COMBUSTION OF CHLORINATED VOCs USING BIMETALLIC CHROMIUM-COPPER SUPPORTED OVER MODIFIED H-ZSM-5 CATALYST

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ABSTRACT

The performance of chromium-copper supported over H-ZSM-5 (Si/Al=240) modified with silicon tetrachloride ($Cr_{1.0}Cu_{0.5}/SiCl_4$-Z) as the catalyst in the combustion of chlorinated VOCs (Cl-VOCs) is reported. A reactor operated at gas hourly space velocity (GHSV) 32,000 h^{-1}, temperature between 100° and 500°C with 2,500 ppm of dichloromethane (DCM), trichloromethane (TCM) and trichloroethylene (TCE) were used for activity studies. Deactivation study was conducted at GHSV 3,800 h^{-1} at 400°C for up to 12 h with a feed concentration of 35,000 ppm. Treatment with silicon tetrachloride improved the chemical resistance of H-ZSM-5 against hydrogen chloride. TCM was more reactive compared to DCM but it produced more by-products due to its high chlorine content. The stabilization of TCE was attributed to the resonance effects. Deactivation of $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z was mainly due to the chlorination of its metal species, especially with higher Cl/H feed. Coking activity in the combustion of Cl-VOC was low, particularly with DCM and TCM. In accordance with Mars-van Krevelen model, the weakening of overall metal reducibility due to chlorination led to loss of activity.

Keywords: Cl-VOC; Deactivation; Reducibility; ZSM-5, Bimetallic.

1 INTRODUCTION

Chlorinated volatile organic compound (Cl-VOC) is an important group of environmental pollutants due to high toxicity, inertness and widespread application in industries (Padilla et al., 1999 ; Ortiz et al., 2003). Catalytic combustion is a viable technology for the abatement of VOC in air stream. Unfortunately with Cl-VOC, this method subjects to several drawbacks as these substances are relatively more stable compared to non-chlorinated ones and also produces hydrogen chloride (HCl), and sometimes, molecular chlorine (Cl_2) which can deactivate the catalyst.

Catalyst deactivation in Cl-VOC combustion is mainly ascribed to physical and chemical changes occurred on the catalyst support and active metal species. Deactivation of zeolite-supported catalyst can originate from interactions between chlorine atoms with certain sites in the support to consequently cause the formation of defects in the framework (Fonseca et al., 2003). Generally, chlorinated molecules can selectively attack the Al-O bonds in the zeolite framework to form aluminum chloride (Padilla et al., 1999). Changes in the active metal species are primarily due to the formation of metal chlorides that are less efficient in catalyzing the combustion reaction (Schneider et al., 2000).

In the present study, a combination of chromium and copper was used. Previous study showed that with this combination, the carbon dioxide yield in the combustion of non-chlorinated VOCs was improved while coking activity was suppressed (Zuhairi et al., 2004). Therefore, in the present paper, the study was extended to Cl-VOC combustion. Silicon tetrachloride treatment on H-ZSM-5 was found to improve the hydrothermal stability of the zeolite while further suppressed coking tendency of the catalyst (Fonseca et al., 2003). In the activity study, dichloromethane (DCM), trichloromethane (TCM) and trichloroethylene (TCE) were used. Emphases were given on characterizing changes occurred either on the active metal species or the zeolite support, and the consequent effects on the activity and deactivation behavior of the bimetallic catalyst.

2 METHODOLOGY

2.1 PREPARATION OF THE CATALYST SUPPORT AND BIMETALLIC CATALYST

H-ZSM-5 (Si/Al=240) (coded H-Z) was prepared by exchanging Na^+ cation in Na-ZSM-5 with NH_4^+ in 2.25 M NH_4Cl for 12 h followed by filtration, drying and calcinations. Chemical modification of H-ZSM-5 was performed by reacting the H-ZSM-5 sample with silicon tetrachloride vapor in nitrogen at 50 ml/min at 500°C for 3 h followed by acid leaching using 2 M HCl solution at 60°C for 2 h. It was then subjected to filtration, washing and drying. Hereafter, the modified zeolite is coded as $SiCl_4$-Z. The bimetallic catalyst was prepared via impregnation method. In this procedure, 5 g of the modified ZSM-5 support was slurried into 100 ml of acidified nitrate solutions of Cr and Cu. The concentrations of these solutions were chosen such to give the final metal loading of 1.0 wt. % and 0.5 wt. % of chromium and copper, respectively. The solution was then evaporated to dryness, calcined at 550°C for 6 h, pressed and sieved to particle sizes of between 250-300 μm. The impregnated catalyst was coded as $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z.

2.2 EXPERIMENTAL SETUP AND CONDITIONS

The experimental setup used in this study consisted of nitrogen and purified air streams, the flow rate of which were controlled using Aalborg (AFC 2600) mass flow controllers. VOC-laden air stream at fixed concentration was generated by bubbling nitrogen gas at suitable flow rate through VOC saturators. The flow of air was used to make up the total flow rate to give the desired gas hourly space velocity (GHSV) in the catalyst bed. The catalytic activity test and the preparation of aged catalyst samples were performed in an 11 mm i.d. borosilicate glass reactor heated with a Lindberg/Blue tubular furnace. The feed and product gases were analyzed using an off-line Shimadzu GC-8A gas chromatograph a Porapak Q and Molecular Sieve 5A columns.

The performance of the catalyst determined at a total feed flow rate of 250 ml/min with a corresponding GHSV of 32,000 h^{-1}. The feed Cl-VOC concentration was kept constant at 2,500 ppm of DCM, TCM or TCE. In order to prepare aged $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z catalyst samples, feeds containing 35,000 ppm of DCM, TCM or TCE was passed through the reactor at a reaction temperature of 400°C and a GHSV of 3,800 h^{-1}. The reaction rate over the catalyst was determined by operating the reactor in differential mode at a GHSV of 78,900 h^{-1} at 400°C using respective Cl-VOC at 2,500 ppm as feed.

2.3 CATALYST CHARACTERIZATION

The catalyst samples were analyzed for surface characteristics using Quantachrome Autosorb-1, while crystallinity was determined using Siemens D2000 X-ray diffractometer. The acidity determination was made using Chembet 3000 system, in which, ammonia adsorption process was carried out at 150° and 250°C for total and strong acidity, respectively (Fonseca et al., 2003). The weak acidity was obtained by taking the difference between these two acidity values. The coke content of aged catalyst, taken as the weight loss of oven dried sample upon heating to 700°C in oxygen, was determined using Perkin Elmer TGA7. The profile of temperature programmed reduction of the catalyst was obtained with a Chembet 3000 instrument.

3 RESULTS AND DISCUSSION

3.1 THE CHARACTERISTICS OF ZSM-5 SUPPORT AND CATALYSTS

Table 1 summarizes important characteristics of the support and metal impregnated catalysts used in the present study. Changes in micropore area gave qualitative indication of the degree of modification experienced by the zeolite framework as they constituted about 80 % of total surface area of the unmodified H-Z support. When treated with silicon tetrachloride, significant drops in BET surface area and micropore area were experienced by the zeolite while mesopore area was adversely affected. These drops signified the presence of defects that contributed to mesoporosity of the material that resulted from partial atomic extraction from the zeolite framework. Impregnation of chromium or/and copper on $SiCl_4$-Z resulted in further decrease in BET surface area and micropore area, but with corresponding drop in mesopore area.

TABLE 1. Characteristics of support materials and catalysts used

Characteristics	[a]Material		
	H-Z	$SiCl_4$-Z	$Cr_{1.0}Cu_{0.5}/SiCl_4$-Z
S_{BET} (m^2/g)	386	346	324
Micropore area (m^2/g)	315	211	198
Mesopore area (m^2/g)	71	134	126
[b]Strong acidity (mmol NH_3 /g)	0.121	0.045	0.044
[c]Weak acidity (mmol NH_3 /g)	0.099	0.063	0.056
Metal content (wt. %)	-	-	1.0 (Cr), 0.5 (Cu)

[a] Z=H-ZSM-5 (Si/Al=240)

[b] Sites retaining ammonia at temperatures higher than 250°C

[c] Difference between total acidity and strong acidity.

It is generally accepted that the type and strength of acid sites on a catalyst play important roles in catalyst coking in VOC combustion process that consequently lead to the deactivation of the catalyst (Fonseca et al., 2003 ; Zuhairi et al., 2004). For this reason, the acidity study of the catalyst was also conducted. Acidity of the support materials used in the present study was characterized by weak and strong acid sites based on the temperature at which ammonia adsorption process was carried out. Weak acid sites were associated with the framework Lewis acid sites and aluminum-rich extraframework species due to its amphotericity while amorphous Si-Al oligomers that were formed during silicon tetrachloride treatment had little contribution to the acidity (Schneider et al., 2000). This was supported by lower value of weak acidity of $SiCl_4$-Z compared to H-Z as some of the acid-soluble extraframework species in $SiCl_4$-Z had been removed during acid leaching process in the preparation step. Strong acid sites were mainly attributed to Brønsted acid sites in the framework of the zeolite (Fonseca et al., 2003). Impregnation of chromium and copper on $SiCl_4$-Z appeared to further weaken the overall acidity, mainly due to the masking of acid sites by metal deposits as indicated by lower BET surface area, micropore area and mesopore area in $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z.

3.2 ACTIVITY STUDY OF $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z

Increasing chlorine content in a VOC molecule was found to positively affect the reactivity of the molecule as suggested by higher conversion of TCM compared to DCM as shown in Figure 1(a). The difference in the reactivity of these two chlorinated organics was more evident at lower temperatures but the gap gradually narrowed down as the temperature increased until total conversion was reached at above 450°C. Meanwhile, TCE with three chlorine atoms and one double bond in its molecule was clearly less reactive compared to DCM and TCM and could not be totally destroyed below 500°C. Despite increasing conversion, higher chlorine content in TCM also promoted the formation of higher by-products as suggested by lower carbon dioxide yield with this substance compared to that of DCM (Figure 1(b)). With TCE feed, low conversion was also accompanied by low carbon dioxide yield.

Chlorine atom is well-known for its high electronegativity and can induce electron cloud in the chemical bond towards its nucleus (Chintawar and Greene, 1997). In DCM and TCM molecules, its presence post withdrawing effect to the electrons forming the covalent bond with carbon atom. As a consequence, partial positive charge center, which was stronger in TCM, formed on the carbon atom and could act as electrophilic sites in the combustion reactions. Also, due to polarity of the C-Cl bonds, carbon center bearing three chlorine atoms in TCM became more reactive than that bearing two chlorine atoms in DCM. The effect manifested as higher reactivity of TCM compared to DCM as indicated by higher conversion observed in this study.

The stabilization of TCE molecules was attributed to the occurrence of resonance effect in the molecule from interactions between lone pair electron in chlorine atoms and the π electron in C=C double bond. First, the more electronegative chlorine atoms sought to pull electrons out of the π system of the C=C double bond. Conversely, lone pairs of electron from chlorine extended the new π-bonding in the C=Cl bond by donating some electron back to the π system (Chintawar and Greene, 1997). This interaction was possible as the electronic configuration of an atom of chlorine was $1s^22s^22p^63s^23p^5$ and the σ-bond formation with the carbon atom left (in the valence shell) one diagonal lone pair ($3s^2$) and two p-orbital lone pairs ($3p_{xy}^2$ and $3p_{yz}^2$). One of these lone pairs was free to overlap with the π-bond (of the C=C entity) to give an extended π-electron system (Scudder, 1992).

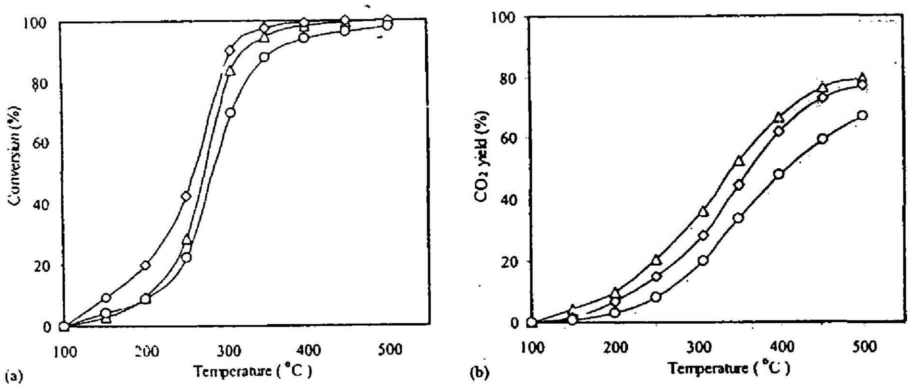

FIGURE 1. Conversion (a) and carbon dioxide yield (b) in the combustion of 2,500 ppm of chlorinated VOCs at a GHSV of 32,000 h^{-1}. (△) DCM, (◇) TCM and (○) TCE.

3.3 DEACTIVATION STUDY

Profiles of $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z deactivation with time on stream after ageing with different feed Cl-VOCs are shown in Figure 2. The profiles were characterized by initial sharp drop followed by a gradual decrease in the activity until relatively stable activity was reached at longer time on stream. $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z catalyst appeared to be resistant to deactivation with less than 15 % activity drop detected for all three types of chlorinated organics. The activity was least affected when DCM was used as the feed with more than 90 % activity retention after 12 h on stream. Compared to TCM, TCE showed initial slower deactivation but as the time progressed, more activity drop was experienced by the catalyst.

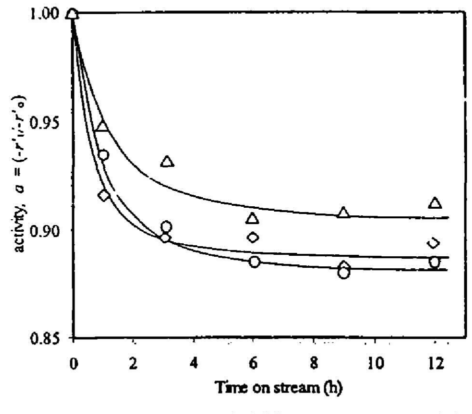

FIGURE 2. Deactivation of Cr1.0Cu0.5/SiCl4-Z catalyst with time on stream in the combustion of 35,000 ppm of chlorinated VOCs at GHSV 32,000 h-1 and 400°C. (△) DCM, (◇) TCM and (○) TCE.

Upon completion of the ageing test, coke deposition on the catalyst was found to be very minimal with less than 1 wt. % for DCM and TCM feeds, and 1.8 wt. % for TCE. Thus, it could be concluded that the catalyst deactivation was mainly attributed to interactions between the catalyst and chlorine bearing in mind that $SiCl_4$-Z support was highly resistant to hydrogen chloride. Low coking activity with DCM and TCM was ascribed to their small molecules and highly reactive intermediates to give high selectivity to gaseous products (Padilla et al., 1999). With increasing molecular size in TCE, the coking activity increased but still low compared to that of non-chlorinated VOCs as reported by Schneider et al. (2000).

Initial interactions between metallic species and chlorine atoms to form metal chloride caused rapid deactivation of the catalyst as indicated by steeper drop in the activity. As the reaction time progressed, more stable activity was obtained suggesting limited capacity of the metallic species to receive chlorine. By theory, highly stable Cr^{3+} could only receive three chlorine atoms to form chloride while it was two atoms with Cu^{2+}. However, with the ability of chromium and copper to present at multiple oxidation states, coupled with the ability of molecular chlorine to act as strong oxidizing agent, these interactions became more complicated. This was probably the governing factor characterizing the deactivation profile of the catalyst with time on stream.

3.4 TPR PROFILE OF AGED $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z

The TPR profile of fresh $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z was characterized by two major peaks occurring at different temperature regions (Figure 3). The peak at around 380°C was assigned to the combined reduction of Cr^{6+} and Cu^{2+} while the second peak occurring at about 100°C higher was attributed to the reduction of Cr^{3+} and Cu^{+}. Upon ageing with TCE, the first peak appeared to be eliminated with time on stream while the overall reducibility of the metal species on the catalyst was found to be on a decreasing trend.

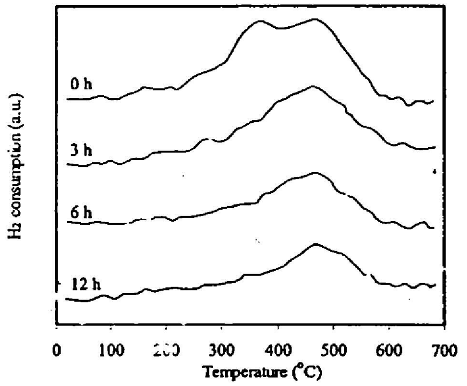

FIGURE 3. TPR profiles of $Cr_{1.0}Cu_{0.5}/SiCl_4$–Z after ageing with 35,000 ppm of trichloroethylene at 400°C for four different times on stream.

TPR result suggests that with the chlorination of the metal species on the catalyst, the overall reducibility of the metals weakened. This could be due to higher electronegativity of chlorine atom compared to oxygen atom that originally formed oxides with metal species in fresh $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z. As a result, the ionic bond in metal chloride should be stronger than that in metal oxide to pose more resistance to reduction during TPR analysis. However, the chlorination and oxidation of the metal species in the combustion reactions were reversible processes that were dictated by reaction temperature and prevalent chloride concentration (Ortiz et al., 2003). This reversibility explained why the catalyst did not show complete deactivation but only achieved relatively stable activity at longer time on stream for all three types of Cl-VOCs.

When present in association with chromium or copper in $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z, chlorine atoms would affect the electron acceptance properties of these metals by strongly forming ionic bond with them (Ortiz et al., 2003). In the TPR analysis, hydrogen had lower ability to reduce these metal chlorides as the first step involved the extraction of chlorine atom to form metal hydrides. Thus, the hydrogen consumption in the TPR profile of the aged catalyst should be attributed to the reduction of remaining oxides of chromium or copper on the catalyst, explaining the decreasing trend in the reducibility of the metals with time.

Changes in the activity with the reducibility of the metal species on the catalyst could be explained with Mars-van Krevelen model which was regarded as the most reliable model to represent VOC combustion process (Minsker et al., 2002). According to this model, the combustion reaction occurred in two separate redox schemes,

(a) Oxidation of the metal species by oxygen form the gas phase, and,
(b) Reduction of the oxidized metal species by the VOC or its intermediates.
Since the chlorination of metal species in $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z reduced some of its metal species while metals in chloride form were generally more resistance to reduction, an overall reduction in redox activity on the catalyst resulted. Thus, according to the Mars-van Krevelen model, a decrease in the overall activity of the catalyst was the likely consequence.

4 CONCLUSIONS

H-ZSM-5 (Si/Al=240) showed high chemical resistance against hydrogen chloride and this desired property was further improved by modifying the zeolite with silicon tetrachloride. TCM was more reactive compared to DCM but produced more incomplete combustion products due to its high chlorine content. The stabilization of TCE was attributed to the resonance effect in the molecule. $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z demonstrated high stability in its activity with time on stream and more deactivation was detected with higher Cl/H ratio feed substance. Coking activity was very low especially with DCM and TCM due to their small molecules and producing highly reactive intermediates to give high selectivity towards gaseous products. Chlorination of metal species in $Cr_{1.0}Cu_{0.5}/SiCl_4$-Z was responsible for loss of activity due to the weakening their overall reducibility. This result was in line with the Mars-van Krevelen model explaining VOC combustion reactions.

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