Catalysis Letters Vol. 81, No. 3–4, August 2002 (©2002)

Ru-promoted CrO_x/Al_2O_3 catalyst for the low-temperature oxidative decomposition of trichloroethylene in air

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Received 29 November 2001; accepted 18 March 2002

A series of Ru-promoted CrO_x/Al_2O_3 as catalysts for the low-temperature oxidative decomposition of trichloroethylene (TCE) were characterized and evaluated in comparison with an unpromoted CrO_x/Al_2O_3 catalyst. Catalyst characterization was conducted by surface area measurement, X-ray diffraction and X-ray photoelectron spectroscopy. Catalyst performance in the TCE decomposition reaction was evaluated with respect to the initial catalytic activity, the rate of catalyst deactivation, and the product concentrations of CO and Cl_2 under dry or wet air conditions. The presence of a small amount of Ru, as much as 0.4 wt% in a CrO_x/Al_2O_3 catalyst, brought about several beneficial effects on the catalytic reaction performance. As compared with the unpromoted CrO_x/Al_2O_3, this Ru-promoted CrO_x/Al_2O_3 catalyst showed enhanced catalytic activity (249 *versus* 264 °C in terms of temperature at which 50% of TCE conversion occurred), a reduced concentration of CO (180 *versus* 325 ppm) in the product, and a decreased propensity to deactivation. Performance improvements of the Ru-promoted CrO_x/Al_2O_3 catalyst were thought to originate from its enhanced oxidation activity due to the coexisting highly-dispersed Ru oxides rendering less active Cr(III) to more active Cr(VI), and facilitating the process of supplying activated oxygen for the reaction system.

KEY WORDS: trichloroethylene; catalytic oxidative decomposition; deactivation; Ru-CrO_x/Al_2O_3; Ru promoter.

1. Introduction

In general, activity, selectivity and stability of a catalyst are important factors for its industrial applications. Particularly, the catalysts for the oxidative decomposition of various chlorinated volatile organic compounds (CVOCs) are required to have enough catalytic activity at low-temperature operation for the operational economics, and to have high selectivity towards environment-friendly products for the prevention of secondary environmental pollution. The catalysts also should be resistant to deactivation at low-temperature operation or poisoning by the Cl_2 or HCl produced. Cr-oxide catalysts have been frequently reported to have high catalytic activity for the trichloroethylene (TCE) decomposition reaction [1–7]. CrO_x/Al_2O_3 catalysts have been commercially applied for the decomposition of CVOCs by virtue of their high activity, low selectivity for Cl_2 production, high resistance to HCl poisoning, and good thermal stability [1,2]. However, there exist also some problems to be solved for the low-temperature application of this catalyst.

It has been reported [1] for the CrO_x/Al_2O_3 catalysts that CO is produced in high concentrations (up to 54% of CO selectivity) from the oxidative decomposition of CVOCs in a fixed-bed reactor. Over an acid catalyst like Cr-Y [8], the formation of CO is highly favored against CO_2. This indicates that the single-component catalyst of Cr does not have sufficient catalytic activity for the oxidation of CO. Furthermore, CO production in higher concentration is expected for the catalysts in their application at lower temperatures and higher space velocities. Such deficiency of oxidation activity can cause the production of partially oxidized products like $COCl_2$, which are more toxic than the original reactants.

Another problem of Cr catalysts encountered in their applications to CVOC decomposition is catalyst deactivation. As the major causes of catalyst deactivation in the CVOC decomposition reaction, coking [3,9] by carbonaceous materials deposited on catalysts, the loss of Cr metal from the catalyst [2,3,10,11] by the formation of volatile CrO_2Cl_2, and the phase transformation of Cr-oxides [3,6] from Cr(VI) to less active Cr(III) have been raised. Among them, coking deactivation is very likely to occur at the initial stage of operation for catalysts of high acidity. According to Chatterjee *et al.* [9], catalyst deactivation by coking is faster for the operation at lower temperatures and higher space velocities. They proposed for the oxidative decomposition of various CVOCs over the acid catalyst of Co-Y that CO could be the reaction intermediate that led to the formation of coke. It can therefore be considered that the production of CO as well as the deactivation by coking may result from the insufficient oxidation activity of the catalyst, by which low-temperature application can be restricted. In order for the low-temperature application

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1011-372X/02/0800-0247/0

of the Cr-oxide catalyst, which has superior initial catalytic activity for the oxidative decomposition of CVOCs, it is crucial for the catalyst to be improved with respect to the high selectivity for CO production and the deactivation originating from its low oxidation activity.

In the previous report [7] where various transition metal oxides were screened as a promoter for an alumina-supported Cr-oxide catalyst in the decomposition reaction of TCE, we reported the activity promotion of the Cr-oxide catalyst coimpregnated with an appropriate amount of Ru, Mn or Ce. Particularly, the alumina-supported Cr-oxide catalyst promoted with a small content of Ru gave higher activity, lower acidity and better reducibility than the single-component Cr-oxide catalyst. This Ru-promoted catalyst with an improved redox cycle property and a lowered acidity suggests the possibility of reducing the CO production as well as the deactivation by coking. In the present study, the possibility of Ru-promoted Cr-oxide as a catalyst for low-temperature oxidative decomposition of TCE has been evaluated in comparison with an unpromoted Cr-oxide catalyst. The effects of reaction temperature and the presence of water vapor in the air-loaded TCE stream upon the initial rate of deactivation, the effluent concentrations of CO and Cl_2, and the conversions of TCE were investigated. Catalysts were characterized using the surface area measurement, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

Catalytic metal was impregnated onto the powdered γ-Al_2O_3 (BET surface area 200 m^2/g) support by evaporating excess solution containing the calculated amount of catalytic metal precursor, chromium(III) nitrate nonahydrate (Aldrich) or ruthenium (III) chloride hydrate (Aldrich). Impregnated samples were dried for 12 h at 110 °C and subsequently calcined for 5 h at 540 °C. For the catalysts of binary metal components, two metal precursors were impregnated at the same time. Powdered samples were pelletized, crushed and sieved to 60–120 mesh for the reaction. In this study, the catalyst was indicated by Cr(10) or Ru(0.4)Cr(9.6), of which numbers mean the weight percents of the corresponding metal components in the oxide catalysts, determined from the AA analysis.

2.2. Catalyst reaction test

Catalytic reaction experiments were conducted in a quartz tube reactor (10 mm i.d.) with a bed of catalyst particles. The reactant was TCE contained in a Pyrex saturator which was immersed into an ice-water bath kept at 0.5 °C. Inlet concentration of TCE to the reactor was adjusted by mixing the flow of N_2 passing through the TCE saturator and the two separate flow streams of N_2 and O_2. The flow ratio of total N_2 to O_2 in the inlet gas stream was adjusted to 79/21 to meet air composition. For the reaction at dried air condition, water vapor in the N_2 and O_2 was removed by passing the gases through the packed beds of molecular sieve 5 Å and silica gel. For the experiments under wet air condition, 10 000 ppm (1 vol%) of water vapor was fed into the reactor by passing a flow of N_2 through a saturator containing distilled water at 16 °C. Catalytic reactions in the water vapor-free or wet air were carried out under the following conditions: total gas flow rate 60 ml/min (GHSV 20 000 h^{-1}), catalyst weight 0.192 g, TCE concentration 730 or 365 ppm.

A GC (Varian 3400) equipped with a packed column (3% OV-17, 80/100 mesh, SS 1.83 m × 3 mm) and FID was used to analyze the concentrations of TCE in the reactant and product streams. The volume of a gas sample injected into the GC column was kept constant using a six-port valve with a sample loop of 1 ml. The conversion of TCE by the reaction was calculated from the GC peak area of TCE in the feed and product streams. Three successive measurements were made for each conversion value. The concentrations of CO and Cl_2 were measured using Dräger detector tubes (Fisher Scientific), carbon monoxide 5/c for CO, and chlorine 0.2/a and 50/a for Cl_2.

2.3. Catalyst characterization

Catalysts were characterized using XRD, BET and XPS. The XRD pattern was obtained using a Rigaku DMAX/1200, and the BET surface area was measured using a Micromeritics 2010. XPS spectra of Al 2p and Cr 2p were measured using the SPECS LHS-10 system of which the X-ray source was Mg K_α radiation (300 W) with pass energy 71 eV and base pressure 7×10^{-9} Torr. XPS spectra measured for the catalysts were referenced to the binding energy (BE) of C 1s, 284.6 eV.

3. Results and discussion

3.1. Characteristics of Ru-CrO_x catalysts

Table 1 lists the light-off temperatures (T_{50}) of TCE decomposition and the surface areas of the catalysts with different compositions of Ru. T_{50} values which indicate the relative activity-ranking of the catalysts for a particular reactant were obtained from the TCE decomposition reaction experiments conducted at GHSV 20 000 h^{-1} and TCE concentration 730 ppm in dried air. The most active catalyst is Ru(0.4)Cr(9.6), which shows the lowest T_{50}. In general, surface areas of

Table 1
Summary of the alumina-supported catalysts

Catalysts	Ru/(Ru + Cr) weight ratio (wt%/wt%)	T_{50} in TCE (730 ppm, dry air) light off (°C)	BET surface area (m^2/g)
Cr(10)	0	264	165
Ru(0.4)Cr(9.6)	0.04	249	170
Ru(1.2)Cr(8.8)	0.12	259	164
Ru(5)Cr(5)	0.5	273	159
Ru(7.2)	1.0	320	150

the catalysts are decreased with increasing Ru composition; however, the presence of a small amount of Ru in the CrO_x/Al_2O_3 catalyst results in an increased surface area.

Figure 1 shows the Cr 2p XPS spectra for the catalysts, Cr(10), Ru(0.4)Cr(9.6) and Ru(1.2)Cr(8.8). Rahman *et al.* [12] reported the BEs of Cr $2p_{3/2}$ of a CrO_x/Al_2O_3 catalyst as 579.7–580.0 eV and 577.2–577.6 eV for Cr(VI) and Cr(III), respectively. BEs corresponding to the Cr $2p_{3/2}$ peak of the catalysts in our study, Cr(10), Ru(0.4)Cr(9.6) and Ru(1.2)Cr(8.8), are 577.6, 579.1 and 578.9 eV, respectively. These results suggest that Cr(III) are the predominant species for the catalyst Cr(10) whereas CrO_3 species of Cr(VI) are present in an increased fraction over the catalyst Ru(0.4)Cr(9.6). As well as for the catalyst Ru(0.4)Cr(9.6), the BE of the Cr $2p_{3/2}$ peak for the Ru(1.2)Cr(8.8) shows the presence of Cr(VI) in an increased fraction as compared with Cr(10). It is therefore concluded that the oxidation state of some parts of the CrO_x has been changed from Cr(III) to Cr(VI) by the presence of the small amount of Ru. Petrosius *et al.* [3] reported for the oxidative decomposition of CH_2Cl_2 using the carbon-supported Cr-oxide catalyst that the catalytic activity was mostly attributed to the Cr(VI) species, and that parts of more active Cr(VI) species were reduced to less active Cr(III) as the reaction proceeded, resulting in the mixed oxidation states of Cr(VI) and Cr(III).

Table 2
Ratio of XPS peak area of Cr $2p_{3/2}$ to Al 2p

Catalysts	Relative peak area, Cr $2p_{3/2}$/Al 2p
Cr(10)	1.0
Ru(0.4)Cr(9.6)	1.1
Ru(1.2)Cr(8.8)	0.57

Therefore it can be understood that the highest activity promotion appearing in the Ru(0.4)Cr(9.6) catalyst is due to the coimpregnated Ru rendering less active Cr(III) to more active Cr(VI). Table 2 lists the ratios of the area of Cr $2p_{3/2}$ peak area to the Al 2p peak for the catalysts Cr(10), Ru(0.4)Cr(9.6) and Ru(1.2)Cr(8.8), which indicate their relative surface coverage of CrO_x on the alumina support surface. As compared with Cr(10), Ru(0.4)Cr(9.6) shows rather increased surface coverage of CrO_x whereas Ru(1.2)Cr(8.8) shows considerably decreased surface coverage. As shown in table 1, the catalyst of Ru-oxide is less active for TCE decomposition reaction than the Cr-oxide. As the content of less active Ru is increased, the relative surface coverage of more active Cr-oxides decreases, and as a result, the catalyst Ru(1.2)Cr(8.8) becomes less active than Ru(0.4)Cr(9.6).

Figure 2 shows the XRD patterns of the Ru-promoted Cr-oxide catalysts in comparison with Cr(10) and Ru(7.2). The same XRD pattern as Cr(10) is observed for the catalyst Ru(0.4)Cr(9.6), which shows the highest

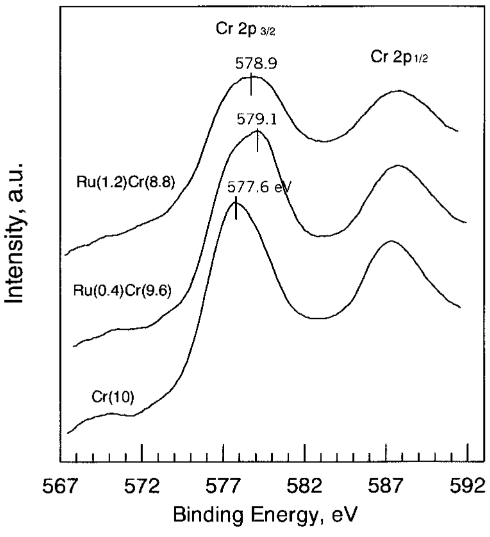

Figure 1. XPS spectra of Cr 2p for the alumina-supported catalysts of Ru and Cr oxides.

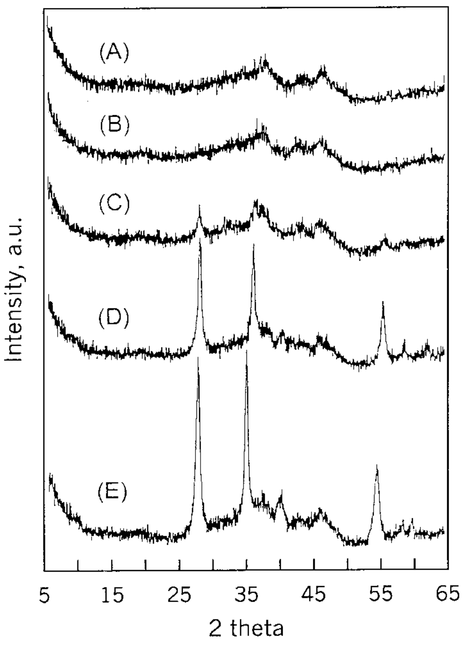

Figure 2. XRD patterns of the alumina-supported catalysts of Ru and Cr oxides: (A) Cr(10), (B) Ru(0.4)Cr(9.6), (C) Ru(1.2)Cr(8.8), (D) Ru(5)Cr(5) and (E) Ru(7).

activity. Although both catalysts contain relatively large amounts of CrO_x, the XRD patterns responsible for amorphous Al_2O_3 only are observed, indicating that CrO_x exists as well-dispersed phases on the support surface without the formation of discernible crystallites. XRD patterns responsible for the RuO_2 crystalline phase appear in weak intensity for the catalyst Ru(1.2)Cr(8.8) and stronger for the catalysts with higher Ru content. This indicates that higher fractions of Ru have wasted in the crystallite formation for the catalysts containing larger amounts of Ru. Decreases in the surface area of the catalysts with increasing content of Ru, as shown in table 1, may be due to the pore blockage of the alumina support caused by the formation of RuO_2 phases with a large size. Also, co-impregnation of the large Ru content with Cr leads to the decreased surface coverage of Cr-oxides, as ascertained by XPS. For the Ru(0.4)Cr(9.6) catalyst, the small Ru content highly promotes the catalytic activity by being effectively dispersed.

The results of surface area, XRD and XPS suggest that the presence of an appropriate amount of highly-dispersed Ru in the alumina-supported CrO_x catalyst makes a contribution to the increase in the catalyst surface area and to the transformation of the Cr(III) species to the Cr(VI), resulting in activity promotion.

3.2. Reaction performance

3.2.1. Catalyst deactivation

Figure 3 shows the TCE conversions over the catalysts Cr(10) and Ru(0.4)Cr(9.6) with time on stream for the reaction at 300 °C. Irrespective of the presence of water vapor in the feed stream, Ru(0.4)Cr(9.6) shows higher catalytic activity than Cr(10). It is also observed that both catalysts deactivate with the time on stream. Figure 3 indicates that Ru(0.4)Cr(9.6) is more resistant to the deactivation than Cr(10) in the oxidative decomposition reaction of TCE. It can also be understood that the presence of water vapor (1 vol%) in the feed stream accelerates the rate of such deactivation.

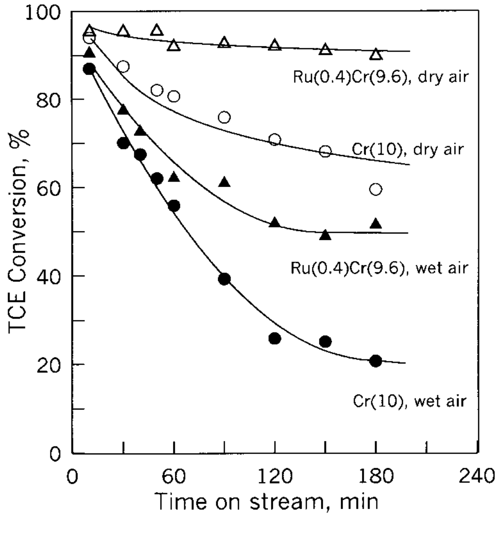

Figure 3. TCE conversions with time on stream of the reaction at 300 °C over the catalysts Cr(10) and Ru(0.4)Cr(9.6) under dry and wet (1% water vapor) air conditions: GHSV 20 000 h^{-1}, TCE 730 ppm.

Among the three major causes of the catalyst deactivation in the CVOC decomposition reaction as mentioned in the introduction section, deactivation by the loss of Cr metal from the catalyst by the formation of volatile CrO_2Cl_2 was reported to occur for the catalyst used for long periods at relatively high temperature [11]. This kind of deactivation can be excluded from the consideration of the cause of catalyst deactivation in the present study because any loss of the metal from the catalysts experimented on is not observed.

Catalyst deactivation by coking usually occurs at earlier stages of reaction by the deposition of cokes onto the active sites or blocking the pores of supports. Chatterjee *et al.* [9] reported for the oxidative decomposition reaction of TCE, CH_2Cl_2 and CCl_4 over Co-Y catalyst that CO formed as a reaction intermediate could be a precursor of cokes on the catalyst. In the reaction where the reaction intermediate [CO] adsorbed on active sites reacts with neighboring activated oxygen to desorb as CO_2, they proposed that cokes can be formed by self-association of the carbon atoms produced by the dissociation of the adsorbed [CO]. As listed in table 3, the concentration of CO in the product stream over the Cr(10) catalyst is 1.8 times higher than that over the Ru(0.4)Cr(9.6). High concentration of CO in the product stream suggests that oxidation reaction is not so much complete that parts of partially oxidized reaction intermediates could stay on the catalyst, probably being formed as cokes. Accordingly, the catalyst Ru(0.4)Cr(9.6) showing less propensity to deactivation can be thought to possess higher oxidation activity than Cr(10). It could be stated that this enhanced oxidation activity of Ru(0.4)Cr(9.6) originates from the well-dispersed Ru-oxide species.

Besides the catalyst deactivation caused by coking, the possibility of the phase transformation of Cr-oxides from Cr(VI) to less active Cr(III) during the reaction cannot be ruled out as a cause of the deactivation in this study. Yim *et al.* [6] reported for the decomposition reaction of perchloroethylene over the catalysts CrO_x/Al_2O_3 and CrO_x/TiO_2 at 350 °C that deactivation of

Table 3
Effluent concentrations of CO and Cl_2 from the oxidative decomposition reaction of TCE (365 ppm) at 350 °C

Catalysts	Feeding air condition	CO (ppm)	Cl_2 (ppm)
Cr(10)	Dry	325	310
	Wet (1 vol% water)	230	–[a]
Ru(0.4)Cr(9.6)	Dry	180	480
	Wet (1 vol% water)	180	–[a]

[a] Not determined.

the Cr-oxide catalysts was mainly attributed to the active phase transformation from more active Cr(VI) to less active Cr(III). This kind of catalyst deactivation was found more significant for the higher feed concentrations of perchloroethylene. In order for the successful application of the Cr-oxide catalysts to the highly concentrated CVOC feeds, they pointed out that the catalysts should be modified to speed up the process of oxygen supplement for the Cr-oxides in the state of deficient lattice oxygen. If the catalyst deactivation observed in figure 3 can be regarded as resulting from the phase transformation of Cr-oxides, Ru(0.4)Cr(9.6) is more resistant to this kind of deactivation than Cr(10). As ascertained by XPS analysis, due to the presence of the small amount of Ru, Ru(0.4)Cr(9.6) has a larger fraction of Cr(VI) than Cr(10). It is therefore surmised that the well-dispersed RuO_2 species might help the Cr-oxides in their neighbors to be maintained as active Cr(VI) during the reaction by providing the Cr(III) with activated atomic oxygen.

As shown in figure 3, the catalyst deactivation is enhanced by the presence of water vapor in the reactant stream. The decreases in TCE conversion by the presence of water vapor are observed nearly the same as 40% for both catalysts after 3 h of reaction time on stream. This indicates that both catalysts suffer from the presence of water vapor to nearly the same magnitude of deactivation. This accelerated catalyst deactivation by water vapor is thought to result from the screening effect of water molecules adsorbed onto some parts of active sites by preventing molecular oxygen or TCE from adsorbing. It was reported [8] that this screening effect of water on the cationic sites of Cr-Y was more pronounced at lower temperature, but disappeared as the reaction temperature increased. After about 3 h on-stream run of the TCE decomposition reaction over the catalysts Cr(10) and Ru(0.4)Cr(9.6) at 300 °C, as shown in figure 3, the reaction continued for a further 25 h at the reactor temperature, 350 °C, and the inlet concentration of TCE, 365 ppm. For this reaction duration, nearly complete conversions of TCE were kept up over both catalysts without any discernible sign of catalyst deactivation in dry or wet air conditions.

3.2.2. *Concentrations of CO and Cl_2 in products*

Table 3 lists the concentrations of CO and Cl_2 in the product stream from the oxidative decomposition of TCE (365 ppm) over the catalysts Cr(10) and Ru(0.4)Cr(9.6) at 350 °C. In the reactions in dry air conditions, the concentration of CO is higher in Cr(10) than in Ru(0.4)Cr(9.6), whereas that of Cl_2 is higher in Ru(0.4)Cr(9.6) than in Cr(10). As discussed above, the production of CO in lower concentration indicates that the catalyst has higher activity for the oxidation reaction. The oxidative decomposition of TCE can be explained by the following modified reaction mechanism, which was originally proposed by Chatterjee and Greene [8] for the reaction of CH_2Cl_2 over the Cr-Y catalyst:

$$C_2HCl_3 + \{\ \} \Leftrightarrow \{C_2HCl_3\} \tag{1}$$

$$O_2 + [\ ] \Leftrightarrow [O_2] \tag{2}$$

$$[O_2] + [\ ] \Leftrightarrow 2[O] \tag{3}$$

$$\{C_2HCl_3\} + 2[O] \Leftrightarrow 2[CO] + \{HCl\} + \{Cl_2\} \tag{4}$$

$$2\{HCl\} + [O] \Leftrightarrow [H_2O] + \{Cl_2\} \tag{5}$$

$$[CO] + [O] \Leftrightarrow [CO_2] \tag{6}$$

$$[CO] \Leftrightarrow [\ ] + CO \tag{7}$$

$$\{HCl\} \Leftrightarrow \{\ \} + HCl \tag{8}$$

$$[CO_2] \Leftrightarrow [\ ] + CO_2 \tag{9}$$

$$\{Cl_2\} \Leftrightarrow \{\ \} + Cl_2 \tag{10}$$

where adsorption sites { } indicate the Brønsted acid sites or protonic sites, and [ ] indicate the metal cationic sites. This reaction mechanism suggests that molecular oxygens adsorbed on the cationic sites are dissociated to be formed as atomic activated oxygens, and reacted with the adsorbed TCE on acid sites to give the partially-oxidized products [CO], {HCl} and $\{Cl_2\}$, as designated in reactions (1)–(4). As to the acid sites on the CrO_x/ZrO_2 catalyst, which is similar to our CrO_x/Al_2O_3, Sohn *et al.* [13] reported that both Brønsted and Lewis acid sites existed on the surface of the catalyst and that the oxidation state of Cr species influenced the acid strength. It can be thought for the CrO_x/Al_2O_3 catalyst that the supported CrO_x species are capable of simultaneously providing the adsorption sites for both molecular oxygen and TCE. The concentrations of Cl_2 and CO in the product stream are governed by reactions (5) and (6), respectively. In the case where the supply of the activated oxygen [O] is facilitated, both reactions (5) and (6) will proceed in a forward direction, resulting in higher concentration of Cl_2 and lower concentration of CO in the product stream. This indicates that Ru(0.4)Cr(9.6) is more active in the catalytic oxidation activity than Cr(10) because the former shows less concentration of CO and higher concentration of Cl_2 in the product stream than the latter, as shown in table 3. This is consistent with the fact that Ru(0.4)Cr(9.6) shows a decreased rate of deactivation as compared with Cr(10), as shown in figure 3. This improved catalytic oxidation performance of the Ru(0.4)Cr(9.6) is thought to be due to the direct involvement of the well-dispersed Ru-oxides as active centers for activating the molecular oxygen.

In the case of reaction in wet air conditions, Cl_2 in the product streams is not detected for both catalysts. It is very likely that the presence of water vapor in the reactant by 1 vol% exerts reaction (5) to proceed in the reverse direction, resulting in the production of HCl instead of Cl_2. Particularly, for the reaction over the catalyst Ru(0.4)Cr(9.6) in which the product concentration of Cl_2 is as high as 480 ppm in dry air, it is very desirable to reduce the Cl_2 concentration to a negligible value by the presence of water vapor in view of the moisture content of atmosphere, about 1 vol%.

4. Conclusions

The low-temperature reaction performance of the CrO_x/Al_2O_3 catalyst for the oxidative decomposition of TCE could be improved by impregnating a small amount of Ru as a promoter. As compared with the Cr(10) catalyst, the Ru-promoted CrO_x catalyst of Ru(0.4)Cr(9.6) showed enhanced catalytic activity, a lowered rate of catalyst deactivation and reduced CO production. This performance improvement of the Ru(0.4)Cr(9.6) catalyst was thought to originate from its enhanced oxidation activity, due to the coexisting highly-dispersed Ru-oxides rendering less active Cr(III) to more active Cr(VI), and facilitating the process of supplying activated oxygen for the reaction system. Owing to its high oxidation activity, the production of Cl_2 in dry air conditions was observed in higher concentration for the Ru(0.4)Cr(9.6) than the unpromoted CrO_x catalyst, but the presence of water vapor by 1 vol% in the feed was enough to make the Cl_2 production negligible. Coimpregnation of the larger contents of Ru with Cr led to decreases in the surface coverage of active CrO_x species and the catalyst surface area, resulting in less activity.

Acknowledgment

This work was supported by the Ministry of Commerce, Industry and Energy.

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