ACTIVITY PROMOTION OF THE CrO$_x$/Al$_2$O$_3$ CATALYST WITH Ce, Mn OR Ru IN THE OXIDATIVE DECOMPOSITION OF TRICHLOROETHYLENE

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Abstract : Alumina-supported metal oxide catalysts of Cr, Co, Ru, Cu, V, Ni, Mn and Ce were prepared and evaluated in their comparative catalytic activities in the oxidative decomposition reaction of trichloroethylene (TCE) in air. The highest catalytic activity was observed for the CrO$_x$/Al$_2$O$_3$ catalyst. Catalytic activity promotion was found to exist for the Cr-based catalysts containing Ce, Mn or Ru as a promoter. The binary component catalytic systems of Ce-Cr, Mn-Cr and Ru-Cr were optimized in their metal compositions to get the highest activity in the TCE decomposition reaction. Ru(0.4 wt%)Cr(9.6 wt%)/Al$_2$O$_3$ catalyst showed the highest activity with the increased reaction rate 2.1 times higher than the Cr(10 wt%)/Al$_2$O$_3$ catalyst. Catalytic activities of the CrO$_x$-based catalysts were discussed in relation with the redox properties and acidities which were determined by temperature programmed reduction (TPR) and temperature programmed desorption of NH$_3$ (NH$_3$-TPD), respectively.

Key Words : catalytic oxidative decomposition, CrO$_x$/Al$_2$O$_3$, Ru, Mn, Ce, promoter effect, trichloroethylene

INTRODUCTION

The increased application and production of chlorinated volatile organic compounds (CVOCs) such as trichloroethylene (TCE), chloroform and methylene chloride have enlarged the concerns over the control and safe disposal of these waste emissions. Among the avaliable disposal processes for decomposing dilute CVOCs into environmentally acceptable species (HCl and CO$_2$), catalytic oxidative decomposition has recently gained great interests as the most economically advantageous method due to its low energy consumption and high efficiency

of destruction at low temperature of operation.[1]

A large number of reports regarding the catalytic decomposition of CVOCs over the supported noble metal and metal oxide catalysts are available on the literatures. In general, noble metal catalysts are highly active for the complete oxidation of non-halogenated VOCs, however, their application to CVOCs seems to be not so successful because of the problem subject to deactivation. Spivey and Butt[2] summarized that Cl$_2$ and HCl produced by the oxidation reaction as well as CVOCs themselves were generally poisons for the supported noble metal catalysts, rendering the active metals to inorganic chlorides with subsequent deactivation. The low temperature operation of a Pt/Al$_2$O$_3$ catalyst for CVOCs accelerated the catalyst deactivation due to the increased

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retention of HCl over the catalyst.[3] These suggest that noble metal catalysts are not suited to the oxidative decomposition of CVOCs. As alternatives to noble metal catalysts, catalysts based on the transition metal oxides such as Cr,[3~8] Cu,[7,9] V,[8,10,11] Co,[7,8,12,13] and Mn[7,14] on various supports have been tried for the CVOC decomposition. Although the supported catalyst of Cr or V oxide has been reported be the most active in the oxidative decomposition of TCE[7] and 1,2-dichlorobenzene,[8] more active catalyst at lower temperature is desirable for better economics of the CVOC decomposition process.

In this study, alumina-supported single metal oxide catalysts of Cr, Co, Ru, Cu, V, Ni, Mn and Ce, which have been well known as catalytic components for the oxidative decomposition reaction, were prepared and screened for their relative catalytic activities in the decomposition reaction of TCE in air. In order to find a metal promoter for the Cr-oxide catalyst which exhibited the highest activity in the preliminary screening experiment, other metals were tried one by one as an activity promoter. The catalytic system showing the possibility of activity synergism were optimized in their metal composition to get the highest activity. Catalytic activities of the Cr-based catalysts were discussed in relation with the redox properties and acidities which were determined by temperature programmed reduction (TPR) and temperature programmed desorption of NH$_3$ (NH$_3$-TPD), respectively.

EXPERIMENTAL

Catalyst Preparation

Catalytic metal was impregnated onto the powdered γ-Al$_2$O$_3$ (BET surface area 200 m^2/g) support by evaporating excess solution containing the calculated amount of metal precursor. Impregnated samples were dried for 12 h at 110℃, and subsequently, calcined for 5 h at 540℃. For the catalysts of binary metal components, two metal precursors were im-

pregnated 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(5) or Ce(5)Cr(5), of which numbers mean the weight percents of the corresponding metal components in the oxide catalysts.

Reaction Tests

Reaction experiments were conducted in a quartz tube reactor (ID 10 mm) with a bed of catalyst particles. TCE was used as a reactant, contained in a pyrex saturator immersed into a ice-water bath kept at 0.5℃. Temperature of ice-water bath was maintained constant using an immersion cooler and an agitator. Concentration of TCE in the influent gas stream to the reactor was controlled by mixing the flow of N$_2$ passing through the TCE saturator and the two separate flow streams of N$_2$ and O$_2$. Water vapor in the N$_2$ and O$_2$ was removed by passing the gases through the packed beds of molecular sieve 5A and silica gel. The flow ratio of N$_2$ to O$_2$ in the influent gas stream was adjusted to 79/21 to meet air composition. Catalytic activities in the water vapor-free conditions were measured by increasing temperature with a rate of 2℃/min under following conditions: catalyst weight 0.192 g (volume 0.18 mL), total gas flow rate 60 mL/min (GHSV 20,000 h^{-1}), TCE concentration 730 ppmv.

A GC (Varian 3400) equipped with a packed column (3% OV-17, 80/100 mesh, SS 6'×1/8") and FID was used to analyse the concentrations of TCE in the reactant and product streams. Oven temperature of the GC was maintained at 100℃, and He was used as the carrier gas. The volume of gas injected into the GC column was kept at 1 mL using a 6-port valve with a loop of 1 mL. The conversion of TCE by the reaction was calculated from the GC peak area of TCE in the reactant and product streams.

Catalyst Characterization

Catalysts were characterized using NH$_3$-TPD,

TPR and X-ray diffraction (XRD). NH$_3$-TPD and TPR were conducted using Micrometrics 2910, and XRD pattern was obtained using Rigaku DMAX/1200. For NH$_3$-TPD, catalyst sample (0.1 g) was pretreated for oxidation and the removal of moisture and impurities in a flow (30 mL/min) of 3% O$_2$/Ar for 5 h at 500 ℃. Following the adsorption of NH$_3$ using 1% NH$_3$/He after cooling down to room temperature, temperature was maintained at 70℃ in a flow (30 mL/min) of He to remove the physisorbed fraction of NH$_3$ until TCD signal had been stabilized. After the stabilization of TCD signal, temperature was raised with a rate of 30℃/min, and TCD signal was recorded. For the TPR, 10% H$_2$/Ar was used for reduction gas and the same method as described in the NH$_3$-TPD was used.

RESULTS AND DISCUSSION

Activities of Single Component Catalysts

Figure 1 shows the light off curves of TCE over the various single component metal-oxide catalysts for evaluating catalytic activity. Oxidative decomposition efficiency of a catalyst could be well represented with the light off curve plotting the conversion of a reactant against reaction temperature. Light off curve is characterized by two characteristic temperatures, T_{50} and T_{90} at which the conversions of a reactant are achieved by 50% and 90%, respectively.[15] T_{50} is termed as the light off temperature by which catalytic activities of catalysts for a particular reactant can be compared. On the other hand, T_{90} is a term governed by the mass transfer limitation of a reactant from bulk gas phase to catalyst surface at higher temperature, which is dependent on the physical properties of a catalyst such as pellet size and shape. The estimated T_{50} values of the various catalysts from the light off curves of TCE are given in the caption of Figure 1. The oxide catalysts in TCE decomposition activity can be ordered as Cr(7.5) > Ru(7.2) > V(7.3) > Mn(4.1) > Co(4.4) >
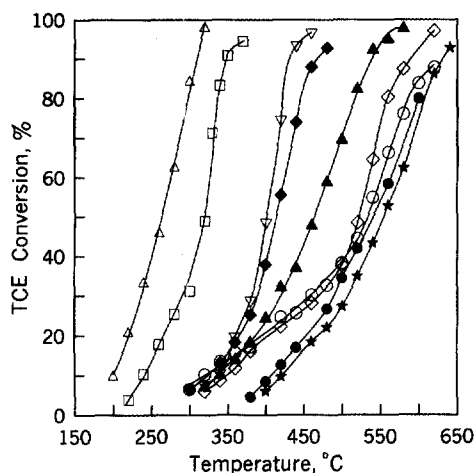

Figure 1. TCE conversion of the Al$_2$O$_3$-supported catalysts of single metal oxides: △Cr(7.5); 266, □Ru(7.2); 320, ▽V(7.3); 402, ◆Mn(4.1); 414, ▲Co(4.4); 465, ◇Cu(4.7); 523, ○ Ni(4.3); 534, ●Ce(10); 542 and ★ Al$_2$O$_3$ support; 554, where the numbers followed by each semicolon are the estimated T_{50} in ℃.

Cu(4.7) > Ni(4.3) > Ce(10). In these catalysts except Ce(10), the metal contents were so adjusted that 2.5 units of the stable metal oxide (as Cr$_2$O$_3$, RuO$_2$, V$_2$O$_5$, MnO$_2$, CoO, CuO or NiO) on a square nanometer of the support surface area could exist. In agreement with Hong et al.[7] and Krishnamoorthy et al.,[8] the supported Cr-oxide catalyst shows the highest catalytic activity for TCE decomposition reaction among the metal oxides catalysts tested.

The effect of the loading amount of Cr onto the alumina support on the catalytic activity has been determined, as shown in Figure 2. At lower temperatures, catalysts with higher Cr contents show higher TCE conversions. However, differences in TCE conversions for the catalysts become smaller as temperature increases, suggesting the presence of mass transfer limitation of TCE at higher temperature. Light off temperatures of TCE over the catalysts Cr(5), Cr(7.5) and Cr(10) are estimated as 277, 266 and 264℃, respectively, indicating that the catalytic activity does not
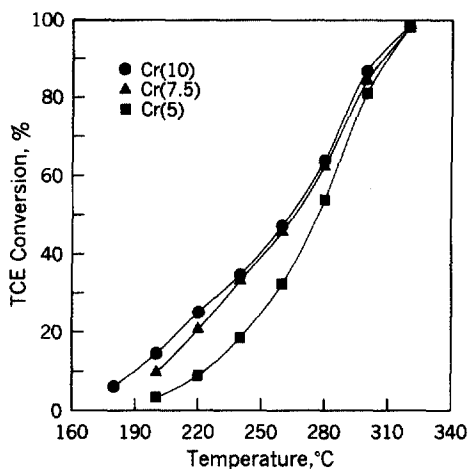
Figure 2. TCE conversion over the Cr-oxide catalysts with different Cr contents.

Figure 3. Light off temperatures of TCE over the Cr-based catalysts each containing a different metal oxide.

increase much more as the Cr content increases from 7.5 to 10 wt%. Therefore, Cr(10) catalyst which shows the lowest T_{50} as a single component catalyst has been used as a reference catalyst for the activity comparison with other catalysts.

Activities of the Promoted Cr-oxide Catalysts

Ru, V, Mn, Co, Cu, Ni or Ce has been tried to investigate its possibility as a promoter for the Cr-oxide catalyst. Figure 3 shows the T_{50} values in TCE decomposition for the various catalysts in which both Cr and a promoter metal are contained by 5 wt% each. Ce(5)Cr(5) catalyst shows lower T_{50} than Cr(10) catalyst, indicating a catalytic activity promotion between Cr and Ce. There also can be a possibility of activity promotion for the catalysts Mn(5)Cr(5) and Ru(5)Cr(5) when comparing their T_{50} values with those of Cr(10) and Cr(5). However, such metals as Ni, Co, V and Cu are not considered to give activity synergism with Cr-oxide catalyst for the TCE decomposition reaction. Subsequently, Ce, Mn and Ru have been selected as a candidate for a possible promoter for the Cr-oxide catalyst.

Figure 4 shows the variation of T_{50} values of TCE with the composition of the promoter metals in the Cr-based catalysts of which total
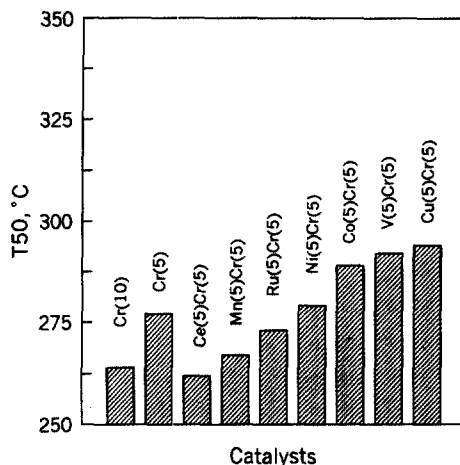
metal contents are kept at 10 wt%. Catalytic activity promotion is observed to exist for all the promoted catalysts Ce-Cr, Mn-Cr and Ru-Cr, as shown in Figure 4(a), (b) and (c), respectively. For the Ce-Cr system, the highest activity promotion appears for the catalyst Ce(2.5)Cr(7.5) of which Ce composition is 0.25. In the case of Mn-Cr, the catalysts Mn(1.2)Cr(8.8) and Mn(2.5)Cr(7.5) show the nearly same activities, so the activity promotion exists in the range of Mn composition from 0.12 to 0.25. In contrast to the catalytic systems of Ce-Cr and Mn-Cr, the activity promotion in the Ru-Cr system is observed to occur within a very narrow range of Ru composition. As shown in Figure 4(c), the highest activity promotion has been obtained for the catalyst Ru(0.4)Cr(9.6) of which Ru composition is so small as 0.04.

T_{50} value of Cr(10) catalyst in TCE decomposition has been determined as 264℃. The lowest T_{50} values which can be obtained from each promoted catalytic system are 252, 254 and 249℃ for the catalysts Ce(2.5)Cr(7.5), Mn(2.5)Cr(7.5) and Ru(0.4)Cr(9.6), respectively. Figure 5 shows the light off curves of TCE over the three catalysts which turn out to be the most active in each systems in comparison with Cr(10). The best light off
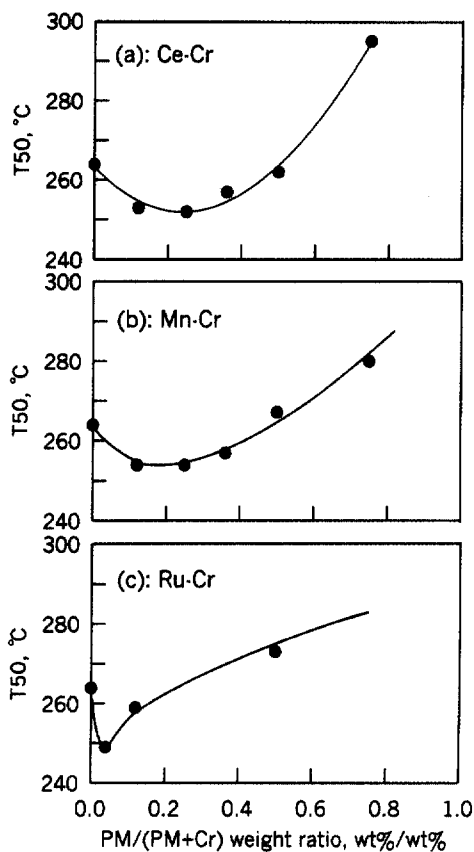
Figure 4. Effect of a promoter metal (PM) composition on the TCE light off temperatures in the Cr-based catalysts: (a) Ce-Cr, (b) Mn-Cr, and (c) Ru-Cr. In all the catalysts, their total metal loadings (PM+Cr) are fixed as 10 wt%.

performance is observed for the catalyst Ru(0.4)Cr(9.6).

Characteristics of Cr-oxide Catalyst

Oxidative decomposition reaction of CVOCs over the metal ion-exchanged acid catalysts has been understood with a dual site mechanism.[3,12] First, CVOC reactants adsorb in the form of carbonium ions onto the Brönsted acid sites and molecular oxygen adsorbs on metal-cationic sites. Oxidized products are in turn produced from the surface reaction between the carbonium ions and the activated oxygen. On the other hand, for the oxidative decomposition
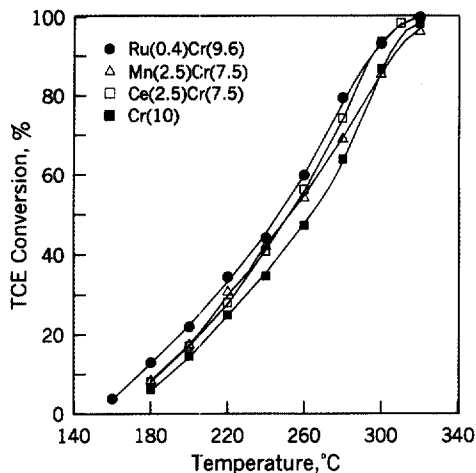

Figure 5. TCE conversion over the Cr-based catalysts promoted by an optimal content of Mn, Ce or Ru.

of VOCs over the non-acid catalysts of metal oxides, it has been reported[13] that the catalytic species are oxidized by molecular oxygen adsorbed, and subsequently the reaction between the activated oxygen and hydrocarbon reactants takes place, and the desorption of products results in the reduction of catalytic species.

It is therefore assured that redox cycle property and acidity of a catalyst can be considered important for the oxidative decomposition reaction of CVOCs. Figure 6 shows the results of TPR and NH_3-TPD for the Cr-oxide catalysts with different Cr contents. As shown in Figure 6(a), the catalysts with more content of Cr are more reducible. As the catalytic content of Cr increases, reduction peak positions shift to lower temperatures and the reduction area increases. Good reducibility means good oxidability, i.e., better redox cycle property. The increase in the reduction peak area for the Cr-oxide catalyst containing higher amount of Cr can be considered to result from weaker interaction between the Cr-oxide phase and alumina support. Park and Ledford[16] conducted the X-ray photoelectron spectroscopy (XPS) study on the oxidation state and surface dispersion of Cr for the Cr-oxide catalysts supported on alumina (BET surface area 202 m^2/g). For the catalysts with low content of Cr,
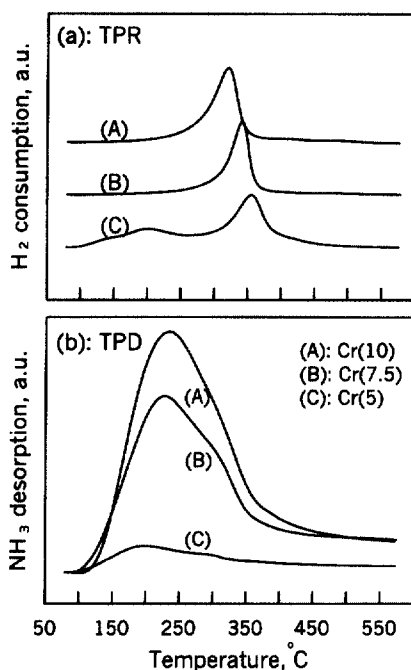
Figure 6. TPR (a) and TPD (b) profiles of the Cr-oxide catalysts.

Cr(VI) was determined as predominant species with high surface dispersion. As the content of Cr increased, surface fraction of Cr(III) increased, but the surface dispersion of Cr decreased. They reported that the Cr-oxide catalyst of high content of Cr (13 wt%) resulted in the formation of crystalline Cr_2O_3 and the large decrease in the surface dispersion of Cr. In our study, BET surface area of the alumina support is 200 m^2/g, similar to that of Park and Ledford.[16] In our study, any XRD pattern responsible for Cr_2O_3 crystallite has not been detected for the Cr(10) catalyst which has the highest content of Cr. However, in view of the XPS study of Park and Ledford,[16] Cr(10) catalyst is supposed to contain both Cr(VI) and Cr(III) species. As the Cr content increases up to 10 wt%, the interaction between the Cr-oxides and support would be weakened in accordance with lowered surface dispersion. This can make a contribution to the increase of the amount of Cr-oxide reduction at lower temperature.

It is also apparent from Figure 6(b) that the

amount of catalytic acid sites increases with the content of Cr although the acidity measured by NH_3-TPD contains Lewis acid sites as well as Brönsted sites. Throughout their study on the acidity of Cr-oxide/ZrO_2, Sohn et al.[17] reported that acidity of the catalyst increased with increasing Cr-oxide content, and that both Brönsted and Lewis acid sites existed on the surface of the catalyst. Mentasty et al.[18] conducted the NH_3-TPD for Cr-oxide/Al_2O_3 catalysts, and reported the nearly same acidity distribution as shown in Figure 6(b). The generation of the acid sites by mixing two oxides is understood to be caused by an excess of a positive or negative charge in a model structure of a binary oxide related to the coordination number of a positive element and a negative element.[17]

It is therefore thought that the superior catalytic activity of alumina-supported Cr-oxide catalysts for TCE decomposition reaction is due to the ability of Cr-oxide species providing both acid sites for TCE adsorption and cationic sites for molecular oxygen activation. In addition, it can be said that the catalyst containing higher content of Cr without the formation of Cr_2O_3 bulk phase has more number of acid sites and better redox cycle property, resulting in higher activity than the catalyst of smaller content of Cr.

Characteristics of the Promoted Cr-oxide Catalysts

Figure 7 shows the results of TPR and NH_3-TPD for the three catalysts, Ce(2.5)Cr(7.5), Mn(2.5)Cr(7.5) and Ru(0.4)Cr(9.6) which exhibit the highest activity promotion in each system, in comparison with those of Cr(10). As shown in Figure 7(a), the largest increase in the reduction peak area is observed for the Mn(2.5)Cr(7.5) catalyst, with a peak temperature nearly same as for Cr(10). Ce(2.5)Cr(7.5) catalyst also shows the increased amount of reduction, but its peak position is shifted to higher temperature than in any other catalysts. It is of particular interest for the Ru(0.4)Cr(9.6)
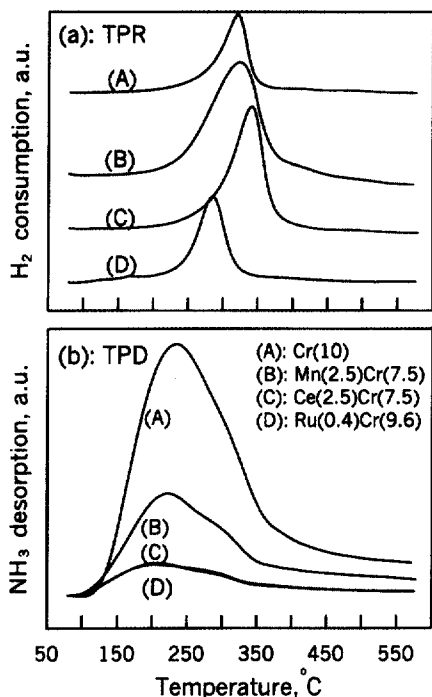
Figure 7. TPR (a) and TPD (b) profiles of the Cr-based catalysts promoted by an optimal content of Mn, Ce or Ru.

Table 1. Summary of kinetic data of TCE oxidative decomposition reaction over the Cr-based catalysts

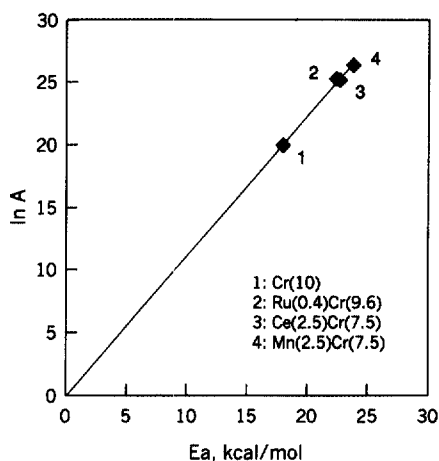| Catalysts	First order rate constant, k (s^{-1}) at 220℃	Activation energy, E_a (kcal/mol)	Frequency factor, A (s^{-1})
Cr(10)	4.9	18.0	5.0×10^8
Ce(2.5)Cr(7.5)	6.2	22.7	8.4×10^{10}
Mn(2.5)Cr(7.5)	7.7	23.8	2.8×10^{11}
Ru(0.4)Cr(9.6)	10.5	22.4	9.3×10^{10}

Figure 8. Compensation effect present in the Cr-based catalysts promoted by an optimal content of Mn, Ce or Ru.

catalyst that its reduction occurs at much low temperature with the increased amount of reduction as compared with Cr(10). Figure 7(b) indicates that co-impregnation of Mn, Ce or Ru with Cr decreases the catalyst acidity which is thought to originate from Cr-oxides. Particularly, for Ce(2.5)Cr(7.5) and Ru(0.4)Cr(9.6) catalysts, much decreases in the amount of catalytic acidity are observed.

Table 1 lists the values of the rate constants, apparent activation energies and frequency factors for the catalysts in the TCE decomposition reaction. Reaction rate constant, k, was obtained assuming the reaction as the first order plug flow kinetics as following:

$$k = - (GHSV/3600) \cdot \ln(1-X_{TCE}) \qquad (1)$$

where, GHSV = gas hourly space velocity (hr^{-1}), and X_{TCE} = fractional conversion of TCE. Apparent activation energies and frequency factors were obtained using the Arrhenius plot in a temperature range, 200 ~

240℃. As compared with the reported activation energies of CrO_x/Al_2O_3 catalysts in a range between 20 and 25 kcal/mol for the TCE decomposition reaction,[7] 18 kcal/mol of the energy obtained for the Cr(10) catalyst is considered to be a reasonable value although a little lower. Ru(0.4)Cr(9.6) catalyst shows the highest catalytic activity with a rate constant 2.1 times higher than Cr(10). It can be understood in Table 1 that the increase in frequency factor is followed by the increase in activation energy. Because the former leads to the increase of the reaction rate while the latter to the decrease, activity promotion of a catalyst is limited by the effect of compensation.[19] A linear relationship between the log values of frequency factors and the values of activation energies, as shown in Figure 8, indicates the

presence of the compensation effect in the Ce, Mn or Ru promoted Cr catalyst system.

In the case of catalytic reaction that the increased frequency factor can be accepted as the increased number of catalytic active sites, Mn-Cr is a catalytic system upon which Mn brings the largest number of active sites. This is consistent with the largest reduction peak area for the Mn(2.5)Cr(7.5) catalyst, as shown in Figure 7(a). The increased amount of reduction in the Mn(2.5)Cr(7.5) catalyst is thought to result from the additional reduction of Mn-oxides as well as Cr-oxides. This can be understood by comparing the TPR of Mn(2.5) Cr(7.5) in Figure 7(a) and that of Cr(7.5) in Figure 6(a). Therefore, Mn-oxides in the Mn (2.5)Cr(7.5) catalyst is thought to participate in the reaction as additional active species. However, because the activity of Mn catalyst is much lower than Cr catalyst, as shown in Figure 1, higher activation energy is required for the reaction over Mn(2.5)Cr(7.5) than the pure Cr(10). As compared with Mn(2.5)Cr(7.5), the catalyst Ce(2.5)Cr(7.5) shows a low reduction area, a high peak temperature and a diminished acidity, resulting in the lowered activity. However, Ce(2.5)Cr(7.5) is more active than Cr(10) because the former has more number of active sites than the latter. Comparison of the TPR profile of Ce(2.5) Cr(7.5) with that of Cr(7.5) in Figure 6(a) suggests that the presence of Ce with CrO_x makes a contribution to the increase in the amount of reduction.

Ru(0.4)Cr(9.5) catalyst shows the increased amount of reduction as well as the much lowered reduction peak temperature, as compared with Cr(10). In this catalyst, the content of Ru impregnated is so small that its reduction, as shown in Figure 7(a), can be mostly ascribed to the reduction of Cr-oxides. In other words, the presence of the small amount of Ru in a Cr-oxide catalyst not only increases the amount of the reduction of Cr-oxide species, but also improves the redox cycle property of the catalyst at much lower temperature. Such improvements in the reduc-

tion characteristics of Ru(0.4)Cr(9.5) should lead to the increase of frequency factor as well as the decrease in the activation energy, however, its activation energy is rather increased as compared with Cr(10), as shown in Table 1. This is possibly due to the significant decrease of the catalyst acidity with the addition of Ru, as shown in Figure 7(b).

CONCLUSION

Alumina-supported single metal oxide catalysts in the TCE decomposition activity is ordered as Cr > Ru > V > Mn > Co > Cu > Ni > Ce. For the CrO_x/Al_2O_3 catalyst which exhibited the highest activity among the single component catalysts, as the content of Cr increased, the catalytic activity increased in accordance with both reducibility and acidity. The activity promotion observed for the Ru, Mn or Ce promoted Cr-oxide catalysts was mainly due to the increase in the reduction amount of catalytic active species, by which more number of active species could be generated and involved in the reaction. However, the diminished amounts of acidity in these promoted catalysts were thought to result in the increases of the reaction activation energies, and subsequently limiting the further activity enhancement. Ru(0.4)Cr(9.6) catalyst showed the highest activity promotion with a reaction rate constant 2.1 times higher than Cr(10). The presence of a small amount of Ru in the CrO_x catalyst gave not only more amount of reduction, but also better reducibility of the catalyst at lower temperature. This suggests that Ru-CrO_x catalytic system is promising as the low temperature decomposition catalyst of dilute CVOCs in air and deserved for further study.

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