 20–40 mesh was loaded in the reactor. A gaseous mixture of dichloromethane and air was introduced to the catalysts, and the concentration of dichloromethane was 3000 ppm (GHSV = 20,000/h). The conversion of dichloromethane was analyzed by a GC-14C (Shimadzu) equipped with a FID detector. The outlet reaction mixture was neutralized by passing through a 0.1 mol/L NaOH solution.

3. Results and discussion

3.1. Reactivities of CrAlO catalysts

Fig. 1 shows the activities of the CrAlO catalysts for CH_2Cl_2 oxidation. It can be seen that the pure Cr_2O_3 and Al_2O_3 samples are much less active compared to the CrAlO catalysts, with conversions of 60% and 5% at 400 °C for the Cr_2O_3 and Al_2O_3 samples, respectively. For the CrAlO catalysts, enhanced activities are obtained with increasing Cr content from 5% to 18%, but further increasing Cr content to 33% results in a suppressed activity. It is found that the 18CrAlO catalyst possesses the highest activity, with the lowest reaction temperature for the conversion of 100% at 350 °C. For CH_2Cl_2 oxidation on CrAlO catalysts, the main reaction products are CO_x, HCl and Cl_2. However, chlorinated organic by-products such as $CHCl_3$ [16] are not detected, indicating that the by-products can be further oxidized over the CrAlO catalysts.

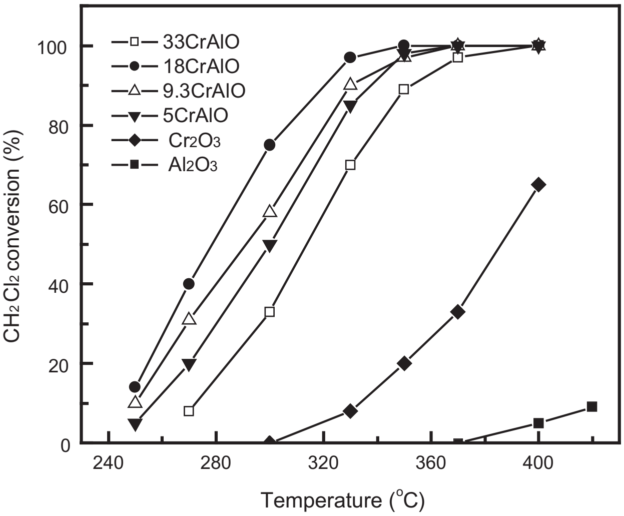

Fig. 1. CH_2Cl_2 oxidation over CrAlO catalysts.

Fig. 2 shows stability of the CrAlO catalyst. It can be seen that the conversion hardly changes and keeps around 70% in 15 h, which indicates that the 18CrAlO catalyst is quite stable during the reaction.

3.2. Cr species characterization

Fig. 3 shows the XRD patterns of fresh and used CrAlO catalysts. It can be seen that for the low Cr content catalysts (5% and 9.3%), only diffraction peaks due to Al_2O_3 are observed (Fig. 3a), implying that the Cr species are highly dispersed. With further increasing Cr content to 18% and 33%, diffraction peaks due to crystalline Cr_2O_3 appear [17] and they become predominant in these catalysts. Compared with Fig. 3a, it is found in Fig. 3b that the diffraction peaks of used catalysts are almost identical to those of the fresh catalysts, suggesting that the phase structure and composition remain stable during the reaction.

As Raman spectroscopy is a very powerful characterization technique to obtain detailed surface information about Cr species [18], the Raman characterization of fresh (a) and used (b) CrAlO cata-

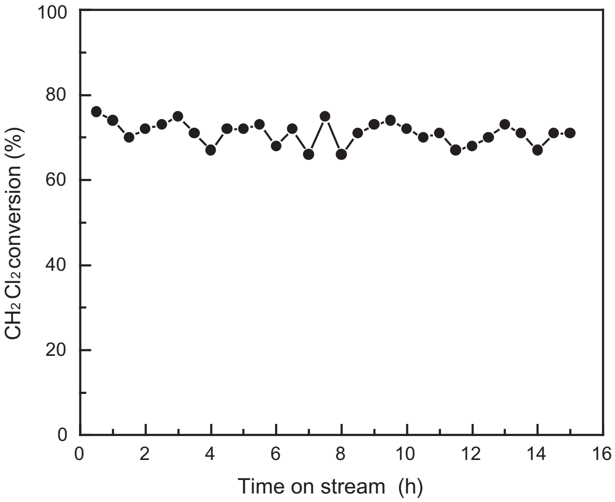

Fig. 2. CH_2Cl_2 oxidation over 18CrAlO catalyst at 300 °C.

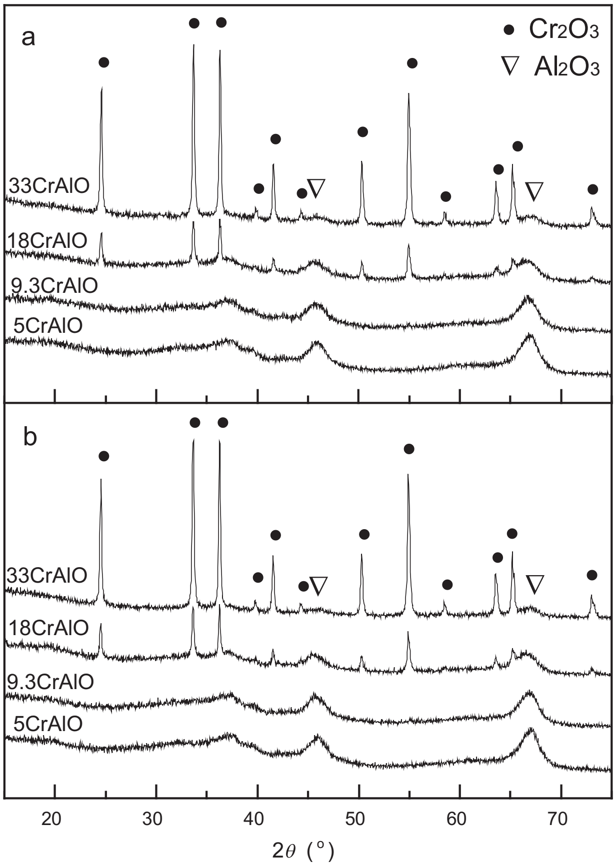

Fig. 3. XRD patterns of fresh (a) and used (b) CrAlO catalysts.

lysts were performed (Fig. 4). For the fresh catalysts in Fig. 4a, a Raman band 864 cm^{-1} assigned to symmetric stretching of Cr(VI) species [19] is observed for the catalysts with low Cr content (5% and 9.3%). The peak becomes weaker with increasing Cr content to 18% and almost disappears when the Cr content is 33%, indicating decreasing amount surface Cr(VI) species in the catalysts. It also imply the cooperation between the Al_2O_3 support and the Cr species, that is, high oxidation state Cr(VI) could be stabilized when the Cr content is low [20]. For the high Cr content catalysts (18% and 33%), additional bands at 307, 351, 550, 609, 1383 cm^{-1} and a band at 1000 cm^{-1} are observed. The former five bands could be assigned to vibration modes of crystalline Cr_2O_3 [21], while the latter is assigned to the polymeric surface Cr species [22]. These bands become more intense with increasing Cr content. The Raman spectra of the catalysts suggest that the low Cr content catalysts contain mainly high oxidation state Cr species (Cr(VI)), while the high Cr content catalysts contain mainly low oxidation state Cr species (Cr(III)). For the used catalysts (Fig. 4b), the Raman bands are almost identical to those of the fresh catalysts, implying that the surface properties of the catalysts remain unchanged during the reaction. Both the XRD and the Raman results suggest that the catalyst remains stable during the reaction, which may explain the stable catalytic behavior of the catalyst.

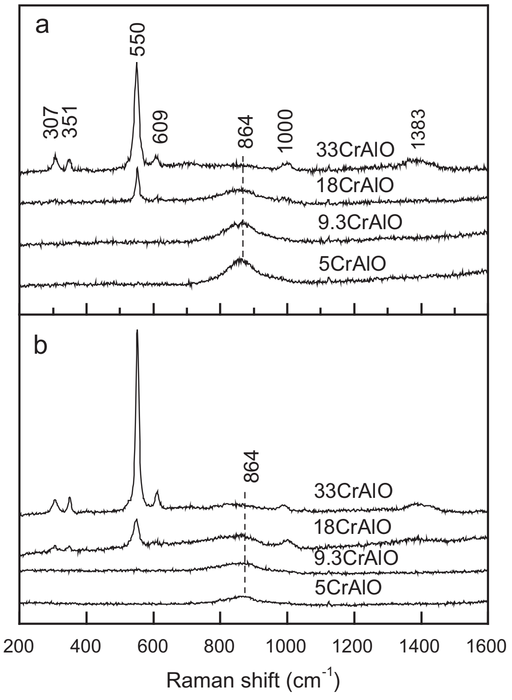

Fig. 4. Raman spectra of fresh (a) and used (b) CrAlO catalysts.

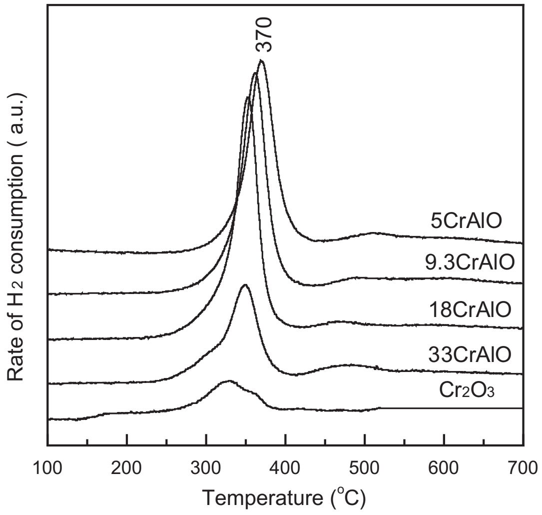

Fig. 5. H_2-TPR profiles of CrAlO catalysts.

3.3. Reducibility of catalysts

Fig. 5 shows the H_2-TPR profiles of the CrAlO catalysts. For the Cr_2O_3 catalyst, a weak and broad reduction peak at about 325 °C is observed. Since crystalline Cr_2O_3 exhibits no reduction peaks before 800 °C [17], the low temperature reduction peak implies that some Cr species in the pure Cr_2O_3 may be oxidized when the sample was exposed in air. For the CrAlO catalysts, the profiles are featured by a reduction peak at 250–450 °C, which is attributed to the ready reduction of high oxidation state Cr species (Cr(VI)) to crystalline Cr_2O_3. It is also seen that the reduction peak shifts to lower temperature with increasing Cr content to 18% and then remains, implying the increased redox property and enhanced activity of the catalyst.

The amount of H_2 consumption is listed in Table 1, which is calibrated by the quantitative reduction of CuO. Also, the

Table 1
H_2 consumption and average valence of Cr in CrAlO catalysts.

Catalyst	H_2 consumption (mmol/g_{cat})	Average valence of Cr
5CrAlO	0.46	3.95
9.3CrAlO	0.50	3.55
18CrAlO	0.53	3.31
33CrAlO	0.27	3.09
Cr_2O_3	0.14	3.01

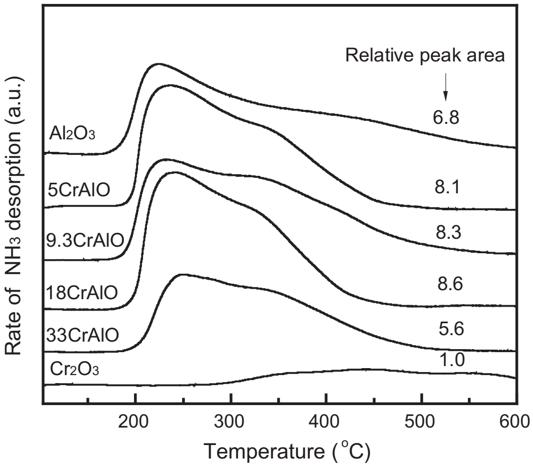

Fig. 6. NH_3-TPD profiles of CrAlO catalysts.

average valence of Cr is calculated according to the amount of H_2 consumption, supposing that the final state of reduced Cr species is crystalline Cr_2O_3. It is found that the total H_2 consumption varies from 0.46 to 0.14 mmol/g_{cat}, with the largest amount of 0.53 mmol/g_{cat} for the 18CrAlO catalyst, which may be one of the reasons for the highest catalytic activity (Fig. 1). The calculated average valance of Cr species in the catalyst declines with increasing Cr content, indicating the ratio of high oxidation state Cr species to low oxidation state decreases. This is in consistent with the XRD and Raman results, as they clear show that low oxidation state Cr(III) dominates in the high Cr content catalysts.

3.4. Surface acidity of catalysts

Fig. 6 shows the NH_3-TPD profiles of the CrAlO catalysts. It can be seen that for all of these, NH_3 desorption peaks appear from 200 °C, and the final temperature of CrAlO catalysts are lower than that of Al_2O_3 support. It indicates that the addition of Cr leads to the decrease in the amount of strong acid sites. Also, the relative areas of the desorption peaks are calculated. It is found that the peak area changes slightly with increasing Cr content, with the 18CrAlO having the largest peak area, which implies the maximum amount of surface acid sites on the catalyst. As the surface acid sites are effective for the adsorption of CH_2Cl_2 and the hemolytic rupture of the C–Cl bond of chloroalkanes [23], large amount of surface acidic sites may be beneficial to the reaction. It may be another reason for the highest activity of 18CrAlO catalyst (Fig. 1).

Fig. 7 shows the FTIR spectra of CH_2Cl_2 adsorption on the Al_2O_3, Cr_2O_3 and 18CrAlO samples. Two bands at 1264 and 1384 cm^{-1} are observed. The former (1264 cm^{-1}) is assigned to ν_{C-Cl} [24], and the latter (1384 cm^{-1}) is assigned to δ_{C-H} [25]. It indicates the chemisorption of CH_2Cl_2 on the catalyst surface. It can be seen from Fig. 7 that the peak intensity of CH_2Cl_2 adsorption is very weak on the Cr_2O_3 catalyst, indicating the adsorption is difficult on the surface of the catalyst. This may be related to the few of surface acid sites on the Cr_2O_3 catalyst. Therefore, for 18CrAlO and Al_2O_3 catalysts with more surface acid sites, the peak intensity of CH_2Cl_2 absorption is stronger. This indicates that surface acid sites are helpful to CH_2Cl_2 absorption on the catalysts.

3.5. Active phase for CH_2Cl_2 oxidation

Fig. 8 presents the relationship between average valence of Cr and reaction rate over CrAlO catalysts at 300 °C. As the catalysts vary in Cr content, the reaction rate is calculated based on unit mass of Cr. As can be seen in Fig. 7, crystalline Cr_2O_3 exhibits almost no activity at 300 °C. The reaction rate increases linearly with increasing average valence of Cr species, that is, it increases with decreasing Cr content in the catalyst. This relationship suggests high oxidation state Cr species play an important role in the reaction [26]. It is in line with the characterization results, as the Raman and H_2-TPR results clearly show that low Cr content catalysts have higher proportion of high oxidation state Cr species (Cr(VI)) compared to those with high Cr content. Therefore, the high oxidation state Cr species (Cr(VI)) are mainly responsible for the growing reaction rate [27]. In addition, it is worthnoting that the surface acidity of catalysts is helpful to decompose CH_2Cl_2 [23].

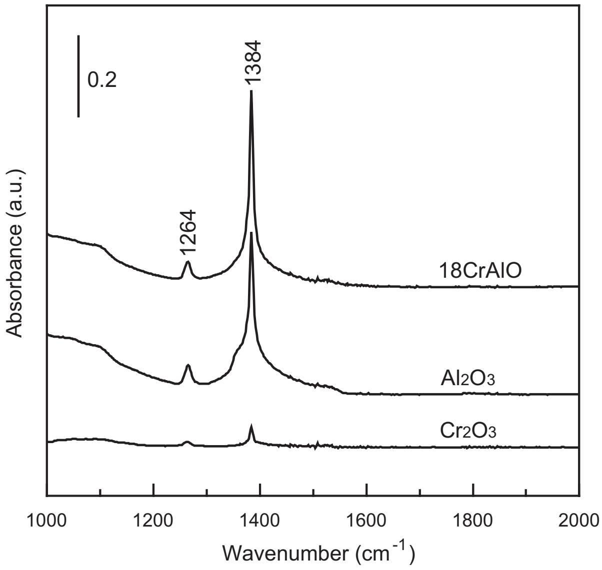

Fig. 7. IR spectra of CH_2Cl_2 adsorption over catalysts.

According to these results above, it can be seen that CH_2Cl_2 was adsorbed on the surface acid sites, and the high oxidation state of Cr species is the active site of CH_2Cl_2 oxidation. The reaction rate for CH_2Cl_2 oxidation increases with increasing average valence of Cr species in the catalysts, and 5CrAlO catalyst gives the highest reaction rate. As for catalytic activity, however, 18CrAlO exhibits the highest due to the largest amount of H_2 consumption and surface acidic sites.

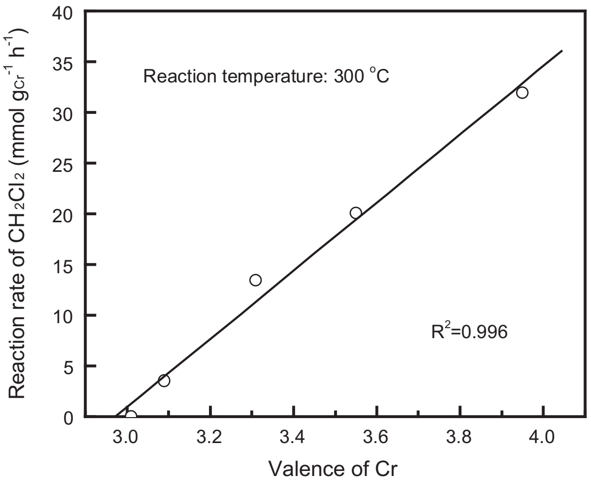

Fig. 8. Relationship between average valence of Cr and reaction rate over CrAlO catalysts.

4. Conclusions

A series of CrO_x/Al_2O_3 catalysts were prepared and tested for CH_2Cl_2 oxidation. Both high oxidation state Cr species and Cr_2O_3 existed in CrO_x/Al_2O_3 catalysts. The highest activity was obtained over the catalyst with 18% Cr content. The reaction rate for CH_2Cl_2 oxidation increased with increasing average valence of Cr species in the catalyst, which indicated that Cr(VI) species played a major role in the catalytic performance for CH_2Cl_2 oxidation, and led to a considerable enhancement of the reaction rate.

Acknowledgment

This work is financially supported by the Plan Project of Science and Technology in Zhejiang Province (2008C21020).

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