ABSTRACT

CATALYTIC OXIDATION OF TRACE CONCENTRATIONS OF TRICHLOROETHYLENE OVER Cr_2O_3 AND 5% Cr_2O_3 ON γ-Al_2O_3

Soyoung Myung

This research addressed the ability of Cr_2O_3 and 5% Cr_2O_3/γ-Al_2O_3 to catalytically oxidize trichloroethylene (TCE). Various types of Cr_2O_3 catalysts were compared with Pt, CuO and Fe_2O_3 which were previously tested in our laboratory. A number of sample catalysts containing 5% Cr_2O_3 on γ-Al_2O_3 were synthesized for this research. Different procedures were evaluated in the synthesis in order to find which procedure gives the most active catalyst. The oxidation of TCE was used as a diagnostic reaction to evaluate catalytic activity. The catalytic oxidation of trichloroethylene was conducted in a tubular reactor system in order to evaluate the activity of the catalysts as a function of temperature and space velocity. Gas chromatography with electron capture and flame ionization detectors was used for quantitative analysis of feed and product streams. The results showed that commercial powdered chromium oxide had lower light-off temperature than powdered iron oxide, but needed a temperature of 600 °C to achieve 99% conversion of trichloroethylene, while Fe_2O_3 showed similar conversion of TCE at 550 °C when 111 ppm TCE are reacted at a space velocity 17,400 v/v/h. In addition TCE was converted by powered Cr_2O_3 to an unknown byproduct which was detected by GC-ECD. Results with supported Cr_2O_3 on γ-Al_2O_3 showed that over 99% conversion of

trichloroethylene was achieved at 400 ^{o}C for the same space velocity. A comparison of catalytic kinetics for oxidation of TCE showed that the best 5 % Cr_2O_3/γ-Al_2O_3 catalyst synthesized in this research is slightly more active than 1.5 % Pt/γ-Al_2O_3. Based on the results presented here, additional research on the new catalyst is warranted. In particular, lifetime comparisons between the new catalyst and 1.5 % Pt/γ-Al_2O_3 need to be conducted.

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by
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This thesis dedicated to my parents.

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CHAPTER 1

INTRODUCTION

Volatile organic compounds, VOCs, emitted from industrial solvents used in paint, ink and adhesive manufacturing, and also from the petrochemical and chemical industries, are involved in environmentally damaging processes. This is a consequence of their toxicity to living things ether by direct reaction with living matter, or indirectly, through chemical reactions within the atmosphere which subsequently affect living matter.

In fact, many industrial processes generate significantly greater quantities VOC emissions than the legislated permitted limits, and therefore, operators need to install pollution control system in order to achieve the required emission levels.(Lawton and Gower, 1994)

One of the most effective ways to assure complete destruction of VOCs present in gaseous emission is by incineration. Thermal incineration of VOCs is a widely used technology, and can be performed by direct-flame oxidation in a combustion chamber, at temperatures of 760 °C or greater, depending upon the nature of the VOCs. However critical operating parameters of time, temperature and turbulence must be satisfied to achieve good result from this technique, otherwise the VOC oxidation will not go to completion, and excess emission levels will be generated. In particular, halogenated organics are often more difficult to oxidize then unsubstituted organics; hence, the presence of halogenated compounds in the input stream requires higher temperature and compounds could produce more toxic components in the effluent than were present in the feed. In addition, this technique is expensive because the high temperatures required for the decomposition of VOCs need additional fuel and special materials of construction that can withstand the high temperatures.

One technology which can help reduced costs and achieve complete oxidation is catalytic oxidation. The technology for the successful catalytic oxidation of VOCs as an alternative to direct thermal incineration has been proven over many years through installation of catalytic oxidation systems to treat VOC emissions from a various industrial processes. The main advantage of catalytic oxidation is from the ability of the catalyst to operate at significantly lower temperatures than direct thermal incineration. The temperature needed for the catalytic oxidation reaction for the majority of VOCs is between 280 °C and 600 °C (Bretschneider and Kurfurst, 1987), and for carbon monoxide which can arise from partially combusted VOCs between 200 °C and 250 °C (Bretschneider and Kurfurst, 1987). Since catalytic oxidizers operate at fairly low temperatures, the addition of a catalytic reactor into the exhaust duct of an incinerator can provide the catalyst with the required temperature to achieve complete oxidation of VOC and carbon monoxide. Catalytic oxidation can reduce capital operating cost because it required much less fuel and no special materials of construction. Moreover, since complete oxidation of halogenated components preferentially form acid gases which are often removed from the effluent gas streams by safe neutralization process, catalytic oxidation is especially desirable and economical to treat haloginated hydrocarbon (Bretschneider and Kurfurst, 1987; Purcell and Shareef, 1988).

Catalytic materials typically used for VOC incineration include platinum and palladium ; other formulations are also used including transition metal oxide for emission streams containing chlorinated compounds. This thesis presents the results of an experimental investigation of the synthesis and operating parameters of a transition metal oxide, Cr_2O_3, used as an oxidation catalysts.

The specific objectives of this research are to check the catalytic ability of Cr_2O_3 to decompose TCE, and find an effective method to synthesized Cr_2O_3 catalyst on a high surface area support. The research also evaluates various synthetic routes those are capable of producing an effective catalyst.

CHAPTER 2

BACKGROUND

Trichloroethylene (TCE) is a chemical that does not occur naturally in the environment. TCE is mainly used as a solvent to remove grease from metal parts. It is used as a chemical (building block) to make other chemicals. In recent years, TCE has been listed as a major contaminant in the workplace and environment in over 460 of 1,179 hazardous waste sites on the National Priorities List (Syracuse Research Co., 1989) and the atmosphere background levels of TCE in the outdoor air we breathe (30 to 460 parts of TCE per trillion, ppt (v)) were found in many sections of the U.S. (Syracuse Research Co., 1989). As suspected human carcinogen, TCE has been found to cause liver carcinoma in experimental animals and is known to affect numerous body organs (Schaumburg, 1990). Like other organohalide solvents, TCE cause skin dermatitis from dissolution of skin lipids and it can affect the central nervous and respiratory systems, liver, kidneys and heart (Syracuse Research Co., 1989). Because of these toxic effects, it has become the subject of extensive governmental regulations and a target chemical in perhaps hundreds of environmental litigations (Schaumburg, 1990).

Catalytic oxidation is one of the most economic and safe methods to decompose low concentrations of VOC in air stream. Catalytic oxidation is an air pollution control technique whereby VOCs in an effluent stream are oxidized with the help of a catalysts. A catalyst is a substance that accelerates the rate of a reaction at a given temperature

Transition metals are good catalysts for reactions involving hydrogen and hydrocarbons. This is a consequence that these substances readily adsorb at metal surfaces. Base metals are seldom used as catalysts because at the reaction temperature they are rapidly oxidized. Thus transition metal oxides are often used as oxidation catalysts (Bond, 1974). Only some noble metals such as platinum are used in metallic form because they resist oxidation at relevant temperatures.

The seriatim of the activity of metal oxide catalysts for the complete oxidation of chlorinated compounds was compiled by Ramanathan, et al., (1989) as follows:

$$\mathrm{Co, Cr > Mn > Cu > Ni > Pt > V\ , Mo}$$

Cr_2O_3 catalysts were shown to have good activity for chlorinated compounds destruction. A chromium oxide impregnated catalyst on the support was used in the oxidation of chlorinated compounds which treated CH_3Cl (Senkan, et al, 1986), hexachlorobenzene and hexachlorobutadiene (Johnston, 1976), and PCB's (Novinson, 1989). In a study by Ramanthane, et al., (1989), the selectivity to chlorine from catalytic oxidation of 1,1-dichloroethane was determined to be 50 % at 500 °C.

Supported metal catalysts are commonly used in industry since supported metal catalysts are often more active than unsupported catalyst. A support is most often a high surface area material containing a complex pore structure into which catalytic materials are deposited (Heck and Farrauto, 1995). The main function of a carrier are to provide a structural framework for the catalytic component and increase the surface area per unit weight of metal above that of the unsupported metal. Other desirable effects may include such factors as increased stability due to small crystallites of metal being sufficiently separated to prevent sintering, and the dispersion inhibits catalyst growth by sintering and the useful life of the catalyst is thereby prolonged (Thomson and Webb, 1968; Bond, 1969).

A very large number of materials have been used as supports depend on the purpose for which the catalyst is required. Low surface area supports are used when the catalytic materials are extremely active. High surface area porous supports are chosen when high activity and stability are required. Alumina is one of the most common carriers used in commercial environmental catalytic applications. There are many different types of alumina having varying surface areas, pore size distributions, surface acidic properties, and crystal structures. The most important alumina, in catalytic applications, is gamma (γ)-Al_2O_3 which is commonly used as a support. The phase transition to γ-Al_2O_3 occurs when boehmite (monohydrate) alumina is converted at roughly 500 °C. This has a tetragonally distorted spinel lattice which typically contains an internal surface area of 100-200 m^2/g.

The most common commercial procedure for dispersing the active catalytic materials within the carrier is by impregnating an aqueous solution containing a salt (precursor) of the catalytic materials. Most preparations simply involve soaking the support in the solution and allowing capillary and electrostatic forces to distribute the salt over the internal surface of the porous network. The solvent is removed by evaporation during drying. When the amount of solution corresponds to the pore volume of support, the method is more precisely referred to as the "incipient wetness impregnation" (IWI) (Purcell and Sharref, 1988; Twigg, 1989). This method is used when there is little or no interaction between the precursor and support. The advantages of IWI are technically simplicity, low cost and reproducible metal loadings (Che and Bennett, 1989).

CHAPTER 3

EXPERIMENTAL

3.1 Preparation of 5 % Cr_2O_3 on γ-alumina

The objective of section 3.1 is to describe the best procedures to synthesize 5% chromium oxide on γ-alumina by the incipient wetness impregnation method.

3.1.1 Methods and Procedures to Prepare Catalyst

The γ-Al_2O_3 support of the active catalytic material was provided by Engelhard Corporation. The aqueous solution in which to γ-alumina was soaked contained chromium salt $Cr(NO_3)_3$. The maximum volume of solution had to be equal to the pore volume of γ-alumina in order to obtain the precise amount of catalytic material, Cr_2O_3, on the support surface structure after drying and calcination. The maximum water uptake by the support is referred to as the water pore volume (Heck and Farrauto, 1995). To determine the water pore volume, deionized water (18 MΩ • cm at 25 °C) is slowly added to a known mass of dried γ-alumina until it is saturated as indicated by beading of excess water. The measured volume of deionized water per unit mass of γ-alumina is used as the value of the water pore volume for the synthesis of catalysts by the incipient wetness impregnation method.

In preparing the catalyst based on conventional incipient wetness method, the γ-alumina is soaked in the exact volume of the aqueous solution of chromium nitrate salt γ-alumina soaked with chromium salt solution is dried. As a part of this research, additional steps were added to modify the conventional catalyst synthesis procedure. For example, the γ-alumina was presoaked with a weak base before soaking in the chromium salt solution because acidic chromium salt solution could then be easily adsorbed on to the basic γ-alumina surface. As a consequences of this additional step, several options regarding concentration and volume were considered. Presoaking solutions at pH 9 and 11 were used because the structure of γ-alumina is stable at these evaluated pH values. The following solution volumes, V, 1/2V and 1/4V based on maximum water pore volume were used. Whenever maximum water pore volume was used, γ-alumina samples were always dried after soaking, but in other cases, drying was not necessary.

Because $Cr(NO_3)_3$ is completely ionized and exists as Cr^{3+} in water, one can calculate the weight of $Cr.(NO)_3$ needed to produce Cr_2O_3 by precipitation or denitration. Even though chromium chloride, $CrCl_3$, can also be completely ionized to Cr^{3+}, chloride ion could deactivate the catalysts and was not used (Simone, et al., 1991). When chromium nitrate solution was prepared, the pH of this solution was adjusted to a pH value higher than 3.5 but lower than pH 6 because chromium nitrate becomes a strongly acidic solution, and this acidic property dissolves γ-alumina. The volume of chromium nitrate solution needed depends on the previous step. If γ-alumina is presoaked in basic solution and dried, the volume of chromium nitrate solution could be equivalent to the maximum water pore volume. Otherwise, the volume of chromium nitrate solution should be half of water pore volume. After soaking γ-alumina with chromium salt solution, water is evaporated leaving the salt on the γ-alumina surface. During calcination at 600 °C, the salt is fixed to the γ-alumina surface and transformed to chromium oxide. Between the drying and calcination steps, precipitation process could be used as an intermediate step since chromium (III) can be precipitated with hydroxide ion as $Cr(OH)_3$. Generally, $Cr(OH)_3$ is formed at pH 6 to 8 and the total pH condition of γ-alumina containing chromium salt must be maintained within the range of pH 6 to 8. When the wet precipitate is heated, it first loses adsorbed water. According to thermoanalytical measurements, the composition of the precipitate at 160 °C corresponds to the formula $Cr_2O_3 \cdot 2H_2O$, and decomposes slowly on further heating until at about 350 °C, $Cr_2O_3 \cdot H_2O$ is formed. Finally, this hydrated structure decomposes rapidly at about 350 °C to Cr_2O_3 (Erdey, 1963). Thus, the precipitate is converted to Cr_2O_3 before the furnace temperature reaches calcination temperature. In addition, when other synthesis procedure which do not contain precipitation step are used, $Cr(NO_3)_3 \cdot H_2O$ is directly oxidized to Cr_2O_3. A thermal gravimetric analyzer (TGA) was used to check the direct oxidation of $Cr(NO_3)_3$ to Cr_2O_3 at elevated temperatures. This TGA experiment is summarized in Table 1 and described in greater detail in Section 3.1.2.

The overall procedure for producing Cr_2O_3 from precursor, $Cr(NO_3)_3$ is diagrammed in Figure 1.

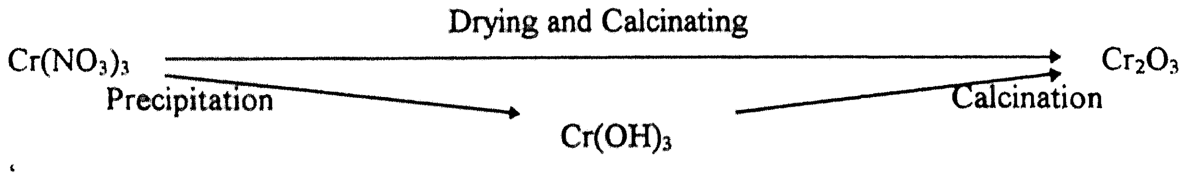


Figure 1 Pathways for converting $Cr(NO_3)_3$ to Cr_2O_3

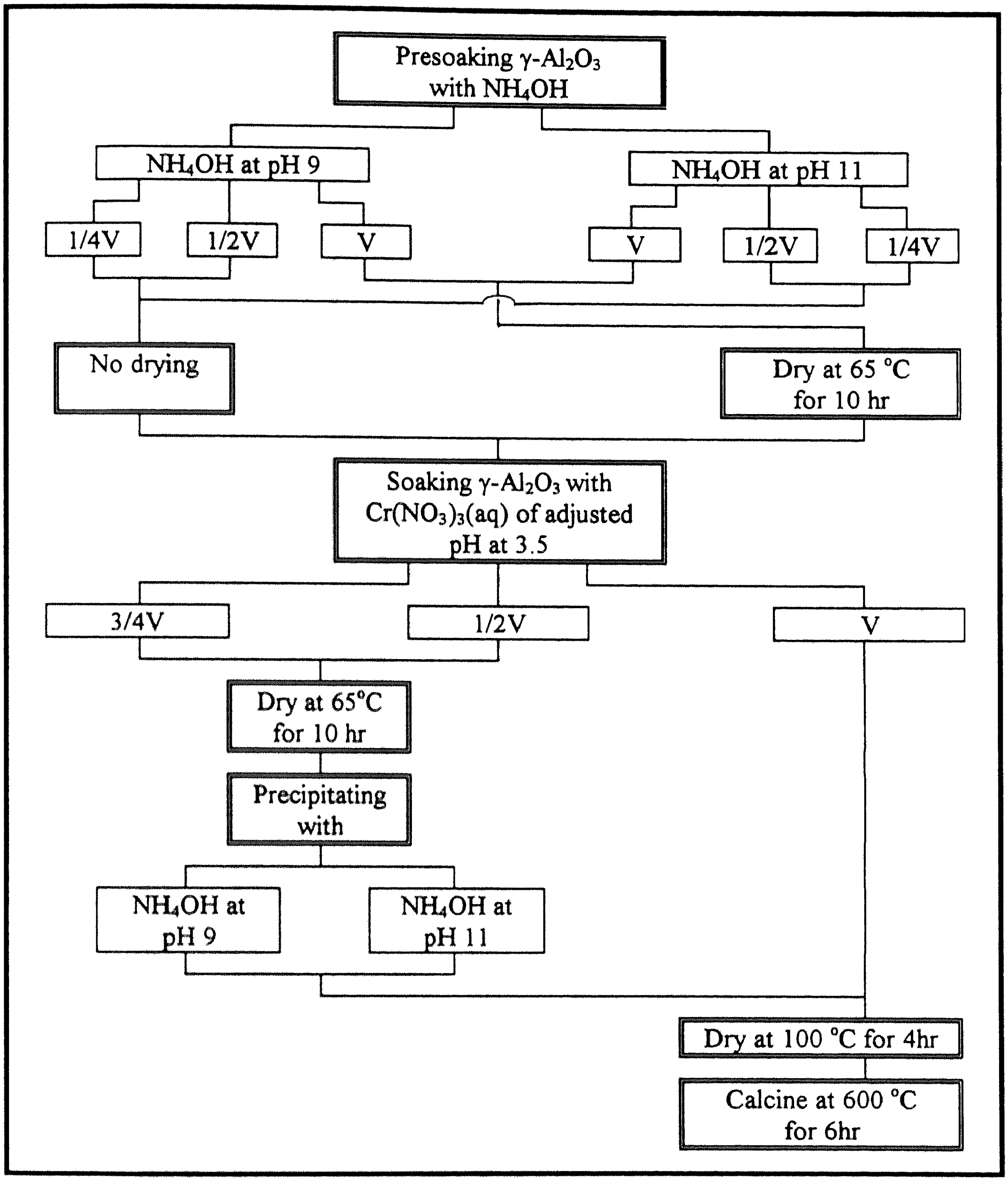
A flow chart of the procedure used to synthesize 5 % Cr_2O_3 on γ-Al_2O_3 which was developed in this research is provided in Figure 2. Table 2 gives key details for the synthetic procedures evaluated in developing the Cr_2O_3 on γ-Al_2O3 catalysts tested in this research. The maximum calcination temperature used was 600 °C, in order to minimize the changes in the γ-Al_2O_3 phase which occurs at the temperatures above 600 °C.

3.1.2 Thermogravimetric Analysis (TGA)

TGA experiments were performed to determine the feasibility of direct denitration of $Cr(NO_3)_3$ to Cr_2O_3 within the temperature region between drying and calcination. With the PE 7500 Professional Computer, the modular TGA 7 permits the measurement of weight changes in a sample material as a function of temperature or time. Under the control of the PE 7500, the TGA 7 is programmed from initial to final temperature and measures weight changes resulting from chemical reactions, decomposition, solvent and water evolution, curie point transitions and oxidation of sample materials. The TGA 7 is made up of two major components: a sensitive ultramicrobalance and furnace element capable of achieving temperatures of 1000 °C. The experimental parameter used to operate the TGA 7 are listed in the Table 1.

Table 1 The parameters used in TGA analysis.

Sample Parameter		Sample weight	: 24.362 mg
		Sample Zero	: - 0.165 mg
Atmosphere Parameter		Purge Gas	: Air
Temperature Program		Temperature, C	Rate, °C/ min
	Initial	30	40.0
	Final	550	-



V = Water pore volume to γ-Al_2O_3

Figure 2. Flow Chart for 5 % Cr_2O_3/γ-Al_2O_3 Synthesis Procedure

Table 2 Procedures tested in synthesizing 5% Cr_2O_3 on γ-Al_2O_3 catalysts

Catalysts Procedure	A	B	C	D	E	F	G	H	I	J	K
Presoaking	pH9 1/4*V	pH9 1/4*V	pH9 1/4*V	pH9 V	pH9 V	pH9 V	pH11 V	pH11 V	pH11 V	pH9 1/2*V	pH11 1/2*V
Drying	no	no	no	65°C 10hrs	65°C 10hrs	65°C 10hrs	65°C 10hrs	65°C 10hrs	65°C 10hrs	no	no
Soaking γ-Al_2O_3 with $Cr(NO_3)_3(aq)$ adjusted as pH3.5	3/4*V	3/4*V	3/4*V	V	V	V	V	V	V	1/2*V	1/2*V
Drying	100°C 4hrs	65°C 10hrs	65°C 10hrs	100°C 4hrs	65°C 10hrs	65°C 10hrs	100°C 4hrs	65°C 10hrs	65°C 10hrs	100°C 4hrs	100°C 4hrs
Precipitation by $NH_4OH(aq)$	no	pH9 V	pH11 V	no	pH9 V	pH11 V	no	pH9 V	pH11 V	no	no
Drying	no	100°C 4hrs	100°C 4hrs	no	100°C 4hrs	100°C 4hrs	no	100°C 4hrs	100°C 4hrs	no	no
Calcination	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs	600°C 6hrs

Note : V = Water pore volume

3.1.3 Comparison Activities of Prepared Catalysts

A. Experimental System

The flow experiments were conducted with a laboratory-scale tubular reactor system shown schematically in Figure 3. The system consists of a 2.5 cm inside diameter quartz tube reactor residing in a vertical three zone tubular furnace. The middle zone has an excellent flat temperature profile of ± 0.5 °C at 500 °C. Eleven different powered 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ catalyst samples synthesized at different conditions were tested one at a time in the tubular reactor. The catalyst samples were contained in the middle zone of the furnace at various residence times and same temperature of 300 °C. The reactor temperature was monitored with 0.16 cm chromel-alumel (K-type) thermocouples which were inserted at the top of the reactor and place in the center line immediately before the catalyst. Measured concentration of TCE in air stream was passed through the reactor from top to bottom (downflow).

A mixture containing 100 ±1 ppm TCE with the balance gas air was obtained from a mixture containing 1000 ppm TCE in air that was obtained from Matheson Gas Products, with analysis, and was used without further purification to make the feed for all evaluations of synthesized catalysts. Its concentration was verified before and after each experiment by bypassing the reactor and analyzing the mixture with the on-line GC using ECD.

B. Gas Chromatography with ECD

The TCE analyses were conducted using a Hewlett Packard 5890 gas chromatography (GC) with an electron capture detector (ECD). The concentration of unreacted TCE

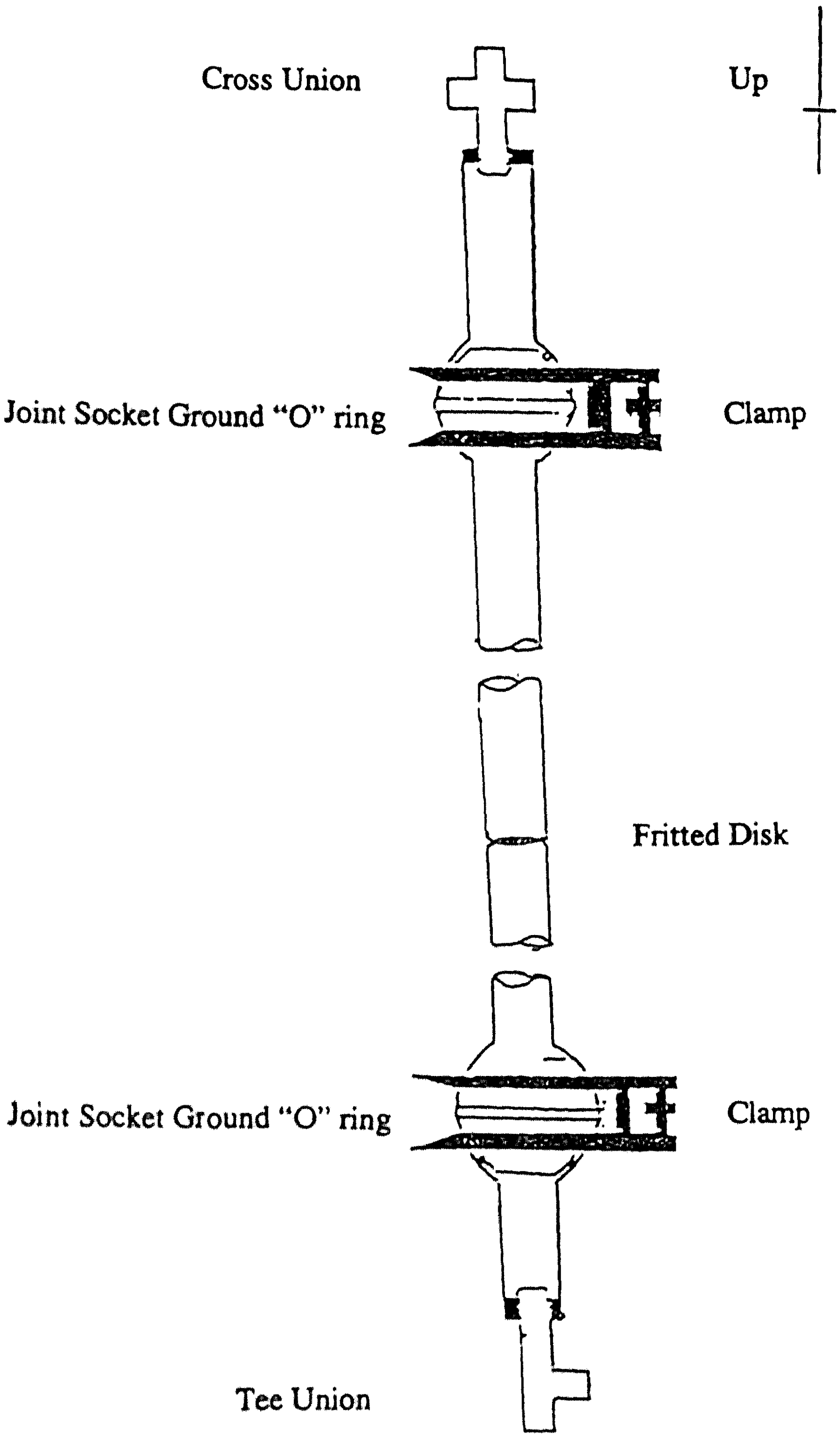
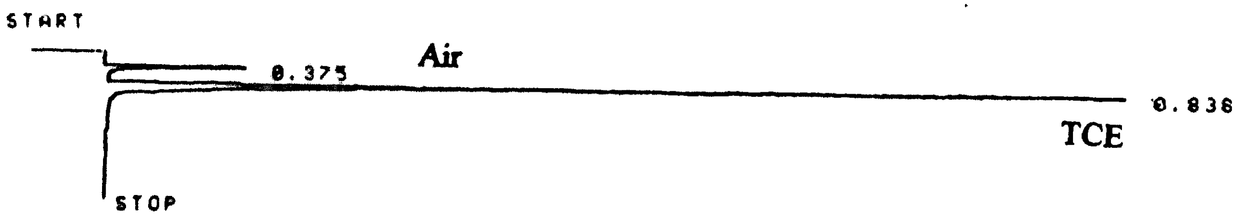


Figure 3 Quartz tube reactor design

remaining in the product gas stream from the reactor was also measured using the same GC-ECD system. A 1/8 inch 10 feet stainless steel column packed with 80/100 mesh Chromosorb GAW was used to separate the product components. The operating conditions of the gas chromatography are listed in Table 3. Figure 4 shows the typical peak resolution and retention time of TCE. The calibration curve for TCE, shown in Figure 5, was made by diluting 1000 ppm TCE in air to five lower concentrations with an exact amount of dry air. A typical gas chromatogram showing the products from TCE oxidation is shown in Figure 6. The analysis was performed on another Hewlett Packard 5890 described in section 3.2.3.



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    .836     8442093   PB    .070     90.65632

TOTAL AREA=9.3122E+06
MUL FACTOR=1.0000E+00
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Figure 4. Typical resolution and retention time for TCE calibration

Table 3 The operating condition of the Hewlett Packard GC used to detect trichloroethylene

Carrier Gas	Nitrogen, 30 cm^3/min
Oven Temperature	100 °C
Injector Temperature	150 °C
Detector Temperature	250 °C
Integrator Attenuation	8
Column packing material	Chromosorb GAW 80/100, 1/8"x 10'

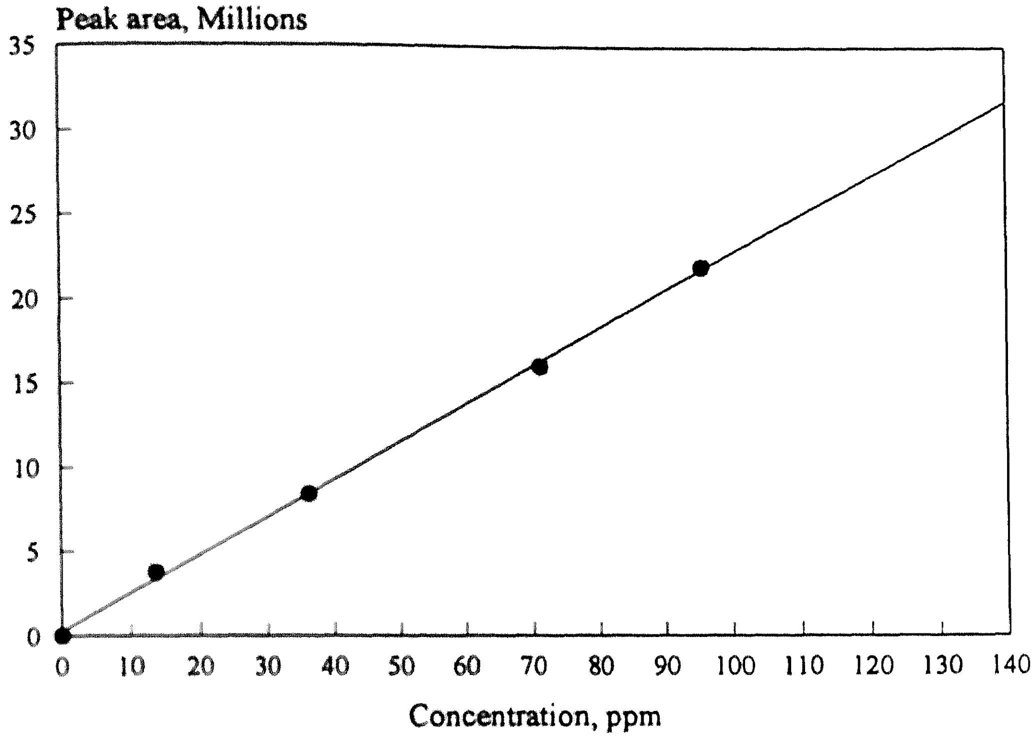
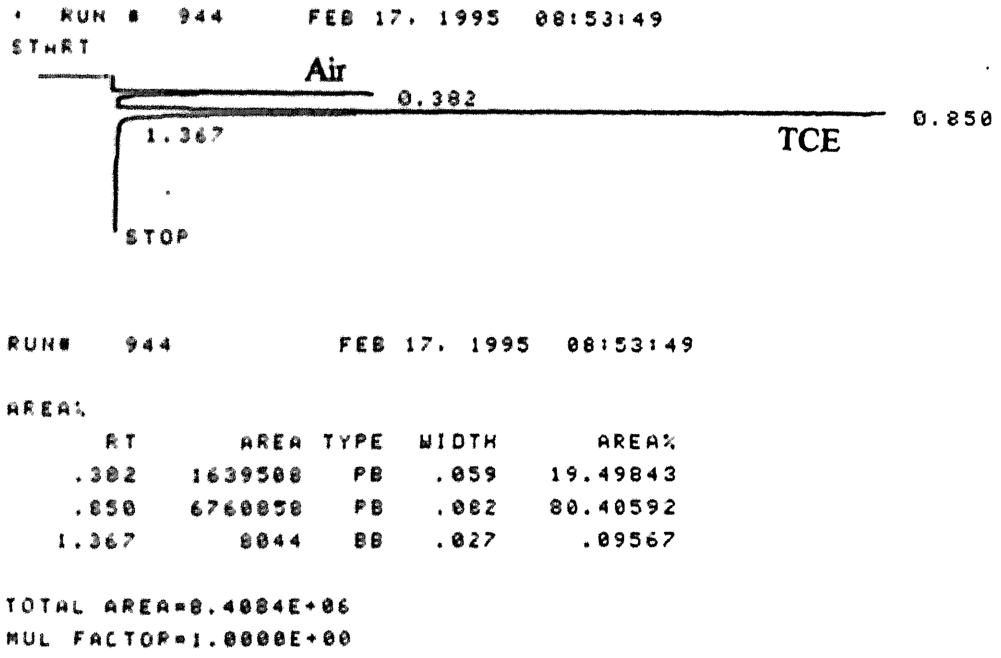


Figure 5 GC Calibration curve for trichloroethylene



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     .850    6760858   PB    .082    80.40592
    1.367       8044   BB    .027      .09567

TOTAL AREA=8.4084E+06
MUL FACTOR=1.0000E+00
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Figure 6 Typical gas chromatography of TCE oxidation product.

C. Catalysts and Space Velocity

The TCE catalytic oxidation activity of each of the eleven 5 % $Cr_2O_3/\gamma\text{-}Al_2O_3$ samples (shown in Table 2) that were synthesized using slightly different procedures was determined. As a surrogate for the activity of eleven samples, conversion of TCE over 0.54 cm^3 of synthesized catalysts was measured. The total flow rate of the air stream containing TCE was 270 cm^3/min. The space velocity was calculated as follows :

$$\begin{aligned}\text{Space Velocity} &= \text{total flow rate / catalyst volume}\\ &= (270\ cm^3/min * 60\ min/hr) / 0.54\ cm^3\\ &= 30{,}000\ v/v/hr \qquad (1)\end{aligned}$$

D. Feed Concentration of TCE

A 100 ppm TCE feed was used to the check catalytic oxidation activity of all synthesized 5 % $Cr_2O_3/\gamma\text{-}Al_2O_3$. In order to obtain 100 ppm TCE, 1000 ppm TCE from a gas mixture cylinder was diluted ten fold with dry air. The actual concentration of TCE was measured by gas chromatography and checked a number of times during each experiment.

E. Temperature Control

The reaction temperature must be reproducible to compare activity of each different synthesized catalysts sample. In this part of experiment, the activity of the eleven synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ was investigated at 300±1 °C. Furthermore, the temperature profile in the middle section of the 3-zone furnace must be uniform (flat) in order to obtain good reaction kinetic parameters. To this end, the temperature in the middle zone could be maintained at ± 1 °C in the temperature range of 200 -600 °C.

3.1.4 Check the Structure of Most Active Synthesized Catalysts

A. X-ray Diffraction

The crystalline nature of the prepared catalysts was checked by x-ray diffraction crystallography. Crystal structures possess planes made by repetitive arrangements of atoms which are capable of diffracting x-rays. The angles of diffraction differ for the various planes within the crystal. Thus,. every compound or element has its own unique diffraction pattern. The differences in these patterns allow the differentiation of various structures. In general, the crystallites of Cr_2O_3 on γ-Al_2O_3 were so small (ca., 7 nm) that no typical Cr_2O_3 spectrum was observed.

B. BET Surface Area Measurement

The Brunauer, Emmett, and Teller (BET) surface area was used to determine the surface area of the prepared catalysts. BET surface area is a standardized measurement for determining the internal surface area of a porous material which is based on the absorption of N_2 gas at liquid N_2 temperature onto the initial surfaces of the support (Heck and Farrauto, 1995). Each adsorbed molecule occupies an area of the surface comparable to its cross-sectional area. By measuring the number of N_2 molecules adsorbed at monolayer coverage, one can calculate the total internal and external surface area.

All the samples used were weighed, inserted in a quartz U tube. The U-tube was installed on the Altamira (AMI-1) catalysts characterization instrument to measure BET surface area. The AMI-1 is a computer operated catalyst characterization instruments, and is used to conduct standard catalyst characterization tests including BET surface area. For example, the Temperature Programmed Desorption (TPD) is used to measurement for active site adsorptive properties and active surface area, and the Temperature Programmed Reduction or Oxidation (TPR/O) for oxidation states of catalysts and for checking reducibility / oxidizability in catalytic studies.

The operating manual for BET measurement was followed exactly. Figure 7 shows the BET operating procedure. The parameters used for a three point BET run are shown in Table 4.

Table 4 Operating Parameters used for BET surface area measurements

Treatment	Treatment Gas	Nitrogen		
	Flow rate	30 cm^3/min		
	Hold Time	5 min		
Flow BET		1st	2nd	3rd
	Adsorbate Gas	10 % N_2 in He	20 % N_2 in He	30 % N_2 in He
	Flow rate	20 cm^3/min	20 cm^3/min	20 cm^3/min
	Adsorption time	4 min	4 min	4 min
	Desorption time	4 min	4 min	4 min
BET Calibration		1st	2nd	3rd
	Carrier gas	10 % N_2 in He	20 % N_2 in He	30 % N_2 in He
	Flow rate	20 cm^3/min	20 cm^3/min	20 cm^3/min
	Response Factor	1.00	1.333	1.280
	Adsorbing gas	N_2		
	Flow rate	30 cm^3/min		
	Time between Pulse	1.5 min		
	Initial Data delay	12 sec		
	Data Collection Interval	60 sec		

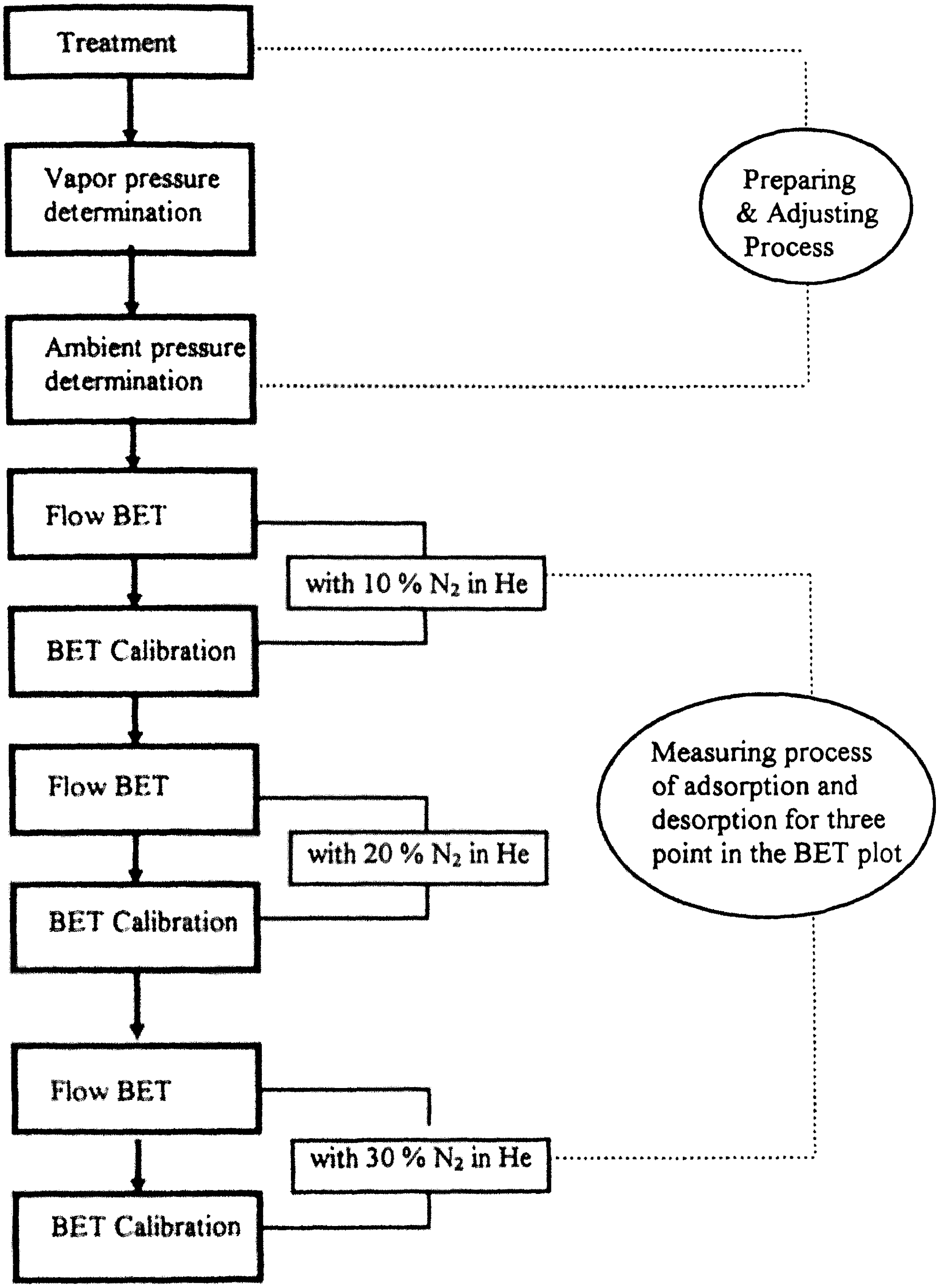


Figure 7 Procedure of BET surface measurement by AMI-1

3.2 Catalytic Oxidation of TCE over Synthesized 5% Cr_2O_3/γ-Al_2O_3

The ability of the synthesized catalysts samples to catalytically oxidize trichloroethylene (TCE) was studied at several controlled temperatures using the quartz flow reactor. The percent conversion of TCE and the product distribution were investigated at a different controlled temperatures The kinetic studies were conducted to investigate catalytic characteristics of synthesized 5% Cr_2O_3/γ-Al_2O_3 to oxidize TCE and to compare the chromia catalysts with other transition metal oxides previously studied in this laboratory.

3.2.1 Measurement of Product from Catalytic Oxidation of TCE over Synthesized 5% Cr_2O_3/γ-Al_2O_3

A. Catalytic Material and Space Velocity

The most active catalyst sample from those synthesized 5% Cr_2O_3/γ-Al_2O_3 catalysts that were prepared according to Figure 2 and Table 2 was selected by comparing conversion using the same experimental conditions of 300°C reactor temperature, 100 ppm TCE and 30,000 v/v/hr space velocity described in section 3.1.3.

A volume of 0.63 cm^3 of the chosen most active synthesized 5% Cr_2O_3/γ-Al_2O_3 catalyst was then checked at another space velocity to compare these result with other results obtained in this laboratory (Xu, 1994). The total flow rate of the air stream containing 1000 ppm TCE was 183 cm^3/min. Thus, the space velocity can be calculated as follows

Space Velocity = total flow rate / catalyst volume

$$= (183\ cm^3/min * 60\ min/hr) / 0.63\ cm^3$$

$$= 17{,}400 \text{ v/v/hr} \tag{2}$$

B. Feed Concentration of TCE

The conversion of 111 ppm TCE was used as an indicator for the effective catalytic oxidation of the most active 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$. In order to obtain 111 ppm TCE, 1000 ppm TCE from the Matheson gas mixture cylinder was mixed at a flow rate 20.3 cm^3/min with flow rate 162.7 cm^3/min of dry air. The actual concentration of TCE was measured by gas chromatography and verified throughout each experiment.

C. Temperature Range

The catalytic oxidation of TCE was studied over the temperature range of 100 to 600°C. The concentration of every product was measured at each of six different temperatures.

3.2.2 Experimental Apparatus

The experimental reactor system is illustrated in Figure 8. The reactor system used for comparing activities of synthesized catalysts described at section 3.1.3 was also used for determining product distributions and kinetics. The tube containing the gas stream passed through reactor and the effluent split into four parts. The first polyethylene tube went to the gas chromatography (GC) with electron capture detector (ECD) to measure unreacted TCE concentration. The polyethylene second tube went to gas chromatography (GC) with nickel hydrogenation catalyst to convert to carbon monoxide and carbon dioxide to methane and measure the methane produced with a flame ionization detector (FID). The third tube went to the methyl orange colorimetric adsorption system to measure

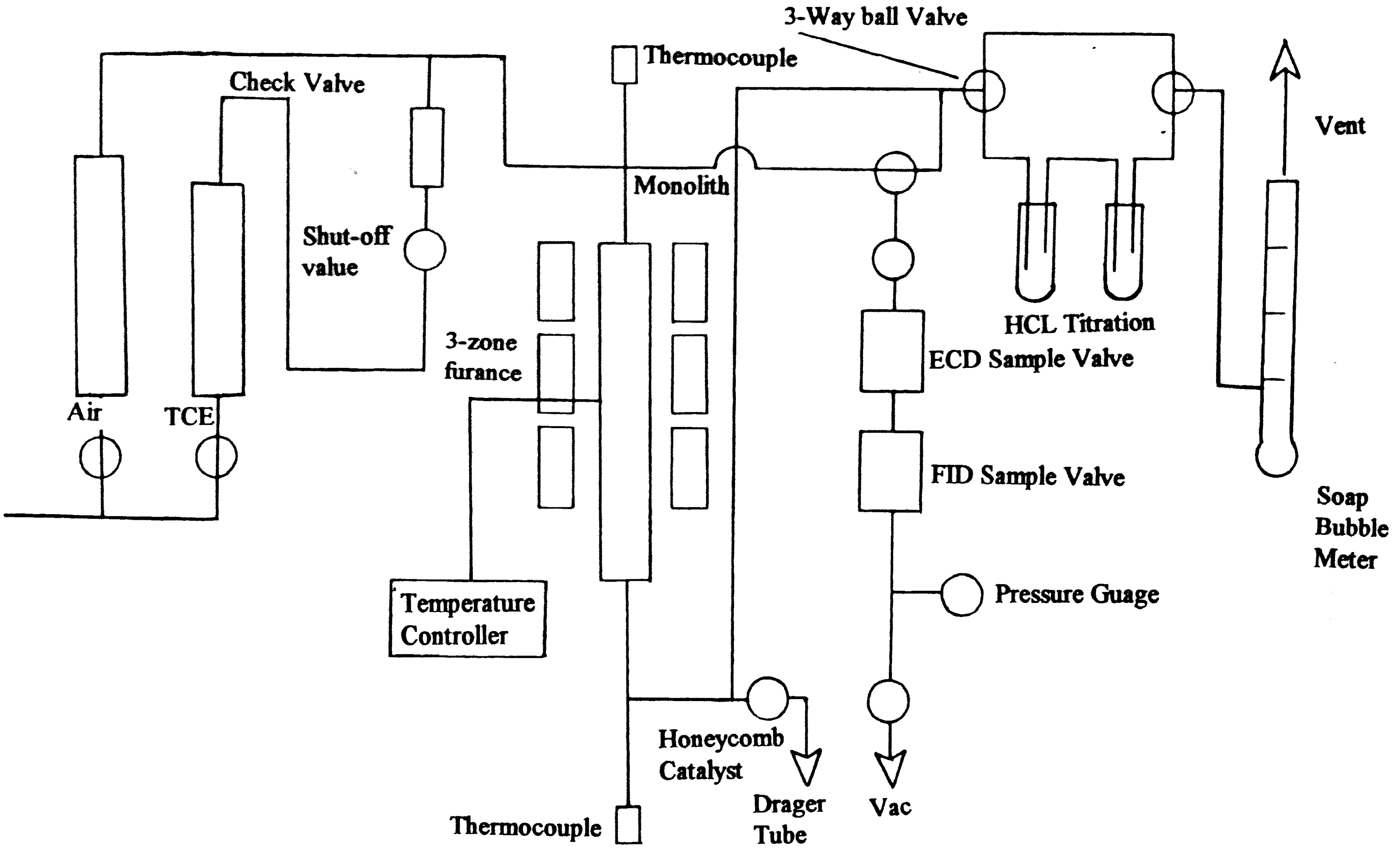


Figure 8 The flow schematic of catalytic oxidation unit

concentration of chlorine, and the fourth tube went to the aqueous solution absorption system to measure hydrogen chloride using a chloride ion selective electrode. The flow rates in each tube were monitored in order to calculate the total quantities of HCl, Cl_2, CO, CO_2, and unreacted TCE that were produced in experimentals designed to conduct chlorine and carbon material balances.

3.2.3 Quantitative Analysis of Products

A. The Concentration of TCE

Gas chromatography with electron capture detector is used to analyze for TCE and any other chlorocarbons that could be produced. However, no other chlorocarbons were detected. The concentration of TCE was quantitatively determined by calibration curve shown in Figure 5. The operating condition of GC-ECD for the experiment are listed in Table 3.

B. The Concentration of Carbon Monoxide and Carbon Dioxide.

Carbon monoxide and carbon dioxide were detected by gas chromatography (GC) using a nickel hydrogenation catalyst to convert carbon monoxide and carbon dioxide to methane after separating these components over a Poropark Q column and measuring the separate methane peaks with a flame ionization detector (FID). This system is described in Figure 9. Both carbon monoxide and carbon dioxide concentrations were calibrated with a certified gas mixtures from Matheson Gas Products. Figure 10 show the typical peak resolution and retention time, and Table 5 summarizes the operating conditions of the gas chromatography with FID used for CO and CO_2 analysis.

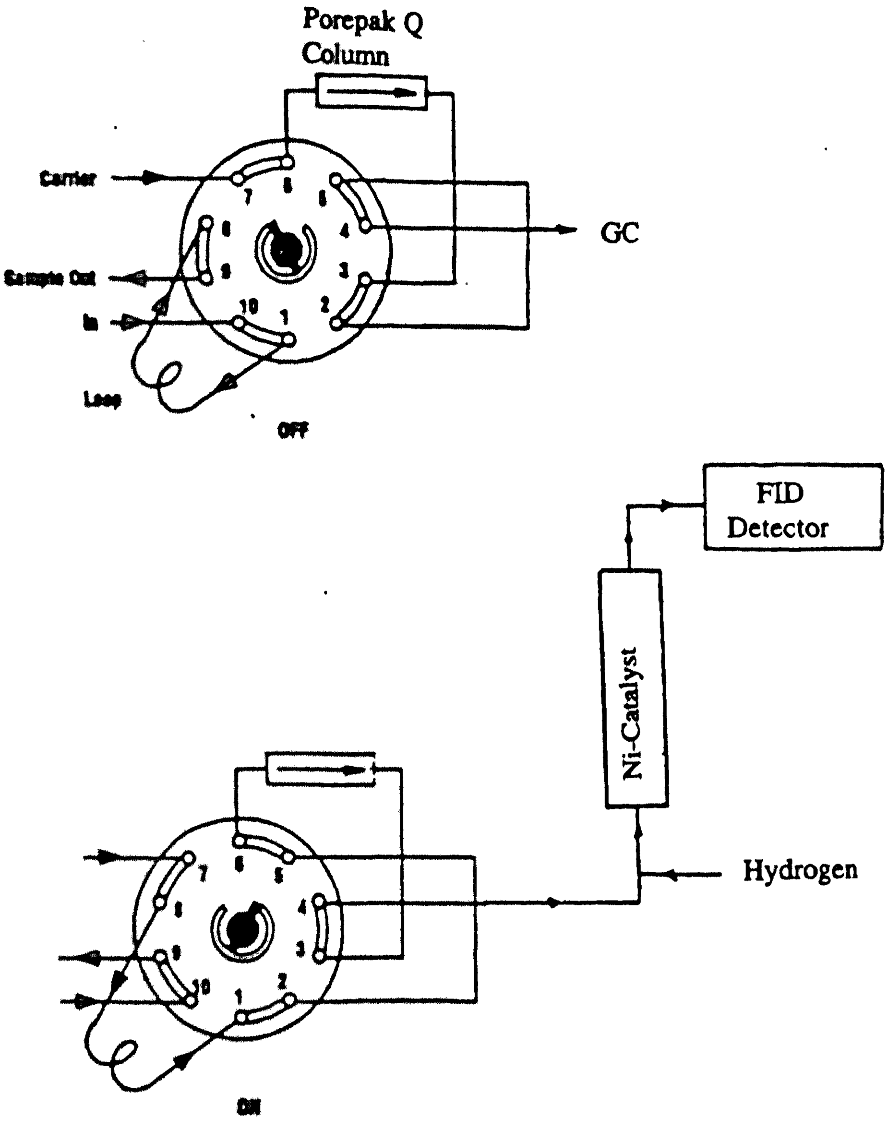
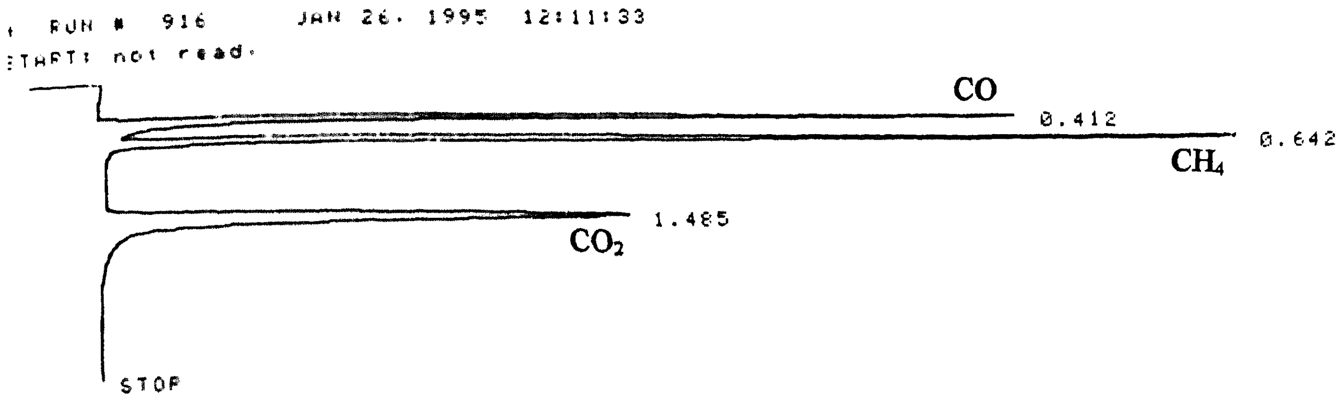


Figure 9 The modified injection system using a nickel hydrogenation catalyst to convert carbon monoxide and carbon dioxide to methane

Table 5 The operating condition of GC to detect CO, CH_4, CO_2

Carrier Gas	He, 20 cm^3/min
Oven Temperature	30 °C
Injector Temperature	350 °C
Detector Temperature	250 °C
Integrator Attenuation	2
Column packing material	Porapak Q, 80/100, 1/8"x 10'



```
+  RUN #  916        JAN 26, 1995  12:11:33
START: not ready.

 STOP
RUN#    916              JAN 26, 1995  12:11:33

AREA%
      RT        AREA TYPE  WIDTH       AREA%
    .412       34916   FE   .045    26.23922
    .642       48926   BE   .042    36.76766
   1.485       49226   BE   .111    36.99313

TOTAL AREA= 133068
MUL FACTOR=1.0000E+00
```

Figure 10 Typical resolution and retention time of CO, CH_4 and CO_2

C. The Concentration of Chlorine gas

The concentration of chlorine gas was measured using methyl orange colorimetric method. About 0 06 g of methyl orange were dissolved in deionized water and diluted to dm^3 and 5 cm^3 of this methyl orange solution was mixed with 100 cm^3 of pH 2 buffer solution. When chlorine gas was absorbed in the prepared methyl orange solution, the red color of methyl orange in pH 2 buffer solution became pale or colorless. Therefore the concentration of chlorine in this solution can be determined by the change in absorbance of visible light. The calibration curve, shown in Figure 11, for chlorine gas was made by reading the adsorbances at 505 nm The five different concentrated standard solutions were prepared by bubbling a certified chlorine gas blend in air that was obtained from Matheson Gas Products through the methyl orange solution for different periods of time.

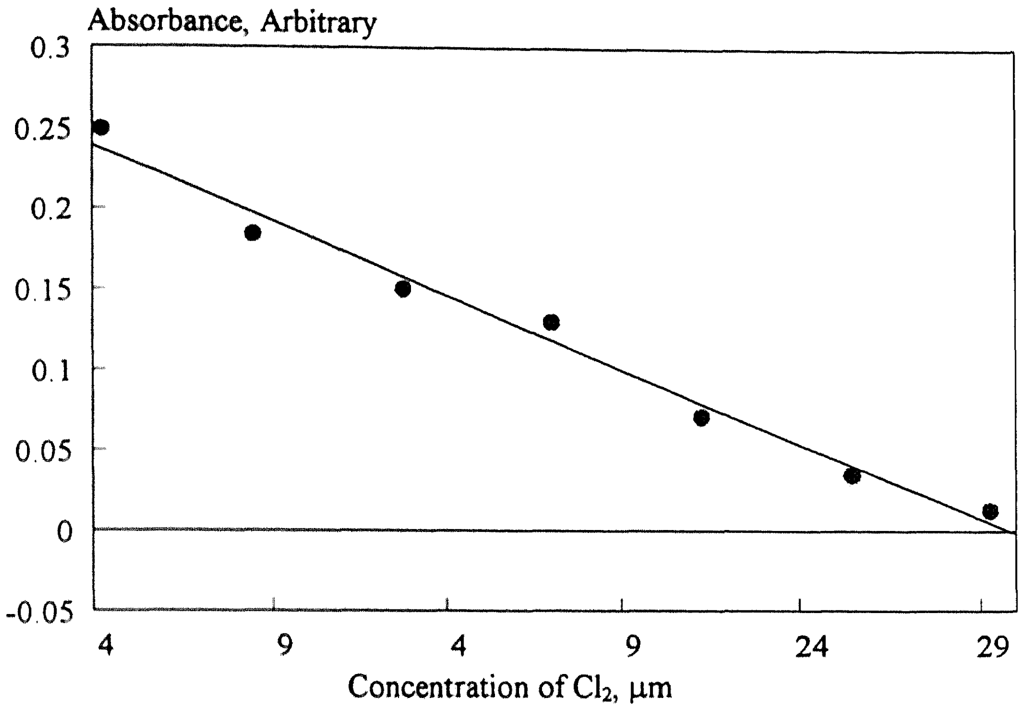


Figure 11 Calibration curve for chlorine gas

D. The Concentration of Hydrogen Chloride

The hydrogen chloride was absorbed in distilled and deionized water and the concentration of chloride ion in the aqueous solution was measured using chloride ion selective electrode. Since chlorine also dissolves in water and one mole of chlorine produces one mole of chloride ion, measured concentration of chloride is total concentration of chloride ion from both hydrogen chloride and chlorine. Therefore the concentration of hydrogen chloride is equal to that total concentration of chloride ion minus the concentration of chlorine. The Jenco model 6071 meter and Orion model 96-17B combination chloride electrode was used. The direct calibration technique used is a simple procedure for measuring a large number of samples, only one meter reading is required for each sample. Calibration was performed using a series of standards. The concentration of the samples was determined by comparison with the standards. Ionic Strength Adjuster (ISA) was added to all solutions to ensure that samples and standard have similar ionic strength. This low level measurement was performed by the following procedure introduced in the instruction manual for Orion model 96-17B combination chloride electrode. First, one cm^3 low level ISA, 1.0 M $NaNO_3$, was added to 100 cm^3 deionized water in 150 cm^3 beaker. The electrode rinsed with deionized water was placed into the beaker and stirred thoroughly. The increments of 1000 ppm chloride standard from a certified gas mixture provided by Matheson Gas Products was added to the beaker following steps outlined in Table 6. The stable millivolt reading was recorded after each increment. The concentration of chloride standard was plotted on a log axis against the millivolts. The sample volume of sample was used for both calibration and during each experiment. The electrode was cleaned with deionized water and then blot dried before the electrode was placed into sample beaker to be analyzed. One cm^3 of low level ISA was added to each 100 cm^3 sample. When the display on the electrometer became stable, the mV reading was recorded and the sample concentration was determined from the calibration curve in Figure 12. The actual quantity of HCl was then calculated by substracting the Cl_2 concentration from the Cl^- measurement.

3.2.2 Kinetic Studies of TCE Oxidation over Synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$

In these experiments, the initial concentration of trichloroethylene was approximately 82 ppm. In order to keep the reaction in the chemical kinetics controlled region, all data were collected at conversions of less than 30%. Four different space velocities, 14,640, 19,520, 29,280 and 58,560 v/v/hr, were used. At each space velocity, experiments were conducted at three different temperatures, 483, 493, 593 K. When space velocity was adjusted, four different volume of catalyst, 0.1, 0.2, 0.3 and 0.4 cm^3 were used to change space velocity and to keep the same flow rate and concentration of trichloroethylene.

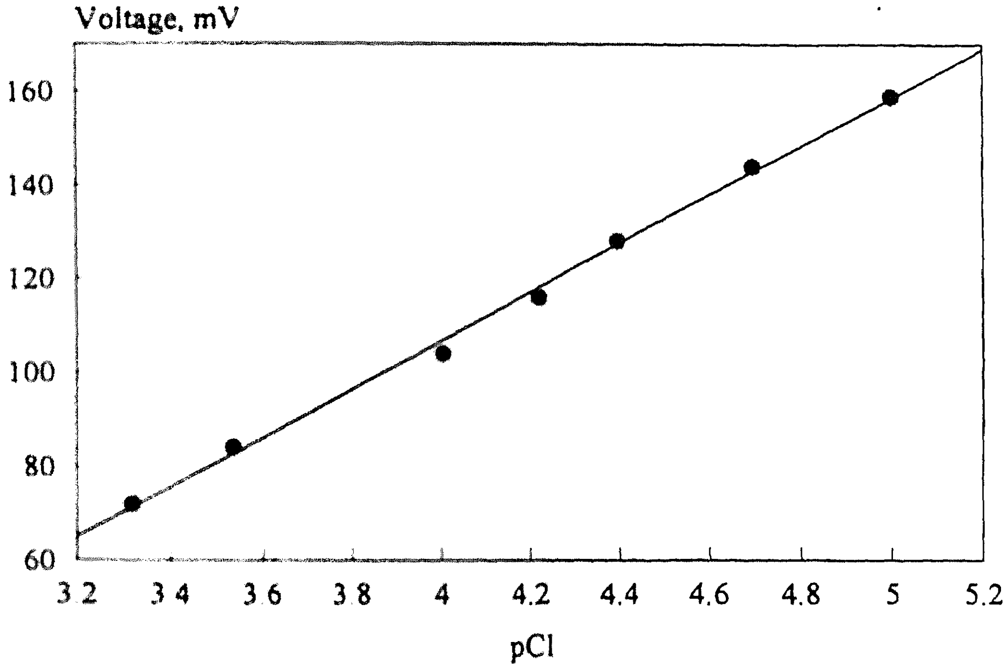


Figure 12 Calibration curve for chloride ion

Table 6 Serial calibration for low level measurements

Step	Added volume	Concentration Molarity
1	0.1 ml	$1.0 * 10^{-5}$
2	0.1 ml	$2.0 * 10^{-5}$
3	0.2 ml	$4.0 * 10^{-5}$
4	0.2 ml	$6.0 * 10^{-5}$
5	0.4 ml	$9.9 * 10^{-5}$
6	2.0 ml	$2.9 * 10^{-4}$
7	2.0 ml	$4.8 * 10^{-4}$

CHAPTER 4

RESULT AND DISCUSSION

4.1 Preparation of 5 % Cr_2O_3 on γ-Al_2O_3

This section discusses the results of the research from testing the modified incipient wetness catalysts that were synthesize to contain 5% Cr_2O_3/γ-Al_2O_3. The various synthetic methods are summarized in Figure 2 and Table 2. The activity of all these synthesized catalysts were determined, and the physical characteristics of most active sample of 5% Cr_2O_3/γ-Al_2O_3 were determined by measuring BET surface area and the crystalline structure of the catalyst by x-ray diffraction crystallography.

4.1.1 Thermogravimetric Analysis

To convert chromium oxide from chromium salt, two pathways were investigated. The first method utilizes $Cr(OH)_3$ precipitates and through heating in air, decomposes these precipitates to Cr_2O_3 The second method converts $Cr(NO_3)_3$ directly to Cr_2O_3 by heating to 600°C The former is the conventional pathway to give Cr_2O_3 from $Cr(OH)_3$ (Erdey, 1963) and the latter pathway thermally decomposes $Cr(NO_3)_3$ to produce Cr_2O_3 and byproduct gases NOx and oxygen This mode of decomposition of $Cr(NO_3)_2$ was confirmed by thermogravimetric analysis (TGA). The result of this analysis is shown in Figure 13

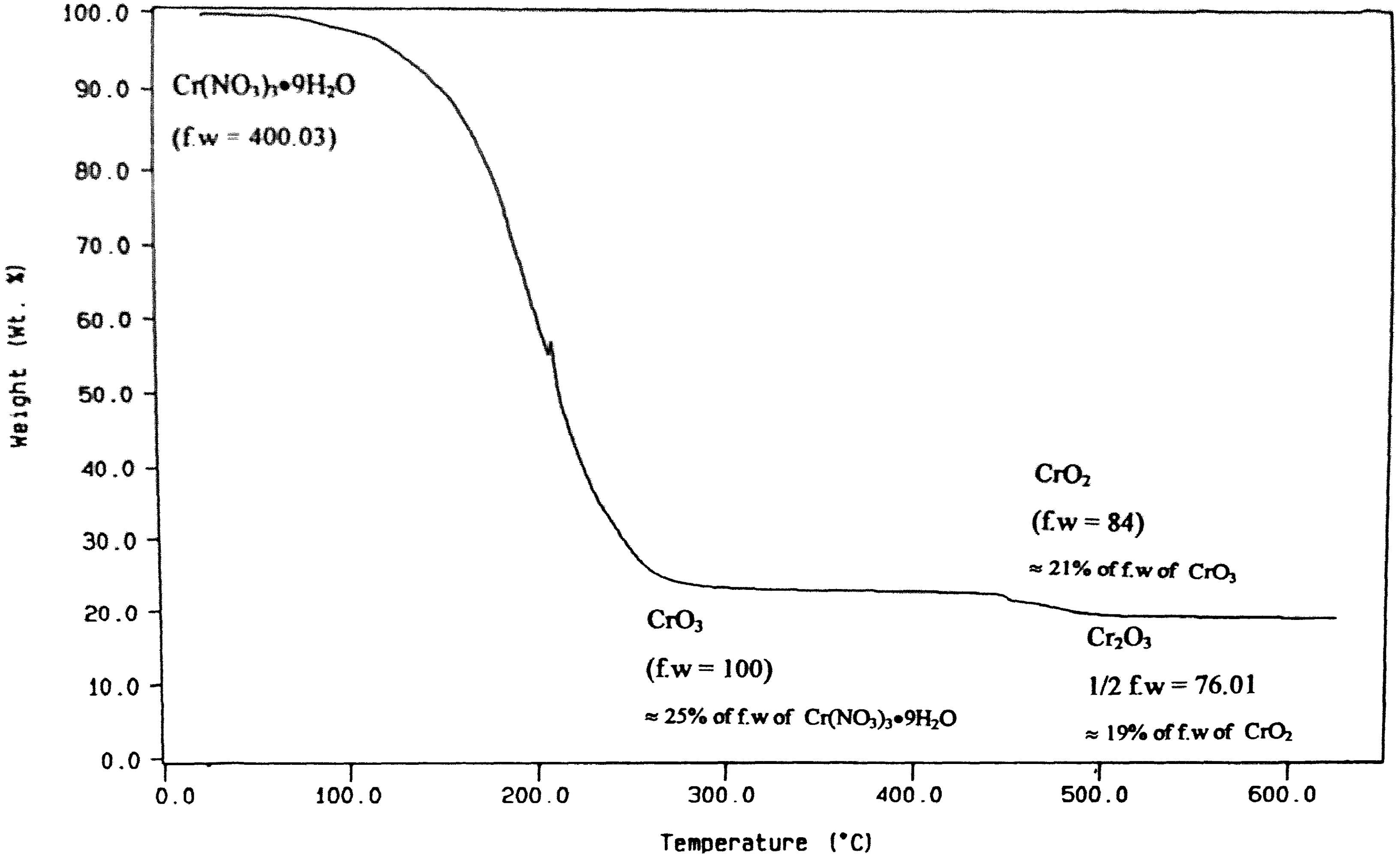
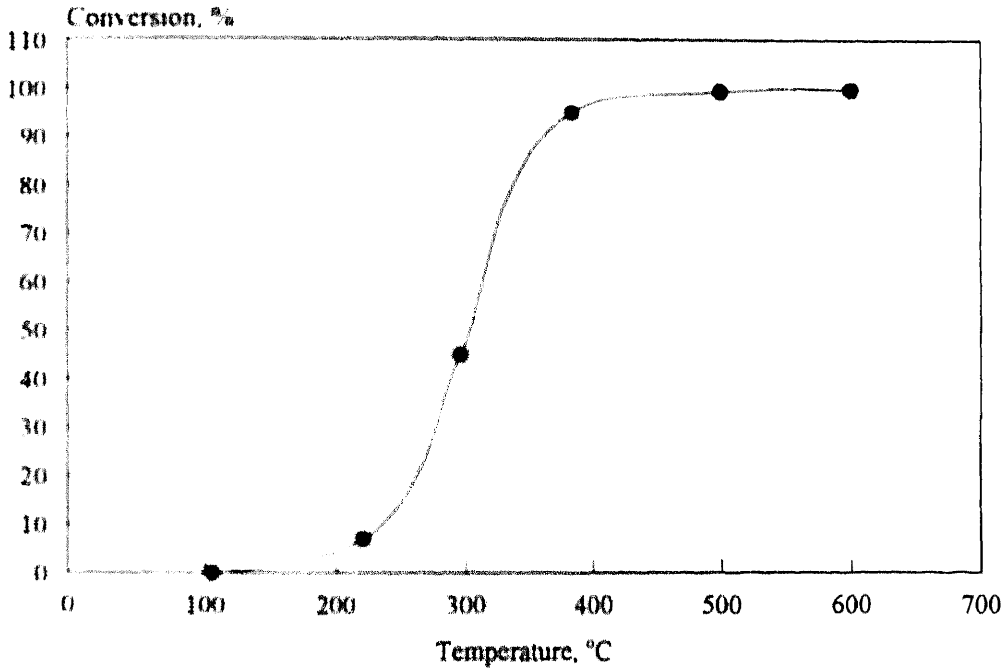


Figure 13 TGA for decomposition of $Cr(NO_3)_3 \cdot 9H_2O$ to Cr_2O_3

4.1.2 Comparison of Activity of Synthesized 5% Cr_2O_3/γ-Al_2O_3

The oxidation of 100 ppm TCE at a space velocity of 30,000 v/v/hr, and in the temperature range 200 °C to 600 °C was used as a diagnostic reaction to determine the most active catalyst among those synthesized. Figure 14 shows the typical TCE conversion curve This type of curve was obtained for each of the 11 synthesized catalysts. The best catalysts were those that were shifted to the left, i.e., the same conversion was achieved at a lower temperature Since all synthesized catalysts showed that the percent conversion is relatively high at temperature between 250 °C and 350 °C, the conversion percentage of each synthesized 5% Cr_2O_3/γ-Al_2O_3 was compared at 300 °C.



Space velocity = 30,000 v/v/hr, Feed concentration 100 ppm

Figure 14 Typical temperature dependent of TCE conversion

The result of this activity test is compared as a bar graph at Figure 16. In this bar graph, it can be seen that the most active synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ catalyst was the one developed using procedure C as listed in Table 2. This catalyst shows 67.2 % TCE conversion at 300 °C. The procedure used to synthesize this catalyst is summarized as follows : First, $\gamma\text{-}Al_2O_3$ is soaked in a quarter of the total volume needed to fill its pores with 0.01 N NH_4OH. The resulting pH is 9. Then this presoaked $\gamma\text{-}Al_2O_3$ is soaked with the remaining three quarters of volume with chromium nitrate aqueous solution whose pH was adjusted with NH_4OH to about 3.5. This $\gamma\text{-}Al_2O_3$ containing the precursor of active catalytic material is then dried. $Cr(OH)_3$ precipitate is formed by soaking in pH 11 NH_4OH solution equal to the total pore volume of $\gamma\text{-}Al_2O_3$. Finally the product is calcined 600 °C for 6 hours This procedure is illustrated in Figure 15.

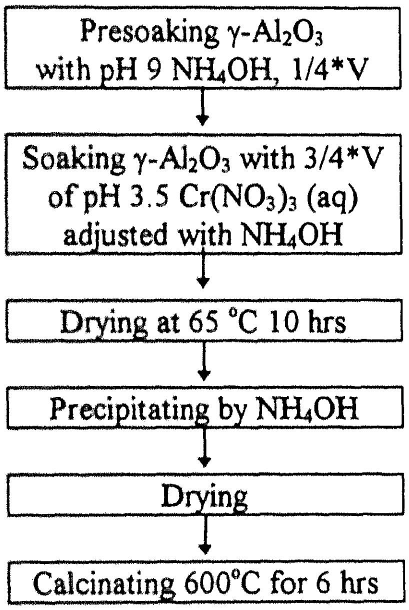
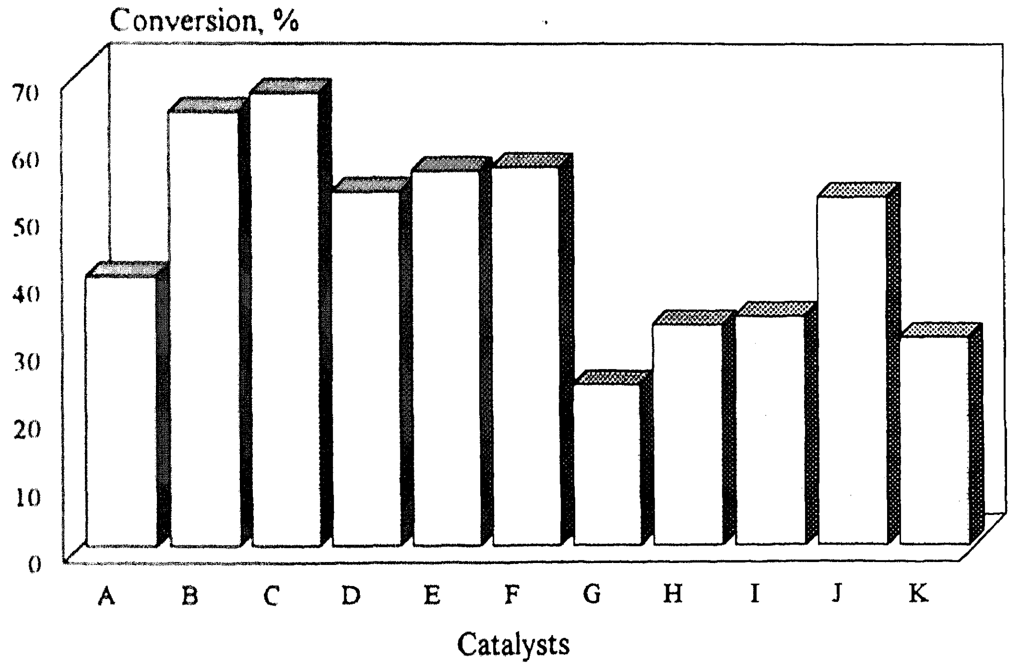


Figure 15 Flow chart of procedure C which is the best method for preparing a microcrystalline Cr_2O_3 catalyst on $\gamma\text{-}Al_2O_3$.

In the course of the research to modify the incipient wetness method to prepare active 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ for TCE catalytic oxidation, and to compare the activity of catalysts prepared by different synthetic methods, several interesting observations were noted and investigated. It was observed that the $\gamma\text{-}Al_2O_3$ presoaked in 0.01 N NH_4OH, the resulting pH is 9, seems to give a more active catalysts than that soaked in 0.1 N NH_4OH, the resulting pH is 11. Catalysts A, B, C, D, E, F and J which were synthesized using a presoak of pH 9 NH_4OH showed generally higher activity than catalysts G, H, I and K which were presoaked in pH 11 NH_4OH. This is most apparent when we see catalysts, catalyst J has higher activity than catalyst K. Catalyst J and K were both synthesized using same procedure except that the J catalyst was presoaked in pH 9 NH_4OH and K was presoaked in pH 11 NH_4OH.



Space velocity = 30,000 v/v/hr, Feed concentration = 100 ppm TCE, and Temperature = 300 °C

Figure 16 Activity comparison of 5% $C_2O_3/\gamma\text{-}Al_2O_3$ catalysts synthesized by different procedures.

It was also observed that the procedure that included a $Cr(OH)_3$ precipitation step obtains a more active catalyst. Catalyst A and B were produced following same procedure except that the Cr_2O_3 in catalyst A was formed by removing the nitrate in $Cr(NO_3)_3$, while Cr_2O_3 in catalyst B was obtained after Cr^{+3} is precipitated by NH_4OH. The differences between catalyst D and E, and G and H are the same as the differences between catalyst A and B. The B, E and H synthetic procedure involving a precipitation step produced catalysts with higher activity than A, D and G catalysts. It was also noted from the activity comparison that Cr_2O_3 formed from the conversion of $Cr(OH)_3$ produced using pH 11 NH_4OH is more active than the Cr_2O_3 from $Cr(OH)_3$ formed at pH 9. In the case of catalysts B and C, these catalysts were synthesized using same procedure, except that $Cr(OH)_3$ is formed using different pH. The comparison of E and F, and catalysts H and I follows that described for B and C. In each case, precipitation at pH 11 NH_4OH produces a slightly more active Cr_2O_3 on γ-Al_2O_3 than was found for pH 9.

4.1.3 The BET surface measurement of synthesized 5% Cr_2O_3/ γ-Al_2O_3

The BET surface area of type C catalyst and a standard γ-Al_2O_3 was measured using the Altamira catalyst characterization instrument model AMI-1. The result of BET surface area measurements are shown in Appendix A, Figure A.1. Figure 17 is the BET plot for the type C catalyst.

The type C catalyst has larger adsorption and desorption surface area than standard γ-Al_2O_3. The BET surface area measurements of γ-Al_2O_3 were 104 m^2/g in adsorption and 100 m^2/g in desorption. The BET surface area of type C 5% Cr_2O_3/γ-Al_2O_3

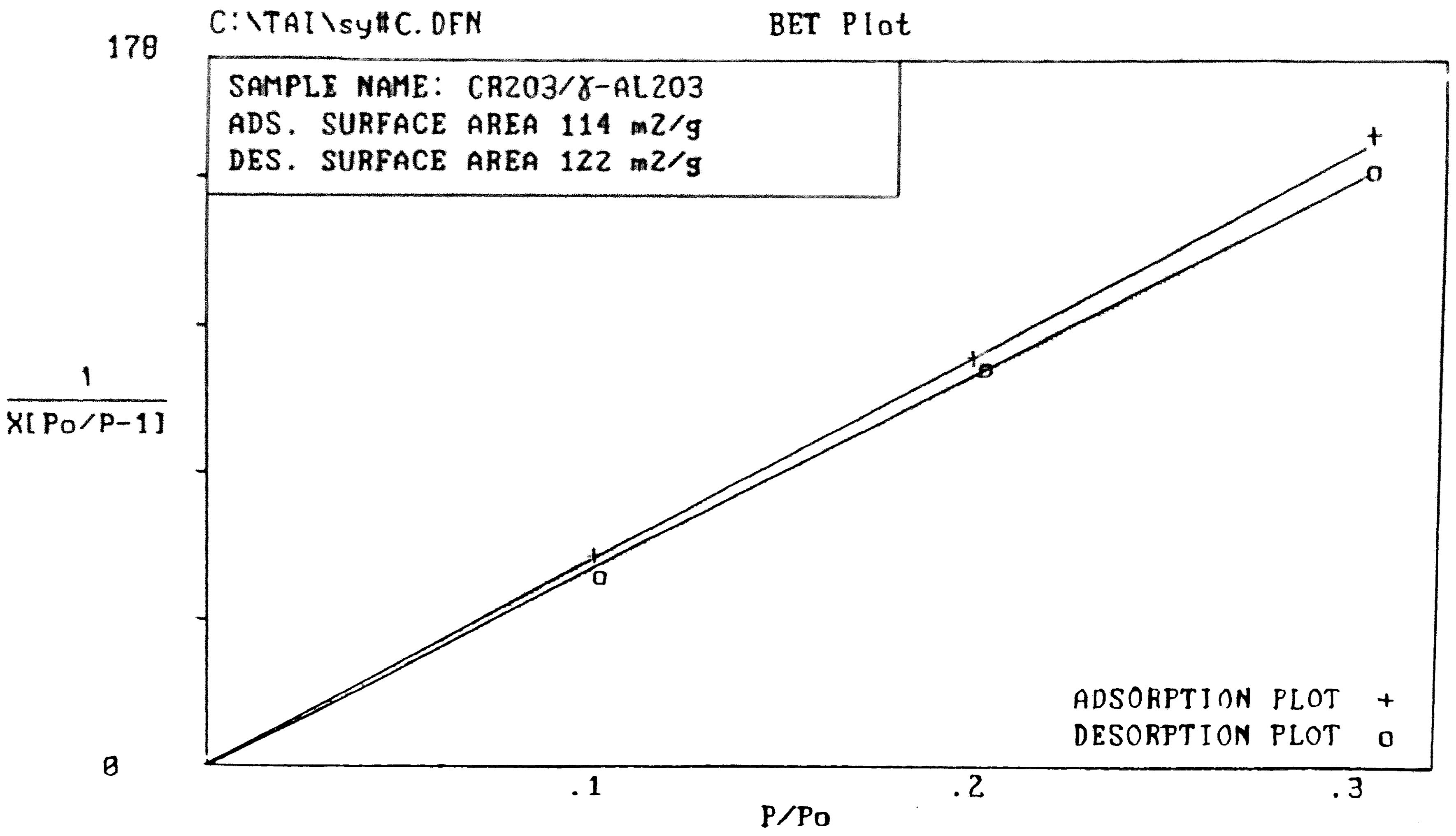


Figure 17 BET plot of most active 5% Cr_2O_3 / γ-Al_2O_3

is obtained as 114 m^2/g in adsorption and 122 m^2/g in desorption. Since the x-ray diffraction crystallography of the surface of synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ is shown to be almost identical with that of $\gamma\text{-}Al_2O_3$, the structure of $\gamma\text{-}Al_2O_3$ in the synthesized catalysts seems not be modified Therefore the $\gamma\text{-}Al_2O_3$ structure of this synthesized catalysts seems to be unaltered by the modified synthetic procedure. Moreover, the surface area of synthesized catalyst is slightly larger than that of $\gamma\text{-}Al_2O_3$. The difference between the surface area of synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$ is believed due to the surface area produced by Cr_2O_3. Using a linear combination of surface areas, one can estimate that the average surface area of the Cr_2O_3 is 422 m^2/g. This number results from the algebraic solution of following equation ;

$$[5\ /\ 100 * \text{S.A.}_{(Cr_2O_3)}] + [95\ /\ 100 * (100 + 104)\ /\ 2] = [\ (114 + 122)\ /\ 2] \qquad (3)$$

based on $\text{W.F.}_{(Cr_2O_3)} * \text{S.A.}_{(Cr_2O_3)} + \text{W.F.}_{(\gamma\text{-}Al_2O_3)} * \text{S.A.}_{(\gamma\text{-}Al_2O_3)}$
$= \text{S.A.}_{(5\ \%\ Cr_2O_3/\gamma\text{-}Al_2O_3)}$

where $\text{W.F.}_{(Cr_2O_3)}$ is weight fraction of Cr_2O_3 in synthesized catalyst

$\text{W.F.}_{(\gamma\text{-}Al_2O_3)}$ is weight fraction of $\gamma\text{-}Al_2O_3$ in synthesized catalyst

$\text{S.A.}_{(Cr_2O_3)}$ is average surface area of Cr_2O_3

$\text{S.A.}_{(\gamma\text{-}Al_2O_3)}$ is measured average surface area of $\gamma\text{-}Al_2O_3$

$\text{S.A.}_{(5\ \%\ Cr_2O_3/\gamma\text{-}Al_2O_3)}$ is average surface area of 5 % $Cr_2O_3/\gamma\text{-}Al_2O_3$

4.1.4 X-ray Diffraction Crystallography

To determine crystalline structure of synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$, the x-ray diffraction crystallography of a standard a $\gamma\text{-}Al_2O_3$ sample and $\alpha\text{-}Cr_2O_3$ sample were compared with x-ray diffraction pattern of synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$. The standard $\gamma\text{-}Al_2O_3$ has broad peaks at 32°, 37°, 39°, 45° and 67° as shown in Appendix B, Figure B 1. The x-ray diffraction peak of standard $\alpha\text{-}Cr_2O_3$ had narrow peak at 2θ values of around 33°, 36°, 41.5°, 50°, 55°, 63°, 65°, 73°, 77° and 79.5° as shown in Appendix B, Figure B 2. The x-ray diffraction pattern of the most active synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ is very similar with that of $\gamma\text{-}Al_2O_3$ as shown Figure 18, thus crystalline structure of $\alpha\text{-}Cr_2O_3$ was not found. However, Cr_2O_3 on a synthesized active catalyst is believed to exist as an undetectable amorphous material or extremely small crystallite. An average particle dimension for Cr_2O_3 on $\gamma\text{-}Al_2O_3$ surface can be estimated as 2.7 nm using BET measurement result as follows,

$$S / V = 6 / D \tag{4}$$

$$S / V = [422\ m^2/g * 5.21\ g/cm^3 * 104\ cm^2/m^2] = 22 * 10^6/cm \tag{5}$$

based on, (Surface area of Cr_2O_3) * (Density of Cr_2O_3) = S / V

$$D = 6\ V / S = 6 / (22 * 10^6)\ cm = 2.7\ nm$$

where S = Surface area of a catalyst particle, m^2

V = Volume of a catalyst particle, m^3

D = Particle size, m

In fact, most catalytic reactions are favored by either amorphous materials or extremely small crystallites. Small crystals can agglomerate or grow and produce large crystallites that diffract x-rays and thus generate easily reproducible patterns, that contain the

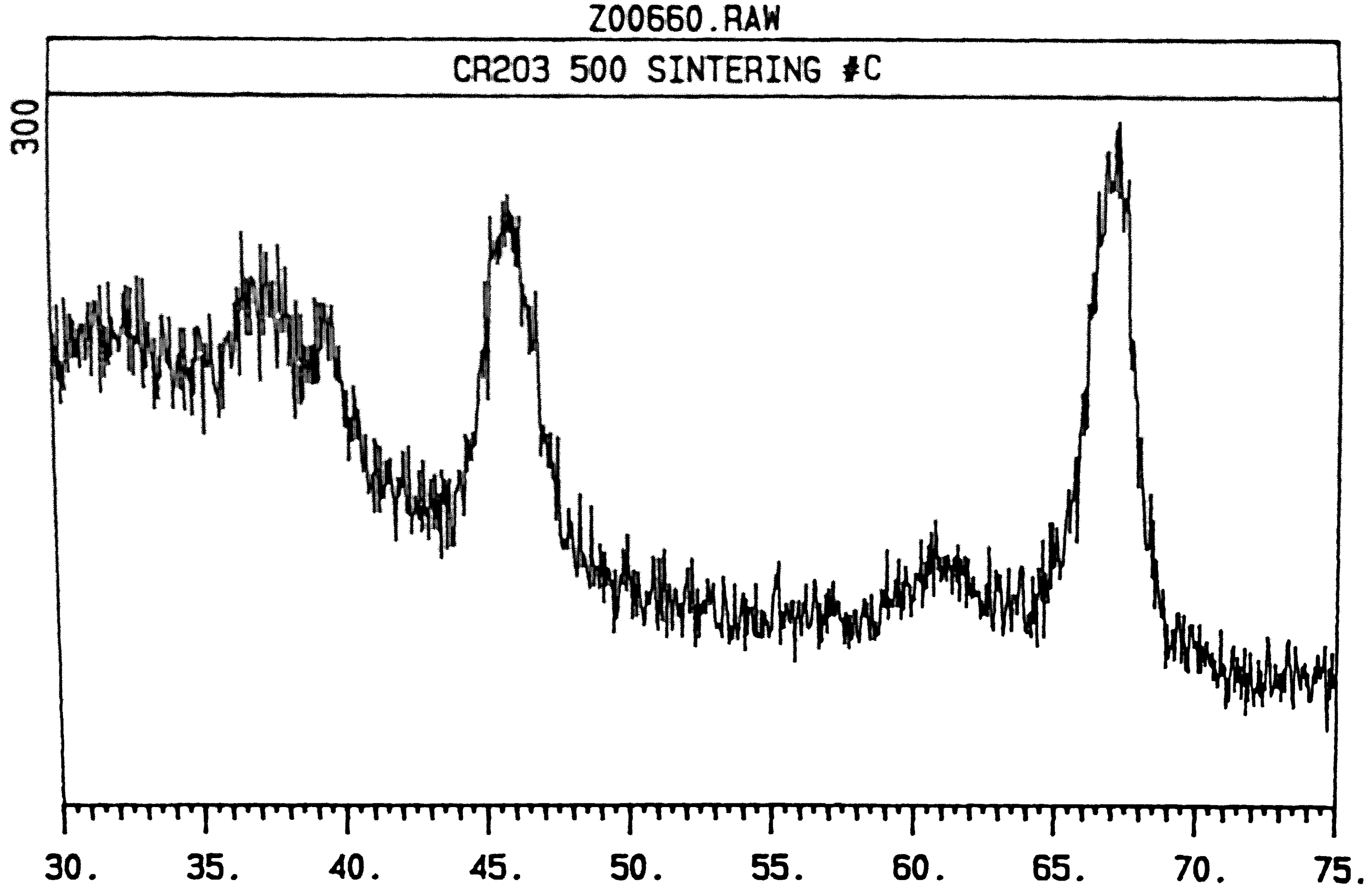


Figure 18 X-ray diffraction pattern of most active 5% Cr_2O_3 / γ-Al_2O_3

expected peaks for crystalline Cr_2O_3. However, when crystalline peaks are observed, usually catalytic activity decrease because most of the active material is inaccessible to reactant molecules The purpose of the preparation technique is to disperse the catalytic components in such a way as to maximize their availability to reactants. When this is done effectively, only small crystals are present, and the diffraction of x-rays is minimized, because little long-range structure exists. As the crystals get smaller and smaller , the x-ray peaks get broader and broader and eventually are undetectable above the background. however, it is this "x-ray-amorphous" species that often are the most active for a given catalytic reaction (Heck and Farrauto, 1995).

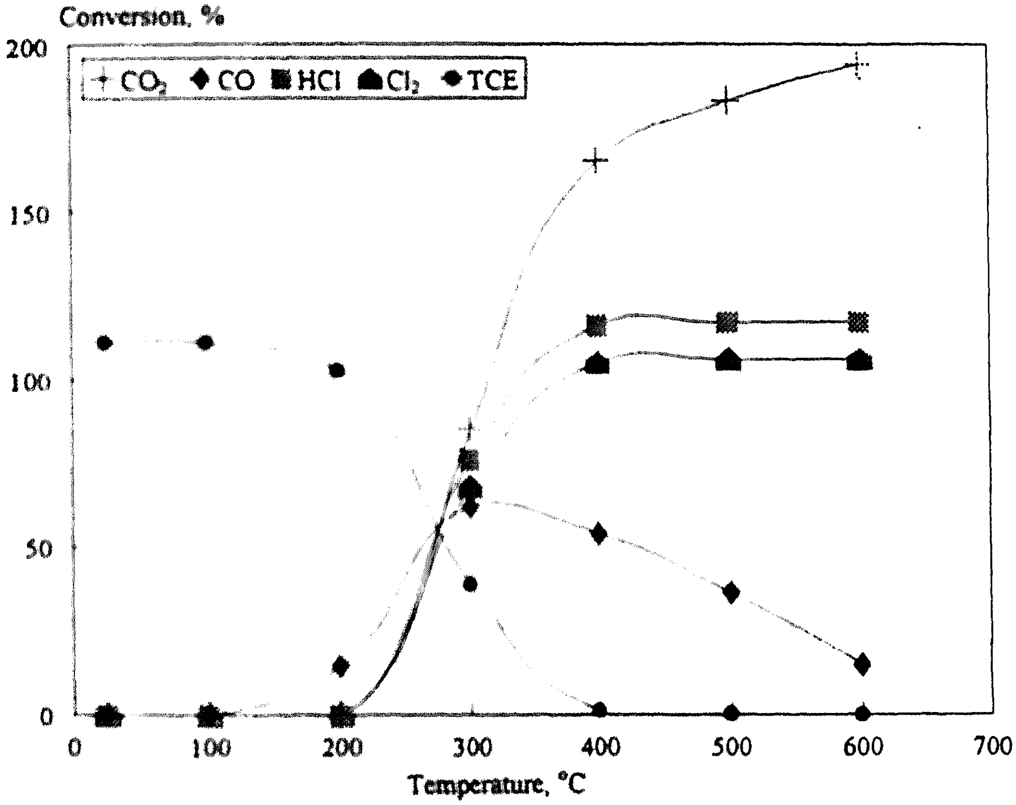
4.2 Catalytic Oxidation of TCE over Synthesized 5 % Cr_2O_3/γ-Al_2O_3

The change in product distribution of catalytic oxidation of trichloroethylene over synthesized catalyst 5% Cr_2O_3/γ-Al_2O_3 at increasing temperatures was investigated and is reported in this section Also, the temperature effect on the rate of oxidation of trichloroethylene and resulting kinetic studies were obtained for the commercial powdered Cr_2O_3 and the best synthetic sample developed in this research.

4.2.1 Product Distribution and Material Balance of TCE Oxidation over Synthesized 5 % Cr_2O_3 / γ-Al_2O_3

Test for product distribution of catalytic oxidation of trichloroethylene over synthesized 5% Cr_2O_3/γ-Al_2O_3 was conducted in the temperature range 25 °C to 600°C, and at the indicated space velocity of 17,400 v/v/hr and initial concentrations of 111 ppm trichloroethylene The dependence of product distribution on temperatures is plotted in

Figure 19. The product distribution and material balances for carbon and chlorine are summarized in Table 7. The main product are carbon dioxide, carbon monoxide hydrogen chloride and chlorine. At the lower oxidation temperature, the concentration of carbon monoxide increase with increasing temperature. At about 300 °C, the concentration of carbon monoxide reaches a maximum and then decrease with increasing temperature. The chlorine content of TCE is converted to HCl and Cl_2 without any chlorocarbon byproducts. Table 9 also shows the excellent carbon balances averaging 99.1 ± 1.4% and chlorine balances averaging 98.2 ± 0.1% for trichloroethlene oxidation.



Space velocity = 17,400 v/v/hr Feed concentration = 111 ppm TCE

Figure 19 The dependence of product distribution on temperature

Table 7 Material Balance of TCE Oxidation over synthesized 5 % Cr_2O_3 / γ-Al_2O_3

Temp °C	**TCE ppm**	**CO ppm**	**CO_2 ppm**	**HCl ppm**	**Cl_2 ppm**	**C balance %**	**Cl balance %**
25	111	-	-	-	-	100±1	-
100	111	-	-	-	-	100±1	-
200	102.63	14.74	-	-	-	99.09±1	-
300	38.92	62	85	76.08	68	101.28±1	98.19±2
400	1.243	54	165	116	104	99.76±1	98.39±2
500	0.28	36.4	83	117	104.6	99.08±1	98.20±2
600	0	15	194	117	104.6	94.14±1	97.95±2

4.2.2 Kinetic Studies of TCE Oxidation over Synthesized 5% Cr_2O_3 / g-Al_2O_3

Rate of reaction for the oxidation of C_2HCl_3 in air can be express using the empirical power law kinetic expression

$$-\text{rate}\ (C_2HCl_3) = k * (\text{concentration of } C_2HCl_3)^a * (\text{concentration of } O_2)^b \qquad (6)$$

Since experiments for this research were conducted in large excess oxygen, the order of TCE catalytic oxidation reaction is pseudo first order. This hypothesis was substantiated by showing the linearity of plots of logarithm of the reactant concentration versus residence time shown as Figure 20.

In addition, the slopes of each plot in Figure 20 are equal to logarithm of the rate constants, ln k, at each temperature. Thus, a plot of the logarithm of the rate constant versus 1/T is shown in Figure 21. The logarithm of the rate constant can be expressed algebraically by the Arrhenius equation as follows:

$$\ln k = \ln A + (-Ea / R) * (1 / T) \tag{7}$$

based on $k = A \exp(-Ea / RT)$

where A is the preexponential factor

Ea is activation energy, MJ / mol

R is gas constant, MJ / mol * K

T is absolute temperature, K

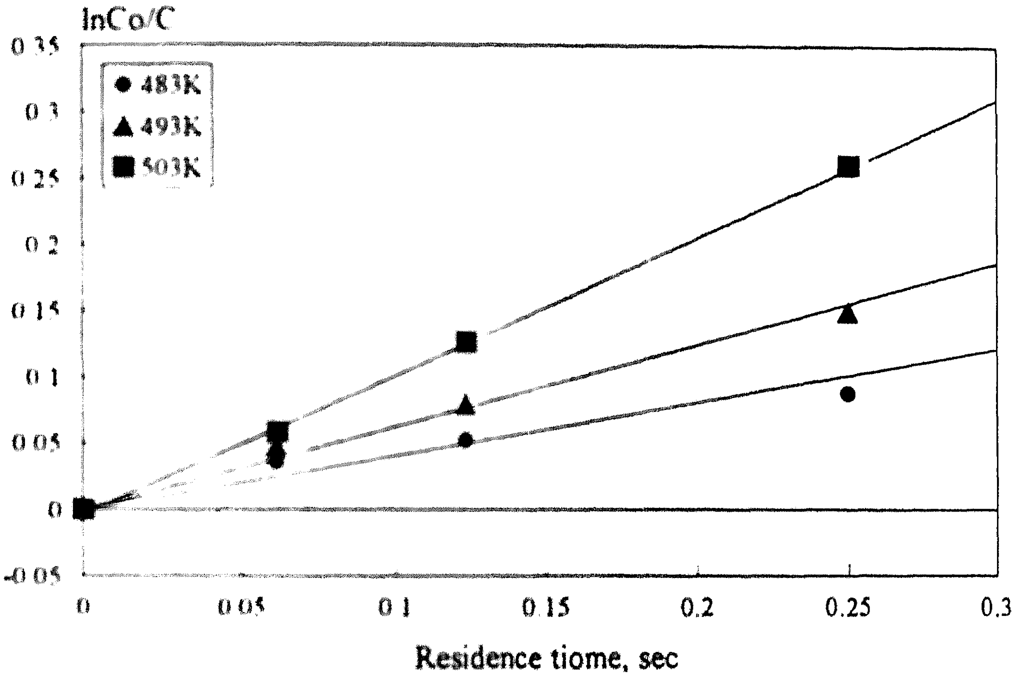


Figure 20 The plot of log reactant concentration versus residence time at different reaction temperatures for TCE oxidation over 5% Cr_2O_3 / γ-Al_2O_3.

Therefor the linear equation of plot in Figure 21 should be equal to Arrhenius equation expressed as a logarithm, and the slope of plot of the logarithm of the rate constant versus 1/T is equal to -Ea / R The preexponential factor, A, is obtained from the intercept of the plot in Figure 21. For this TCE oxidation reaction over synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$, The activation energy, Ea, is calculated as 71.5 MJ/mol (17.1 kcal/mol) and the preexponential factor, A, is 7.6*10^7 sec^{-1}. Thus, the reaction rate equation for TCE catalytic oxidation over synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ is expressed as follows:

$$-rate(C_2HCl_3) = k * (\text{concentration of } C_2HCl_3) \qquad (8)$$

$$= A \exp(-Ea / RT) * (\text{concentration of } C_2HCl_3)$$

The Arrhenius parameters for 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ are compared to those of 1.5% $Pt/\gamma\text{-}Al_2O_3$ of Ea = 81.2 MJ/mol (19.4 kcal/mol) and the preexponential factor, A, is 2.23 * 10^7 sec^{-1} (Shaw, 1993). Consequently the new catalyst is comparable in activity with Pt and should be further developed.

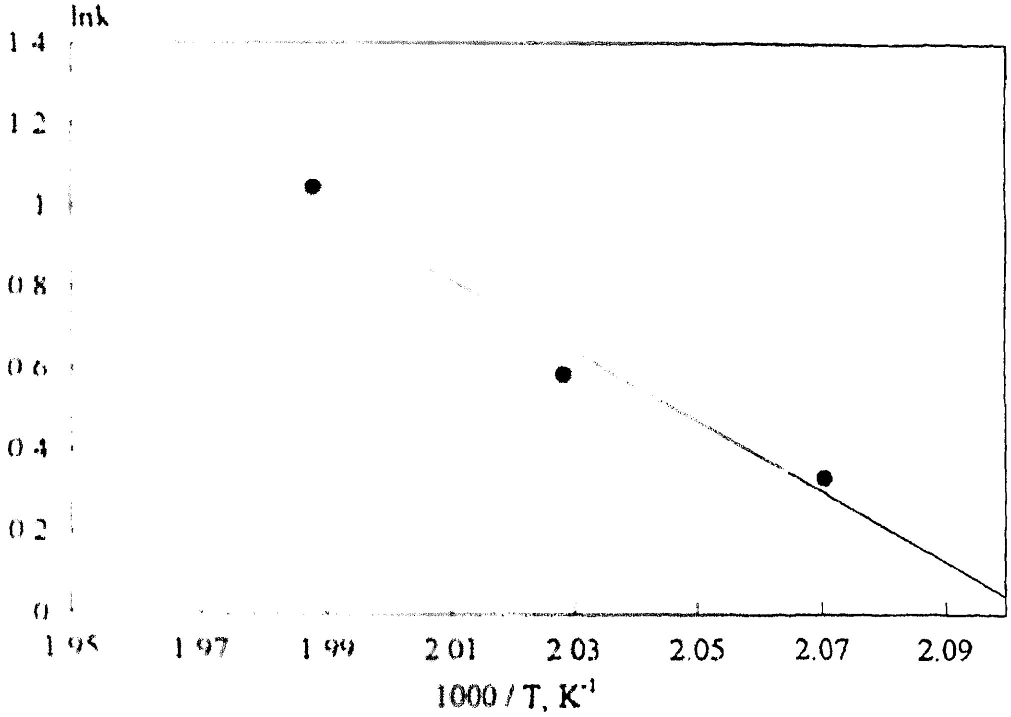


Figure 21 Arrhenius plot of first order rate constant for TCE oxidation over 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$

4.2.3 Comparison of Temperature Effect of TCE Oxidation over 5% Cr_2O_3/γ-Al_2O_3, Fe_2O_3 and CuO.

Since the slope of the conversion versus temperature curve can give a qualitative picture of the rate-controlling step, comparing conversion versus temperature profile of each catalyst is very useful to evaluate the factors for controlling each catalyst. The TCE conversion versus temperature curve for TCE catalytic oxidation over synthesized 5% Cr_2O_3/γ-Al_2O_3 can be obtained from material balance data in Table 9. Besides, the TCE conversion curve for Fe_2O_3 catalyst against temperature was also obtained using data from a material balance study of TCE oxidation observed by increasing temperature. This study conducted by Xu, 1994 and is recorded in her thesis on page 37, Table 4. Therefore the temperature effects of both synthesized 5% Cr_2O_3/γ-Al_2O_3 catalyst and powdered Fe_2O_3 catalyst can be studied by comparing these two TCE conversion curves, shown as Figure 22. The steeply rising curves observed at low temperatures and conversions indicate that they are occuring in the chemical kinetic control region which is related to the chemical interactions of reactant TCE with O_2 on the catalysts surface. In case of Fe_2O_3 catalyst, chemical kinetic region was found to occur at about 325 to 425 °C, while this region in the curve of synthesized 5% Cr_2O_3/γ-Al_2O_3 catalyst is exist at about 200 to 300°C. The temperature-insensitive mass transfer control zone reflected as a relatively flat portion occur at temperature over 450°C on the curve based on Fe_2O_3 catalyst and at over approximately 380°C by synthesized 5% Cr_2O_3/γ-Al_2O_3 catalyst.

TCE conversion over powdered Cr_2O_3 was also studied to compare with synthesized 5% Cr_2O_3/γ-Al_2O_3 at the same space velocity, 17400 v/v/hr, same initial TCE concentration, 111 ppm. The TCE conversion curve over powdered Cr_2O_3 versus temperature shows an unusuals shape in Figure 22. The slope rises sharply after light off to about 250 °C, like the other two curves. However, the slope decreases after about 250 °C, achiving 100 % TCE conversion at 600°C. Within the temperature region between 400 to 600, an unknown GC peak was observed by GC-ECD before the TCE peak shown Figure 23 The GC operating condition is described at Table 8. The experiments were repeated three time and essentially the same results were observed.

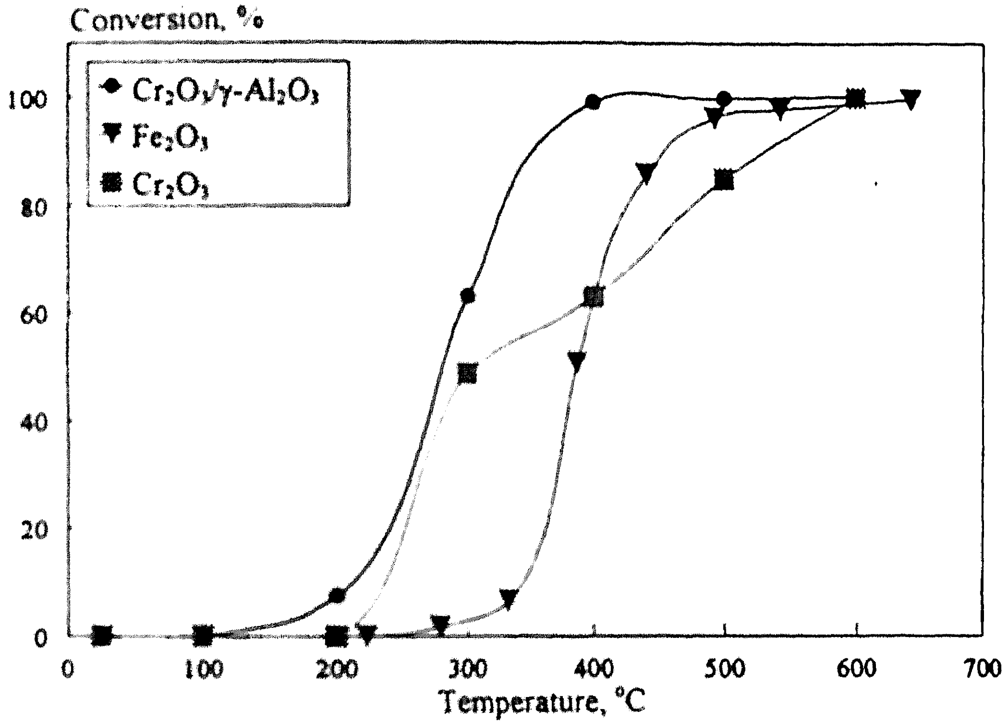
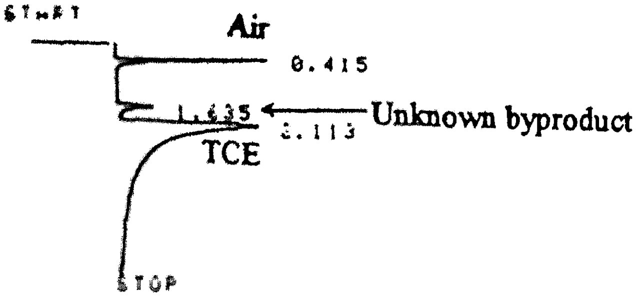


Figure 22 Temperature effects of TCE conversion over Cr_2O_3, 5% Cr_2O_3 γ-Al_2O_3 and Fe_2O_3

Research on the catalytic oxidation of trichloroethylene over Fe_2O_3 and CuO catalyst which was conducted by the Sanmei Xu 1994, conversion versus temperature curve based on CuO indicate that TCE conversion over CuO catalyst occurred at higher temperature ranges than that for Fe_2O_3. Therefore, Fe_2O_3 catalyst was investigated as a more effective catalyst than CuO catalyst for TCE oxidation. (Xu, 1994).

It was found in this study that synthesized 5% $Cr_2O_3/\gamma\text{-}Al_2O_3$ catalyst is more effective for oxidizing trichloroethylene than Fe_2O_3 or CuO catalysts.



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   2.113     3473026   PB    .454    82.24291

TOTAL AREA=4222086
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Figure 23 Gas chlomatography of TCE oxidation over powered Cr_2O_3

Table 8 GC operating condition for detect TCE oxidation over Cr_2O_3

Carrier Gas	Nitrogen, 30 cm^3/min
Oven Temperature	60 °C
Injector Temperature	150 °C
Detector Temperature	250 °C
Integrator Attenuation	8
Column packing material	Chromosorb GAW 80/100, 1/8"x 10'

CHAPTER 5

CONCLUSION

As a consequence of the research the following conclusions were reached:

- Modifications to the incipient wetness method used in the preparation 5% Cr_2O_3/γ-Al_2O_3 catalysts for trichloroethylene (TCE) oxidation give conversions in the range of 20 to 67 % at 300°C and 30,000 v/v/hr
- X-ray crystallography shows that the catalytically active Cr_2O_3, supported on γ-Al_2O_3, exist as a microcrystalline or amorphous substance, i.e., no Cr_2O_3 peaks were detected
- The BET surface area measurement of the most active synthesized 5% Cr_2O_3/γ-Al_2O_3 catalyst showed 114 m^2/g adsorption surface area and 122 m^2/g desorption surface area, which is slightly larger than that for γ-Al_2O_3 support. The difference between the surface area of synthesized 5% Cr_2O_3/γ-Al_2O_3 and that of γ-Al_2O_3 is due to the small size of the Cr_2O_3 crystallites which are estimated provide 422 m^2/g or an average crystallitic dimension of 2.7 nm
- Material balances for oxidation of trichloethylene over synthesized 5% Cr_2O_3/γ-Al_2O_3 at the space velocity of 17,400 v/v/hr and at six temperatureaverage 99.1 ± 1.47 % for carbon and 98.2 ± 0.1 % for chlorine
- The main products from the catalytic oxidation of trichloethylene over synthesized 5% Cr_2O_3/γ-Al_2O_3 are carbon monoxide, carbon dioxide, chlorine and hydrogen chloride.

- The oxidation reaction of trichloroethylene obeys first order reaction kinetics with respect to trichloroethylene
- The activation energy, Ea, for the oxidation of trichloroethylene over synthesized 5% Cr_2O_3/γ-Al_2O_3 is 71.5 MJ/mol (17.1 kcal/mol), and the preexponential factor, A, is 7.6 *10^[illegible] sec^{-1}
- The light-off temperature for catalytic oxidation of 111 ppm trichloroethylene over synthesized 5% Cr_2O_3/γ-Al_2O_3 at 17,400 v/v/hr is 150 °C, and 99 % conversion is achieved at 400°C. At the same condition, the light-off temperature for Fe_2O_3 occurs at 300 °C and 99 % conversion at 550 °C as investigated by Xu, 1994. Also Fe_2O_3 has been reported as a better catalyst than CuO in Xu's thesis. Consequently, 5% Cr_2O_3/γ-Al_2O_3 is more effective oxidizing trichloroethylene than Fe_2O_3 and CuO.
- Commercial powdered Cr_2O_3 shows a light-off temperature at 200 °C, and 99 % TCE conversion at a higher temperature of 600 °C. Between 300 to 600 °C, TCE is partially converted to an unknown byproduct which is detected by GC-ECD.
- Synthesized 5 % Cr_2O_3/γ-Al_2O_3 has very similar activity to 1.5 % pt/γ-Al_2O_3 and therefore warrants further development (Shaw, 1993).

APPENDIX A

BET SURFACE AREA MEASUREMENT

Table A 1 The Result of BET surface area measurement

	γ-Al_2O_3	5% Cr_2O_3 / γ-Al_2O_3
Sample weigh (g)	0.0549	0.0563
Ambient Pressure	781	781
Saturated Vapor Pressure	780	781
Adsorption Plot Slope Adsorption Intercept Correlation Coefficient Adsorption Surface area (m^2/g)	614.4713 -6.989487 0.9980522 104	551.4989 -8.682922 0.9991993 114
Desorption Plot Slope Desorption Intercept Correlation Coefficient Desorption Surface Area(m^2/g)	643.2955 -9.624222 0.9996467 100	506.2411 -1.488991 0.9997456 122

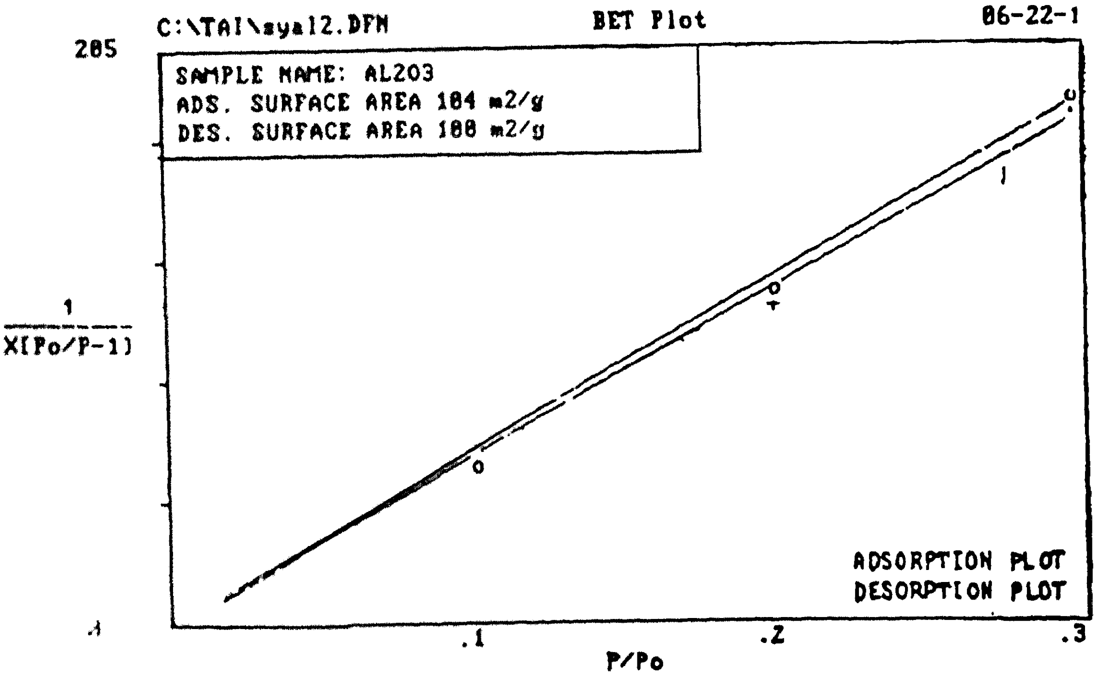

Figure A 1 BET plot for γ-Al_2O_3

APPENDIX B

X-RAY DIFFRACTION CRYSTALLOGRAPHY

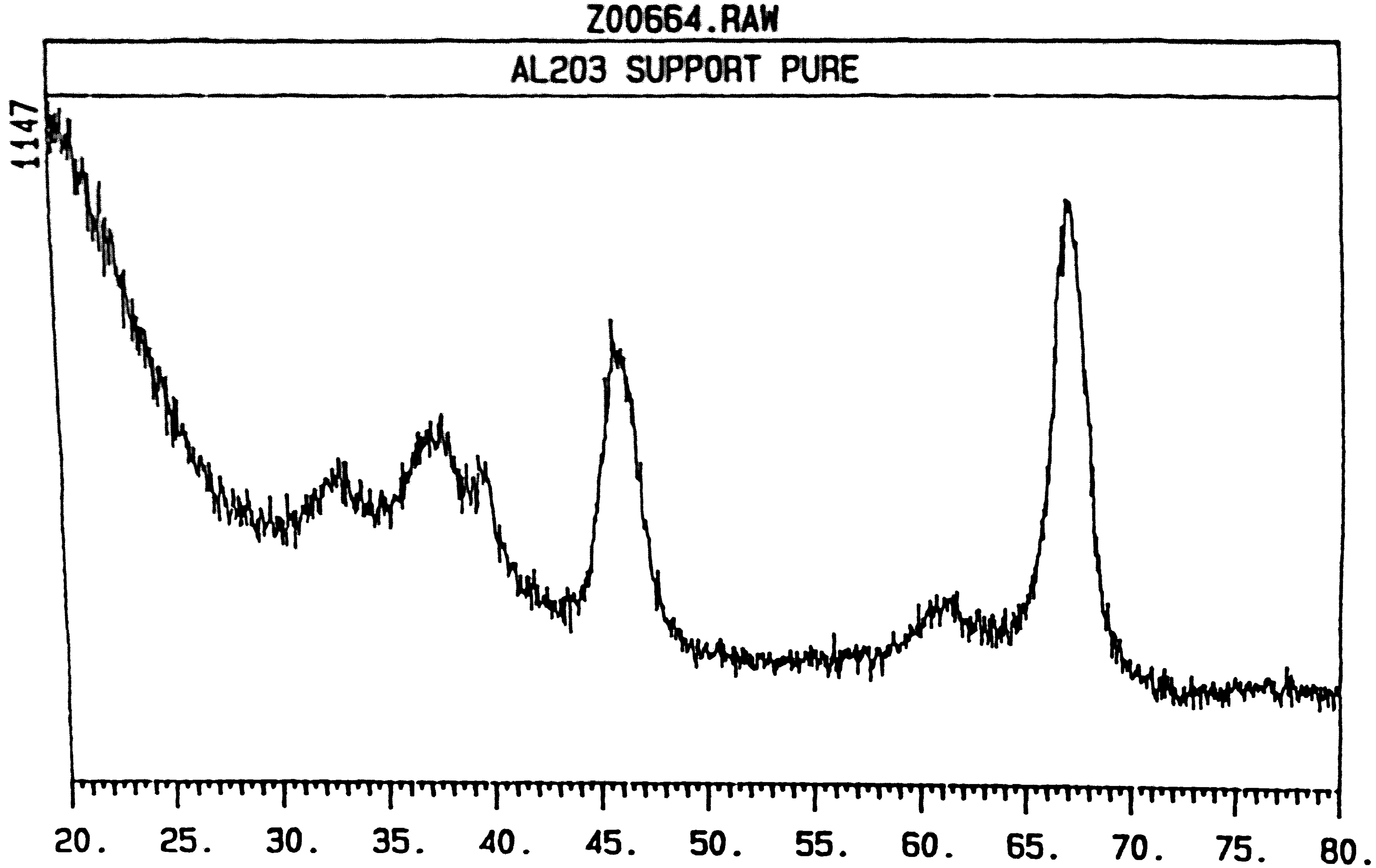

Figure B 1 X-ray diffraction crystallography of γ-Al_2O_3

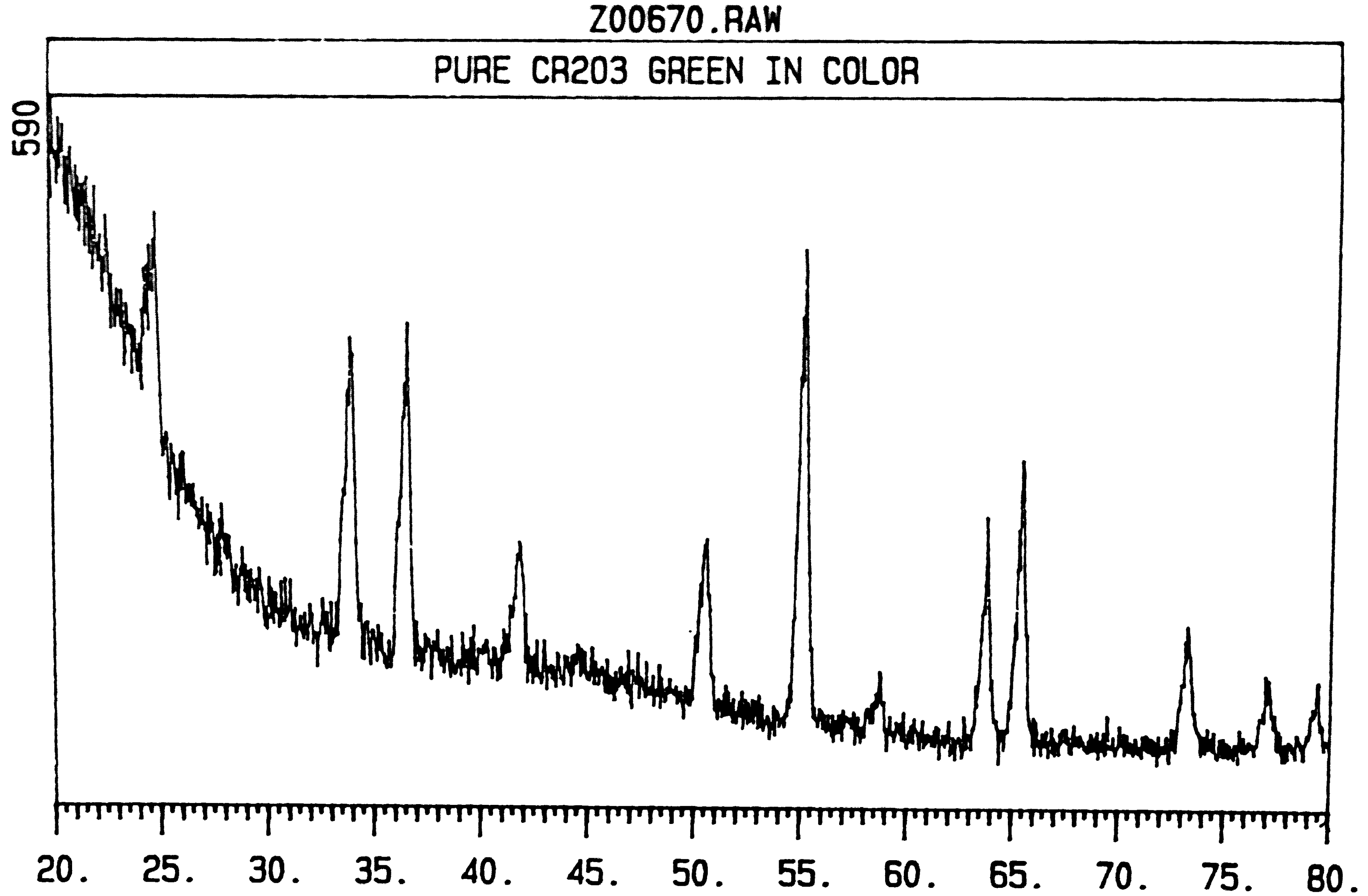

Figure B 2 X-ray diffraction crystallography of α-Cr_2O_3

APPENDIX C

KINETIC STUDIES

Table C 1 Data used in the chemical kinecs studies

Residence time (sec)	Conversion (%) at 483 K	Conversion (%) at 493 K	Conversion (%) at 503 K
0	0	0	0
0.0164	3.53	4.68	5.62
0.123	5.1	7.7	11.84
0.184	6.72	10.76	17.3
0.25	8.42	13.93	23.28

Table C 2 Data to achieve Arrhenius equation described in Figure 21.

$[\text{Temperature}]^{-1}$ (1000/K)	Slope (ln K)
2.07	0.336
2.08	0.59
1.98	1.05

REFERENCES

Bond, G. C. 1973. *Catalytic Destruction of Chlorinated Hydrocarbons* U.S. Patent No. 1485735.

Bond, Geoffrey Colin. 1969. *Catalysis by Metals.* Academic Press, London, Chap. 3.

Bretschneider, Boris and Kurfurst, Jiri. 1987. *Air Pollution Control Technology.* Fundamental Aspects of Pollution Control and Environmental Science series **8,** New York, pp. 170-173.

Che, Michel and Bennett Carroll O. 1989. "The Influence of Particle Size on The Catalytic Properties of Supported Metals." *Advances in Catalysis,* Academic Press, London, vol **36**. pp. 60-62.

Erdey, Laszlo. 1965. *Gravimetric Analysis* Edited by Ilona Buzas Pergamon press, New York, part II, Chap.21.

Johnston, E. L. et al. 1976. *Low Temperature Catalytic Oxidation of Chlorinated Compound to Recover Chlorine Values Using Chromium-Impregnated Supported Catalysts.* U.S. Patent 3989807, No. 2.

Lawton, T. J. and Gower, R. J. 1994. "Catalysis Aid Cleaner Environment Thermal Incineration Process Enhanced by Platinum-based Catalyst." *Platinum Metals Review* Edited by Johnson Matthery, Environmental Products Catalytic Systems Division, Royston, vol. **38**, No. 4, pp. 160-161.

Novinson, T. 1989. *Chemical Detoxification of Polychlorinated Biphenyls (PCBs).* U.S. Patent 4804779. Feb. 14.

Purcell, Robert Y. and Shareef, Gunseli Sagun. 1988. *Handbook of Control Technologies for Hazardous Air pollution.* Science Information Resource center, Hempshere Publishing Corporation, New York, Chap. 4, pp. 47-53.

Ramanathan, K. and Spivey, J. J. 1989. "Catalytic Oxidation of Dichloroethane." *Combustion Sci. & Tech.* vol. **63**, pp. 247-255.

Schaumburg, F. D. 1990. "Banning Trichloroethylene: Responsible Reaction or Overkill." *Environ. Sci. & Tech.* vol. **24**, No. 1.

Senka, S. M., Chang, W. D. and Karra, S. B. 1986. "A Detailed Mechanism for The High Temperature Oxidation of C_2HCl_3." *Combustion Sci. & Tech.*, vol. **49**, pp. 107-121.

Shaw, H., Wang, Y., Yu, T. C. and Cerkanowicz, A. E. 1993. "Catalytic Oxidation of TCE and Methane Chloride with Noble Metals." Emerging Technologies for Hazardous Waste Management III, ACS, Advances in Chemistry Series No. **518** Chap. 17, pp. 358-379.

Simone, D.O., Brungard, N.L. Kennell, and Farrauto, R.T. 1991. "Reversible Poison of Palladium Catalysts For Methane Oxidation" *Applied Catalysis*, **70**, pp. 87-100

Syracus Research Corp. 1989. *Toxicological Profile for Trichloroethylene.* Oak Ridge National Laboratory under DOC Interagency Agreement No. 1857-BO26-Al pp. 3-5

Thomson, Samuel J and Webb, G. 1968. *Heterogeneous Catalyst.* Edited by T. L. Cottrell, John Wiley & Son Inc., New York Chap 1

Twigg, Martyn V. 1989. *Catalyst Handbook.* Wolfe Publishing Ltd., London, Chap.1 pp. 41-43