CATALYSTIC WET OXIDATION OF WASTEWATER CONTAINIG ACRYLIC ACID

LAU WENG KEONG

UNIVERSITI MALAYSIA PAHANG

CATALYSTIC WET OXIDATION OF WASTEWATER CONTAINIG ACRYLIC ACID

LAU WENG KEONG

Thesis submitted in partial fulfillment of the requirements
for the award of the degree of Bachelor of Chemical Engineering

Faculty Of Chemical And Natural Resources eNGINEERING
ENGINEEING UNIVERSITI MALAYSIA PAHANG

February 2013

SUPERVISOR'S DECLARATION

I declare that this report is the result of my own work except as cited in the references and summaries which have been duly acknowledge.

Signature : -----------------------------------

Name : -----------------------------------

Date : -----------------------------------

STUDENT’S DECLARATION

I declare that this report is the result of my own research except as cited in the references and summaries which have been duly acknowledge. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature : -----------------------------------
Name : -----------------------------------
ID Number :
Date : -----------------------------------

ACKNOWLEDGEMENT

I wish to express my eternal gratitude and sincere appreciation to my supervisor Dr. Chin Sim Yee, from Faculty of Chemical & Natural Resources Engineering for her invaluable guidance, empowering support and profound advice throughout the preparation and realization of this thesis.

My sincere appreciation also extends to all of my friends and other lecturers from Universiti Malaysia Pahang (UMP) who had provided their full support and co-operation to make this study possible. I am grateful to my family members too.

I would also like to thank Faculty Chemical and Natural Resources Engineering of Universiti Malaysia Pahang for providing me resources and facilities Finally, above all, I feel pleasure to have good health, strength and perseverance to complete this proposal.

TABLE OF CONTENTS

CHAPTER 1 - INTRODUCTION

CHAPTER 2 – LITERATURE REVIEW

CHAPTER 3 – METHODOLOGY

CHAPTER 4 – RESULT AND DISCUSSION

CHAPTER 5 – CONCLUSION AND RECOMMENDATION

REFERENCE

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

AA = acrylic acid
Mn = manganese
Ce = cerium
CWO = catalytic wet oxidation
WO = wet oxidation
COD = chemical oxygen demand
AOP = advanced oxidation process
UV = ultraviolent
BET = Brunauer, Emmett, and Teller
BJH = Barrett, Joyner, and Halenda
XRF = X-ray fluorescence
XRD = X- ray diffraction

PEMANGKIN PENGOKSIDAAN UNTUK AIR SISA MENGANDUNGI AKRILIK ASID

ABSTRAK

Akrilik asid (AA) adalah salah satu sebatian organik berbahaya yang boleh ditemui di air sisa industri yang boleh menyebabkan kerosakan yang serius kepada alam sekitar dan kesihatan.. Dari Kajian ini, pemangkin pengoksidaan (CWO) telah digunakan dengan kehadiran pemangkin Mangan Serium oksida untuk mengoksidakan acid akrilik dalam keadanan operasi yang kurang ketat. Dalam penyelidikan ini, pemangkin Mangan Serium Oksida (Ce-Mn-1) telah disediakan oleh co-pemendakan dan dicirikan dengan menggunakan pembelauan sinar-X (XRD), X-ray flusoncen (XRF), Brunauer, Emmett, dan Tellerteori (BET) dan Barrett, Joyner, dan Halenda (BJH) analisis. Di samping itu, prestasi pemangkin dalam CWO air sisa mengandungi Asid Akrilik telah diperolehi dengan memanipulasi parameter operasi yang berbeza, yang suhu dan kepekatan Asid Akrilik. Aktiviti pemangkin telah dianalisis oleh chemical oxygen demand (COD) kaedah analisis. Pemangkin dengan nisbah mangan / serium 67/33 telah berjaya disintesis dengan kawasan permukaan tertentu, 83,1155 m2g-1 dan isipadu liang 0.3031cm3g-1. Walaupun pemangkin yang disintesis menunjukkan ciri-ciri fizikal yang baik tetapi data sastera pengurangan COD yang diperolehi adalah tidak sismatik disebabkan oleh tindakbalas sampingan, pempolimeran dan pembentukan asid karbonik semasa eksperimen. Kesimpulan, walaupun ciri-ciri pemangkin menunjukkan hasil yang baik tetapi disebabkan reaksi sebelah berlaku semasa eksperimen, aktiviti pemangkinan tidak dapat ditentukan.

CATALYSTIC WET OXIDATION OF WASTEWATER CONTAINIG ACRYLIC ACID

ABSTRACT

Acrylic acid (AA) is one of the hazardous organic compounds that can be found in industrial wastewater which can cause serious damage to the environment and health. From this research, catalytic wet air oxidation (CWO) process has been used with the presence of Manganese-Cerium Oxide catalyst in order to oxidise acrylic acid in the less severe operating condition. In the present research, the Manganese-Cerium Oxide catalyst (Ce-Mn-1) was prepared by co-precipitation and characterized by using X- ray diffraction (XRD), X-ray flusoncen (XRF), Brunauer, Emmett, and Teller theory (BET) and Barrett, Joyner, and Halenda (BJH) analysis. In addition, performance of the catalyst in CWO of wastewater containing Acrylic Acid was obtained by manipulating different operating parameters, which are temperature, and the concentration of Acrylic Acid. The catalytic activity was analyzed by Chemical Oxygen Demand (COD) analysis method. The catalyst with manganese/cerium ratio 67/33 was successful synthesized with specific surface area, 83.1155 m^2g^{-1} and pore volume $0.3031cm^3g^{-1}$. Although the synthesized catalyst showed good physical characteristic but the literature COD reduction data obtained is fluctuating due to the side reaction polymerization and formation of carbonic acid during the experiments. As the conclusion the characteristics of catalyst shown a good result but due to the side reaction occur during the experiments, the catalytic activity can’t be determined.

CHAPTER 1

INTRODUCTION

1.1 Background of the Proposed Study

Water is used in industrial plants frequently and in large quantities. The spent water (wastewater) may be contaminated with toxic and hazardous organic compounds which cause serious damage to the environment and health. Acrylic acid (AA) is one of the hazardous organic compounds that can be found in industrial wastewater. Acrylic acid is by product of many industries (painting, chemical fibers, adhesives, detergents) and can cause serious damage to the environment when it is released into industrial effluents due to its highly toxicity to aquatic organisms (Silva et al, 2003).

Due to the increased awareness to environmental and health risks, several techniques such as esterification, adsorption, and wet oxidation have been developed to remove acrylic acids from the wastewater but most of the treatment methods are ineffective or uneconomical. Wet oxidation (WO) process is one of the early methods used for the treatment of toxic wastewater. By generation of active oxygen species such as hydroxyl radicals, takes place at high temperatures and pressure, the refractory compounds can break down into simpler, easily treated material before released into the environment (levec & Pintar, 2007). However, WO process is prohibitively expensive due to the severe operating condition; catalytic oxidation process which is an improvement of wet oxidation process by use of catalyst was developed (Hendricks, 2006 &Wolfovich, 2006).

The presence of catalyst accelerates the oxidation rate and reduces the severe operating condition (levec & Pintar, 2007). However, the operating condition for CWO remains severe and not economical (Hendricks, 2006). Therefore a development of new catalyst is highly desirable. In the present, metal oxide catalyst was developed to and tested in the catalytic wet oxidation of acrylic acid.

1.2 Research Objectives

There are two objectives for this research.

1.2.1 To synthesize and characterize the Manganese – Cerium Oxide catalysts.

1.2.2 To determine the activity of the synthesized catalyst in the catalytic wet air oxidation of wastewater containing acrylic acid.

1.3 Scope of the Proposed Study

The Manganese - Cerium Oxide catalyst was prepared by co-precipitation method and characterized using X- ray diffraction (XRD), X-ray Fluorescence (XRF), Brunauer, Emmett and Teller method (BET) and Barrett, Joyner, and Halenda (BJH). In addition, the performance of the catalyst in various parameters was determined at the end of the experiment. Two operating parameters, initial concentration of acrylic acid and temperature were studied in this research. The catalyst activity was evaluated by calculating the reduction of acrylic acid and the organic compounds amount after the experiments. The analysis methods used to determine the concentration of acrylic acid will be chemical oxygen demand (COD).

1.4 Significance of the Proposed Study

The significance of the present study is to develop a metal oxide catalyst which is more eco friendly, economical and reduce the severity of the operating condition for the wet oxidation of acrylic acid. This catalyst can be used to reduce the cost of wastewater treatment and the treated water is less hazardous to the environment. This will give a very great impact to the environment and the industry.

CHAPTER 2

LITERATURE REVIEW

The background of wastewater containing acrylic acid and its' wastewater treatment techniques including catalytic wet oxidation (CWO), heterogeneous catalysts for wet oxidation and catalyst synthesis method were review in this chapter.

2.1 Acrylic Acid in Industrial Wastewater Containing Acrylic Acid

Treatment of wastewater containing acrylic acid is extensively studied in recent years, due to it widely use in industry and toxicity. According to the National Pollutant Release Inventory (NISH), the industrial sectors contributing to acrylic acid emissions are the chemical products sector and the plastic products industries (NISH, 2012). The chemical products sector includes industries producing industrial organic chemicals, plastics, resins, soaps, cleaning compounds, adhesives, plastic products and other chemical product (NISH, 2012). The plastic products industries include the foamed and expanded plastic products industries and other plastic products industries (NISH, 2012). National Institute of Health Sciences reported that acrylic acid might occur in wastewater effluent from industrial facilities at concentrations not exceeding 0.5 mg/litre, whereas effluent levels of 2500 mg/litre were reported at a methyl acrylate production facility in India and treated acrylic acid concentration was below the limit of detention (0.1 mg/litre) in wastewater from a production facility in Europe.

Acrylic acid (AA) is a moderately strong carboxylic acid which is colorless, corrosive, flammable and miscible with water. A detail report done by the National Institute of Health Sciences states that acrylic acid is low to moderate acute toxicity by oral route. However, diluted acrylic acid is less harmful to human, but serious damage to the environment when it is released into industrial effluents due to it's highly toxicity for aquatic organisms. Acrylic acid has moderate acute toxicity in aquatic organisms; a toxicity value between >1 mg/L and 100 mg/L has been reported (U.S. Environmental Protection Agency, 1994). Several wastewater treatment techniques have been developed to remove acrylic acid from the waste water.

2.2 Wastewater Treatment for the Waste Containing Carboxylic Acid

Nowadays, water scarcity becomes an increasingly severe problem all over the world. Rapid economic growth and increasing urbanization cause a great increasing amount of industrial wastewater containing toxic and hazardous organic compounds. Because of the increasing awareness of environmental and health risks combined with strict waste treatment regulations, many industrial treatment plants were constructed in the 1970s and 1980s (Coppen, 2004), but still wastewater treatment is an ardent issue today. There are a number of wastewater treatment techniques available such as separation treatment, biological treatment, and destruction treatment (Nor Habibah, 2006, and Wang et al, 2007).

2.2.1 Separation Treatment

In separation treatment, the carboxylic acids are removed from the wastewater by using a variety of physical separation, such as adsorption (Wolfovich, 2006). But there is a lot of drawback of separation technique such as high cost and require the additional stage to separate the additional chemicals or adsorbent which are difficult to remove from the treated water.

Adsorption is one of the separation treatments use to treat wastewater containing carboxylic acid. Carboxylic acids can be removal by adsorption method. Various substances will adsorb on various adsorbents. Adsorbates include organic compounds, particles, and metal ions (Hendricks, 2006). In a patent of Kawabata et al. (1982), carboxylic acids were separated by using a polymer adsorbent of pyridine skeletal structure and cross-linked structure. Ever though the carboxylic acids can be removed by adsorption method but the cost of commercial adsorbents associated with adsorbent regeneration for adsorption operation is very expensive, especially when the concentration of carboxylic acids is high on the wastewater (Hendricks, 2006 & Kumar, 2006).

2.2.2 Biological Treatment

A wide variety of hazardous organic compounds can be removed using biological treatment. The bacteria and other microorganisms are used to degrade wastewater compounds (Hendricks, 2006). This method is highly effective for organic and inorganic solutions and its operational costs are relatively low (Peavy, 1985). But still there are some short comings for biological treatment; it cannot completely remove soluble components and taking long residence times (Nor Habibah, 2006).

2.2.3 Destruction Treatment

The destruction treatments were advanced wastewater treatment techniques which can achieve the high contaminants elimination levels by breakdown or decompose the organic molecules to form carbon dioxide and water (Wolfovich, 2006 and Wang at el, 2007). Advanced oxidation process (AOP) on the basis of UV and H2O2, supercritical water oxidation and wet air oxidation are including in destruction treatments (Wolfovich, 2006). These approaches along with their drawback are outlined in Table 2.1.

Table 2.1 Destruction Treatment method

Method	Description	Disadvantage	Reference
Advanced oxidation process	Generation of very reactive species such as hydroxyl radical to oxidise organic pollutants.	Requires long reaction time and large doses of chemical.	Hendricks. D., 2006 & Stasinakis. A. S., 2008

Continue Table 2.1

Method	Description	Disadvantage	Reference
supercritical water oxidation	Using supercritical fluids as a medium for oxidation of organic.	Extreme severe operating condition and high energy cost.	Hendricks. D., 2006 & Eliaz. N. et al , 2003
Wet air oxidation	Using high energy to breakdown the complex organic compound.	No complete oxidation process and severe operating condition	Hendricks. D., 2006 & Levec & Pintar, 2007

2.3 Wet Air Oxidation

Wet air oxidation is a technology used to treat the waste water steams which are too dilute to incinerate and too concentrated for biological treatment (Wang et al, 2007). WAO process takes place at high temperatures and pressures and breakdown (oxidation) the toxic contaminants to low molecular weight oxygenated compounds in liquid phase by using oxygen gaseous source as the oxidizing agent (Levec & Pintar, 2007). Typical condition for WAO are 423-593K for temperature, 2-15 MPa for pressure, and 15-10min for residence time (Luck, 1999 & Debellefontaine, 2000). A study of Levec and Pintar (2007) state that by taking place at temperature around 473-593K and pressure above 20 bar, the extent of COD removal may typically be about 75%-90%. But there are a lot of drawbacks for WAO process. The drawbacks of WAO are severe operation conditions, non-complete oxidation process and prohibitively expensive. In order to improve the efficiency of WAO, catalysts have been used to reduce operating condition with higher oxidation rates (Wolfovich, 2006). However, the operating condition for CWO still severe and not economical.

2.4 Catalytic Wet Oxidation

Catalytic wet oxidation (CWO) process is a further development of the WAO process which an active catalyst is used. The development of commercial CWAO processes started as early as the mid-fifties in the United States (levec & Pintar, 2007). Compare with WAO process, CWAO has lower energy requirement. The presence of a catalyst increases the oxidation rate and consequently reduces the severity of the operating conditions. CWAO process is capable to oxidize all organic contaminants ultimately to carbon dioxide and water and preferred for wastewater those are highly concentrated or contain component which are toxicity to biological treatment system (Wang at el, 2007). CWAO process can be conducted by using homogeneous and heterogeneous catalysts. The soluble homogeneous transition metal catalysts are operating successfully to treat industrial effluent and being applied in several wet air oxidation plant. But, the homogeneous transition metal catalysts require a subsequent separation step to separate the homogeneous catalyst from the treated water and recycle back to the reactor inlet (levec & Pintar, 2007). Therefore, the application of solid heterogeneous catalysts is more viable. The heterogeneous catalysts that have been employed in CWO can be divided into two main groups, oxides of the transition metal (pure or mixed) and supported noble metals (Silva, 2003)

2.4.1 Noble Metal

Noble metals provide high activity in oxidation effective in of different pollutants such as phenols, carboxylic acids (including refractory acetic acid), ammonia and aniline. Table 2.1 summarizes the application of noble metal catalysts for different CWO reactions.

Table 2.2 Process Data of CWO using Noble Metal Catalysts

Noble Metal	Support	Substrate	T (°C)	P (MPa)	Reference
Pt, Pd, Ru	Al_2O_3, CeO_2, AC	P-chlorophenol	120	2.6	Qin et al, 2001
Ru, Pd, Pt	CeO_2	Aniline, Phenol, carboxylic acid	200	0.69	Barbier et al, 2005
Ru, Ir, Pd, Ag	CeO_2, TiO_2, ZrO_2	Acetic Acid	200	2.0	Barbier et al, 1998
Pt	C	Maleic acid, malonic acid, phenol	120-170	1.5-1.8	Zacharia, 2004
Pt	Al_2O_3	Phenol	150	1.4	Lee D.K. et al, 2010
Pt	C	Phenol	120-180	1.5-2.0	Zacharia , 2004
Ru	CeO_2/ ZrO_2	Phenol	170	3	Wang et al, 2007
Ru	CeO_2, C, Ce/C	Phenol Acrylic acid	160	2.0	Oliviero, 2000

Table 2.2 shows that different substrate/pollutants and different metals may present optimum result. Catalyst activity is based on pollutant. This is proven by the reports of Barbier (1998) and Qin (2001). For acetic acid oxidation, Barbier et al (1998) showed that the catalyst activity of Ru higher than Pd, whereas Qin (2001) showed that for the p-chlorophenol oxidation, catalytic activity of Pt higher than Pd. Besides that, the noble metal supports also influence catalyst performance. This has

been provin by the study of Oliviero (2000) on the oxidation of phenol and acrylic acids under Ru noble metal catalyst based in carbon, cerium and carbon-cerium. Oliviero et al (2000) stated that the catalyst performance affect by the support and their result shown that the conversion of acrylic acid using cerium as the support of rubidium is than the catalyst using carbon contain cerium supports, (Ru/C-Ce and Ru/C).

In most reactions, supported noble metals catalysts are generally found to be more active than metal oxide catalysts. However noble metal catalysts are expensive and less resistant to poisoning, which may be due to the limited metal loading on the support (Wolfovich, 2006).

2.4.2 Metal Oxides

The use of pure or mixed metal oxide is common in wastewater. Copper oxide and manganese oxide, separate or combined with other oxides, have received special attention in the CWO of aqueous effluents. Manganese oxide is reported to exhibit good activity and much active than homogeneous copper catalyst (Imamura, 1999). Table 2.3 summarizes the applications of metal oxide catalyst in the CWO process.

Table 2.3 Process Data of CWO using Metal Oxide Catalysts

Metal Oxide	Substrate	T (°C)	P (MPa)	Reference
Ni/MgAlO	Phenol	180	2.5	Vallet et al, 2012
CoO/BiO	Acrylic acid	140-180	0.4	Kumar et al, 2006
CuO/MnO_x	Ethylene glycol	160-220	1.5-2.5	Silva et al, 2004
$Ni/Al2O_3$	Ammonia	230	2.0	Kaewpuang et al, 2004
MnO/CeO	Acrylic acid	140-180	0.4	Kumar et al, 2006
MnO/CeO	2,4-dichlorophenol	160	1.0	Lee et al, 2002

Continue table 2.3

Metal Oxide	Substrate	T (°C)	P (MPa)	Reference
MnO/CeO	Formaldehyde	190-220	1.5-3.5	Silva et al, 2003
MnO/CeO	Phenol	80-130	1.0	Wolfovich, 2006
MnO/CeO	Acrylic acids	200	1.5	Silva et al, 2004
MnO/CeO	Ethylene glycol	160-220	1.5-2.5	Silva et al, 2004

Manganese/Cerium combined oxide catalyst is widely used for different substrate/pollutants such as Formaldehyde, Phenol, Acrylic acid, Ethylene glycol and 2,4-dichlorophenol in CWO process and showed an excellent performance (Silva et al, 2003, Wolfovich, 2006 and Silva et al, 2004). The research of Silva et al (2003) states that the catalytic wet oxidation efficiency of different cerium based catalyst, Cobalt-Cerium(Co/Ce), Silver-Cerium(Ag/Ce) and Manganese-Cerium (Mn/Ce) for waste water containing acrylic acid in 2 h increased by the order Co/Ce < Ag/Ce < Mn/Ce. Therefore, manganese showed to be the best metal to be combined with Cerium in terms of catalytic activity. Therefore, Manganese/Cerium combined oxide catalyst which is an economical composite catalyst and widely used for CWO process, showed the highest potential for CWAO of acrylic acid (Silva, 2003).

2.5 Catalyst Preparation Methods

Noble metal and metal oxide catalyst are the most important type of heterogeneous catalysts in industrial practice. Therefore, the synthesis of noble metal and metal oxide catalyst are significant in scientific and industrial. Many methods can be use to synthesis heterogeneous catalyst such as co-precipitation, impregnation and so gel synthesis, but the preference of the synthesis method is highly depend on the physical (such as particle size and morphology) and chemical (such as catalyst active site and chemical path way) characteristics desired in the catalyst (Perego & Villa, 1997 and Haber et al, 1995). Basically, heterogeneous catalyst can classify into three categories with respect to the synthesis method, there are supported catalyst, bulk catalysts (unsupported catalyst) and mixed catalyst (Perego & Villa, 1997).

2.5.1 Bulk catalyst and supported catalyst

Bulk catalyst can define as unsupported catalyst. Generally, bulk catalysts are comprised of active catalyst that do not require high surface or intrinsically have a large surface area. Usually, bulk catalysts are used for high temperature applications such as refractory aluminates for catalytic combustion (King, nd). Typically synthesis methods for bulk catalyst are co-precipitation and sol-gel synthesis (Perego and Villa, 1997). Supported catalyst is the combination of active catalyst and supporter, co-catalyst. The co-catalyst which has a higher surface area is use to support and disperse the primary catalyst (King, nd). Generally, the supporter is prepared as the bulk catalyst synthesis method and then the active catalyst is immersed on the supporter. Typically synthesis methods for support catalyst are impregnation method (Perego and Villa, 1997). Mn/Ce oxide catalyst is categorized as bulk catalyst and the catalyst synthesis method is co-precipitation due to simplicity in composition control and high yield.

2.5.2 Co-precipitation

Co-precipitation is the most common method used to synthesis mixed metal oxide bulk catalyst. Precipitation is accomplished by combining a selected cation in solution with a suitable anion in sufficient concentrations to exceed the solubility of the resulting salt (combination of cations and anions) and produce a supersaturated solution. Nucleation occurs and growth of the crystalline substance then proceeds in an orderly manner to produce the precipitate (MARLAP, 2004).

In this method, catalytically active mixed metal salt solution is mixed with a precipitating agent. Generally, nitrates and chlorides metal salt are use due to their high solubility and precipitating agent hydroxides and hydroxyl are common used to form insoluble salt (precipitating). After a time hydroxides or hydroxyl salts start to precipitate and form a homogeneous mixture is filtered off. The filter cake (precipitate) is wash with ultra water to remove the excess precipitating agent and then undergoes thermal treatment (drying and calcinations) to remove water and activate the catalyst (Perego and Villa, 1997).

There are several factors affect the physical character and crystallite of the precipitation. These factors are rate of precipitation, concentration of ion, solubility of salts, temperature, pH, stirring and degree of superaturation. There are many researchers using co-precipitation to synthesis transition metal catalyst. Table 2.4 Shown the catalysts synthesis by different researcher using co-precipitation method.

Table 2.4 Catalyst Synthesis by Different Researcher

Catalyst	Researcher	Reference
Manganese-cerium	Wolfovich	Wolfovich, 2006
Cobalt-Cerium Silver-Cerium Manganese-Cerium	Silva, Rita, Marques, Rose and Ferreira	Silva et al, 2003
Cobalt-Bismuth	Kumar, Raghavendra and Chand	Kumar, 2006
Iron-Molybdate	Soares, Portela, Kiennemann and Hilaire	Soares et al, 2002

2.5.3 Sol gel method

Sol gel method is an advance method using to synthesis bulk catalyst. Instead of precipitation process, Sol gel synthesis method using flocculation and gelation to form heterogeneous catalysts. Sol, a stable suspension colloidal solid particle in liquid has been use to flocculate the precursors in the liquid and form a porous and three dimensional solid networks (gel) in the liquid after a time (King , nd).

Sol gel process occurs in several steps, there are formations of sol, gelation, ageing and thermal treatment. First, prepare a sol by adjusting pH and Silicon alkoxides. Then, the precursors are mixed into the organic solvent to form a colloidal suspension and then the sol is introduced in moulds for casting operation. After that the colloidal partials and condensed silica species (sol) link together to become a three-dimensional network. At gelation point, the viscosity of the sol rapidly increases and forms a gel. After a time for aging the gel, remove the solvent and undergoes thermal treatment to obtain catalyst (Düzenli, 2010). Sol gel method is an advance method and the preparation condition for each steps are no detailed.

2.6 Catalyst Characterisation

The technique for the characterisation of heterogeneous catalyst has been improved during the past ten years. The physical techniques can be applied to the real catalysts used in every industrial. The principal physical characterisation techniques used by industry are listed in Table 2.5.

Table 2.5 Techniques Used In Industrial Catalyst Characterisation

Techniques	Catalyst characterisation
• Gas adsorption • BET model • HK model • BJH model • Langmuir model	• Surface area • pore size distribution • Pore Volume • Pore size
• X-ray Diffraction (XRD) • X-ray Fluorescence (XRF) • Scanning Electron Microscopy (SEM) • Transmission Electron Microscopy (TEM)	• Chemical characterisation of functional group • Crystal structure • Phase structure

2.6.1 BET & BJH

Brunauer, Emmett and Teller (BET) analysis provides precise specific surface area evaluation of material. Generally, BET analysis is used to determine the specific surface area of solid by evaluate the physical adsorption of nitrogen onto the surface of the solid at liquid nitrogen temperature. BET device dose the nitrogen gas incrementally to the solid and the pressure is allowed to equilibrate for each dosed of nitrogen gas and the quantity of nitrogen is recorded. The amounts of nitrogen at each pressure define an adsorption isotherm and using this isotherm to calculate surface area by using BET equation (Norcross, nd).

Barrett, Joyner, and Halenda (BJH) device further increase the nitrogen gas pressure until the monolayer of nitrogen gas condenses to fill all the pores with nitrogen liquid and then the nitrogen gas pressure incrementally to evaporate the condensed nitrogen liquid. The adsorption and desorption define isotherms and the hysteresis between the isotherms is used to determine the pore size and volume by using BJH calculation. The pore diameter limits for macroporous material is more than 50nm and mesoporous material is pore between 50nm and 2nm, no suitable for microporous material which the pore diameter is less than 2nm (Trunschke, 2007). BET and BJH device has widely application in the study of catalyst, adsorbents, zeolites, pharmaceutical and artificial bone material to determine the specific surface area and pore volume (Norcross, nd).

2.6.2 XRF

X-Ray Fluorescence (XRF) was first proposed at 1928, X-ray fluorescence has only become common in archaeological uses within the past few decades (Adan-Bayewitz et al, 1999). XRF transfer high-energy gamma rays to the sample and measures the secondary X-ray that pass through the sample, or fluorescent x-rays. When sample is exposed to the gamma rays, their component atoms eject one or more electrons in a process known as ionization. Electron ejection only takes place if the atom is exposed to radiation with a greater energy than its ionization potential. XRF measures the energy dispersed in the ejection of these electrons (Rice, 1987). XRF has been successfully used for chemical analysis of major and trace- elemental concentration. In this research, XRF was used to analysis the metal oxide and trace metal composition in the catalyst. In recently research, XRF has been used by Vallet et al (2013) to characterize Ni and Fe catalyst supported over hydrotalcite.

2.6.3 XRD

X-ray diffraction (XRD) is one of the most importance technique used for illumination of structural information relating to the crystalline. Diffraction was occur when parallel X-rays passing through a sample and bent at a specific angle (). The diffracted angle used by Bragg's law to calculate the space distance between adjacent layers of atom or ions. The space distance between adjacent layers of atom determine the peak position and the peak intensity is determined by what atoms are in the diffracted plane (Bruker, 2001). The diffracted angle and the intensities of the diffracted X-ray were records and form a diffractogram to identify the characteristic of the sample. The compounds in the sample were identified using software to compare with the experimental diffraction date from the known compounds which is match with the diffraction date in the diffractogram (Speakmen, nd). Generally, The experimental diffraction dates from the known compound were compiled into PDF database by the Joint Committee on Powder Diffraction Standard, (JCPDS) (Scintag inc, 1999).

CHAPTER 3

METHODOLOGY

3.1 Research Design

This research focuses on the catalytic wet air oxidation (CWAO) of acrylic acid with presence of manganese - cerium oxide catalyst. The catalyst synthesis, catalyst characterization and catalysts testing will be discussed in this chapter.

3.2 Manganese-Cerium oxide Catalyst Preparation

For this research, the manganese - cerium oxide catalyst was prepared by co-precipitation to carry out the experiment.

3.2.1 Catalyst Reagents and Apparatus

Table 3.1 shows the chemical reagents that will be used in the catalyst preparation. The table has also covered the chemicals' purity, phase and its function respectively in catalyst preparation.

Table 3.1 The Chemical Reagent Used With Its Purity and Its Function.

Chemical reagent	Phase	Purity	Function
Manganese (II) Nitrate Hydrate	Solid	98%	Raw material to prepare Manganese Oxide in catalyst.
Cerium (II) Nitrate Hexahydrate	Solid	99%	Raw material to prepare Cerium oxide in catalyst.
Sodium Hydroxide	Solid	99%	Precipitating agent for precipitation.

Figure 3.1 shows the system scheme and apparatus was used in the catalyst preparation. Apparatus needed to synthesis manganese – cerium oxide catalyst are volumetric flask, breaker, funnel, filter paper and conical flask.

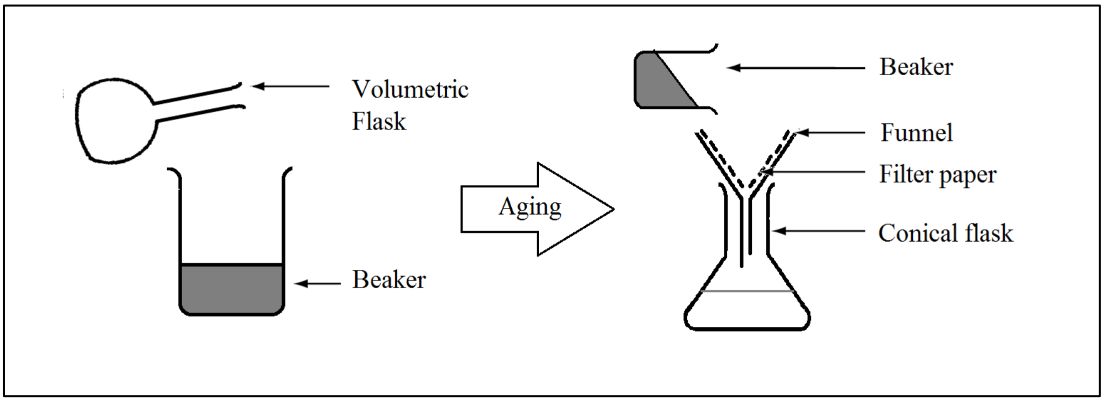


Figure 3.1: Catalyst preparation system scheme

3.2.2 Catalysts Synthesis Procedure

The manganese - cerium oxide catalyst with molar composites ratio for Mn/Ce was 70/30 was prepared by co-precipitation from a mixed aqueous solution of manganese (II) nitrates ($Mn(NO_3)_2$*xH_2O) and cerium (III) nitrates ($Ce(NO_3)_3$*6H2O) as described by Silva, et al (2003). The concentration with 15 g of metal salt/100 ml of mixture solution was prepared using volumetric flask and poured at room temperature into 200 mL of 3 M aqueous sodium hydroxide (NaOH, 97%). After 30 minutes of aging, the resultant dense brown gel was separated by filtration, washed with deioned water, and dried in air at 100^{o}C for 16 h followed by calcination at 350^{o}C for 3 h in air using glass furnace.

3.2.3 Catalysts Characterization

Catalyst will be characterized by using X- ray diffraction (XRD), X- ray Fluorescence (XRF) and BET & BJH analysis methods. Catalyst surface and pore volume were obtained using conventional BET method and BJH, while elemental composition was by XRF and crystalline structure was identify by XRD. 0.4365g of Mn-Ce catalyst sample was degassed under vacuum at 180 °C and became 0.4326g of degassed catalyst sample before BET and BJH analyst. The isotherms were measured at liquid nitrogen temperature with Thermo Scientific Surfer instrument. The Surface area was calculated using BET modal whereas the pore volume and pore size were calculated using BJH. For XRF, 10g of catalyst sample required for the XRF analysis. XRF measurements were performed using a Quantexpress method, with software for data acquisition and analysis. For XRD, 2g of catalyst was operated at 30 kV and 150 mA and the data were collected in the range of $2\theta=3^{\circ}.90^{\circ}$ with a step size of 0.005°.

3.3 Catalyst Testing and Sampling

The catalyst was tested in batch reactor at atmospheric pressure.

3.3.1 Reagents and Apparatus

Table 3.1 shows the chemicals that will be used in the catalyst testing. The table has also covered the chemicals' purity and its function respectively in catalyst testing.

Table 3.2 The Chemicals Used With Its Purity and Its Function.

Reagents	Phase	Purity	Function
Acrylic acid	Liquid	99.7%	To be used as chemical component remove by CWO
Manganese-Cerium catalyst	Solid	-	To be used to removal acrylic acid in the CWO

Figure 3.1 shows the batch reactor system scheme and apparatus was used in the catalyst testing. The apparatus and their function are listed in Table 3.3

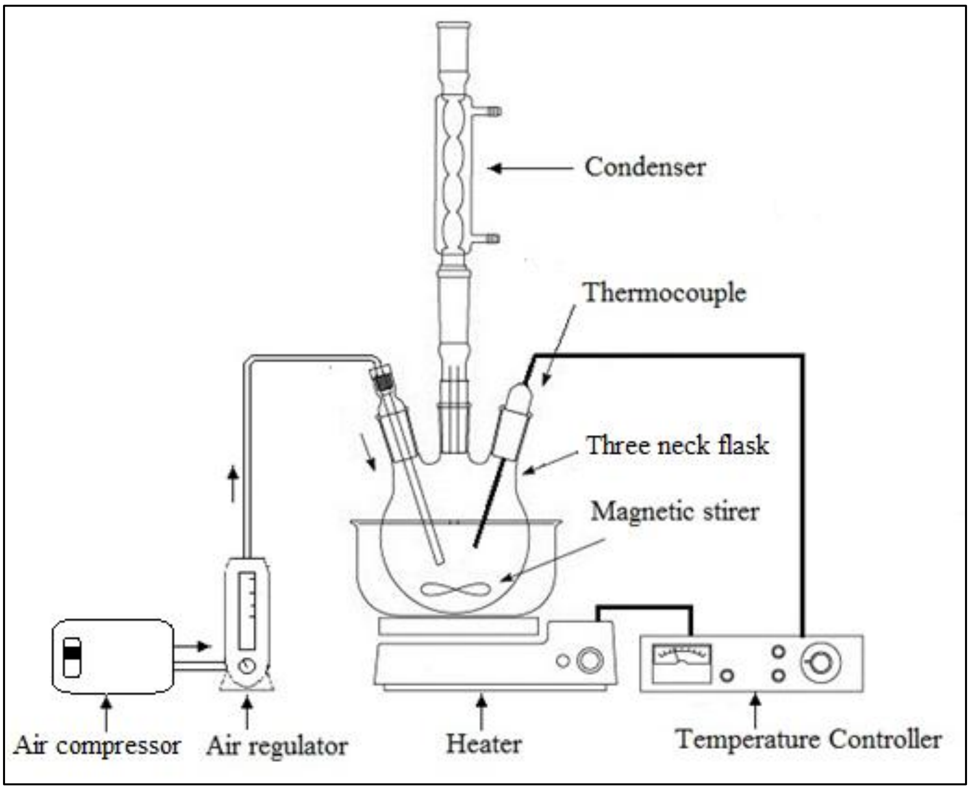


Figure 3.2 Batch reactor system scheme

3.3.2 Experimental Procedure

The initial testing of catalysts was performed in a batch reactor for wet air oxidation of acrylic acid (CH_2=$CHCO_2H$, 99%) solution. The oxidation was carried out at 50^oC (±2°C), 1 bar, 40000ppm acrylic acid, 4 L/min oxygen flow rate in a complete magnetic stirrer three-necked flask (reactor). The reactor initially was charged with deionized water and agitation will be started. The reactor will be heating by using modifier heating mantle. The temperature inside the reactor was measured by type J thermocouples and the temperature was controlled by temperature controller. As soon as temperature was attained, the catalyst and acrylic acid were injected in to reactor to attain a concentration of desired ppm. Experiment was repeated by varying the temperature and initial concentration of acrylic acid. All catalyst experiments were carried out with 2.5g/l of catalyst. 2ml of samples was taken periodically through the three-necked flask by syringe. 2ml of the samples with reaction times of 1, 5, 10, 20, 30, 60, 90, 120, 150, 180, 240, 300 minutes were taking out and the catalyst will be separated by using syringe filter. The filtrate was analyzed by chemical oxygen demand.

3.3.3 Range of Parameter

For the temperature manipulation experiment, temperature 50°C, 60°C, 70°C, and 80°C was carried out. For the initial concentration acrylic acid manipulation experiment, different concentration 4000ppm, 20000ppm and 40000ppm of arylic acid was carried out.

3.4 Performance Analysis Methods

Sample was analysis by COD instrument.

3.4.1 Reagents and Apparatus

Reagents needed to determine performance of manganese - cerium oxide catalyst are:

I. COD Digestion Reagent Vial High Range

II. Test tube

Apparatus needed to determine manganese – cerium oxide catalyst are:

I. COD Digester Reactor

II. Spectrophotometer, HACH DR/2400

III. COD rack

3.4.2 Analysis Procedure

In this procedure, 2ml of water sample is pours into vials containing the pre-measured reagents (strong oxidant, potassium dichromate). Then, the vials are heated under 150⁰C for 3hour until digestion is complete and then cooled. The COD value was determined using the spectrophotometer.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalysts characterization

The catalytic properties of synthesised Mn-Ce catalyst were determined and compared with the Mn-Ce catalyst synthesis by other researchers. The surface area, pore volume, microstructures Mn-Ce atomic ration of synthesised catalyst were compare with the Mn-Ce catalyst prepared by Wolfovich (2006).

4.2 Atomic ratio of Mn/Ce catalyst revealed by XRF

The atomic ratio of Mn/Ce catalyst (Mn-Ce-1) was analysed using XRF. 10 g of the Mn/Ce catalyst was used for the XRF analysis. Table 4.1 shows the major and trace element and their weight percent.

Table 4.1 XRF result for major and trace element weight percent of Mn/Ce catalyst

No	Metal/Metal oxide	Mass percent, %
1	Cerium Oxide	52.92
2	Manganese Oxide	44.52
3	Sodium Oxide	0.72
4	Europium Oxide	0.53
5	Calcium Oxide	0.39
6	Silicon Dioxide	0.26
7	Neodymium Oxide	0.23
8	Magnesium Oxide	0.14
9	Sulphur Trioxide	0.09
10	Aluminium Oxide	0.08
11	Rhodium	0.04
12	Nickel Oxide	0.04
13	Cobalt Oxide	0.02
14	Vanadium Oxide	0.02
15	Copper Oxide	0.01

The XRF result show that 97.43 weight percent of the catalyst is desired component, manganese Oxide and cerium oxide. The other metal oxide, which is 2.565 weight percent in the catalyst is due to the trace metal in the raw material, $Mn(NO_3)_2.6H_2O$ (sigma) with 2% of trace metal inside and the impurity in the deionized water (magnesium, calcium and sodium). The XRF result shows the atomic ratio of Mn/Ce is 67/33 which is about 12% error compare to the desired Mn/Ce with atomic ratio 70/30. The reason of 12% error is due to the raw material $Mn(NO_3)_2.6H_2O$ is a strong moisture absorbent and having unpredicted hydrate state (Sigma, year). Low storage temperature (2-8°C) has caused the water moisture in air condenses. The condensate was adsorbed by Manganese Nitrate surface and decreasing the purity of Manganese in the metal salt.

4.3 Crystal structural characteristics of Mn/Ce catalyst revealed by X-ray diffraction analysis

The crystal structural characteristics of Mn/Ce catalyst with atomic ration 67/33 were analysis by using XRD. Figure 4.1 show the comparison between the XRD intensity graph of the synthesized catalyst in the present study, Mn-Ce-1 with the catalysts synthesized by Wolfovich (2006) with atomic ratio 60/40 by calcinations in air (Mn-Ce-WA) at atmospheric pressure and calcinations in vacuum at 85 mbar (Mn-Ce-WV). The figure show the graph profile and the peaks of represent on the XRD intensity graph of Mn-Ce-1 is similar to the XRD intensity graph of Mn-Ce-WV. The sharp peaks indicated the dispersion of manganese oxide and cerium oxide phase.

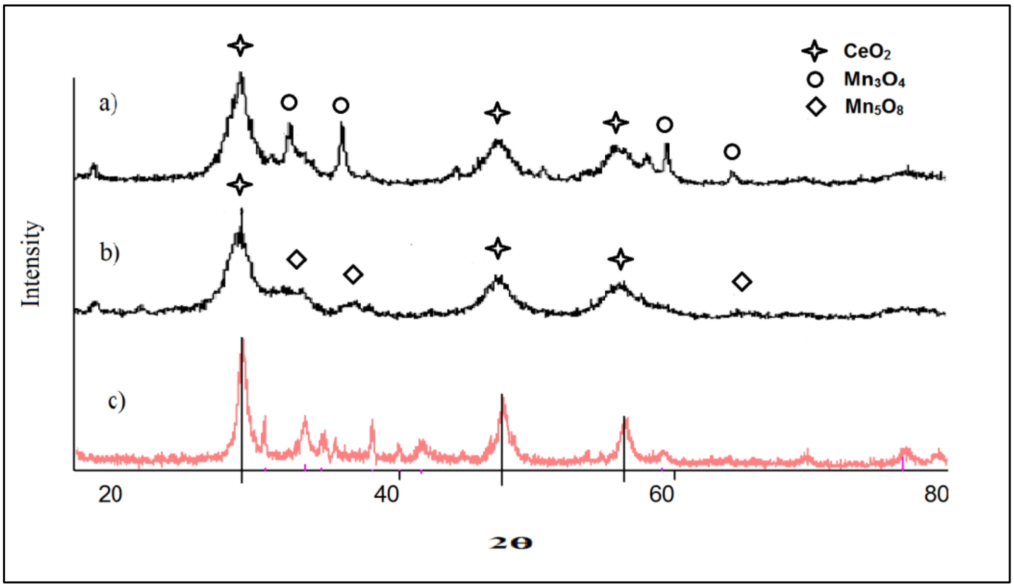


Figure 4.1 X-ray diffractograms of Mn/Ce catalysts: Mn-Ce-WV(a), Mn-Ce-WA(b), Mn-Ce-1 (c).(source: Wolfovich, 2006)

4.4 Surface area and pore volume of Mn/Ce catalyst revealed by BET & BJH

The surface area and pore volume of Mn-Ce-1 (Mn-Ce catalyst with atomic ratio 67/33) were derived from Nitrogen adsorption-desorption isotherms using BET and BJH method. Figure 4.2 is the Isotherm graph for the Nitrogen adsorption-desorption.

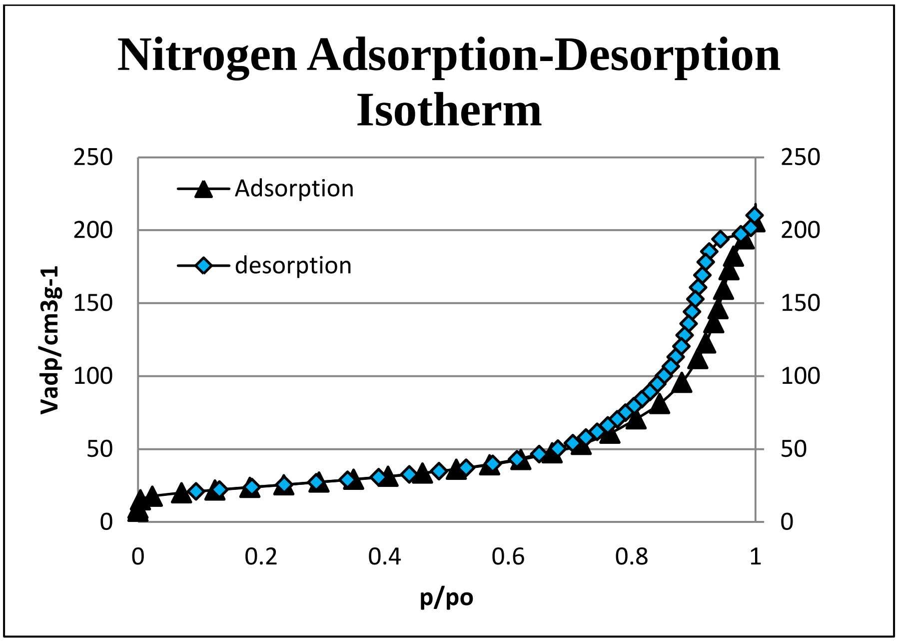


Figure 4.2 Nitrogen adsorption- desorption Isotherm

The sharp of adsorption isotherm shown in Figure 4.1 is similar to the type IV isotherm. The intermediate flat region in the isotherm (around p/p^0 from 0 to 0.01) corresponds to monolayer formation. The low slope region in the middle of the isotherm corresponds to the formation of multilayer and the hysteresis at the end of the graph was correspond to the gases condensation in capillary pore and indicate the presence of mesopores.

The Langmuir model state the surface is of Mn-Ce catalyst is 219.13 m^2g^{-1}. The Langmuir theory was based on the assumption that adsorption is monolayer in nature but in the true picture of adsorption, multilayer formation has to be considered (Hwang & Barron, 2011). Therefore, this theory is only applicable under the conditions of extreme low pressure where monolayer formation on the solid surface. Therefore the result of Langmuir is inaccurate.

BET theory extends the Langmuir theory to multilayer adsorption. BET theory states that multilayer adsorption would occur under the condition of high pressure and low temperature due to the thermal energy of gaseous molecules decreases and more gaseous molecules available per unit surface (Hwang & Barron, 2011). Therefore BET model is well fits to type IV isotherm which isotherm shows the formation of monolayer followed by formation of multiplayer. Besides that, Hwang & Barron (2011) state that type IV isotherm gives the characterization of mesoporus material (pore diameter between 2 to 50nm).

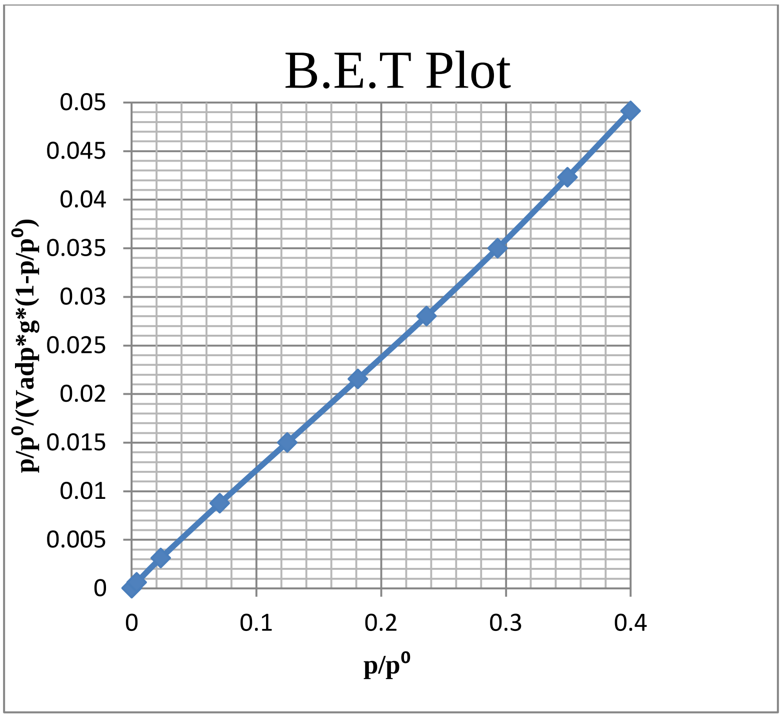


Figure 4.3 B.E.T Plot

The surface area was calculated by using BET method. Figure 4.3 is the BET plot. The calculation used adsorption branch from initial p/p^0 = 0 to final p/p^0 = 0.4 due to the monolayer formation and multilayer formation occur and no gases condensation occur at this region. The calculated specific surface area of the Mn/Ce catalyst with atomic ratio 67/33 is 83.155m2/g, which is lower than the Mn/Ce catalyst synthesis by Wolfovich with atmic ratio 60/40. The reason of the surface area of synthesized catalyst in the present study is lower than the Mn/Ce catalyst synthesis by Wolfovich with atmic ratio 60/40 is due to the dispersion of manganese oxide on the cerium oxide and been discussed at the section 4.1.4.

The pore properties of Mn-Ce catalyst with atomic ration 67/33 was calculated by using mesopores BJH method. The Figure 4.4 is the mesopores B.J.H plot (Groen et al 2003). The calculation used desorption branch from initial p/p^0 = 0.3 to final p/p^0 = 0.95. The calculated cumulative Pore volume is 0.3031cm^3/g^{-1} and the median pore radius is 8.507nm. BJH method is the most widely used for calculation of the pore properties of mesopores material.

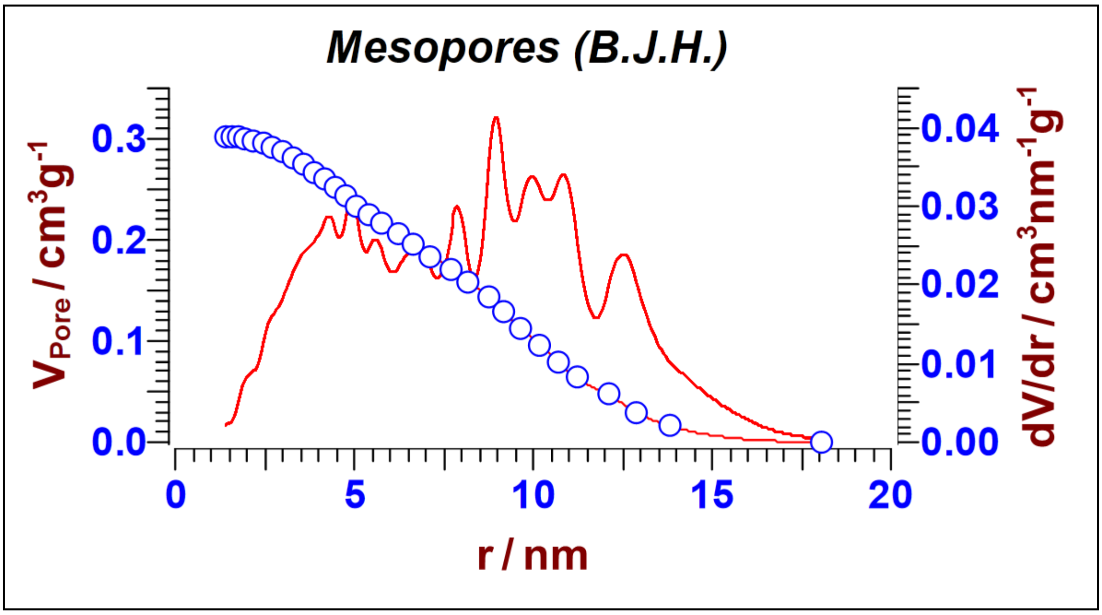


Figure 4.4 Mesopores B.J.H plot

The pore properties of Mn-Ce catalyst with atomic ration 67/33 was calculated by using mesopores BJH method. The Figure 4.4 is the mesopores B.J.H

plot (Groen et al 2003). The calculation used desorption branch from initial p/p^0 = 0.3 to final p/p^0 = 0.95. The calculated cumulative Pore volume is 0.3031cm^3/g^{-1} and the median pore radius is 8.507nm. BJH method is the most widely used for calculation of the pore properties of mesopores material.

4.5 Comparison of catalytic properties of Mn-Ce base catalyst

Table 4.2 show the comparison of catalyst properties between Mn-Ce catalyst with atomic ratio 67/33 (Mn-Ce-1) and Mn/Ce catalyst synthesis by Wolfovich with atomic ratio 60/40 by calcinations in air (Mn-Ce-WA) at atmospheric pressure and calcinations in vacuum at 85 mbar (Mn-Ce-WV).

Table 4.2 Comparison of Catalytic Properties of Mn-Ce Base Catalysts

Catalyst	Mn-Ce-1	Mn-Ce-WV	Mn-Ce-WA
Surface area (m^2g^{-1})	83.155	98	128
Pore diameter (nm)	17.014	14.8	11.5
Pore volume (cm^3g^{-1})	0.3031	0.36	0.37
Mn/Ce atomic ratio	67/33	60/40	60/40

From Table 4.2, Mn-Ce-1 has the smallest surface area (83.155m^2g^{-1}) follow by Mn-Ce-WV (98m^2g^{-1}) and Mn-Ce-WA (128m^2g^{-1}) and the pore volume show the similar trends that Mn-Ce-1 has the smallest pore volume (0.30 cm^3g^{-1}) follow by Mn-Ce-WV (0.36cm^3g^{-1}) and Mn-Ce-WA (0.37cm^3g^{-1}). However the pore diameter of Mn-Ce-1 show the highest value, 17.014nm follow by Mn-Ce-WV, 14.8nm, and Mn-Ce-WA, 11.5nm. From the trends, the surface area of Mn-Ce catalyst is directly proportional to the pore volume but inversely proportional to the pore diameter. The pore volume is derived from the amount of vapour adsorbed at a relative temperature close to unity and calculated by using BJH method. The results obtain are line with the theory, the pore volume is directly proportional to the surface area of the catalyst because larger the volume, higher the porosity of the catalyst and bigger the surface in the pore (Peng & Wang, nd). The pore diameter is inversely proportional to the surface area of catalyst because the pore diameter is estimate from the pore volume by assuming cylindrical pore geometry and using the equation below (Leddy N. 2010):

$$S = \frac{2V_{liq}}{r_p} \quad \text{..Eq 4.1}$$

Where r_p is average pore radius

V_{liq} is the volume of saturated liquid nitrogen in pores

S is the surface area of the catalyst

Therefore, the surface area is inversely proportional to pore diameter but directly proportional to the pore volume.

The study of Cu-Mn-Si catalysts, which done by Zheng et al (2007) was stated that there are two reasons for the high surface area. First is that the silica itself has large surface area, Second is that the copper or manganese are well dispersed on silica leading to the increase of BET surface areas of Copper or manganese. Wolfovich (2006) also state that the relatively high surface area of mixed oxides is determined mostly by CeO_2 phase that displayed a much higher dispersion and comprised of the catalyst by weight. The catalyst synthesized by Wolfovich (2006), Mn-Ce-WA catalysts content 60% weight of CeO_2 and the result of XRF shows that the weight of CeO_2 comprised in Mn-Ce-1 catalyst is 54% only. This explains the reason of Mn-Ce-1 has smaller surface area compare with others.

The preparation method and the raw materials used may affect the catalytic properties of Mn-Ce catalyst. Table 4.3 show the preparation step for each Mn-Ce catalyst.

Table 4.3 Comparison of Synthesis Step of Mn-Ce Based Catalysts

Catalyst	Mn-Ce-1	Mn-Ce-WV	Mn-Ce-WA
Synthesis method	Co-precipitation	Co-precipitation	Co-precipitation
Raw material			
Manganese Salt	$Mn(NO_3)_2.XH_20$	$MnCl_2.4H_20$	$MnCl_2.4H_20$
Cerium Salt	$Ce(NO_3)_3.6H_2O$	$CeCl_3.7H_2O$	$CeCl_3.7H_2O$
Mn/Ce ratio	67/33	60/40	60/40
Precipitation agent	NaOH	NaOH	NaOH
Aging			
Temperature (^oC)	Room temperature	Room temperature	Room temperature
Time (hr)	0.5	0.5	0.5
Stirrer (rpm)	0	0	0
Separation method	Filtration	Filtration	Filtration
Drying			
Temperature (^oC)	100	100	100
Time (hr)	16	16	16
Calcination			
Temperature (^oC)	350	350	350
Time (hr)	3	3	3
Pressure (atm)	1	0.85	1

The Mn-Ce-1 catalyst was prepared by using similar synthesis method and the synthesis condition state by Wolfovich’s (2006)research, only the raw material used is different. The difference anion size of nitrate salt and chloride salt may affect the size of crystal formed. However there is no detail study on the effect of anion salt on the co-precipitation method.

4.6 Catalysts performance in acrylic acid oxidation

Mn-Ce catalyst was tested in a batch reactor. The catalysts tested in atmospheric pressure with optimal CWO Mn/Ce atomic ratio of 7:3 as established in study of (Silva, 2003). This operating condition was selected to test the catalyst activity. The operating conditions include temperatures and initial concentrations of acrylic acid amounts were varied during the study.

4.7 Comparison between Wet Oxidation and Catalytic Wet Oxidation

The catalyst efficiency was measured taking into account the COD concentration of the solution as principal parameter, since the COD is a measure of total quantity of oxygen required to oxidize organic material. Figure 4.5 represents the COD reduction as a function of time for non catalytic wet oxidation and catalytic wet oxidation. Even thought the graph for wet oxidation (without catalyst) and catalytic wet oxidation (5g/L catalyst) are very fluctuating but the COD reduction with catalytic wet oxidation showed slightly increase in COD reduction compare with wet oxidation. The result show that wet oxidation reach to a highest COD reduction of 31.7% at 150 minutes and catalytic wet oxidation reach highest COD reduction 34% at 120 minutes. The research done by Silva et al (2003) reported there is no conversion of Acrylic acid inside a 200^{o}C and 15bar Batch reactor without using catalyst, but the result show that the COD reduction happen in the wet oxidation. By compare the highest COD reduction of catalytic wet oxidation and wet oxidation the COD reduction rate of catalytic wet oxidation are slightly higher than wet oxidation, which mean the activity of Mn-Ce catalyst for conversion of acrylic acid is very low under atmospheric pressure with 50^{o}C. The result is similar as the research done by Kumar et al (2006), which conclude that the catalytic wet oxidation of acrylic acid under atmospheric pressure is not encouraging due to low COD reduction. The study of Kumar et al (2006) also states the maximum 16% COD reduction at atmospheric pressure at 80⁰C with a reaction time of 30 h. However, the COD reduction for both reactions are too fluctuating which mean there are side reactions were happen during the experiment.

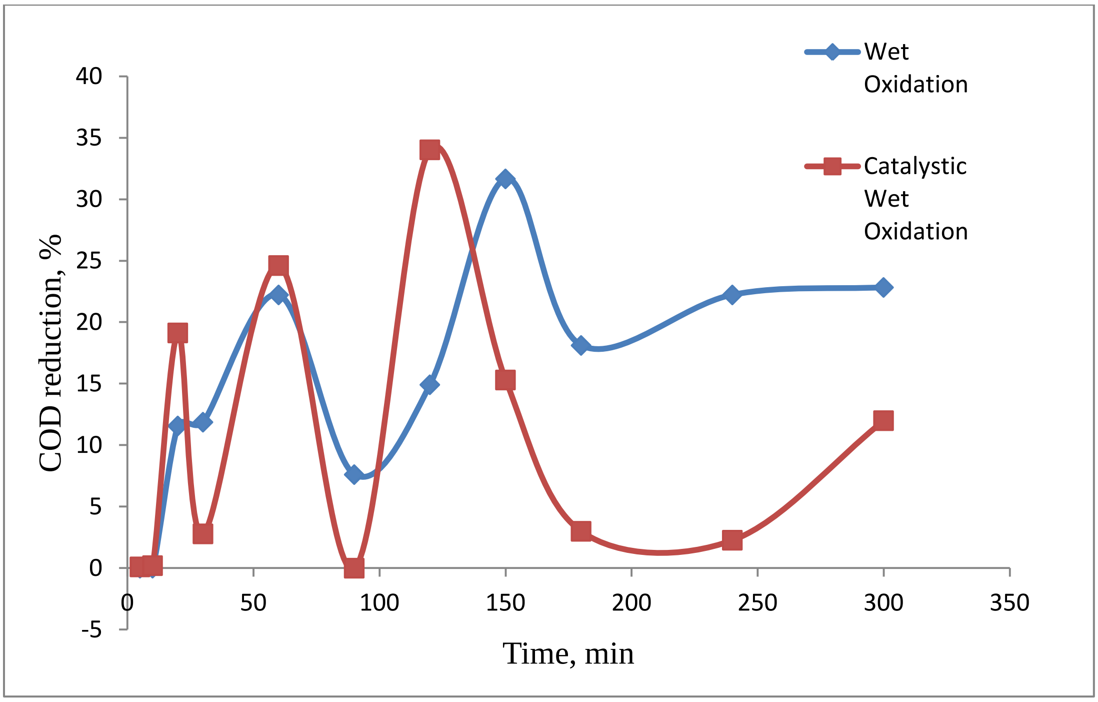


Figure 4.5 COD reduction of wet oxidation and catalytic wet oxidation.

4.8 Side Reaction

The fluctuation of COD reduction for the catalytic wet oxidation in the experiment is abnormal phenomenon was due to the side reactions were happen during the experiment. In heterogeneous oxidation, hydrocarbon molecules activate by adsorption of hydrogen and form an activated hydrocarbon molecular present at the surface of catalyst. The present of oxygen in the gas phase dissolve in the solution became electrophilic oxygen and present at the surface of catalyst to oxidize the hydrocarbon (Wolfovich, 2006). The Full oxidation of hydrocarbon is show below

$$R^{\cdot} + O2 \rightarrow CO2 + H2O$$

Therefore the COD reduction for catalytic wet oxidation should be slowly increased due to the acrylic acid degradation.

4.8.1 Polymerization

Polymerization is one of the undesired reaction may happen in the experiment. Acrylic acid polymerizes easily when exposed to heat, light or metals. Acrylic acid reacts readily with free radicals and electrophilic or nucleophilic agents. Commonly, acrylic acid polymerization involves the following typical steps initiation, propagation and termination. In initiation step, the acrylic acid activates by free radical, electrophilic or nucleophilic agents to initiate a live chain. In propagation step, acrylic acid units add to the live chain the activated acrylic acids, where the hydrogen of one radical is transferred to another added acrylic acid and acrylic acid can be continues added until form a long live polymer chain. The last step is termination step, where the live polymer combines with another free radical or live polymer to form one saturated dead polymer (Li & Schork, 2006). The initiation step was occur when acrylic acid molecules activate by present of catalyst.

However, the polymerization is still happen during the reaction, the figure 4.6(a) show there is a grey colour gluey solid stick on the three necked flask after the experiment. The figure 4.6(b) show that the syringe filter used for filter sample at 30 minutes, 2 hour and 5 hour (from left to right). The amounts of solid on the syringe filter become large from time to time. Both figures prove that the polymerization was happen during the experiment.

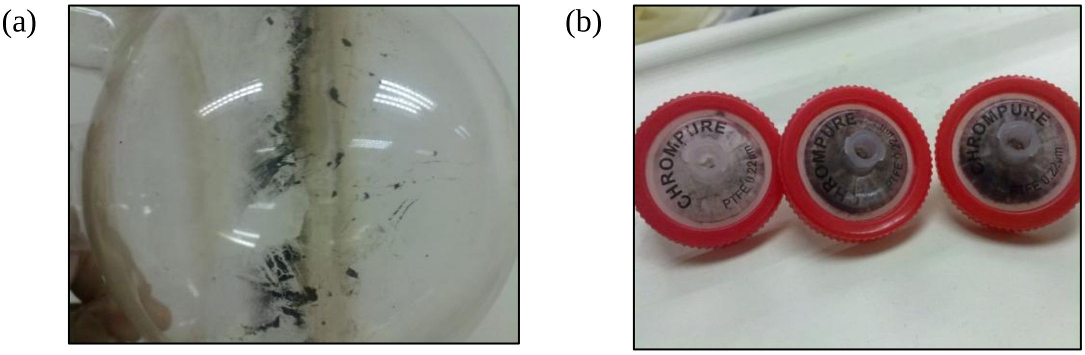


Figure 4.6(a) Gluey solid on the three necked flask; (b) Syringe filter syringe filter used for filter sample at 30 minutes, 2 hour and 5 hour

The acrylic acid (Sigma Aldrich, 99% purity) was stabilized by 200ppm monomethyl ether of hydroquinone (MEHQ) as polymerization inhibitor and used along the experiments. Acrylic acid is miscible in the water and organic solvent, but MEHQ only miscible in organic solvent and partly dissolves in water. The solubility of MEHQ is very low in water, only 40g/L under 200^{o}C (Chemiblink, 20013). Therefore, polymerization was happened during experiment due to the absence of MEHQ in the solution.

The present of polymer, the product of acrylic acid polymerization was affected the COD test. Chemical oxygen demand is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant (Boyles, 1997). Chemical oxygen demand (COD) test uses dichromate, a strong chemical oxidant in an acid solution and heat to oxidize organic carbon. However, some organic compounds are only partially oxidized and some of the organic compounds are not oxidized (Boyles, 1997). A polymer with long carbon chain is partially oxidized in the dichromate; therefore less green chromic ion (Cr3+) is form and spectrophotometer show low COD value. This explain the high conversion (30% ~ 40%) occur within 30 minutes compare with the research done by Kumar et al (2006), the maximum 16% COD reduction at atmospheric pressure at 80^{o}C with a reaction time of 30 h. Besides that, oxidative polymerization may happen during the two hour digestion time and more oxygen is required to polymerise the acrylic acid.

4.8.2 Formation of Carbonic Acid

Carbon dioxide is one of the products produce from the full oxidation of acrylic acid (Wolfvich, 2003). Carbon dioxide is the most common source of acidity in water. Carbon dioxide dissolves in water and form carbonic acid, which is the organic compound with the formula H_2CO_3 (Peavy et al, 1985). Therefore the increasing of COD value does not mean acrylic acids are generated during the experiment, is the formation of carbonic acid occurs during the experiment.

4.9 Comparison between Various Temperatures

The effect of temperature on COD reduction of acrylic acid was studied. Figure 4.7 show the result of COD reduction of Acrylic acid under atmospheric pressure with 5g/L catalyst for different temperature (50⁰C, 70⁰C and 80⁰C).

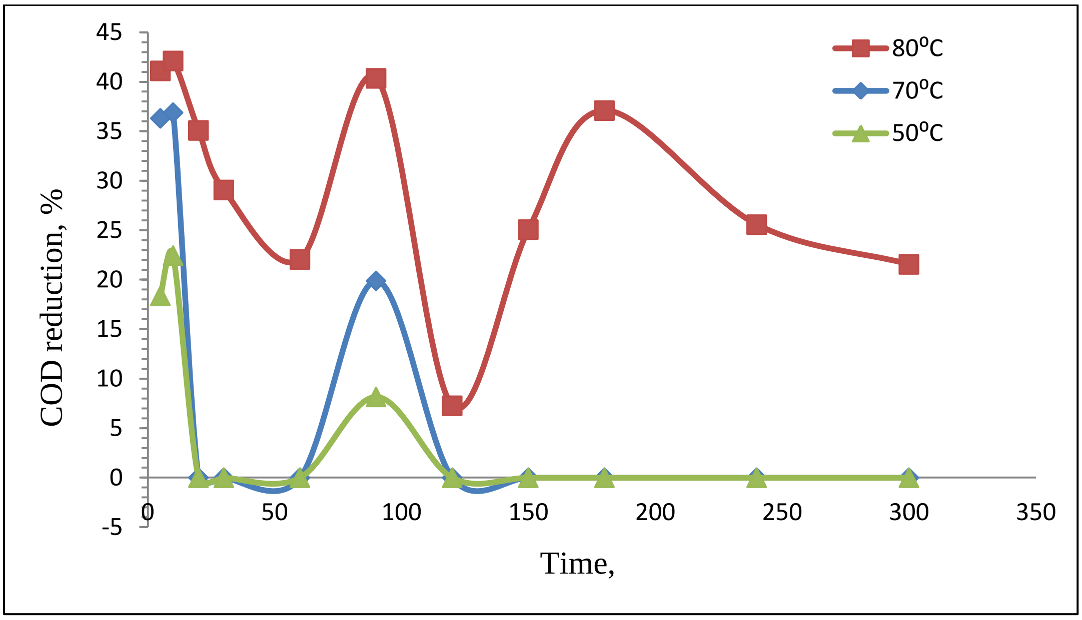


Figure 4.7 COD Reduction with Different Temperature

Figure 4.7 shows that higher temperature would lead to higher conversion. The highest COD conversion for 50⁰C, 70⁰C and 80⁰C was achieved at 10 minutes. The highest COD conversion for operating temperature at 50⁰C is 22.4%, for 70⁰C is 36.9%, and for 80⁰C is 42.1%. However, the trends show that the COD values are increasing rapidly after 10 minute and reduce again after 60 minutes. The second highest COD conversion was achieved at 90 minutes. The COD values are then increasing again. The COD value increase may due to the effect of the formation of carbonic acid during the experiment. Carbon dioxide is one of the products produce from the full oxidation of acrylic acid (Wolfvich, 2003). The increasing of COD value was due to the formation of carbonic acid occurs during the experiment.

4.10 Comparison between Various Acrylic Acid Concentrations

The effect of acrylic acid initial concentration on COD reduction of acrylic acid was studied. Figure 4.8 show the result of COD reduction of Acrylic acid under atmospheric pressure with 5g/L catalyst for various acrylic acid initial concentrations (40000ppm, 20000ppm and 4000ppm).

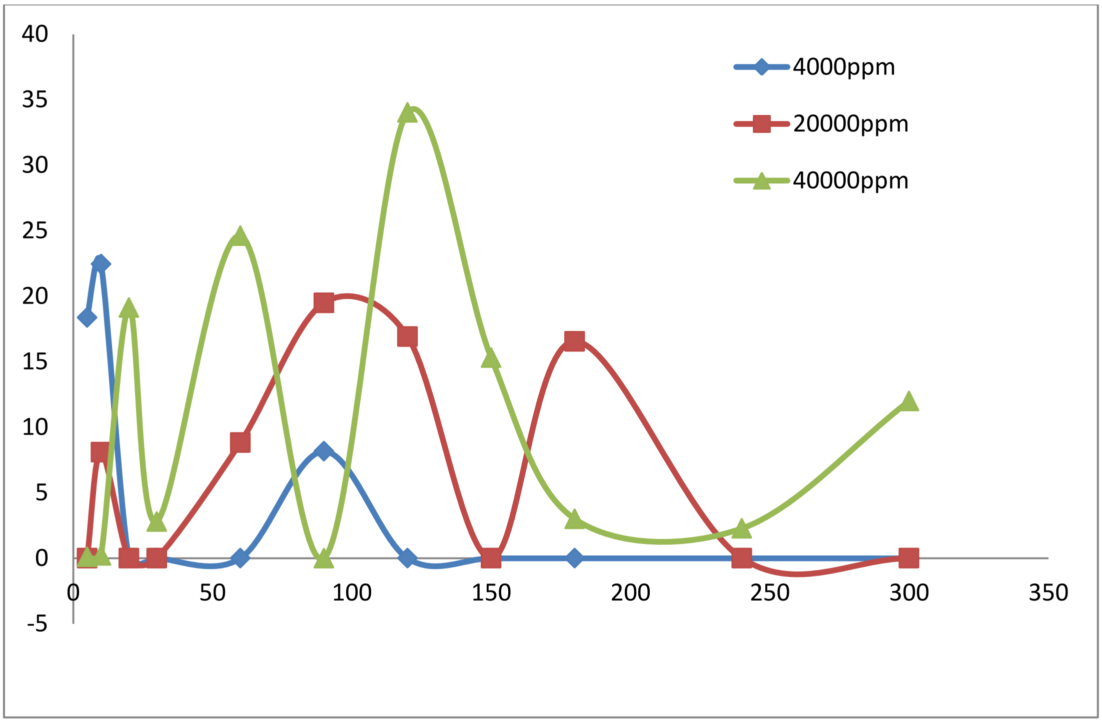


Figure 4.8 COD Reduction with Different Acrylic Acid Initial Concentration

Figure shows that the higher the initial concentration of acrylic acid slower reaches the highest COD reduction could be obtained. For the 40000ppm Acrylic acid concentration, the reaction reaches highest COD reduction at 120 minutes which is slower than 20000ppm concentration of Acrylic acids, 90 minutes and followed by 4000ppm, 10 minutes. This reason of this phenomenal happen is the deactivation of catalyst occurs more rapidly at high acrylic acid concentration (Fogler, 2006). The surface area of catalyst block with carbonaceous matter formed in the pore due to the polymerization of acrylic acid (wolfvoch, 2003). Therefore, higher acrylic acid concentration, expedite the formation of carbonaceous matter and hence accelerate the deactivation of catalyst. Hence, more catalyst might be needed to achieve the same conversion if the initial concentration of AA is higher.

CHAPTER 5

CONCLUSION AND RECOMMENTATION

5.1 Conclusion

The manganese cerium oxide catalyst with Mn/Ce ratio 67/33 was synthesized and characterised. Specific surface area, pore volume, crystal structural and Mn/Ce ratio were determined and compared with the manganese cerium oxide catalyst synthesized by Wolfovich at 2006. The specific surface area and pore volume of the catalyst is $83.155 m^2 g^{-1}$ and $0.3031 cm^2 g^{-1}$. The synthesized catalyst was tested at temperature range, 50 to 80℃ and various initial concentrations of acrylic acid, 4000ppm, 20000ppm and 40000ppm. Althought the synthesized catalyst show a good physical characteristic but the literature COD reduction data was fluctuating due to the side reaction, polymerization and formation of carbonic acid in the reaction.

5.2 Recommendation

There are many others characteristics of the catalyst such as oxidation state, thermal stability and leaching of catalyst can be studied for manganese cerium oxide catalyst. High temperature and water soluble polymerization inhibitor should be used during the experiment to reduce the rate of side reaction. The analysis method such as total organic carbon (TOC) analysis, high performance liquid chromatography (HPLC) and gas chromatography (GC) should be used to obtain more data.

REFERENCES

Adan-Bayewitz, David, Frank Asaro, and Robert D. Giauque (1999). Determining Pottery Provenance: Application of a New High-Precision X-Ray Fluorescence Method and Comparison with Instrumental Neutron Activation Analysis. Archaeometry 41:1-24.

Barbier J., Delanoe, Jabouille, Duprez, Blanchard & Isnard (1998). Total oxidation of acetic acid in aqueous solutions over noble metal catalysts. Retrieved from http://pubget.com/paper/pgtmp_5baad788bfe88c9dd71fa875af398958/Total_oxidation_of_acetic_acid_in_aqueous_solutions_over_noble_metal_catalysts

Barbier J., Oliviero L., Renard B. & Duprez D. (2005). Role of ceria-supported noble metal catalysts (Ru, Pd, Pt) in wet air oxidation of nitrogen and oxygen containing compounds. http://link.springer.com/article/10.1007/s11244-005-2509-1#page-1

Barbier J., Oliviero L., Renard B., Duprez D., Guerrero R.A., Bachiller B.B. & Rodriguez R.I. (2000). Catalytic wet air oxidation of phenol and acrylic acid over Ru/C and Ru–CeO_2/C catalysts. Retrieved from http://www.sciencedirect.com/science/article/pii/S0926337399001411

Biachi, C.L., Ragaini, V., & Carvoli, G. (2002). A new method to clean industrial water from acetic acid via esterification. Retrieved from http://www.sciencedirect.com/science/article/pii/S0926337302001443

Boyles W. (1997). The science of chemical oxygen demand – technical information series, booklet no. 9 Retrieved from http://www.hach.com/asset-get.download-en.jsa?code=61786

Bruker AXS (2001). Introduction to powder X-ray diffraction Retrieved from http://www.smcr.fisica.unam.mx/8temasutiles/articulosutiles/Bas-XRD.pdf

Chemblink. (2013). Chemical list- 4-methoxyphenol. Retrieved from http://www.chemblink.com/products/150-76-5.htm

Coppen, J. (2004). ADVANCED WASTEWATER TREATMENT SYSTEMS. Retrieved from http://pssurvival.com/PS/Water/Waste/Advanced_Wastewater_Treatment_Systems_2004.pdf

Debellefontaine, H & Foussard, J. N. (2000). Wet air oxidation for the treatment of industrial application in europe. Waste manage. 20, 15-25 . Retrieved from http://www.researchgate.net/publication/222690818_Wet_air_oxidation_for_the_treatment_of_industrial_wastes._Chemical_aspects_reactor_design_and_industrial_applications_in_Europe

Düzenli D. (2010). Development of sol-gel catalysts by use of fast combinatorial synthesis and high throughput testing Techniques for catalytic oxidation of propylene to propylene oxide. Retrieved from https://etd.lib.metu.edu.tr/upload/12612675/index.pdf

Fogler, 2006 Catalyst Decay.Retrieved from http://www.umich.edu/~essen/html/byconcept/cdchap/10chap/ECRE_CD-CH10.pdf

Groen J.C., Peffer L.A.A., Perez R.J. (2003) Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis http://144.206.159.178/ft/748/92429/14465368.pdf

Haber J., Block J.H.,& Delmon B. (1995). Manual Of Methods And Procedures For Catalyst Characterization. Retrieved from http://pac.iupac.org/publications/pac/pdf/1995/pdf/6708x1257.pdf

Hendricks. D. (2006). Water treatment unit processes, physical and chemical. Boca Raton, londan and new York: taylor & francis

Howard, S. P., Donald, R. R. & George, T. 1985. Environmental Engineering. McGraw-Hill. Singapore.

Hwang N. and Barron A.R. (2011). BET Surface Area Analysis of Nanoparticles Retrieved from http://cnx.org/content/m38278/1.1/

ICDD. (2013). Electron Diffraction. Retrieved from http://www.icdd.com/resources/tutorials/index.htm

Imamura, S.(1999). Industrial and Engineering Chemistry Product Research and Development. American Chemical Society.

Kaewpuang-Ngam S., Inazu K., Kobayashi T. & Aika K. (2004). Selective wet-air oxidation of diluted aqueous ammonia solutions over supported Ni catalysts

Kawabata, N., Yasuda, S., Yamazaki, T. (1982), US patent 4323702.

King L. Y. (nd). Catalyst Design and Preparation. Department of Chemical Engineering Hong Kong University of Science and Technology. Retrieved from http://teaching.ust.hk/~ceng510/notes/CENG511/Lecture7.pdf

Kumar P., Raghavendra P. V. K. & Chand S. (2006) Catalytic wet oxidation of carboxylic acid present in waste water. Retrieved from http://nopr.niscair.res.in/bitstream/123456789/4971/1/JSIR%2065(10)%20 838-842.pdf

Leddy N. (2012) Surface area and porosity. Retrieved from http://www.tcd.ie/CMA/misc/Surface_area_and_porosity.pdf

Lee B.N., Lou J.C. & Yen P.C. (2002). Catalytic wet oxidation of 2,4-dichlorophenol solutions: activity of the manganese-cerium composite catalyst and biodegradability of the effluent stream. Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/11995864

Lee D.K., Song B.K., Jeong S.E., Kim D.S., Kim T.H., Le Y.K., Le N.T., Cho M.J., & Henam S.D. (200. Catalytic Wet Oxidation of Phenol Using Regeneration of Pt/Al2O3. Retrieved from https://www.jstage.jst.go.jp/article/jpi/53/3/53_3_184/_pdf

Levec, J., & Pintar, A. (2007). Catalytic wet-air oxidation processes: A review. Catalysis Today 124, 172–184. Retrieved from http://www.sciencedirect.com/science/article/pii/S092058610700199X

Li R. & Schork F.J. (2006). Modeling of the Inhibition Mechanism of Acrylic Acid Polymerization Retrieved from http://pubs.acs.org/doi/abs/10.1021/ie0512439

Luck, F. (1999). Wet air oxidation: past, present and future, Catal. Today 53, 81-91. Retrieved from http://www.ingentaconnect.com/content/els/09205861/1999/00000053/00000001/art00112

MARLAP (2004). Separation techniques. Retrieved from http://www.epa.gov/radiation/docs/marlap/402-b-04-001a-01-final.pdf

National Institute of Health Sciences, NISH. (nd). Environmental Health Criteria for Acrylic Acid. Retrieved from http://www.inchem.org/documents/ehc/ehc/ehc191.htm#SectionNumber:10.2

National Pollutant Release Inventory, NISH (2012). Acrylic acid: Overview. Retrieved from http://www.npi.gov.au/substances/acrylic-acid/index.html

Nor Habibah Binti Mohd Rosli. (2006). Development of biological treatment system for reduction of cod from textile wastewater. Retrieved from http://eprints.utm.my/4902/1/NorHabibahMohdRosliKPFS2006TTT.pdf

Norcross. (nd). Gas Absorption Theory. micromeritic Instrusment Corporation.

Oliviero, L., Barbier Jr.J., Duprez, D., Guerrero-Ruiz, A., Bachiller-Baeza, B., & Rodr´ıguez-Ramos, I. (1999). Catalytic wet air oxidation of phenol and acrylic acid over Ru/C and Ru–CeO2/C catalysts. Applied Catalysis B: Environmental 25, 267–27. Retrieved from http://www.sciencedirect.com/science/article/pii/S0926337399001411

Peavy H., Rowe D.R., Tchobanoglous G. (1985). Environmental Engineering . McGRAW-HILL. Singapore.

Peng J & Wang c.h. (nd) An Investigation on the Influence of Pore Size and Porosity of Sponge on Maximum Cell Concentration Retrieved from http://www.nus.edu.sg/nurop/2010/Proceedings/FoE/Peng%20Jiajie.pdf

Perego C.& VillaP. (1997)Catalyst preparation methods. Retrieved from http://chemistits.files.wordpress.com/2008/07/catalyst-preparation-methods-perego1.pdf

Qin J., Zhang Q. & Chuang K.T. (2001). Catalytic wet oxidation of p-chlorophenol over supported noble metal catalysts. Retrieved from http://www.sciencedirect.com/science/article/pii/S0926337300002009#

Rice, Prudence M. (1987). Pottery Analysis: A Sourcebook. University of Chicago Press, Chicago.

Scintag inc. (1999). Chapter 7: basics of X-ray diffraction. Retrieved from http://epswww.unm.edu/xrd/xrdbasics.pdf

Sigma-Aldrich, (2013). Manganese(II) nitrate hydrate MSDS Retrieved from http://www.sigmaaldrich.com/catalog/product/aldrich/203742?lang=en&region=MY

Silva A.M.T., Isabel M. Castelo-Branco, Rosa M. Quinta-Ferreira & Janez Levec (2003). Catalytic studies in wet oxidation of effluents from formaldehyde industry. Retrieved from https://estudogeral.sib.uc.pt/bitstream/10316/3816/1/file64404e2a704643f1b6644bde58b319f4.pdf

Silva A.M.T., Oliveira A.C.T. & Quinta-Ferreira R.M. (2004). Catalytic wet oxidation of ethylene glycol: kinetics of reaction on a Mn–Ce–O catalyst. Retrieved from http://www.sciencedirect.com/science/article/pii/S0009250904006347

Silva, A.M.T., Marques, R.R.N., Quinta-Ferreira, R.M. (2003) Catalysts based in cerium oxide for wet oxidation of acrylic acid in the prevention of environmental risks. Applied Catalysis B: Environmental 47, 269–279. Retrieved from https://estudogeral.sib.uc.pt/bitstream/10316/3811/1/file4dbbd3a33b634e939b780b02a6046572.pdf

Speakman, (nd). Basics of X-ray Power diffraction. Retrieved from http://prism.mit.edu/xray/Basics%20of%20X-Ray%20Powder%20Diffraction.pdf

Trunschke A. (2007). Surface area and pore size determination. Retrieved from http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2007_2008/trunschke_surface_area_pores_191007.pdf

U.S. Environmental Protection Agency (1994). Chemical summary for acrylic acid. Retrieved from http://www.epa.gov/chemfact/s_acrlac.txt

Vallet A, Ovejero G., Rodriguez A., Peres J.A., Garcia J. (2012). Ni/MgAlO regeneration for catalytic wet air oxidation of an azo-dye in trickle-bed reaction.

Wang J.B, Zhu W.P, Wang W. & Yang S.X. (2007). Catalytic wet air oxidation of phenol with Ru/ZrO2-CeO2 catalyst. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/17891952

Wang, L. K., Huang, Y., Shammas, N.K. (2007). Advanced physicochemical treatment technologies. Totowa, new jersey: humana press

WBK & Associates Inc. (2002). Assessment report on acrylic acid for developing an ambient air quality guideline. Retrieved from http://www.assembly.ab.ca/lao/library/egovdocs/alen/2002/140570.pdf

Wolfovich, M. A. (2006). Catalytic Wet Oxidation of Phenol and its Halogenated Derivatives on Nanostructured Metal Oxides. Retrieved from http://aranne5.lib.ad.bgu.ac.il/others/Abecassis-WolfovichMeyrav.pdf

Zacharia P.G.M. (2004). Catalytic wet oxidation of organic wastes using platinum catalysts. Retrieved from http://alexandria.tue.nl/extra2/200411596.pdf

Zheng H.Y., Zhu Y.L., Huang L., Zeng Z.Y., Wan H.J. & Li Y.W.(2007). Study on Cu–Mn–Si catalysts for synthesis of cyclohexanone and 2-methylfuran through the coupling process. Retrieved from http://144.206.159.178/FT/11730/539224/12529988.pdf

APPENDIX A

X-Ray Fluorescence Result

No	Metal/Metal oxide	Result	Unit	Test method
1	Cerium Oxide (CeO2)	58.74	%	Quantexpress (Best Detection)
2	Manganese Oxide (MnO)	49.42	%	Quantexpress (Best Detection)
3	Sodium Oxide (NaO2)	0.80	%	Quantexpress (Best Detection)
4	Europium Oxide (Eu2O3)	0.59	%	Quantexpress (Best Detection)
5	Calcium Oxide (CaO)	0.43	%	Quantexpress (Best Detection)
6	Silicon Dioxide (SiO2)	0.29	%	Quantexpress (Best Detection)
7	Neodymium Oxide (Nd2O3)	0.26	%	Quantexpress (Best Detection)
8	Magnesium Oxide (MgO)	0.15	%	Quantexpress (Best Detection)
9	Sulphur Trioxide (SO3)	0.10	%	Quantexpress (Best Detection)
10	Aluminium Oxide (Al2O3)	0.09	%	Quantexpress (Best Detection)
11	Rhodium (RH)	0.04	%	Quantexpress (Best Detection)
12	Nickel Oxide (NiO)	0.04	%	Quantexpress (Best Detection)
13	Cobalt Oxide (CoO)	0.02	%	Quantexpress (Best Detection)
14	Vanadium Oxide (V2O5)	0.02	%	Quantexpress (Best Detection)
15	Copper Oxide (CuO)	99	ppm	Quantexpress (Best Detection)
16	Rubidium Oxide (Rb2O)	45	ppm	Quantexpress (Best Detection)
17	Zirconium Oxide	32	ppm	Quantexpress (Best Detection)

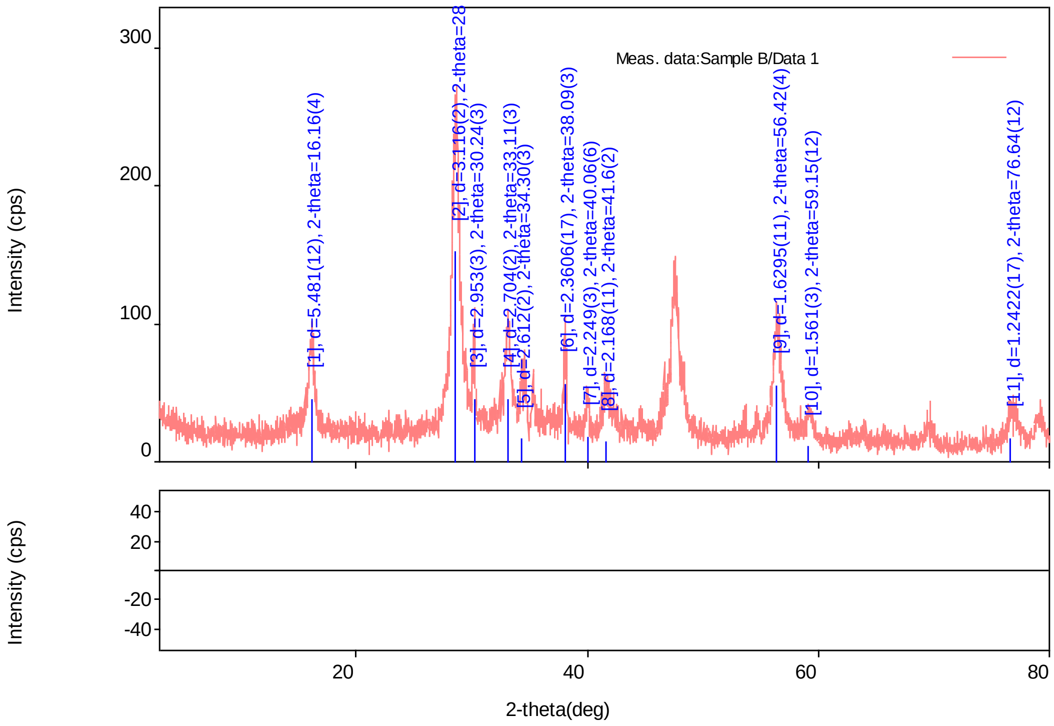
APPENDIX B

X-ray Diffraction Analysis Results

General Information

Analysis date	11/6/2012 9:57:11 AM		
Sample name	XRD Analysis	Measured time	10/21/2012 4:10:33 PM
File name	Sample B.raw	Operator	administrator
Comment	UMP		

Measurement profile



APPENDIX C

BET and BJH result

Analytical Conditions

Blank done with: Helium

Adsorbate: Nitrogen

Adsorption data

p/p^o	V ads cm3/g-1
8.80E-05	7.3463
0.00015	9.4406
0.0041	15.236
0.0234	17.702
0.0707	20.051
0.1248	21.949
0.1814	23.759
0.2364	25.532
0.2934	27.416
0.3494	29.337
0.4052	31.362
0.461	33.588
0.5158	36.188
0.5697	39.235
0.6203	42.857
0.671	47.471
0.7181	53.204
0.7646	60.904
0.807	70.737
0.8451	81.216
0.881	95.754
0.9069	112.04
0.9197	122.76
0.9328	136.64
0.9397	146.25
0.9486	159.52
0.9575	172.95
0.9647	182.22
0.982	194.09
0.9996	205.83
1.0001	217.83

Desorption Data

p/p^o	V ads cm3/g-1
210.18	0.9989
201.61	0.9928
197.19	0.9767
193.89	0.9436
185.41	0.9255
178.19	0.9198
169.19	0.9144
160.81	0.9074
152.8	0.903
144.14	0.8975
135.95	0.892
128.04	0.8856
120.43	0.8803
113.15	0.8711
106.64	0.8632
100.22	0.852
94.632	0.8413
89.126	0.8293
84.17	0.8162
79.408	0.8034
74.949	0.7897
70.388	0.7764
66.214	0.7612
61.838	0.7439
57.906	0.7257
54.031	0.7045
50.303	0.6803
46.546	0.65
42.984	0.614
39.836	0.5747
37.175	0.5317
34.836	0.4877
32.624	0.4396
30.707	0.39
28.932	0.3396
27.238	0.289
25.573	0.2371
23.923	0.1847
22.231	0.1321
20.999	0.0942

APPENDIX D

COD value

Concentration AA	4000ppm	
Temperature	70^{o}C	
Time	COD	COD reduction %
0	17350	0
5	11050	36.31124
10	10950	36.88761
20	17350	0
30	17350	0
60	17350	0
90	13900	19.88473
120	17350	0
150	17350	0
180	17350	0
240	17350	0
300	17350	0

Concentration AA	4000ppm	
Temperature	80^{o}C	
	COD	COD reduction %
0	19950	0
5	11750	41.10276
10	11550	42.10526
20	12950	35.08772
30	14150	29.07268
60	15550	22.05514
90	11900	40.35088
120	18500	7.26817
150	14950	25.06266
180	12550	37.09273
240	14850	25.56391
300	15650	21.55388

Concentration AA	4000ppm	
Temperature	$50^{o}C$	
Time	COD	COD reduction %
0	19600	0
5	16000	18.36735
10	15200	22.44898
20	19600	0
30	19600	0
60	19600	0
90	18000	8.163265
120	19600	0
150	19600	0
180	19600	0
240	19600	0
300	19600	0

Concentration AA	40000ppm	
Temperature	$50^{o}C$	
Time	COD	COD reduction %
0	65700	0
5	65700	0
10	65700	0
20	58100	11.56773
30	57900	11.87215
60	51100	22.22222
90	60700	7.61035
120	55900	14.91629
150	44900	31.65906
180	53800	18.11263
240	51100	22.22222
300	50700	22.83105

Concentration AA	20000ppm	
Temperature	$50^{o}C$	
Time	COD	COD reduction %
0	27200	0
5	27200	0
10	25000	8.088235
20	27200	0
30	27200	0
60	24800	8.823529
90	21900	19.48529
120	22600	16.91176
150	27200	0
180	22700	16.54412
240	27200	0
300	27200	0