

EFFECTS OF BASE METAL PROMOTERS IN VOC CATALYSTS FOR CHLOROCARBONS AND n-HEXANE OXIDATION

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Abstract – The oxidation reactions of dichloromethane, dichloroethane and n-hexane were carried out over honeycomb type platinum basic VOC catalyst (BVC) containing vanadium, chromium, manganese, cobalt, copper or barium. In dichloromethane and dichloroethane catalytic oxidation up to 450 °C, chromium was found as the most active component. Although vanadium was also effective initially, it was deactivated after treatment in the furnace at 800 °C for 120 hours. Chromium, cobalt, vanadium and barium promoted catalysts showed higher activities than BVC in the reaction of n-hexane.

Key words : Chlorocarbons, n-Hexane, VOC Oxidation, Chromium, Promoters

INTRODUCTION

At the present time, there is great concern about contamination of the environment by volatile organic compounds (VOCs). VOCs include a variety of organic compounds such as aliphatic and aromatic hydrocarbons, alcohols, ketones, esters, formaldehyde, phthalic anhydride and many others. VOCs are vented or discharged from a wide range of manufacturing processes, from can coating and automobile painting to semi-conductor manufacture including baking, printing, and lithography.

One of the most widely used methods of reducing VOCs from industrial exhausts is thermal incineration, which operates between 750 °C and 1,000 °C. In the case of catalytic thermal oxidation, the same reaction occurs at significantly lower temperatures between 250 °C and 500 °C. Therefore, the main advantage of catalytic oxidation over thermal incineration is its ability to destroy VOCs at a far lower temperature. It also offers more advantages: high destructive efficiency that generally exceeds 99 %, lower operating temperature than thermal combustion systems, lower capital cost and smaller units.

The active components for the oxidation of VOC and chlorinated hydrocarbons are usually the noble metals such as platinum, palladium and platinum-palladium or the oxides of base metals such as cobalt, copper, manganese, vanadium, chromium, tungsten and so forth [Mazzarino et al., 1993; Cordi et al., 1996; Vigneron et al., 1996; Jones et al., 1997; Drago et al., 1994; Greene et al., 1996]. One of the most significant advantages of precious metal catalysts for the removal of VOCs and halogenated solvents is their ability to form complete combustion products. Platinum is typically used alone in a straightforward oxidation catalyst where it oxidizes the hydrocarbons in the presence of a large excess of oxygen.

Earlier formulations of the catalyst were quickly inhibited

by the presence of trace amount of halogens. Halogenated hydrocarbons have traditionally been considered as reversible poisons for precious metal catalysts. With today's poison resistance technology, catalysts are available that are capable of destroying chlorine-, fluorine-, or bromine-containing organic compounds [Bertelsen, 1992]. Several tests on the subject of catalytic oxidation of halocarbons were carried out, but some people only revealed the general name of catalysts, not active components [Noordally et al., 1993; Freed et al., 1993].

The work described in this paper was undertaken to identify suitable base metals as the promoter for the oxidation of dichloromethane, dichloroethane and n-hexane.

EXPERIMENTAL

1. Preparation of Catalyst

The catalysts used in this work were prepared by the incipient wetness method using Condea SBa-150 Al_2O_3 and an aqueous solution of $\text{H}_2\text{Pt}(\text{OH})_6$ and other base metals on cordierite monolith having 400 cpsi (cells per square inch). The precursors were vanadium (III) chloride (VCl_3 , Aldrich Chem. Co.), chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Junsei Chemical Co., Ltd.), manganese (II) acetate tetrahydrate ($\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, Junsei Chemical Co., Ltd.), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Shinyo Pure Chemicals Co., Ltd.), cupric acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Junsei Chemical Co., Ltd.) and barium hydroxide octahydrate crystal ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, Nippon Chemicals Industrial Co., Ltd.).

In order to evaluate the effect of the addition of V, Cr, Mn, Co, Cu, Ba to wet slurry of $\text{Pt}/\text{Al}_2\text{O}_3$ on the activity, three groups of catalyst were made as shown in Table 1. BVC means basic VOC catalyst for hydrocarbon oxidation containing 2 wt% platinum, 70 wt% alumina and 28 wt% ceria/zirconia. CVC means a commercial VOC catalyst added with barium oxide (6 wt%) to BVC catalyst made in Heesung

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Table 1. Base metal loading rate and BET surface area of fresh and aged catalysts

Group	Catalyst	BM loading rate as oxide form (%)	BET surface area (m ² /g)
Group 1	BVC ¹⁾	-	28.3
	CVC ²⁾	BVC+6 wt% Ba	29.3
	V2	BVC+12 wt% V	33.7
	Cr2	BVC+12 wt% Cr	32.1
	Mn2	BVC+12 wt% Mn	27.8
	Co2	BVC+12 wt% Co	28.0
	Cu2	BVC+12 wt% Cu	37.8
Group 2	V1	BVC+6 wt% V	40.4
	V3	BVC+18 wt% V	21.5
	Cr1	BVC+6 wt% Cr	45.9
	Cr3	BVC+18 wt% Cr	36.3
Group 3	BVC (a) ³⁾	-	23.4
	V2 (a)	BVC+12 wt% V	5.4
	Cr2 (a)	BVC+12 wt% Cr	24.3

¹⁾BVC means basic VOC catalyst which is composed of 2 wt% Pt, 70 wt% alumina and 28 wt% ceria/zirconia.

²⁾CVC means commercial VOC catalyst which is added with 6 wt% barium oxide to BVC catalyst.

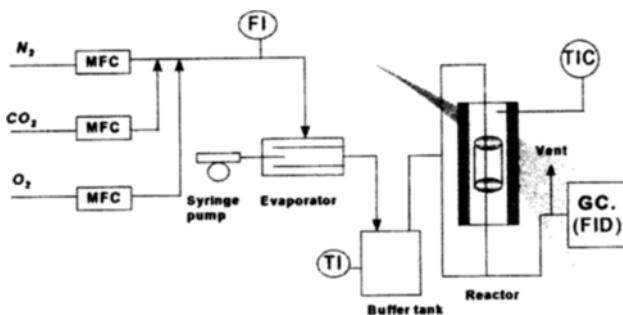
³⁾(a) means that the catalyst is aged in air for 120 hours at 800 °C.

Engelhard Corp. V2 means that vanadium (V) was added two times as much as the barium loading to BVC catalyst. The catalysts of first group were prepared with 12 wt% base metal oxides, while those of second group were prepared with 6 wt% and 18 wt% base metal oxides. The catalysts of third group were aged at 800 °C for 120 hours in a box furnace.

The catalyst preparation steps were as follows: For BVC catalyst, basic slurry which is composed of alumina, ceria, zirconia and the platinum solution was made in the first place, and the slurry was milled by using a ball mill. Then the solid fraction was adjusted to 49 % by adding DI water. After the precursors were added to the basic slurry, it was mixed well. The monolithic substrate of 400 cpsi (cell per square inch) was dipped in the slurry, and then surplus slurry was blown off by air. The slurry loading was 142 g/l-substrate as a dry basis. The catalysts were dried at 120 °C for 20 minutes in a continuous dryer to remove excess water and other volatile species from the pores of cordierite substrate followed by calcination at 500 °C for 1 hour in a continuous oven to remove all traces of decomposable salts used to prepare the catalyst.

2. Reactivity Test

Catalytic activity data were obtained by using a conventional fixed-bed flow reactor at atmospheric pressure (Fig. 1). The sample of honeycomb catalyst (dia. 25.4 × 47.4 mm) was placed in the stainless steel reaction tube with 27 mm i.d. and heated in a continuous stream of the reactant gas mixture. The furnace temperature was controlled with a maximum variation of 2 °C by a PID controlled electric furnace. Oxidizing feedstream consists of 10 % CO₂, 4 % O₂, 1,000 ppm HC with N₂ balance. Each reactant gas was controlled by mass flow controller (M. J. Technics, model MR). The liquid hydrocarbon fed with a syringe pump (Keuna Mechatronics, model

**Fig.1. Schematic diagram of bench rig.**

KASP 005/150 MT) was vaporized in an evaporator which was kept at 150 °C. Total flow rate was 6.88 l/min and VHSV (Volumetric Hourly Space Velocity) was kept at 20,000 hr⁻¹. For the homogeneous mixing of the reactant gas, a buffer tank with heating mantle was placed between the evaporator and the reactor. The feed line located behind the evaporator was wrapped with a heating band to avoid the condensation of hydrocarbon vapor. After steady state was obtained, the measurements were carried out from ambient temperature to 450 °C under atmospheric pressure at a rate of 5 °C/min. Conversion data were determined by analyzing the unreacted hydrocarbon with a gas chromatograph (Donam system Inc., DS 6200) equipped with FID (Flame Ionization Detector) and capillary column (J&W Science, DB1, 0.5 mmID × 30 m).

3. Measurement of Total Surface Area

The specific surface areas of fresh and aged catalysts were measured using a BET measuring apparatus (Micromeritics : 2200A) which can measure from 0.5 to 1,500 m²/g. The accuracy and reproducibility are ±4, ±1 %, respectively. The catalysts were aged in a box furnace at 800 °C for 120 hours. Before N₂ adsorption was allowed, the catalyst was evacuated at 250 °C for 45 minutes.

4. Others

The percent solid of slurry was measured by rapid percent solid measuring apparatus (LECO, model TGA-1064). The micrographs of fresh and aged catalysts were taken by using SEM (JOEL, model 5800) at the condition of 15 kv.

RESULTS AND DISCUSSION

The conversions of n-hexane, DCM (dichloromethane) and DCE (dichloroethane) over fresh BVC, CVC, V2, Cr2, Mn2, Co2, and Cu2 catalysts are shown in Fig. 2. Fig. 2(a) shows the results of n-hexane oxidation reaction over seven different catalysts mentioned above. Platinum appears to be the preferred catalyst for saturated hydrocarbons and higher molecular weight species. Palladium is preferred for methane and low molecular weight olefins [Heck et al., 1995]. The basic catalytic oxidation reaction of n-hexane occurs as follows: C₆H₁₄+19/2 O₂ → 6 CO₂+7 H₂O. Except for Cu2 catalyst, all catalysts promoted the n-hexane oxidation compared with BVC catalyst. Among these catalysts, Cr2 catalyst was superior by far to the others in the full range of temperature. Co2 catalyst also showed good activity. V2, Mn2 and CVC catalysts also expedited the conversion to some extent, but Cu2 catalyst in-

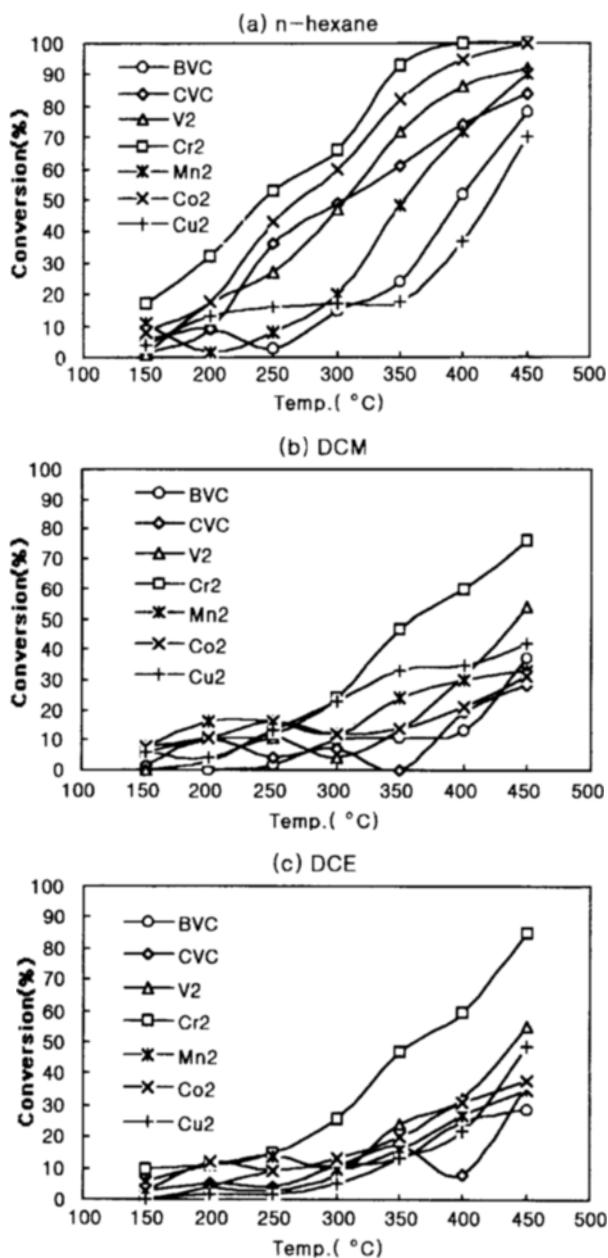


Fig. 2. Conversion of (a) n-hexane, (b) DCM (dichloromethane), (c) DCE (dichloroethane) over BVC, CVC, V2, Cr2, Mn2, Co2 and Cu2 catalysts.

dicated a poor activity.

DCM (dichloromethane) and DCE (dichloroethane) oxidation reactions over seven catalysts prepared in the present study proceeded as shown in Fig. 2(b), (c). DCM is one of the most refractory halocarbons compared with compounds with larger carbon-carbon linkages or increasing numbers of halogen atoms, which can be destroyed at lower temperatures than DCM. Comparative conversion tests were run on n-hexane, DCM and DCE. The complete oxidation temperatures of n-hexane, DCM and DCE were reported about 350 °C, 470 °C and 430 °C, respectively [Noordally et al., 1993]. Bond energies for C-Cl bonds in chlorinated methane are typically on the order of 20-25 kcal/mol lower than the corresponding C-H bond

energies, indicating thermodynamic favorability of C-Cl bond cleavage over C-H bond cleavage [Drago et al., 1994]. DCM and DCE contain sufficient hydrogens for complete oxidation to HCl with formation of CO₂ or CO₂ plus H₂O as following reactions : CH₂Cl₂ + O₂ → 2 HCl + CO₂, C₂H₄Cl₂ + 5/2 O₂ → 2 HCl + 2 CO₂ + H₂O. It was demonstrated that destruction of CCl₄ without water vapor in the feed caused catalyst deactivation and, consequently, produced significant amounts of Cl₂ instead of HCl [Freed et al., 1993]. This demonstrates the importance of water vapor in stabilizing the catalyst performance, as well as producing the desired HCl rather than Cl₂. In comparison with BVC catalyst, the conversion of DCE with Cr2 catalyst was 85 % at 450 °C, which was the highest value. Since chromium is considered little affected by chlorine, Cr catalyst destroys the chlorocarbons with a high efficiency. It has been known that chromium-based catalysts are effective in the destruction of chlorocarbons such as dichloromethane and trichloromethane [Nguyen et al., 1993]. Cr₂O₃ and V₂O₅ + Pt catalysts are effective in the oxidation of chlorinated hydrocarbons [Heck et al., 1995] and alumina-supported Cr₂O₃ is reported to be effective in the catalytic decomposition of methylene chloride [Drago et al., 1994]. In all catalytic oxidations of halocarbons the first step can be viewed as metal chloride formation : Cr₂O₃ + 2 C₂HCl₃ + 3 O₂ = 2 CrCl₃ + 4 CO₂ + H₂O. The metal chloride then hydrolyzes to HCl, which goes into the vapor phase and this regenerates the Cr₂O₃ catalyst : 2 CrCl₃ + 3 H₂O → Cr₂O₃ + 6 HCl. The HCl can be oxidized to chlorine, just like in the Deacon process [1870]; 4 HCl + O₂ → 2 Cl₂ + 2 H₂O [Berty, 1997]. When water was present in the feed, TCE (trichloroethylene) capacity dropped significantly on Cr-ZSM-5. This is due to the competitive adsorption of the sites between water molecules and TCE molecules and also to the water molecules forming clusters around these sites, thereby creating a diffusion block for TCE molecules [Greene et al., 1996]. This agrees with our results. Vanadia supported on an alumina-modified zirconia shows a resistance to poisoning by HCl, but it is slowly poisoned by SO₂ if present [Jones et al., 1997]. V2 and Cu2 catalysts also accelerated the oxidation of DCM and DCE to some extent. TCE sequential adsorption runs were carried out on Cr-ZSM-5. These runs consisted of three phases : (1) sorbing TCE on the sorbent until saturation followed by heating to desorb all TCE, (2) sorbing either water, CCl₄ or MeCl₂ on the same sorbent and (3) sorbing TCE again on the sorbent presaturated with either water, CCl₄ or MeCl₂ [Greene et al., 1996]. The activities of Mn2, Co2 and CVC catalysts were lower than those of Cr2, V2 and Cu2 catalysts. These catalysts seem to absorb chlorocarbons because their conversions became lower in a certain moment by desorbing the halocarbons from the sites before in the process of the temperature is raised. CVC catalyst especially seems to absorb them near 350 °C to 450 °C.

Cr2 and V2 catalysts were selected because of their good oxidation properties for DCM and DCE. We made V1, V3, Cr1 and Cr3 catalysts with different loadings of vanadium and chromium compared with V2 and Cr2 catalysts (refer to Table 1). The conversion of DCM and DCE over fresh V1, V3, Cr1 and Cr3 catalysts is shown in Fig. 3 and Fig. 4. The performances of vanadium catalysts were improved as vanadium

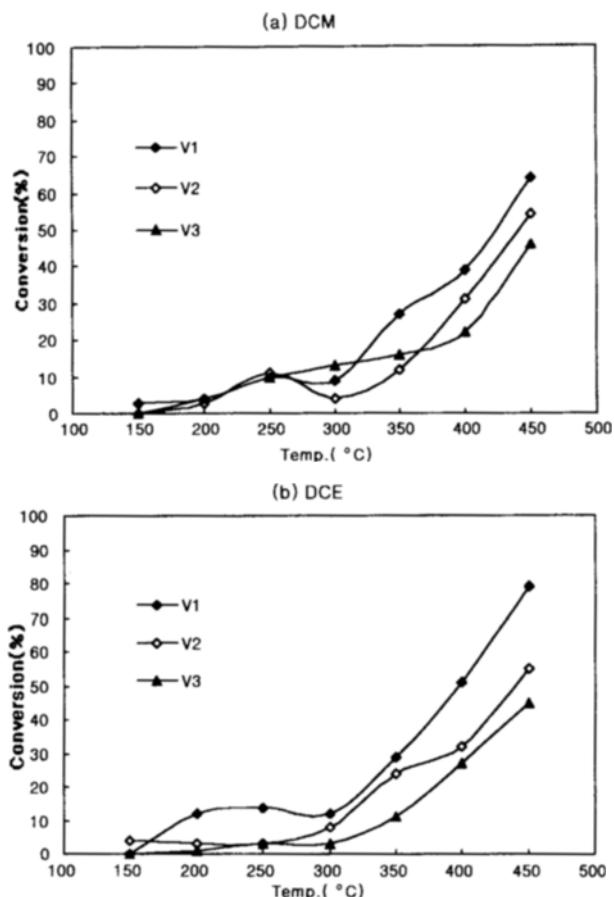


Fig. 3. Conversion of (a) DCM (dichloromethane), (b) DCE (dichloroethane) over V1, V2 and V3 catalysts.

loading was decreased as shown in Fig. 3(a), (b). It was considered that the surface of vanadium catalysts was decreased abruptly; specifically, the surface areas of V1, V2 and V3 measured by BET apparatus were $40.4\text{ m}^2/\text{g}$, $33.7\text{ m}^2/\text{g}$ and $21.5\text{ m}^2/\text{g}$, respectively, as shown in Table 1. In the case of chromium catalysts, these were reversed because the performance of chromium catalysts improved better when the chromium loading was increased as shown in Fig. 4(a), (b).

In order to investigate the deactivation by thermal aging, BVC, V2 and Cr2 catalysts were pre-treated at 800°C for 120 hours in a box furnace. The performances were evaluated for the oxidative destruction of dichloroethane. It is desirable to form haloacids instead of molecular halogens for two reasons. First, an acid such as HCl is much more easily trapped and neutralized from the effluent gas stream than chlorine (Cl_2), thereby reducing corrosion problems in downstream processing equipment. Second, molecular halogen can attack the components of the catalyst much more easily than haloacids, thereby decreasing the life of the catalyst. For example, in the absence of water chlorine converted the chromium oxide to a volatile red chromium oxychloride resulting in the deactivation of the catalyst [Nguyen et al., 1993]. Fig. 5 shows the conversion of the three aged catalysts mentioned above. The conversion of all aged catalysts was much lower than that of the fresh ones. The per-

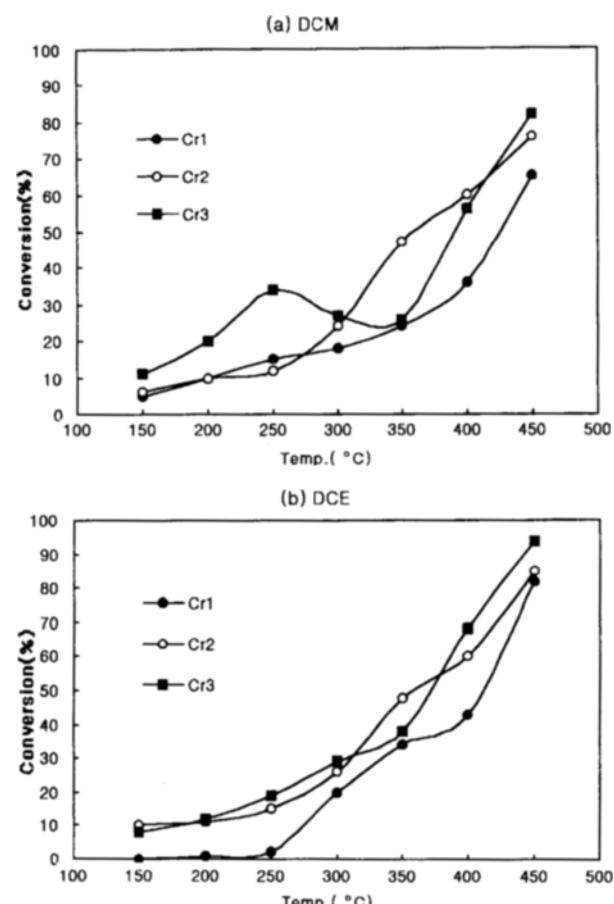


Fig. 4. Conversion of (a) DCM (dichloromethane), (b) DCE (dichloroethane) over Cr1, Cr2 and Cr3 catalysts.

formance of Cr2(a) catalyst was the best, although the activity reduced to about a half the activity of the fresh one. However, a rapid drop in the activity of this catalyst occurred by loss of the metal as volatile CrO_2Cl_2 [Drago et al., 1994]. BVC(a) catalyst showed a similar conversion pattern at all temperature ranges except 450°C. Vanadia-containing catalysts supported on different oxides were studied. For the most part,

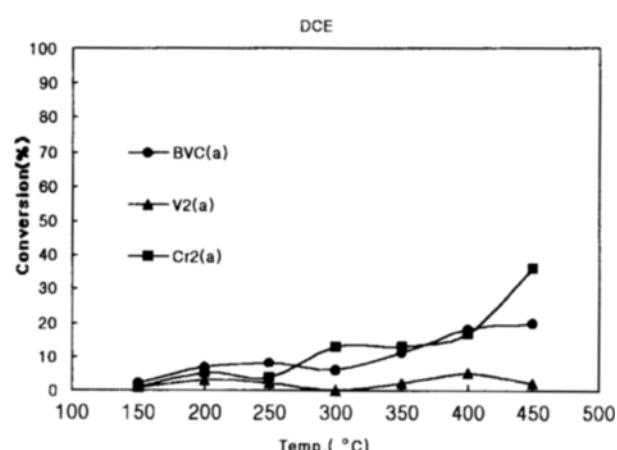


Fig. 5. Conversion of DCE (dichloroethane) over aged BVC, V2 and Cr2 catalysts.

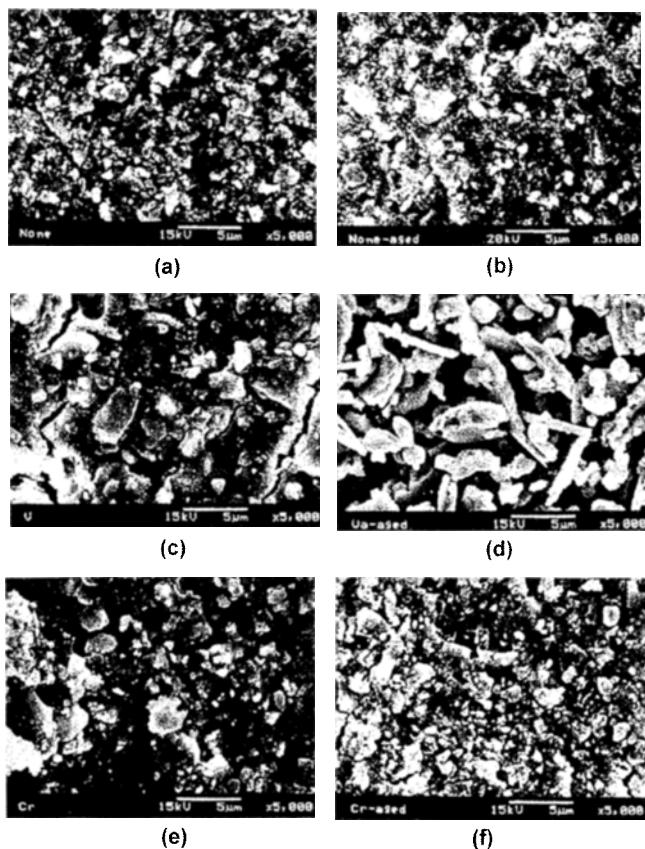


Fig. 6. SEM micrographs of fresh catalysts and aged catalysts at 800 °C for 120 hours.

(a) BVC, (b) BVC(a), (c) V2, (d) V2(a), (e) Cr2, (f) Cr2(a).

the area of the vanadia after aging in air for 4 hours at 500 °C was significantly lower than that of the fresh support, possibly because the vanadia had blocked micropores in the support or had encouraged sintering of the smaller pores [Jones et al., 1997]. In case of V2(a) catalyst, the activity nearly disappeared, presumably due to its surface area reduction from 21.5 to 5.4 m²/g.

SEM micrographs of BVC, BVC(a), V2, V2(a), Cr2 and Cr2(a) catalysts are shown in Fig. 6(a)-(f). Most of the vanadium was coagulated or evaporated after thermal aging at 800 °C for 120 hours as shown in Fig. 6(c), (d), because the melting point of vanadium is 690 °C. The loss of BET surface area for V2(a) catalyst was 84 %. Sintering results in the lowest activity as shown in Fig. 5. Therefore the vanadium containing catalyst should be used below a temperature of approximately 500 to 600 °C at most. Unlike V2(a) catalyst, the SEM micrographs of BCV(a) and Cr2(a) catalysts are almost the same as those of BVC and Cr2 catalysts, as shown in Fig. 6(a), (b), (e), (f). BET surface areas for BVC and Cr2 catalysts after aging were reduced 17 % and 24 %, respectively. Therefore, the activities of these two catalysts were reduced to a lesser extent than the activity of the V2 catalyst.

CONCLUSION

The oxidation reactions of n-hexane, DCM and DCE were

carried out over honeycomb type platinum basic VOC catalysts (BVC) promoted by vanadium, chromium, manganese, cobalt, copper or barium. Tests were executed up to a temperature of 450 °C over fresh catalysts and aged ones which were put in a box furnace at 800 °C for 120 hours.

From the results of the reaction for n-hexane using fresh catalysts mentioned above, it was found that the chromium promoted catalyst was the best one. Cobalt, vanadium or barium which was added to BVC promoted the oxidation to some extent. For DCM and DCE oxidation, the activity of chromium-promoted catalyst was superior by far to the other catalysts. Vanadium and copper catalysts accelerated the oxidation of chlorocarbon to some degree.

From the results of the reaction for DCM and DCE over fresh catalysts with different loadings of vanadium and chromium, it was observed that the conversion increased with a decrease of vanadium loading or with increased chromium loading.

For DCE oxidation over aged BVC, vanadium-promoted and chromium-promoted catalysts, aged chromium-promoted catalyst showed relatively less reduction in activity among the catalysts investigated. On the other hand, aged vanadium-promoted catalyst lost almost all the activity by aging at 800 °C for 120 hours. Vanadium is suggested to be used for hydrocarbon oxidation below the temperatures of approximately 500 to 600 °C at most, because the melting point of vanadium is 690 °C.

Continued study of the chromium promoted catalyst for chlorocarbon oxidation will be needed because it showed excellent performance for DCM and DCE oxidation.

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