Decomposition of Chlorinated Volatile Organic Compound by Metal Catalytic Incineration

Chih Ming Ma, Gui Bing Hong, and Chang Tang Chang

Abstract—In this study, the oxy-DE chlorination of 1, 2-dichloroethane with excess oxygen fuels was performed in laboratory scale tubular reactor with packed Pt and Fe_2O_3 catalyst. It is important to understand the influence of operation parameters, such as catalysts, temperature, and retention time on removal efficiency. The catalysts, including noble metal catalyst (Pt) and metal support catalyst (Fe_2O_3), were used in this experiment. Additionally, the temperature and retention time were operated from 450 ℃ to 650 ℃ and from 0.3 to 1.5 s, respectively. Reactants and products were analyzed quantitatively by gas chromatography with a flame ionization detector (GC/FID) and Mass Spectrometer (GC-MS). In order to evaluate the oxidation kinetic behavior of 1, 2-dichloroethane with Pt and Fe_2O_3 catalyst, the Arrhenius equation was used in this study. The experimental data were compared with those predicted results from the kinetic model. The results showed that the removal efficiency was relative to intermediate, final product profiles, retention time, and temperature. Furthermore, the optimum operation conditions of the reactor with Pt catalyst and Fe_2O_3 catalyst were determined.

Index Terms—Volatile organic compound, dichloromethane, metal catalyst.

I. INTRODUCTION

Volatile organic compounds (VOCs) are defined as the organic compounds that have high vapor pressure and are easily vaporized at ambient temperature and pressure. Halogenated VOCs emissions are associated with a wide range of industrial processes. For instance, dichloromethane is mainly used in metal degreasing processes and known to be hazardous to the environment and public health. Treatment of environmental pollution caused by Cl-VOC (e.g. dichloromethane, 1,2-dichloroethane) emissions has become an important topic recently [1]. Methods usually used to abate VOCs include incineration with or without catalyst, adsorption, absorption, and condensation. Among these methods, thermal incineration and catalytic incineration are the most effective control technologies [2]. Thermal incineration requires temperatures in excess of 750°C, with the attendant disadvantages of high fuel cost and production of undesirable by-products. Catalytic incineration requires lower temperatures within the range of 200-500°C effectively to remove CL-VOCs [3].

Recently, catalytic incineration has being attracted due to its lower reaction temperature, energy efficiency, and low NOx formation. Catalysts reported for oxidation of chlorinated VOCs consist of base metal oxides and noble metals with acidic supports [4]-[6]. Pope *et al.* [7] used a Pt catalyst catalytically to convert n-butanal in the mixture with methyl mercaptan. They have found that the conversion of n-butanal was suppressed by methyl mercaptan if operating temperature was below 300°C. Besides, Chu and Lee [8] used a Pt/Al_2O_3 catalyst to convert ethanol in mixtures with dimethyl disulfide. They found out that the conversion of ethanol was significantly suppressed by existence of $(CH_3)_2S_2$ by temperature lower than 300°C. Barbosa et al. [9] noted the activity of Fe_2O_3 supported on silica for total combustion to CO_2 when iron content reached values above a certain level, and showed existence of a linear dependence of the rate of methane oxidation on total iron content of catalyst. By the way, SOx,and NOx reduction, PM (particulate matter) oxidation and wastewater treatment will be carried out over different type catalysts [10]-[15]. There is very few information about the study of combustion of chlorinated VOCs over base metal oxides [16]-[18]. On the other hand, base metal oxides are much less expensive and allow higher catalyst loading. Higher catalyst loading will bring to higher active surface area in metal oxide [19]. Although very active, the application of catalyst is using to low operating temperatures because of volatile formation and toxic chromium oxy-chloride. [1].

This study we also notice that function of the oxy-dechlorination of 1, 2-dichloroethane with excessive oxygen was carried out during laboratory scale tubular reactor with packed Pt and Fe_2O_3 catalyst. Spivey [3] indicated that those major parameters affecting catalytic incineration of VOCs included catalyst type, VOC speciation, VOCs concentration, operating temperature, space velocity and O_2 concentration. In order to understand importance and influence of operating parameters on degradation of 1, 2-dichloroethane, the catalyst characteristics were examined first. Related kinetic equations were also established based on observed experimental results. The catalytic reaction of 1, 2-dichloroethane over Pt and Fe_2O_3 catalyst was fulfilled in continuous scale catalytic incinerator for this study. Present work, the kinetic model of Arrhenius was used to analyze the results. The results show that the Arrhenius model is suitable for predicting the kinetic behavior of 1,2-dichloroethane catalytic incineration. These results suggest that the adsorption of VOCs or O_2 molecule is important in the process of catalytic incineration of 1, 2-dichloroethane.Additionally, the optimum operating conditions in reactor with Pt catalyst and Fe_2O_3 catalyst were

also defined in this study.

II. MATERIALS AND METHODS

A. Preparation of Catalyst

The first to prepare the catalyst is to preheat 700 mL H_2O to 70 ^{o}C in an oven. An aqueous solution will be obtained by adding 35 g Fe_2O_3 and 14.2 g FeO, immediately followed by precipitation with an ammonia solution (45 mL). The precipitate was filtered off, washed and dried at 105 ^{o}C for 12 h. Prior to the catalytic runs, the catalysts were thermally activated in air at 500 ℃ for 60 minutes. The commercial catalyst (DASH-220N Pt/Al_2O_3) was used to compare the 1,2-dichloroethane treatment performance with the prepared catalyst in this study. The basic properties of DASH-220N Pt/Al_2O_3 catalyst are shown in Table I.

B. Experimental Instruments

The catalytic incineration of this study was preformed in a bench scale fixed bed reactor, as shown in Fig. 1. The system is divided into three parts: VOC gas system, catalytic incineration system, and effluent gas analyzing system. The gas generation system was composed of an Argon cylinder (99.9%, San Fu), an oxygen cylinder (99.9%, San Fu), three mass flow meters (Teledyne Hasting-Raydist, HFC-202), a water bath and a 1,2- dichloroethane generator (Pyrex). The temperature of simulated gas was measured by K type thermocouples before going through the catalytic reactor. The material as pipes, valves, regulators or fittings used was either SS-316 or Teflon. The catalytic incineration system was composed of a custom-made SS-316 tube reactor and a high temperature heater. The catalysts were set in the center of quartz tube and length, internal diameter, and outer diameter of the reactor were 400 mm, 15 mm and 24 mm, respectively. Furthermore, the gas analysis system was composed of gas chromatograph with FID (HP5890II) and MS (Finnigan TRACE GC2000/TRACE MS) detectors.

III. RESULTS AND DISCUSSION

A. Effect of Various Conditions

In this study, three sets of experiments were performed to compare degradation efficiency of 1, 2-dichloroethane with Equation (1).

$$\text{Degradation efficiency} = 1- [C_2H_4Cl_2] / [C_2H_4Cl_2]_0 \quad (1)$$

where $[C_2H_4Cl_2]$ is the outlet concentration (mol/ L) of 1,2-dichloroethane and $[C_2H_4Cl_2]_0$ is the inlet concentration (mol/ L) of 1,2- dichloroethane.

The degradation efficiency is a function of temperature and the results are shown in Fig. 2. No significant reduction of 1, 2- dichloroethane (about 2~ 3%) is attributed to temperature effects without using catalyst, case (a), in the incineration system. In case (b) of Fig. 2, the degradation efficiency was 30.2 % at T = 500°C with using packed Fe_2O_3 catalyst. However, the decomposition efficiency of 1,2-dichloroethane was 78.2% at 500°C for case(c) (with Pt catalyst). Fig. 2 shows that the degradation efficiency of 1, 2-dichloroethane under various conditions following the

sequence: Pt catalyst > Fe catalyst > No catalyst in the incineration system.

TABLE I: THE BASIC PROPERTIES OF DASH-220N Pt/Al_2O_3

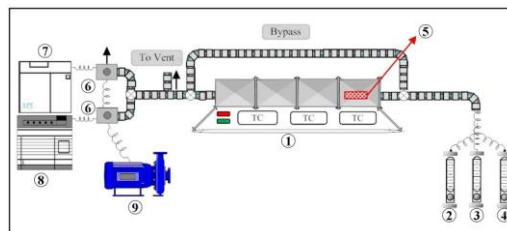| Catalyst	Shape	Bulk density (g/L)	Pore volume (cm³ g⁻¹)	BET surface area (m² g⁻¹)	Average pore radius (Å)	Average diameter (mm)
Pt/ Al_2O_3	Pellet	770	0.44	166.62	76.12	0.44

Fig. 1. A schematic diagram of a bench-scale catalytic incinerator. (experimental instruments : 1. high temperature reactor; 2. 1-2-dichloroethane generator; 3. oxygen cylinder; 4. argon cylinder; 5. catalyst; 6. six- port valve; 7. GC-ms; 8. GC-fid; 9. pump)
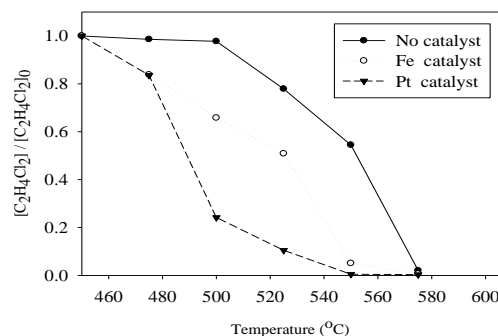

Fig. 2. Control efficiency of 1, 2-dichloroethane under various conditions. (Experimental conditions: case (a): no catalyst; case (b): Fe2O3 catalyst; and case (c): Pt catalyst in the incinerator at the retention time of 1.0s.)

B. The Composition of Products

Fig. 3 shows 1, 2- dichloroethane was oxidized over the Pt and Fe_2O_3 catalyst. The experiment shows that the conversion is increased rapidly at 550°C, and the decomposed products of 1, 2- dichloroethane are C_2H_4, C_2H_6 and C_3H_8. Fig. 3(a) shows that the concentration of C_2H_6 and C_3H_8 is increased with the increasing of C_2H_4 concentration. The concentration of C_2H_6 is also increased with the increasing of C_3H_8 concentration but there is no relation to C_2H_4 for case (b) in Fig. 3. The maximum concentration of C_2H_6 and C_3H_8 with Pt catalyst and C_2H_4 with Fe_2O_3 was observed at retention time 0.7sec.
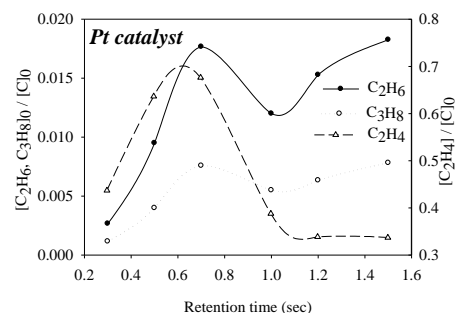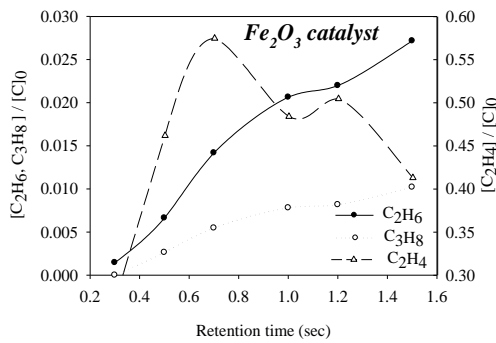

Fig. 3 (a). Products of 1, 2-dichloroethane decomposition over Pt catalyst of 550 ℃.

Fig. 3(b). Products of 1, 2-dichloroethane decomposition over Fe_2O_3 catalyst of 550 ℃.

C. Effect of Retention Time

Retention time is one of the important process parameters affecting the conversion efficiency of catalytic incineration. Spivey [3] indicated that the catalytic incineration requires retention time, in the range of 0.3 ~ 1.5 seconds to decompose VOCs. In this study, the retention time was operated between 0.3 to 1.5 s. The effect of retention time on the conversion efficiency of 1,2 -dichloroethane is shown in Fig. 4. The decreasing of retention time can cause the increasing of flow rate. The larger flow rate results in smaller oxidation rate since that mass transfer is limited. Fig. 4(a) shows that the conversion efficiency of Fe_2O_3 catalyst at incineration temperature increased to 525℃ with the retention times in the range of 0.5~1.5 s, the conversion efficiency of Fe_2O_3 catalyst was above 50%. When Fe_2O_3 catalyst changes to Pt catalyst in the catalytic incineration at the retention times 0.5~1.5 s, the conversion efficiency of Pt catalyst was above 80% in the incineration temperature 550℃, as shown in Fig. 4(b).
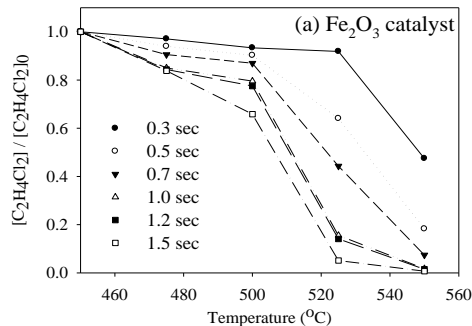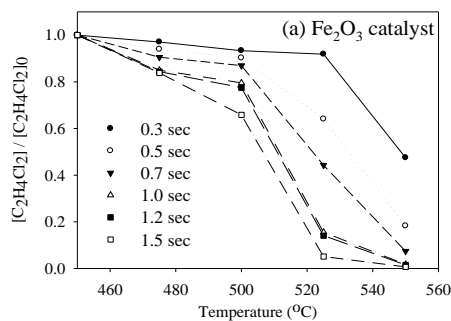

Fig. 4(a). Effect of different retention time of 1, 2-dichloroethane over the Fe_2O_3 catalyst.

Fig. 4(b). Effect of different retention time of 1, 2-dichloroethane over the Pt catalyst.

D. Effect of Incineration Temperature

This study also evaluated different catalytic incineration temperatures of 1-2-dichloroethane from 450℃ to 600℃. In Fig. 5, the conversion efficiency of Pt and Fe_2O_3 catalysts at the incineration temperature of 475℃ was not obvious. Fig. 5(a) shows the reaction with Pt catalyst became active while the temperature was increased to 500℃, even with small retention time. In contrast, Fig. 5(b) shows obvious larger conversion efficiency of Fe_2O_3 catalyst at the incineration temperature of 525℃. In addition, the conversion efficiency (η) of Pt catalyst and Fe_2O_3 catalyst at 550℃ was 66~99.8% and 53~99%, respectively. In general, the conversion efficiency of 1-2-dichloroethane was increased with the increase of the temperature with these two catalysts.

E. Kinetic Analysis of Arrhenius Equation

The temperature dependence of kinetic parameter k_{obs} (1/sec) in Eq. (2) can also be described by the Arrhenius equation as follows:

$$k_{obs} = A \exp\left(-\frac{Ea}{RT}\right) \quad (2)$$

where:
k_{obs}: kinetic parameter (1/ min)
A: frequency factor (1/ min)
Ea: activation energy (kcal/mole)
T: temperature (K)
R: gas constant (1.987×10^{-3} kcal/mole K)

Integration of Eq. (2) yields an expression as follows:
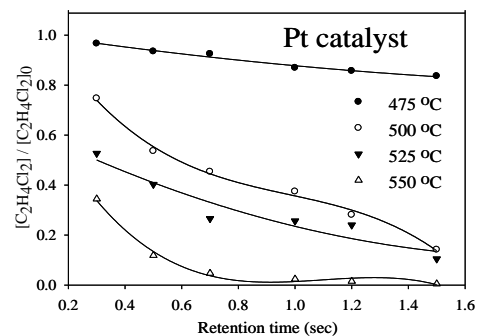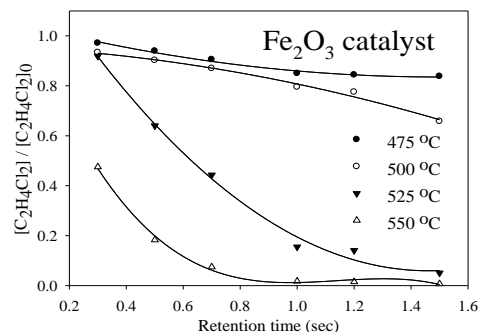
$$\ln k_{obs} = \ln A - \frac{Ea}{RT} \quad (3)$$

Fig. 5(a). Effect of temperature of 1, 2-dichloroethane over the Pt catalyst

Fig. 5(b). Effect of temperature of 1, 2-dichloroethane over the Fe_2O_3 catalyst
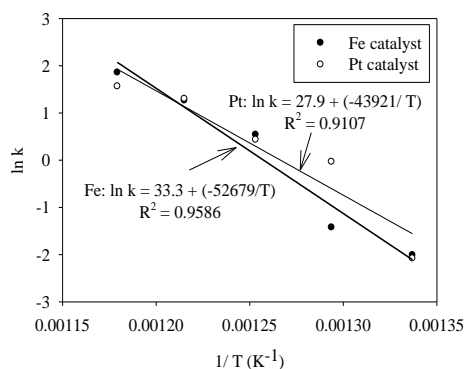
Fig. 6. Arrhenius plot showing two catalyst relationships for 1/kobs with 1, 2-dichloroethane

Based on Eq. (3), the linear expression can also be obtained by plotting the reciprocal degradation rate ($1/k_{obs}$) as a function of the reciprocal of temperature ($1/T$). The values of k_{obs} are shown in Fig. 6 with Pt catalyst and Fe_2O_3 catalyst for 1,2-dichloroethane. The fitting results in Fig. 6 seem well and the R^2 value of Pt catalyst and Fe_2O_3 catalyst was 0.911 and 0.958, respectively. The frequency factor (A) and the activation energy (*Ea*) can be evaluated by means of a lowest square/best fitting procedure by using Equation (2). The results show that the values of A and *Ea* for the catalytic conversion of 1,2-dichloroethane with Pt catalyst were roughly 27.9 (sec^{-1}) and 43.92 (kcal/mol), respectively. In addition, the values of A and *Ea* with the Fe_2O_3 catalyst were approximately 33.3 (sec^{-1}) and 52.68 (kcal/mol), respectively.

IV. CONCLUSION

The oxy-dechlorination of 1,2-dichloroethane with excess oxygen was performed in laboratory scale tubular reactor with packed Pt and Fe_2O_3 catalyst. The results show that the degradation efficiency of 1,2-dichloroethane under various conditions followed the sequence: Pt catalyst ＞ Fe catalyst ＞ No catalyst in the incineration system. In this study, the decomposition products of 1,2-dichloroethane were identified as C_2H_4, C_2H_6 and C_3H_6. In general, the experimental data could be correlated well with the Arrhenius equation. The regression equation was identified as K =1.438×10^{12} exp (-22.10 kJ/RT) and K =3.004×10^{14} exp (-26.51 kJ/RT) with Pt catalyst and Fe_2O_3 catalyst, respectively. Retention time is one of the important operation parameters affecting the catalytic oxidation rate since the higher flow rate in the reactor and smaller retention time will decrease the activity of catalyst to decompose the pollutants. In addition, the conversion efficiencies of Pt catalyst and Fe_2O_3 catalyst will be increased at any retention time while the incineration temperature was increased. Additionally, the optimum operation conditions of the Pt catalyst and Fe_2O_3 catalyst were determined as 0.7s/550°C and 1.0 s/525°C, respectively.

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