OXIDATION OF ETHANOL AND CARBON MONOXIDE ON ALUMINA - SUPPORTED METAL/METAL OXIDE XEROGEL CATALYSTS

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Selcan ATEŞ

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We approve the thesis of **Selcan ATEŞ**

Assoc.Prof.Dr. Erol ŞEKER
Supervisor

Prof.Dr. Sacide ALSOY ALTINKAYA
Committee Member

Prof.Dr. Levent ARTOK
Committee Member

16 December 2011

Prof.Dr. Mehmet POLAT
Head of the Department of
Chemical Engineering

Prof.Dr. R. Tuğrul SENGER
Dean of the Graduate School of
Engineering and Sciences

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ABSTRACT

OXIDATION OF ETHANOL AND CARBON MONOXIDE ON ALUMINA-SUPPORTED METAL/ METAL OXIDE XEROGEL CATALYSTS

The main goal of the study is to investigate the effect of metal type, metal oxide type and metal/oxide loading on the conversion as a function of temperature for the complete combustion of ethanol and CO in air over single step sol-gel made Al_2O_3 supported metal and mixed metal oxides. Two types of catalysts, Pt/Al_2O_3 (1, 2, and 3 % Pt loaded) and $CuO\text{-}Mn_2O_3/Al_2O_3$, with Cu/Mn molar ratio of 1:1, 5:1 and 12:1, and 50, 70, and 90% metal loading, were synthesized by impregnation and single step sol-gel methods, respectively. In addition, by synthesizing CuO/Al_2O_3, Mn_2O_3/Al_2O_3 and $Pd\text{-}Mn_2O_3/Al_2O_3$, the catalytic activity relationship between metal and metal oxides were clarified.

Characterization of the samples was performed by XRD, BET, and FT-IR techniques and it was observed that among the metal oxide catalysts, $CuO\text{-}Mn_2O_3/Al_2O_3$ (70 wt%; $(Cu/Mn)_{molar}=1$) showed the highest activity due to the formation of $Cu_{1.5}Mn_{1.5}O_4$ phase while 3% Pt loaded alumina was the catalyst demonstrated the highest catalytic activity among the noble metal catalysts. Also, Pd addition enhanced the activity of metal oxide catalyst by lowering the temperature at which ~99% ethanol conversion was obtained. Moreover, deactivation of $CuO\text{-}Mn_2O_3/Al_2O_3$ mixed oxides was observed due to the irreversible adsorption of CO_2 on catalyst surface at low temperatures.

Except for Pt containing catalysts, the catalysts that showed high catalytic activity in ethanol oxidation was also tested for CO oxidation and CO_2 formation was detected qualitatively at varying operating temperatures.

ÖZET

ALUMİNA-DESTEKLİ METAL/METAL OKSİT XEROGEL KATALİZÖRLERİ ÜZERİNDE ETANOL VE KARBONMONOKSİT OKSİDASYONU

Bu çalışmanın asıl amacı, havadaki etanol ve karbonmonoksit'in tek basamaklı sol-gel yöntemiyle yapılan alumina destekli metal ve karışık metal oksit üzerindeki tam yanmasında; metal çeşidinin, metal oksit çeşidinin ve metal/oksit yüklemesinin sıcaklığa bağlı dönüşüm üzerindeki etkisini incelemektir. İki çeşit katalizör, Pt/ Al_2O_3 (%1, %2 ve %3 Pt yüklenmiş) ve Cu/Mn mol oranları 1:1, 5:1 ve 12:1; metal yüklemeleri % 50, % 70 ve % 90 olan CuO-Mn_2O_3/Al_2O_3, sırasıyla impregnasyon ve tek basamaklı sol-gel metodlarıyla sentezlenmiştir. Ayrıca, CuO/Al_2O_3, Mn_2O_3/Al_2O_3 and Pd-Mn_2O_3/Al_2O_3 sentezlenerek, metal ve metal oksitler arasındaki katalitik aktivite ilişkisine açıklık getirilmiştir.

Örneklerin karakterizasyonu XRD,BET ve FT-IR teknikleri kullanılarak yapılmıştır ve soy metal katalizörleri arasında % 3 Pt yüklenmiş alumina yüksek aktivite gösteren katalizör iken, metal oksit katalizörleri arasında, CuO-Mn_2O_3/Al_2O_3 (%70 ;$(Cu/Mn)_{mol}$=1:1) katalizörünün $Cu_{1.5}Mn_{1.5}O_4$ faz oluşumu sebebiyle en iyi aktivite gösterdiği gözlenmiştir. Ayrıca, Pd ilavesi ~ %99 etanol dönüşümünün olduğu sıcaklığı düşürerek metal oksit katalizörünün aktivitesini artırmıştır. Bunun yanı sıra, katalizör yüzeyi üzerinde tersinir olmayan CO_2 adsorpsiyonundan kaynaklanan CuO-Mn_2O_3/Al_2O_3 deaktivasyonu tespit edilmiştir.

Pt içeren katalizör hariç, etanol oksidasyonunda iyi aktivite gösteren katalizörler aynı zamanda CO oksidasyonu için de test edilmiş ve değişen sıcaklıklarda CO_2 oluşumu kualitatif olarak tespit edilmiştir.

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CHAPTER 1

INTRODUCTION

Throughout the history, the urbanization and improvements in the living conditions along with the increase of the life expectancy of human beings have resulted in urgent needs for producing and developing novel products/methods to sustain healthy growth of the population. This hence has led a rapid consumption of the natural resources and also caused an adverse change on the environment. Due to the developments in industry, toxic exhaust gases emitted by the vehicles and the production of power have caused a serious change in the natural balance; hence, increasing environmental problems. In addition, day by day, these problems together with increasing population and high amount of toxic gases in the atmosphere have reached to dangerous levels for human beings. In this sense, most of volatile organic compounds (VOCs), which include over a thousand of different organic and inorganic molecules, contribute to the rise of hazardous pollutants in air. Since almost all of industrial products are made up of organic chemicals, VOCs present in the atmosphere are mainly due to consumer products, chemical industries, organic solvents and combustion sources depending on hydrocarbon fossil fuels. In the developed countries, such as USA, fossil fuels, such as coal, oil, and natural gas, which supply the great amount of world primary energy needs are major energy sources for transportation fuels, electricity, heat, and air-conditioning. However, the combustion of fossil fuels in chemical processes leads to the emission of carbon monoxide, nitrogen oxides, and organic by-products into air due to incomplete combustion and imperfect air/fuel mixing. Emission of fossil fuels combustion products, particularly nitrogen oxides (NO_x) and VOCs, are much more dangerous for environment since the combination of these pollutants (VOC and NO_x) in the atmosphere cause acidic rain and photochemical smog where nitrogen oxides and VOCs react together to produce ozone and peroxy compounds in the presence of sunlight. Therefore, by-products and unused reactants, VOCs emitted from fossil fuels, industrial process and motor vehicle exhausts accumulate in the atmosphere and being an important challenge for the societies to solve. Additionally, in the next decades, without policies, this accumulation is expected to reach dangerous levels for living creatures as a result of high volatility, toxicity, reactivity and persistence of these organic gases. In light of these characteristics, it is vitally important to take precautions for these organic gas emissions either to control the air quality or to maintain good human health.

For the last decades, besides, progressive increase of VOCs emissions, information about their effects on human health, accumulations and their role in the formation of photochemical smog make governments act together and force them to determine stricter regulations as well as efficient and economic methods for the reduction of these pollutants' emission. Since problems related to hazardous organic compounds in air are one of the major concerns for the globe as well as local regions, control strategies and regulations for improvement of air quality approach the problems on an international and regional basis due to long distance travel of some organic pollutants from source regions. Despite of applying stricter regulations as well as economic and efficient types of methods and techniques to control VOC emission and their cross-border, in some part of the world, emissions are still increasing due to industrial and commercial processes' by-products. Thus, it's expected that Chinese VOCs emissions from solvents and paints will be about 5 times higher in 2020, compared to 1990 (Klimont et al., 2002).

As well as the great amount of VOCs emitted from different types of emission sources, there are many highly toxic chemical organics (e.g. polycyclic aromatic hydrocarbons) released in small (even extremely small) quantities in the atmosphere. Apart from damage caused when exposed to high concentrations, even minute amounts of them may have strong effect on human health, animals, and vegetation. It's reported that methane, which is the lightest volatile organic, is almost 20 times more effective green house gas than its complete oxidation product, carbon dioxide (Bunce, 1991). It's expected that reducing significant amount of methane concentration within a decade could give much more quick and significant result than similar reductions in CO_2 emission. Thus, carbon oxides may be released to the environment with minimal environmental implications compared to the release of the VOCs themselves. However, it's primarily important and necessary to understand the nature of the gases emitted into air and the chemical transformations they undergo before take a necessary action for reduction of toxic gas emission. In this regard, it is reported that high concentration of organic compounds are generally not removed efficiently (Junge, 1974) and also their life time in the atmosphere are important factor as some can continue to be present in the atmosphere for thousand years, while others can be consumed in a minute after they have been emitted. For instance, lifetime of carbon dioxide in air is between 50 and 200 years, while it is 12 years for methane and is about 3,200 years for sulfur hexafluoride (UNFCCC). In addition to this, VOCs concentrations in urban and rural sites show differences due to atmospheric transportation and regional sources of these hazardous gases. Benzene level in the atmosphere, for example, might be exposed to 1000 times the levels measured in remote regions (OECD, 1994). However, whether these gases have very small amount in the air or not, it should be taking into the account that, these gases and their effects, heat-holding potential and addition to global warming will continue. In this regard, for the last decades, concerns about increasing amount of VOCs in the air have catalyzed several countries including European, Canadian, and U.S governments to implement national emission policies either to reduce hazardous pollutant levels or to meet air quality standards for clean environment. In 1990, in United States of America, the US Clean Air Act called for a 90% reduction by 1998 in the emissions of 189 toxic chemicals, 70 % of which were classified as VOCs (Parkinson, 1991). For that call, Environmental Protection Agency (EPA), working for cleaner environment for many years, has been implementing reduction programs to reduce emissions from different type of mobile and stationary sources. In addition to applied national action programs, international agreements and plans have also been accepted around the world. Therefore, total emissions of VOCs, released from different type of emission sources, are decreasing for many years in European countries.

Although regulations vary considerably from country to country, recent policy developments to control the level of hazardous organics in the atmosphere is mainly based on economic and regulatory instruments, air quality standards, risk limits of compounds for both health and environment, and technological improvements. A series of protocols establishing reduction objectives and signatories on international agreements show differences between countries policies as a result of application sequences and starting point of the regulatory procedure. In this way, national legislation is already in place or being drafted in many European countries. For instance, in the United Kingdom, in 1990s, it was covered by the Environmental Protection Act. In Netherlands, quantitative risk assessment was used primarily, whereas a technology driven approach for setting emission standards was used in Germany, Sweden, and Switzerland, complemented by environmental standards or ambient air quality standards (Wiederkehr, 1994). In addition, currently, many countries including France, Germany, United Kingdom, and Sweden have already reached emission levels far below their Kyoto target (EEA Technical Report, 2009).

Global concerns about the environmental issues and governments restrictive regulations have encouraged the development of effective and economic methods in the reduction of volatile organic compounds (VOCs). However, as in many industrial plants, vest streams show differences in volumes, flow rates, temperatures, compositions, physical and chemical properties of VOCs with respect to their emission sources. Basically, emission control techniques depending on process and equipment modifications, are generally used to minimize the volatilization or formation of VOCs or to prevent the escape of these gases in which operation takes place in the process. However, it is not always possible to modify the process or process equipments easily. On the other hand, to minimize the emission and control the process, emission sources can be either identified or modified and organic solvents used in the process can be replaced or minimized to the milder levels. However, the efficient removal of volatile organic compounds from sources such as waste streams, tank loading/unloading operations, sometimes is a challenging problem with some pollution abatement technologies due to VOCs containing streams with a wide range of concentrations. Therefore, the variation in the nature of existing VOC compounds and their physical and chemical properties, have given rise to a corresponding wide range of VOC control methods that can be classified into two groups based on two approaches. The first is VOCs destruction method that they are generally destroyed to carbon dioxide and water and the second one is VOCs recovery methods in that they are captured for reuse and subsequent disposal. Common type of VOC control techniques and their operating conditions are shown in Table 1.1. However, it should be kept in mind that operating conditions may change as a function of the type and concentration of material. In addition, due to the potential explosion hazards, inlet concentrations in excess of 25% of the LEL (Lower Explosive Limit) should be avoided (AIChE, 1992).

Table 1.1. VOCs destruction methods and conditions
(Khan, 2000)

		VOC Concentration (ppm)	Temperature (^{o}F)	Removal Efficiency (%)
Destruction Methods	Catalytic Incineration	100-1000,but always less than 25% of LEL	300	90-98
	Thermal Incineration	Greater than 20 but less than 25% of LEL	700	95-99
	Bio-filtration	<5000	50-105	60-95
Recovery Methods	Absorption	500-15000	Normal	95-98
	Adsorption	700-10000 but always less than 25 % of LEL	<130	80-90
	Condensation	5000-10000	Ambient	70-85

In detail, condensation technique for the recovery of VOCs is one of the efficient and safe alternatives for VOCs recovery. It requires high concentration of volatile organics, of which boiling points above 100 ^{o}F, and having low gas flow rates. Thus, its commercial applicability is limited.

Adsorption of VOCs, classified as physical adsorption and chemisorption, is based on the interaction between adsorbate and adsorbent to separate dilute organic compounds from waste streams. Activated carbons, zeolites, silica gel and alumina are mostly used types of adsorbent and among them, activated carbons provide one of the best options due to their high surface area. In most cases, adsorption control technique is used for recovery of expensive and unreacted raw material treatments. However, efficiency reaches 95 % to 98 % when treating waste streams contain single compounds or relatively simple mixtures of compounds of which concentrations ranging from 10 ppm to 10,000 ppm. Therefore, in industrial process adsorption-based methods are favorable for removal of low concentration of hydrocarbon vapors from gaseous stream. Also, VOCs molecular weights between 50 and 200 are favorable for adsorption since lower molecular weight organics do not generally adsorb well and higher molecular weight organics are difficult to remove during regeneration (EPA, 1984). In addition to adsorption of VOCs, absorption control technique is generally used to remove VOCs from gas streams by contacting the contaminated air with a liquid solvent. Transformation between gas stream and liquid solvent consists of diffusion of gas stream to the solvent and dissolution into it. The absorbing liquids are generally chosen by their high capability to solve VOCs. Thus, any soluble VOCs will transfer to the liquid phase. Absorption systems can treat waste stream gases containing very high concentrations of VOCs ranges from 500 to 5000 ppm but it may require to pretreatment of VOCs containing solvents.

Membrane separation in VOC reduction control is based on using a semi-permeable membrane to separate VOCs from a waste gas stream. In this system, the membrane is permeable to VOCs but not air. Therefore, VOCs can pass through the membrane as the purified air stream is released to the atmosphere. However, this technique is sensitive to flow and concentration changes. In addition, their usage is rare and costly.

Alternatively, the destruction of VOCs is the most common and effective way in the control of volatile organic compounds. For instance, biological control system is based on the capability of certain microorganisms to transform organic and inorganic pollutants to water, carbon dioxide, and bio-mass. The most commonly used form of biological degradation is biofilter that is selective and concentration sensitive. In biological treatments, solubility and biodegradability of the contaminants are important parameters for the process (Kiared et al., 1996). Compounds such as alcohols and alkanes generally degrade well, whereas compounds such as chlorinated hydrocarbons are difficult to treat in biofilter. In addition, one of the advantages of biological treatment methods over physical and chemical techniques is that they can be conducted at room temperature and atmospheric pressure. Moreover, biological methods are inexpensive and easy to operate, however, due to incomplete oxidation their efficiency may be low and may even form by-products more toxic than the original compounds (Webster et al., 1996).

Combustion of VOCs is rapid and exothermic process that may result in either complete or incomplete oxidation of VOCs. Since many fuels and organic compounds consist of carbon and hydrogen, their complete combustion by oxygen, produce carbon dioxide and water. Many odors and VOCs containing streams can be burned or oxidized by application of two basic types of competitive combustion technologies; thermal and catalytic oxidation. Incineration (thermal oxidation), which is used most often in abatement of VOCs, destroys organic compounds by burning them at high temperatures between 1,300 and 1,800 ^{o}F and usually provides VOCs destruction efficiencies varying from 95% to 99 %. Thermal oxidizers have wide applicability and can be used for almost any volatile organic compounds. However, these compounds used in the thermal oxidizer may require different operating temperature and show different destruction efficiencies as a function of type and concentration of material in the vent stream. Thermal oxidizers can also be used for gas streams having VOC concentrations at very low concentration range of less than 10 ppm up to the very high concentrations approaching 10,000 ppm. However, they are rarely used on gas streams that have VOC concentrations exceeding approximately 25% of the lower explosive limit (LEL) due to explosion risk. Despite broad applicability of this incineration technique, large amount of fuel requirement of thermal oxidizers to heat the gas stream to necessary temperature cause additional and expensive operating costs, large and heavy constructions. Moreover, at high temperatures, undesirable by-products such as nitrogen oxides, dibenzofurans and dioxins can be formed in significant amounts.

In catalytic combustions, waste gas stream and air are contacted over a catalyst in order to allow reaction to occur at sufficiently lower reaction temperature than thermal incineration; hence, eliminating the formation NO_x and toxic byproducts. The operating temperature, of the catalytic combustors, which is between 500 and 1000 ^oF, is lower because of the catalysts. In this catalytic system, VOC destruction efficiency changes with respect to catalysts volume per unit volume of gas processed, reaction temperature, and VOC concentration and composition in the waste stream. A catalytic system is able to be operated at low concentration of VOCs, between 100 to 2,000 ppm and gives high destruction efficiencies ranging from 95 % to 99 %. However, this system can produce hazardous combustion by-products such as sulphur compounds as in the thermal oxidizers and additionally, due to poisoning effect, the catalyst used in the process may require to be replaced. Despite of these disadvantages, the benefits, such as reduced NO_x emission, having high destruction efficiency, lower operating temperatures, reducing fuel consumption, smaller units and less expensive operating conditions make catalytic combustion more desirable and effective long-term solution for reducing emissions of hazardous organic compounds. In particular, catalytic combustion is a key process for applications such as industrial air purification, automotive emissions control, and CO elimination in flue gases. The catalysts, used for catalytic combustion of VOCs, fall into two categories. The first is the supported noble metal catalysts and the second one is transition metal oxide catalysts. Noble metal catalysts, typically platinum and palladium, show high activity at low temperatures but are expensive and their availability is limited. Therefore, it is important to use them at low concentrations in catalyst or ensure well dispersion on support oxides, such as Al_2O_3 and SiO_2. In the catalytic combustion, the other types of catalysts are metal oxide catalysts that are usually oxide of the transition metals, such as oxides of cobalt, copper, nickel, and manganese. They are used in both supported and non-supported forms and cheaper but less active than noble metals at low temperatures. In this study, emission of organic compound, specifically ethanol released from commercial bakeries, and carbon monoxide, which is the common type of hazardous pollutants released from any combustion process was reduced on the supported metal and mixed oxide catalysts. The presence of low concentration of these compounds in the air is hazardous. In this sense, in bakery operations, where equimolar amount of carbon dioxide, ethanol, and small amount of by-products are produced and released as a result of anaerobic fermentation process are considered to have significant contribution to air pollution.

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2 \qquad (1.1)$$

Based on the measurements, the fermentation of 100 lbs sugar produces nearly 49 lbs ethanol, 47 lbs carbon dioxide, and 4 lbs of by-products, such as glycerol and organic acids (Sanderson et al., 1983). Since a commercial bakery can produce 300,000 pound of bread or other bakery products per a day, the great amount of ethanol is released into the atmosphere. Since upper and lower explosion limits of ethanol vapor in air are 3.3 and 19, the emission of produced gases in bakery operations are generally controlled by simple local exhaust ventilation in order to keep gas concentration in the bakery below the exposure limits. Otherwise, high concentration of ethanol leads to flame or long-term exposure may cause adverse reproductive and fatal effects, such as visual disorders, allergic skin reactions, brain damage and central nervous system depression in human. However, local ventilation control system is not sufficient way in the control of emission of volatile organics. Therefore, ethanol emission from bakeries must be managed and controlled by efficient type of VOCs control and reduction routes. Similarly, carbon monoxide, which is produced from generally incomplete combustion of any combustion process, furnaces, gas stoves, and automobile exhausts, is also fatally dangerous for human due to its ability to inhibit oxygen intake to blood. Addition to health effect, the significant contribution to photochemical smog and ozone depletion makes carbon monoxide important pollutant that has to be reduced.

In this study, the objective is to investigate the effect of metal type, metal oxide type and metal/oxide loading on the ethanol combustion and CO oxidation in air over single step sol-gel made alumina supported metal and mixed metal oxides. For this purpose, platinum supported on alumina (Pt/Al_2O_3) with the loadings of 1, 2, 3 wt.% and different metal ratios of copper-manganese mixed oxide on alumina ($CuO-Mn_2O_3/Al_2O_3$) with the loadings of 50, 70, and 90 % were tested as solid catalysts in the catalytic combustion. In addition, CuO/Al_2O_3, Mn_2O_3/Al_2O_3, and $Pd-Mn_2O_3/Al_2O_3$ was also synthesized to shed light on the catalytic activity relationship between metal and mixed oxides. The reason behind choosing Pt/Al_2O_3 catalyst for ethanol combustion is that it shows high activity at low temperatures. In addition, $CuO-Mn_2O_3/Al_2O_3$ mixed oxide catalyst was synthesized because it is cheap as compared to noble metal catalysts.

This thesis contains five chapters. In chapter one, addition to the general introduction for volatile organic compounds an their potential effects on both human health and environment, governments VOCs reduction strategies, the emission control methods and also the aim of this thesis are introduced. In chapter two, a literature survey on the properties of volatile organic compounds and catalytic reduction of them on both noble metal and transition metal oxide catalysts are presented. In chapter three, the specifications and pretreatment procedures (if any) of the chemicals used in this study and also experimental set-up, material preparation methods, such as the single step sol-gel and the impregnation method for the catalyst preparation is explained in details. In addition, the material characterization methods, such as X-Ray diffraction and the surface area measurement using N_2 adsorption are given. In chapter four, the catalyst activities and the behaviors of ethanol and carbon monoxide combustions are presented and discussed in this thesis. Finally, the conclusions and some recommendations are listed in chapter five.

CHAPTER 2

LITERATURE SURVEY

2.1. Volatile Organic Compounds (VOCs)

Increasing concern about the environmental issues, especially air pollution, have subjected to stricter legislation about air pollutants, particularly volatile organic gas emission that is being involve in every part of our life. Besides involving in chemical products, they are the major contributors of photochemical smog leading to formation of dangerous hazards and pollutants affecting human health, environment, and all living things. Therefore, in order to control their emission, it is extremely important to determine volatile organic compounds, their properties, and their emission sources. In this regard, although there is no general quantitative definition of what VOCs are, any compound (excluding carbon monoxide and carbon dioxide) that participates in atmospheric photochemical reactions are frequently described as 'volatile organic compounds' as defined by Environmental Protection Agency (EPA) in the United States. In addition, there have been subsequent attempts to give a more quantified definition as the term volatile organic compounds refers to those organic compounds which are present in the atmosphere as gases, but which under normal conditions of temperature and pressure would be liquids or solids. In addition to this, unlike traditional major air pollutants (e.g. CO, SO_x, NO_x) volatile organic compounds contain mixtures of numerous organic substances such as alkanes, alkenes, alkynes, aromatics found in gaseous and they show different physical and chemical behaviors and emitted from a variety of sources. With few exceptions, these organic compounds present in the atmosphere originate from anthropogenic processes, related to human activities mainly from stationary combustion, petrol storage and distribution, solvent and fuel evaporation and vehicular emissions (Singh et al., 1992). More specifically, they can be emitted from either household products such as office supplies, inks, cleaning products, insulating and painting materials or they can be originated from industrial process and automobile exhausts that are mainly responsible for outdoor VOC pollution.

2.1.1. Catalytic Oxidation of VOCs

In the oxidation of various types of VOCs, a variety of catalysts including either supported or unsupported noble metal catalysts (Pt, Pd, Au, Rh) and metal oxide catalysts (MnO_x, CuO_x, CeO_x, ZrO_x) have been intensively studied in literature. Activities of these materials depend on the nature and morphology of the support and the type of VOCs to be oxidized in the system and have been generally evaluated in terms of active sites, metal loading, electronic, and geometric effects between the catalyst components as investigated widely in literature.

Toluene oxidation was studied by Verykios et al. (2009) over supported Pt catalysts as well as over variety of metal oxide (M_xO_y) catalysts (M=Cu, Mn, Ce, V, Mg, Zr, Cr, Nd, Cs). Result showed that supported metal oxides, especially over 60% MnO_x, 70-90% CeO_2 and 5-10 % CuO_x supported on alumina, exhibit high activity as compared to single component catalysts. They concluded that reducibility of dispersed active phases could enhance the catalytic performance of these catalysts.

A similar study was carried out for the oxidation of benzene, toluene, and xylene over various type of metals (Cu, Mn, Fe, V, Mo, Co, Ni, Zn) on γ-Al_2O_3 (Kim, 2002). Among the catalysts, Cu/ γ-Al_2O_3 was found to have high catalytic activity and it was observed that increasing copper enhanced the catalytic activity. In this regard, they observed that Cu/ γ-Al_2O_3 which include 5 % Cu loading, showed the highest activity. By changing the support, activity of 5 % Cu/ γ-Al_2O_3 catalysts was observed and it was concluded that increasing in activity resulted in strongly due to well distribution of copper, not because of the surface area of the supports. Marion et al. (1990) showed that CuO dispersed on alumina was active for methane combustion. They claimed that low Cu loading on alumina led better dispersed ionic CuO while high CuO loading resulted in poorly dispersed catalyst. For the oxidation of methane, catalyst with ionic character was found to be more active. Catalytic methane oxidation was also investigated over Co_3O_4 catalysts supported on alumina and it was observed that catalysts were deactivated due to the reaction of the active phase with the support material (Garbowski et al., 1990).

2.2. Ethanol Combustion and CO Oxidation

Ethanol which is a common type of VOC, has a wide application area, such that, it is produced in bakeries as a by-product, used as a solvent in a printing process and is a great potential fuel for vehicles. With the progressive increased of production and usage of ethanol, its emission to the atmosphere should be treated to reduce the concentration at levels tolerated by current regulations. Although traditional removal techniques still in use such as keeping toxic gas concentration by simple exhaust ventilation, alternative control technologies are available and much more effective in the elimination of VOCs. In this regard, catalytic combustion is one of the more frequently used types of elimination technology (Campesi et al., 2011) especially when the low concentration of VOCs in a great volume of gases has to be treated (Morales et al., 2006). In general, low temperature catalytic combustion technique show better efficiency, produce no secondary pollution, and conserve the energy. For the purpose of the total oxidation of ethanol, the optimal catalysts should have good activity at low temperature and high selectivity to undesirable by-products, such as acetaldehyde and stability against catalyst deactivation (Monceaux et al., 2003). In addition, oxidation catalysts for the combustion of carbon monoxide is an important research topic due to wide application area in industrial, environmental and domestic fields mainly in automobile or industrial emission control applications and proton exchange membrane fuel cells. For these application areas, low temperature operation condition is a crucial requirement, thus, researchers have studied to develop catalysts, which are active even at room temperature. In this sense, Haruta et al. (1989) showed that supported gold catalysts are active even at temperatures below 0 ºC. In the study, Haruta and co-workers studied the oxidation of 1.0 % CO in air over supported nano gold catalyst, and showed that total oxidation of carbon monoxide to CO_2 occurred at temperature as low as – 70 ºC. However, in catalytic systems, several factors influence the catalytic activity such as volatile organic compound structure, concentration, and loading. It is widely known that inert support leads better catalytic performance than simple bulk catalyst due to high surface area and new species that supports provide. Thus, support characteristics, chemical properties, and texture are important parameters for its interaction with active phase on reducibility, dispersion and therefore activity and product selectivity of the catalyst (Aguero et al., 2008). In addition, space velocity has significant effect on destruction efficiency that increasing the space velocity decreases the conversion of VOCs to the desirable products (Vigneron et al., 1993). In this regard, temperature is also prominent that at higher temperatures, VOCs destruction is much more efficient from the system, but it can also accelerate catalyst deactivation, thus reduce the catalyst activity. In catalytic oxidation, selecting type of catalyst for the exact hydrocarbon reaction is also very important. In this sense, two main types of catalysts become prominent: Noble metal catalysts and metal oxide supported catalysts.

2.3. Catalysts for Ethanol Combustion and CO Oxidation

2.3.1. Noble Metal Catalysts

For the combustion of volatile organic compounds, supported noble metals, especially Platinum (Pt) and Palladium (Pd), are mostly used and desirable catalysts since they have high activity at relatively low temperatures, and show high selectivity for the formation of carbon dioxide and water, with lower partial oxidation products. Depending on the nature of VOCs and type of catalysts used in the catalytic system, activities show differences. Thus, it’s reported that noble metal catalysts are appropriate for non-halogenated VOCs destruction (Spivey, 1987). In contrast, usage of other noble metals, such as Au and Ag, is rare for high temperature reactions and high space velocity applications, as Rh_2O_3 is known to react with alumina (Ferrandon, 1999). Although platinum and palladium are known as active catalysts for VOC degradation, they exhibit different catalytic activities that Pd is more active for the oxidation of short –chain hydrocarbons, while Pt exhibits higher activity toward long- chain hydrocarbons (Abbasi et al., 1996). Cant et al. (2000) studied the oxidation of toluene, benzene, and 1-hexene alone and in mixtures with carbon monoxide and isooctane over platinum, palladium, and rhodium supported on alumina catalysts. Results showed that each metal exhibits different activity order for individual reactions that platinum is the most active for the oxidation of benzene as palladium with toluene.

Besides type of metal and VOCs, preparation method is crucial particularly for the carbon monoxide oxidation over Au catalyst with small particle size and high dispersion on metal oxide supports (Santos et al., 2010). In order to investigate the influence of preparation method and metal type effect on the catalytic activity, Figueiredo and coworkers (2010) studied several noble metals (Pt, Pd, Rh, Ir and Au) supported on commercial titania prepared by two different preparation method (liquid phase reduction deposition-LPRD and incipient wetness impregnation-IMP) for the catalytic oxidation of toluene, ethanol and CO. It was observed that for the CO oxidation, Au prepared by IMP was the worst catalyst while Au LPRD was the most active catalyst indicating that different particle sizes obtained depending on the dispersion over different supports. For all types of VOCs, except for CO, it was found that LPRD method produced better results, although difference between the two methods was not significant. For both preparation methods, the catalyst activity between those metals was observed in this manner: $Pt/TiO_2 > Pd/TiO_2 >> Rh/TiO_2 \approx Ir/TiO_2 >> Au/TiO_2$.

Catalytic performance of ethanol (500 ppm) in air also investigated by Avgouropoulos and coworkers (2006) over pure alumina, platinum supported alumina, and alkali (K^+ and Na^+) promoted Pt/Al_2O_3 catalysts. They found that ethanol oxidation over pure alumina produced diethyl ether and ethylene as by-product while Pt/Al_2O_3 catalyst produced acetaldehyde and acetic acid as partially oxidized compounds. In addition, oxidation of ethanol to CO_2 occurred at high temperature at about 300 ºC for Pt/Al_2O_3 and higher than 400 ºC for pure Al_2O_3, respectively. They noticed that at high alkali content promoted catalysts were more active than un-promoted Pt/Al_2O_3 catalysts and produce no acetic acid. They also investigated the catalyst stability towards deactivation and stated that under the standard reaction conditions stable operation for promoted Pt/ Al_2O_3 catalyst was achieved after a period of 5h, with 91% conversion to CO_2, 8 % conversion to acetaldehyde.

In commercial applications of catalysts, catalytic stability is an important factor as well as its activity. In this respect, supported Pt and Pd particles can be poisoned and sintered that leads to decreasing in the catalyst activity. Tahir and coworkers (1998) stated that the presence of halogenated VOCs deteriorate and temporarily poison the performance of precious metal catalysts when supported on alumina. Another important aspect about the oxidation of VOCs over noble metal catalysts is that the reaction is generally recognized to be structure sensitive (Santos et al., 2010). However, it's worthwhile to notice that correlation between catalyst activity, selectivity and metal dispersion depends on the type of VOCs. In this regard, study on ethanol selectivity over Cu and Pt catalyst was carried out by varying the space velocity through the reactor (Ismagilov et al., 1979). By changing space velocity, it was found that acetaldehyde and carbon dioxide different in amount over Cu catalyst. However, they observed that selectivity of carbon dioxide, meaning that high conversion of ethanol, reached over the Pt catalyst. McCabe and Mitchell (1983) also studied the 0.1 vol. % ethanol oxidation over 4 wt % Cu, 2 wt % Cr, 4 wt % Mn and 0.1 wt % Pt supported on alumina catalyst. They conclude that all three catalysts produce acetaldehyde, carbon monoxide, and carbon dioxide in the oxidation of ethanol. In addition, acetaldehyde amount was found to increase as temperature raised over each catalyst.

In recent years, researchers try to develop catalysts having good activity at lower temperatures as well as noble metal have and want to decrease the cost of the catalyst by developing new one. For this purpose, supported metal oxide catalysts are known as good alternative and highly active catalyst for VOC oxidation reactions. Lahousse et al. (1998), for instance, compared the combustion activity of VOCs over γ –MnO_2 and Pt/TiO_2. It was found that for the oxidation of benzene and methanol, γ –MnO_2 was superior compared with Pt/TiO_2 that 90% of 250-300 ppm of mixtures of VOCs is removed at 533 K with metal oxides. In addition, they also found that the presence of the water vapor shortened the time required to reach stable activity over γ –MnO_2 catalyst.

2.3.2. Metal Oxide Supported Catalysts

Despite high activity, stability, and susceptibility of supported noble metals to deactivation by poisoning, and the high cost of the noble metal component have initiated research into other possible catalysts for VOC abatement. Transition metal oxides, specifically metal oxide based catalysts can be an alternative way for noble metal due to noble metals cannot overcome the problem of carbonaceous deposits, including particulate matter (Odenbrand, 1999). An advantage of transition metals is that they are much cheaper and thermally more stable alternative as compared to noble metals. Another advantage of metal oxides is that they have an unlimited potential for modifications. For these reasons, metal oxides are accepted to show a catalytic activity as good as noble metals do.

In the oxidation of organic compounds, Cr, Mn, Co, Ni, Fe, Cu, and V are mainly applied oxides of transition metals. In the study carried out by Li et al. (2009), complete oxidation of ethanol was evaluated over $V_2O_5/\gamma\text{-}Al_2O_3\text{-}TiO_2$ catalyst prepared by the mixing sol-gel and co-impregnation method. They investigated the support effect, preparation methods, and vanadium content in the comparison of the catalysts performance. For 5% V_2O_5 catalyst supported on γ-Al_2O_3-TiO_2 prepared by mixing sol-gel method showed the best performance that ethanol conversion was reached 92% at 200 ºC while conversion on single γ-Al_2O_3 and TiO_2 supports were only 47% and 19%, respectively.

Among the transition metals, manganese oxides (MnO_x) including bulk MnO_2, Mn_2O_3 and Mn_3O_4 as well as those supported on carriers such as alumina has received the attention of many researchers as a cheaper alternative catalysts. Due to the low reactivity with Al_2O_3, Mn is comparatively stable over Al_2O_3 supports (Strohmeier, 1984). As a result, their highly stable feature makes supported or unsupported MnO_x important and to have been extensively studied for VOCs oxidation (Kalantar and Linfors, 1998). Ferrandon et al. (1999) studied a series of alumina-supported MnO_x catalysts for oxidation of CO, CH_4, C_2H_4, and $C_{10}H_8$. It's known that, as well as the nature of the phase of Mn oxide, the activity of alumina-supported catalysts depend on the nature of the support. Therefore, they used two alumina supports with different surface areas (α- Al_2O_3 5 m^2 g^{-1} and γ - Al_2O_3 50–250 m^2 g^{-1}). Results showed that despite the low surface area, Mn oxide supported on α- Al_2O_3 showed high activity for the carbon monoxide oxidation as a result of available sites on the surface during the calcination step (600 ºC).

In progressive studies, Cadu´s and coworkers (2008) prepared manganese oxide catalysts supported on Al_2O_3 and Mg-Al_2O_3 composite from two different precursors and with two manganese loadings for the catalytic performance of ethanol combustion. It was observed that higher manganese loading leads higher catalytic activity and the best catalytic performance was obtained when manganese oxide species are highly dispersed on the catalytic surface. At the same manganese loading, regarding to support and thus; dispersion effect, they found that the catalysts prepared from manganese acetate are more active than the catalysts prepared from manganese nitrate that oxidation reaction starts below 100 ºC on the catalysts prepared from acetate and 130-150 ºC for the catalysts prepared from nitrate precursor. In addition, influence of support treatment on the catalytic activities in ethanol and toluene combustion studied by the same research group. Alumina treated with water and diluted nitric acid was used as a support for the preparation of MnO_x/Al_2O_3 catalysts with two different loadings. They evaluated that modifying alumina affected interaction between support and active phase, dispersion and reducibility of catalysts due to changes in physicochemical properties of alumina in porosity, surface area, and surface acidity. They also detected that at high manganese loading, catalyst showed better catalytic activity for the ethanol combustion due to high capacity for adsorbing oxygen. In this sense, Chen et al.(2009) prepared $MnO_x/Al_2O_3/Ce_{0.45}Zr_{0.45}M_{0.10}O_y$ (M = Mn, Y, La) catalysts by impregnation method and investigated that doping of Mn enhance the oxygen storage capacity. Hence, oxygen vacancy density and oxygen mobility resulted in the improvement of the catalyst activity.

Another research about complete oxidation of VOCs (formaldehyde and methanol oxidation) over MnO_x (with and without Pd) supported on alumina was showed that synergy between supported manganese and palladium phase improved the activity of the bimetallic catalyst that, as Pd was added to Mn/Al_2O_3, the light off temperature decreased from 220 to 90 ºC (Alvarez-Galvan et al., 2004). This is associated with the ability of manganese oxide to release oxygen, thereby facilitating the formation of PdO phase. Ferrandon and coworkers (1999) indicated that addition of small amounts of platinum had favorable synergetic effect on the manganese oxide behavior. In addition, they studied effect of calcination temperature on the catalysts performances and claimed that different calcination temperature (500 ºC and 800 ºC) result in different manganese oxide phases. Formation of Mn_2O_3 phase at 500 ºC was claimed to be active manganese oxide catalyst for the oxidation of CO and naphthalene. As reported in literature, Mn_2O_3 is also a stable phase and it’s widely known that catalytic activities of mixed oxides are generally much higher than those of separate components. Thus, it is published that catalysts which are consisted of manganese oxides and other oxides exhibit good catalytic activity as compared to a single one due to interaction between support and with other components. In this sense, the synergy between Mn_2O_3 and Fe_2O_3 on VOCs studied by Duran and his coworkers (2009). They have prepared Mn_2O_3-Fe_2O_3 mixtures with different Fe/Mn atomic ratios by means of citrate method. They observed that formation of Mn_2O_3-Fe_2O_3 solid solution has better catalytic performance on ethanol, ethyl acetate and toluene oxidation than on Fe_2O_3 and Mn_2O_3 pure oxides. In addition to this, Mn-Cu mixed oxides prepared by co-precipitation were tested on propane and total oxidation of ethanol by Cadus and coworkers (2006). They studied different aging time (4,18 and 24 h) for those oxidation reactions and results showed that prepared mixed oxides exhibit better catalytic performance than Mn_2O_3 and CuO pure oxides due to the existence of a $Cu_{1.5}Mn_{1.5}O_4$

mixed phase and the easier reducibility of the catalysts. In addition, it was observed that stated that higher aging time resulted in better catalytic activity. However, the effect of ageing time on the activity of the final catalysts also studied by Taylor and coworkers (1997). They prepared a series of copper/ manganese oxide catalysts with varying ageing times (4, 18, and 24 h) using coprecipitation procedure and calcined them at 500 ºC for 17 h. They claimed that increasing the ageing time plays important role in the formation of the mixed $CuMnO_x$ oxides and found that the best catalytic performance obtained on the catalyst aged for 12 h.

It is well known that hopcalite catalysts, which comprise a mixture of copper and manganese oxide, show better catalytic performance in carbon monoxide and volatile organic compounds combustion. They are known as highly active catalysts even at low temperatures, but at above 600-700 ºC, single oxide phases of CuO and Mn_2O_3 are not longer available in the catalyst mixture and crystallization of the copper manganite spinel starts to appear (Buciuman and Hahn, 1999). Therefore, at this temperature range, they lose their activity and stability, irreversibly. Larsson and Andersson (2000) studied several catalysts including CuO_x/Al_2O_3, $CuO_x–CeO_2/Al_2O_3$, $CuMn_2O_4/Al_2O_3$, and Mn_2O_3/Al_2O_3 in the combustion of carbon monoxide, ethanol, and ethyl acetate. In order to promote the complete oxidation activity for CO, they modified the alumina with ceria prior to the deposition of CuO. The activity increased with CuO_x loading until formation of crystalline CuO particles. However, it was found that $CuO-CeO_2/Al_2O_3$ catalyst was more active compared with hopcalite catalyst for the oxidation of CO, on the other hand, $CuMn_2O_4/Al_2O_3$ catalyst was more active for the combustion of ethanol and ethyl acetate. The enhancement of activity is attributed to high dispersion of CuO and oxygen storage ability of CeO_2. Crystalline $CuMn_2O_4$ and Mn_2O_3 phases were observed over $CuMn_2O_4/Al_2O_3$ catalyst.

Although hopcalite catalysts are well known for low temperature carbon monoxide oxidation, copper manganese oxide loses activity for CO oxidation at above 500 ºC due to the possibility of crystallization of $CuMn_2O_4$ (Larsson and Andersson, 2000). However, catalyst calcined at 500 ºC can display high activity because of the consequence of the low surface area of the material but not due to a high CO oxidation activity (Hutchings et al., 2009). Copper-containing manganese oxides (Cu/Mn molar ratio =0-1/1) prepared by sol-gel method was examined for 1 vol. % CO oxidation by Miyake et al (2009). As they compared catalysts, they observed that catalysts prepared by sol-gel method showed better activity than Meso Mn and commercial hopcalite catalyst. This activity explained by incorporation of copper and electron transfer between oxygen and manganese. It is generally accepted that activity of hopcalite catalyst result from a quick charge exchange between Mn^{+3} and Cu^{+2} cations which are regenerate active sites. However, a study carried out by Buciaman et al. showed that high activity of hopcalite catalyst arose from synergistic cooperation of CuO and Mn_2O_3 phases in physical mixture, but not from the interaction of copper and manganese cations within the spinel lattice of $CuMn_2O_4$. In the synthesis of the hopcalite precursor, drying and calcination steps are recognized to be crucial. Hence, effect of calcination temperature on the development of the surface area was investigated by Hutchings et al. (2009). They prepared the catalysts by coprecipitation and calcined them at different temperatures then tested for the oxidation of carbon monoxide at ambient temperature. They examined that as they increased the calcination temperature, loss of crystallinity occurred. At 400 ºC, new crystallite phase was observed and considered to be the microcrystalline $CuMn_2O_4$ hopcalite phase with small amount of copper and manganese oxides. They observed that the most active catalyst was that calcined at 410 ºC and also surface area of those catalyst calcined between 410-470 ºC were very similar and were more active than commercial hopcalite. On the other hand, calcination of unaged precursor at 500 ºC for 18 h led to totally inactive material.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

In this study, Pt/Al_2O_3 powder catalysts having Pt loadings of 1, 2 and 3 wt % and $CuO-Mn_2O_3/Al_2O_3$ with various metal ratios and weight loadings were synthesized via impregnation and single step sol-gel method, respectively. In addition, to figure out the synergy between CuO and Mn_2O_3 species and to compare them with $CuO-Mn_2O_3/Al_2O_3$ catalyst, CuO/Al_2O_3 and Mn_2O_3/Al_2O_3 with weight loading of 70% was synthesized through the same way. Moreover, $Pd-Mn_2O_3/Al_2O_3$ was synthesized in order to observe the addition of small amount of noble metal effect on the catalytic activity. In the synthesis of Pt/Al_2O_3 catalysts, dihydrogen hexachloroplatinate (IV) hexahydrate was used as a precursor for platinum. In addition, for the synthesis of $CuO-Mn_2O_3/Al_2O_3$ catalysts, copper (II) nitrate dihydrate (Sigma) was used as a precursor for copper oxide; manganese (II) nitrate tetrahydrate (Merck) was used as a precursor for manganese oxide, respectively. For all type of catalysts, aluminum isopropoxide (Alfa Aesar) was used as a precursor for alumina. Deionised water (DIW) was used as solvent and nitric acid (HNO_3) was used as a peptizer in the sol-gel method. Used chemicals are summarized in the Table 3.1.

Table 3.1. Properties of materials used in catalysts synthesis

Chemicals used in the experiments	Chemical formula	Molecular Weight (g/mol)	Purity (%)
Aluminum isopropoxide	$Al(OCH(CH_3)_2)_3$	204.24	98
Copper (II) nitrate dehydrate	$Cu(NO_3)_2.2H_2O$	223.56	98
Manganese (II) nitrate tetrahydrate	$Mn(NO_3)_2.4H_2O$	251.01	96
Platinic Acid	$H_2PtCl_6.6H_2O$	517.91	99.9
Nitric Acid	HNO_3	63.01	65

3.2. Methods

In this study, experiments can be categorized into three groups as seen in Figure3.1;

-Preparation of catalysts

-Characterization of catalysts

-Testing of catalysts in the experimental set-up

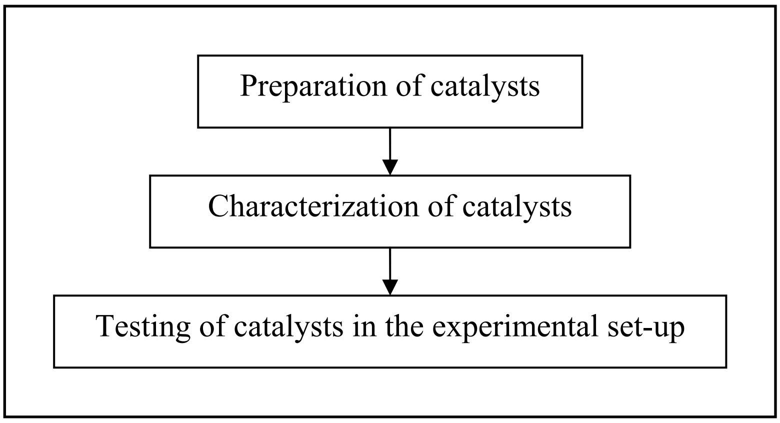

Figure 3.1. Experimental Procedure

3.2.1. Preparation of Catalysts

Platinum supported on alumina catalysts were prepared via incipient wetness impregnation method. As a starting point, to prepare alumina, necessary amount of alumina isopropoxide (AIP) and water were mixed at 85 ºC for 1 h. Then, in order to obtain high surface area, a known amount of glycerol (2 % wt) were added to AIP-water mixture at the same temperature and stirred for 3 hours before the peptization step in which HNO_3 were added and kept at 85 ºC again for 1 h. The mixture was left overnight for ageing and calcined at 500 ºC with a heating rate 10 ºC /min for 6 h. Finally, obtained powders were ground and sieved to 60 mesh (250 μm) size. For the impregnation step, pore volume of alumina was found by wetting the alumina with required amount of water until alumina powders saturated. Therefore, by considering the appropriate loading of platinum on alumina, platinic acid was solved in an amount of water found earlier. Finally, Pt containing solution was impregnated to alumina powders and dried at 120 ºC for 6 h then calcined at 500 ºC for 6 h before any testing.

For catalytic combustion of ethanol, three different loading of Pt/Al_2O_3 were synthesized with weight loadings of 1%, 2% and 3%.

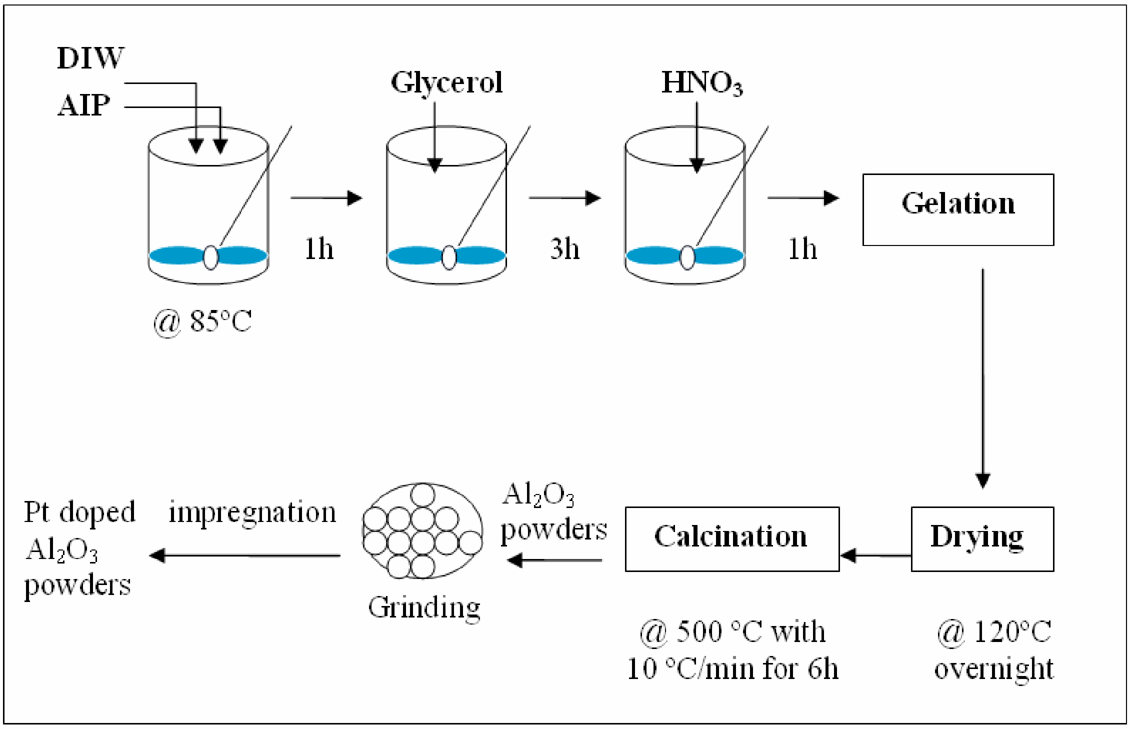

Figure 3.2. Experimental procedure for the preparation of alumina supported Pt catalyst

On the other hand, copper manganese on alumina ($CuMn_2O_4/Al_2O_3$) catalysts with the weight loadings of 50, 70, and 90 % were synthesized for each Cu/Mn molar ratios of 1,5,12 via single step sol-gel procedure. In Figure 3.3, experimental procedure for the synthesis of CuO-Mn_2O_3/Al_2O_3 catalyst is shown. First, to prepare alumina supported catalysts, a known amount of alumina isopropoxide (AIP) in deionized water was stirred for 1 h at 85 ºC, after which 65% HNO_3 was added to mixture and stirred together at 85 ºC again for 1 h. On the other side, needed amount of copper (II) nitrate and manganese (II) nitrate were solved in deionised water, separately and prepared in order to add to alumina sol. After that, separate solutions were added to prepared alumina sol in one step and mixed together at 85 ºC. Gelation occurred within 3 hour. Finally, gels were dried at 120 ºC for 12 h and calcined at 500 ºC with a heating rate 10 ºC /min for 17 h. Finally, catalysts were ground and sieved to 60 mesh (250 µm) size. Moreover, to synthesis CuO/Al_2O_3, Mn_2O_3/Al_2O_3 and Pd-Mn_2O_3/Al_2O_3 catalysts, alumina sol was prepared by the same procedure then appropriate metal precursor was added into sol for each catalyst. For the catalysts mentioned, gels were dried at 120 ºC for 12 h, then calcined at 500 ºC for 17 h, and finally sieved to 250 µm before their usage in an experimental reaction.

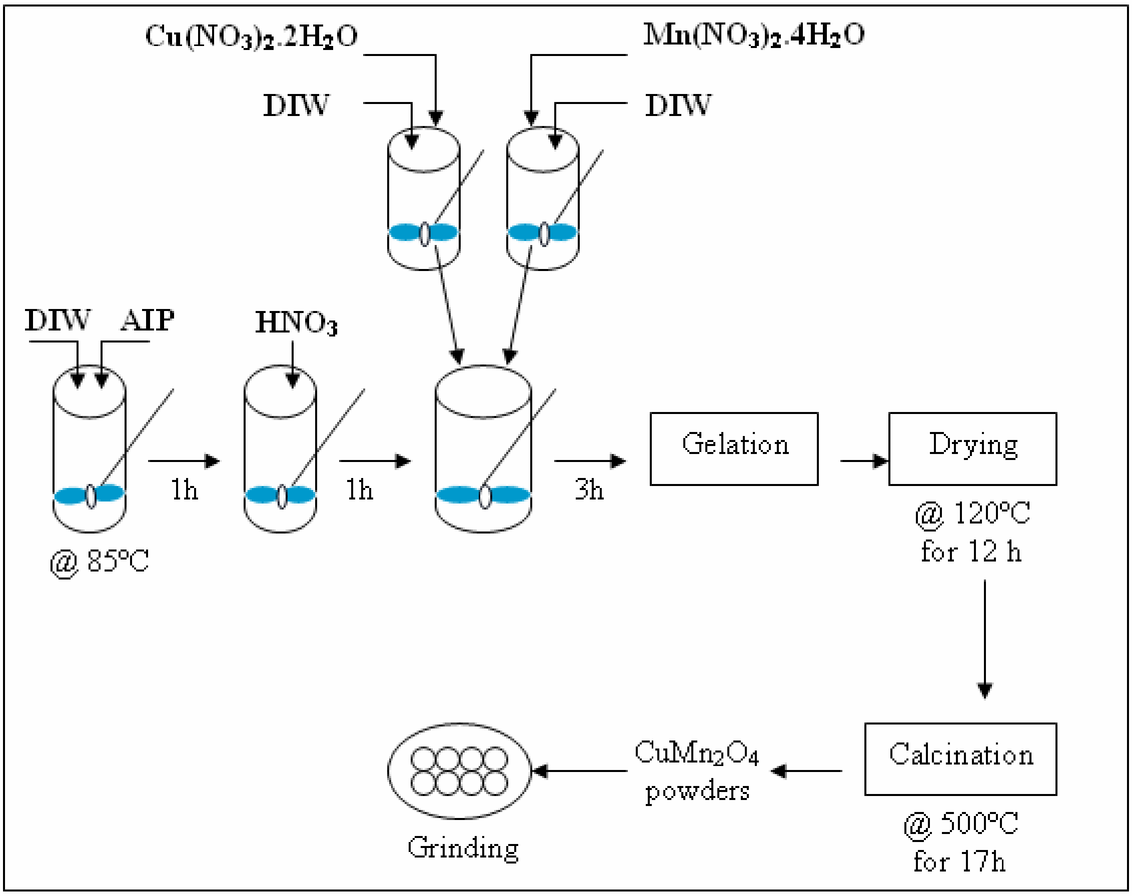

Figure 3.3. Experimental procedure for the preparation of $CuO-Mn_2O_3/Al_2O_3$ catalysts

3.2.2. Characterization of the Materials

In the characterization of the samples, X-ray diffraction (XRD), BET and GC-FID were used. In order to determine the crystallite phase and the average crystallite sizes of samples, XRD pattern of the samples were determined using a Philips Xpert XRA-480 Model X-ray diffractometer. BET surface areas of the prepared samples were determined by using Micromeritics ASAP2020 analyzer at scan mode 77 K in the presence of N_2. Inlet and outlet composition of ethanol and by-products released during the reaction were detected using a gas chromatography with a flame ionization detector

(GC-FID, Shimadzu GC-14A) which has 30 m length, inner diameter of 0.25 cm, HP-5 capillar column.

3.2.3. Experimental Setup and Catalysts Testing

3.2.3.1. Experimental Instruments

The catalytic oxidation of ethanol was performed in a fixed-bed reactor system at atmospheric pressure and in the temperature range of 50-350 ^{o}C. The tubular quartz reactor, with dimensions 30 cm long and an inner diameter of 1 cm, was filled to 0,6 cm with catalyst, which was placed in the middle of the reactor and supported by quartz wool. The reactor was placed in a high-temperature furnace made up of with a grinded zeolite inside to avoid thermal loses and electrical heating system inside the furnace controlled by a proportional integral derivative (PID) controller with a K type thermocouple positioned on the catalyst bed to get an accurate measurement of the reaction temperature. In addition, for accurate and stable controlling of gas flow rates, the concentration of air and nitrogen were adjusted by Brooks Instrument (Brooks model 5850).

3.2.3.2. Activation Procedure before Catalyst Testing

After the synthesis process of catalysts, the fresh catalyst powders loaded to known catalyst volume in a quartz reactor and treated by 1.5 ml of liquid ethanol at room temperature. In the activation procedure, first, necessary amount of nitrogen flow was passed through the reactor tube in order to carry the excess ethanol from the reactor and then dry air was passed through the tubular reactor in order to oxidize the adsorbed ethanol or other species on the catalyst surface. Finally, washed catalysts was kept at 120 ^{o}C for 1 hour in a ventilation stream and then calcined at 500 ^{o}C for 2 hour.

3.2.3.3. Catalyst Testing

In the evaluation of prepared catalysts in experimental set-up, first, concentration of dry air and nitrogen gases is adjusted by mass flow controllers. Flow of gases is controlled by a digital flow meter and in order to have ethanol vapor in the stream, nitrogen flow is send to a bubbler filled with liquid ethanol at room temperature. Furnace, having an electrical system inside, is set to a temperature point that experiment will be carried out. After ensuring that needed amount of ethanol vaporized, and getting steady state condition for each step, feed gas (total flow rate:100 cc/min and average ethanol concentration is 1500 ppm) is sent to the reactor containing catalysts. After the steady state condition reached for the reaction, product gas and reactants are collected into quartz gas-holders, separately and their analysis are carried out by a gas chromatographer equipped with FID detectors.

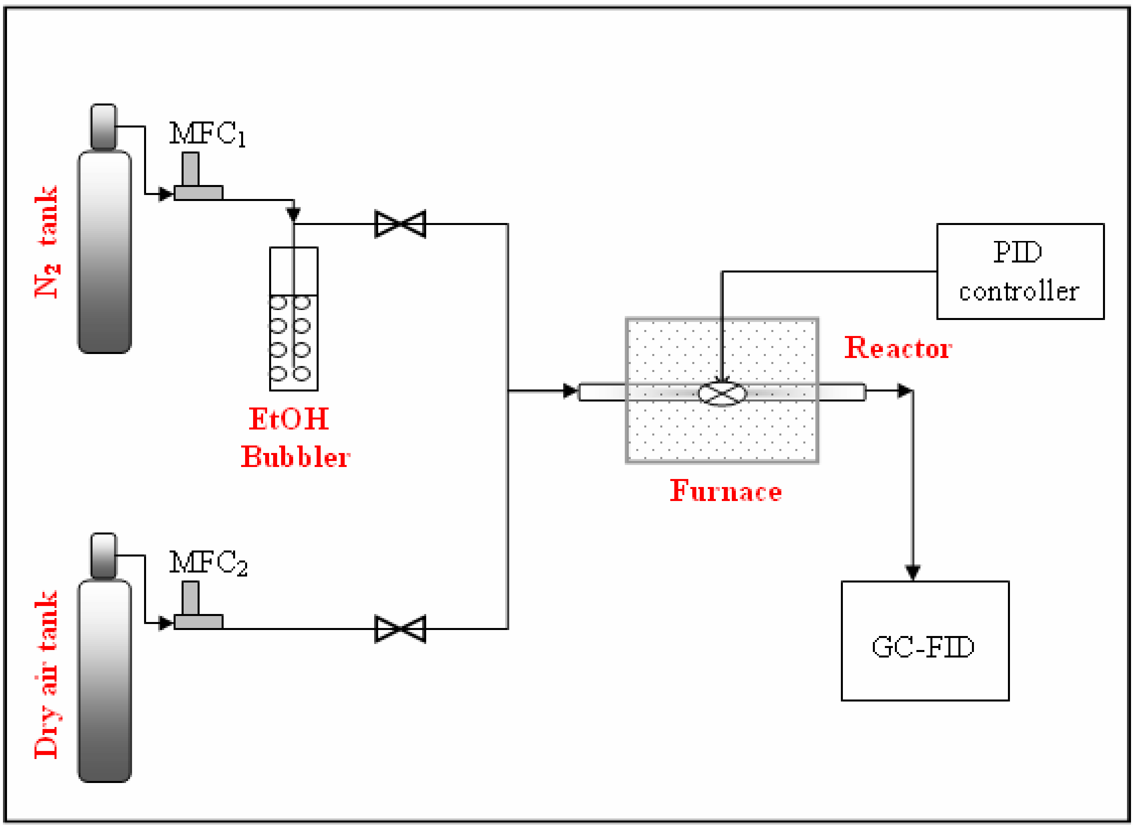

Figure 3.4. Experimental set-up of ethanol combustion

Figure 3.4 demonstrate a diagram of ethanol oxidation process. However, in the oxidation of carbon monoxide, without any vaporization step, flow of 1 % CO in balanced, diluted with dry air to 0.5 % CO and sent to a reactor replaced in furnace. Product composition of outlet gas was analyzed by using GC-MS equipment.

CHAPTER 4

RESULTS AND DISCUSSION

The complete oxidation of ethanol was studied over mixed metal oxide and mixed oxide supported noble metal catalysts with various metal ratios and the loadings, prepared by using a sol-gel method, which allows one to control the chemical reactions; hence, indirectly tailoring the textural and chemical properties of the catalyst. The most effective catalysts for the ethanol combustion were selected by considering the lowest temperature at which 100% ethanol conversion is obtained.

All the catalysts were tested in a tubular quartz reactor filled with a catalyst to have a catalytic bed length of 0.6 cm (i.e. ~0.3 g of the catalyst). Ethanol was vaporized in a bubbler at room temperature (24-27 ^{o}C) before being mixed with dry air to obtain an inlet ethanol concentration of 1000-2000 ppm and a space velocity of 12000 h^{-1} and the reaction was performed at temperatures ranging from 50 to 350 ^{o}C. Prior to the catalytic tests, all the catalysts were activated under the dry air flow at 500 ^{o}C for 2 h. At each reaction temperature, the catalysts were kept under the reaction condition for a reasonable time (e.g. 1 h to 2 h) to reach at steady-state. The concentrations of the reactants and the products were determined after being at steady-state using a gas chromatography equipped with a FID detector.

Table 4.1. Operating conditions for ethanol oxidation

Operating parameters	Operating range
Reaction temperature	50-350 ^{o}C
Inlet ethanol concentration	1000-2000 ppm
Total flow rate	100 ml/min
Space velocity	12000 h^{-1}

In carbon monoxide oxidation, the reaction conditions were kept the same as that of the ethanol combustion but CO concentration was 5000 ppm in the inlet.

4.1. Blank Test

To observe if there is a gas phase ethanol oxidation, ‘Blank test’, which refers to the absence of catalyst on the catalytic bed, was tested in a tubular reactor containing only glass wools inside. Figure 4.1 shows the total ethanol conversion amount of homogeneous reaction of ethanol as a function of different reaction temperature and it clearly shows that total ethanol conversion increases with increasing reaction temperature.

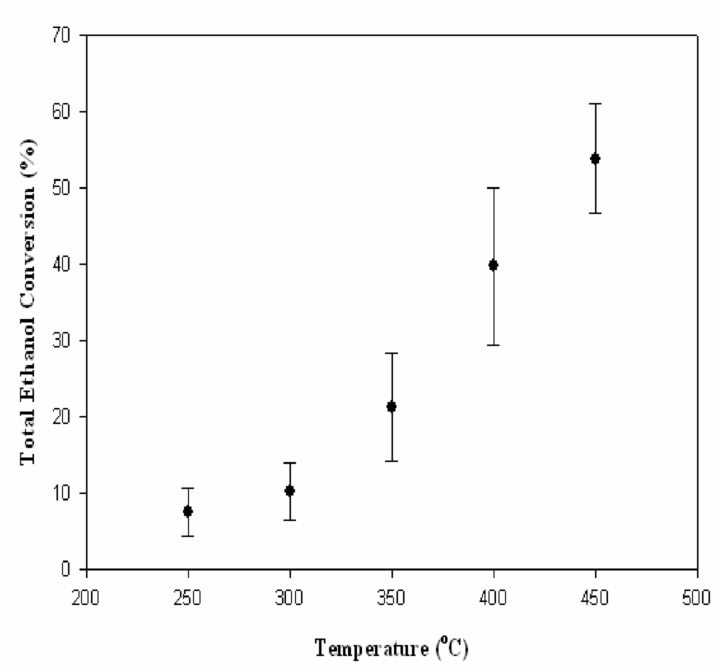

Figure 4.1. Total Ethanol Conversion of Blank Test

According to the results obtained from gas chromatography-mass spectrometry (all products obtained using the catalysts at different operating temperatures were showed in Table A.1 in Appendix A), ethanol conversion to carbon dioxide started to be observed at 400 ^{o}C. However, below this operating temperature ethanol can be converted to other products that could not measured quantitatively. Therefore, homogeneous reaction of ethanol combustion without catalyst did not appreciably occur below 400 ^{o}C.

4.2. Catalytic Performance of Noble Metal Catalysts in Ethanol Combustion

Previous studies in literature show that the noble metal catalysts, in particular Pt and Pd catalysts, exhibit a high catalytic activity in the reduction of VOCs. Hence, in this study, for the ethanol combustion, platinum was selected and impregnated on sol-gel made alumina support with various metal loadings. Figure 4.2 shows the total ethanol conversion obtained over 1, 2, and 3 % Pt/Al_2O_3 catalysts as a function of reaction temperatures.

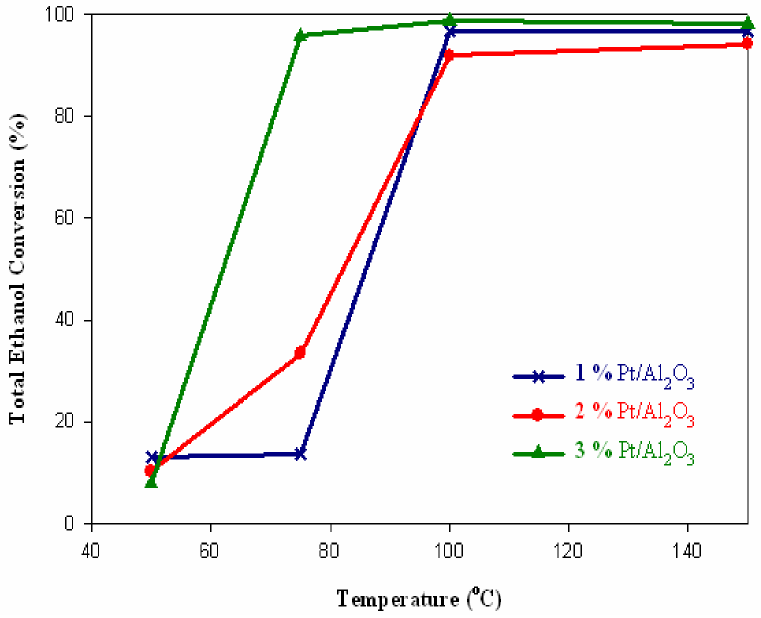

Figure 4.2. Comparison of varying Pt loadings of Pt/Al_2O_3 catalysts in ethanol combustion

As seen in the figure above, increasing Pt loading from 1% to 3% lowers the highest ethanol conversion temperature from 100 ° to 75 °C. In fact, at 75 °C, Pt/Al_2O_3 showed 96 % ethanol conversion while it was 13 % and 33 % over 1% and 2% Pt/Al_2O_3 catalysts, respectively. Each run was repeated 3 times under the same reaction condition and the results are tabulated in Table 4.2. It should be noticed that, at lower temperatures where the ethanol conversion decreased, the experimental error was high due to the tendency of ethanol to adsorb onto the surface at low reaction temperatures; hence requiring longer time to reach at the reaction steady state.

Table 4.2. Total Ethanol Conversion on Pt/Al_2O_3 Catalysts with Experimental Errors

Catalysts	**Total Ethanol Conversion (%)**		
	@ 150 °C	**@ 100 °C**	**@75 °C**
1 % Pt/Al_2O_3	96.66 (±0.84)	96.87 (± 0.02)	13.55 (±6.14)
2 % Pt/Al_2O_3	94.16 (±2.57)	91.86 (±5.75)	33.40 (±17.27)
3 % Pt/Al_2O_3	98.20 (±1.38)	98.70 (±3.80)	95.79 (±3.80)

To find out the main reason behind the difference in ethanol conversion vs. temperature behavior observed among the catalysts with varying Pt loadings, XRD characterization method was used.

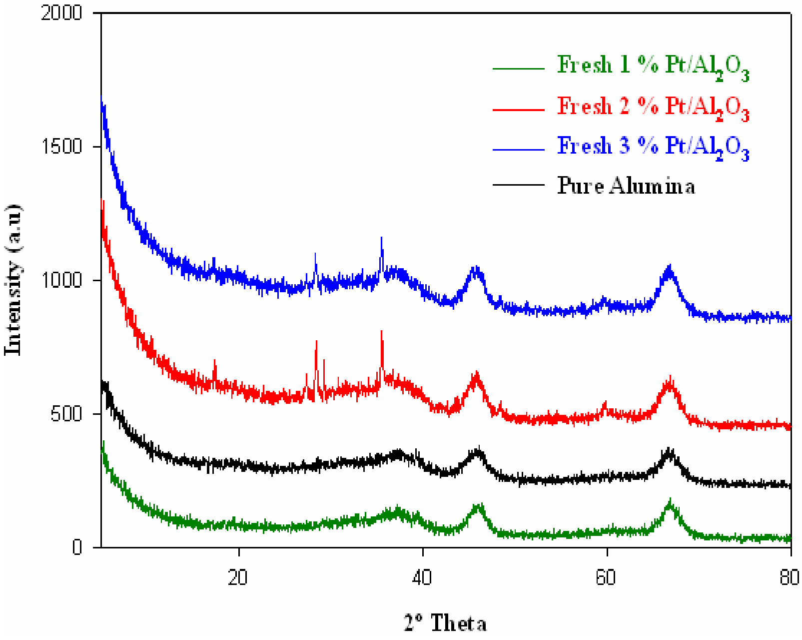

Figure 4.3. XRD patterns of different weight loadings of Pt/Al_2O_3 catalysts

Figure 4.3 shows XRD patterns of the Pt/Al_2O_3 for all the Pt loadings and pure alumina before using them in activity tests. At 37.44, 46.03 and 67.76 of 2Θ angles, alumina peaks are seen (other related peaks are shown in Figure A.1-7 in Appendix A). As figure demonstrated, Pt loaded Al_2O_3 and pure alumina show similar XRD pattern, which means that Pt crystallite size is less than 5 nm for all the Pt loadings and also, there are no diffraction lines associated with Pt metal that located at 39.67 and 46.28 of 2Θ angles (XRD pattern of Pt is shown in Figure A.1 in Appendix A). This is plausible since XRD method is not sensitive to crystallite sizes below 5 nm. In other words, this indicates that on fresh catalysts (i.e. unused) platinum was highly dispersed on alumina support regardless of the Pt loading. It is well known that the catalytic activity increases with increasing the number of available "active" sites at the surface. In other words, increasing Pt loading while keeping the crystallite size as small as possible, such as less than 5 nm, seems to provide additional active sites; hence, resulting in an increased conversion. Thus, one may expect to obtain increased conversion for all the Pt loadings since crystallite size is less than 5 nm for all the catalysts. However, 1% and 2%Pt loadings show the same conversion vs. temperature behavior within the experimental errors but there is a significant difference between 3%Pt and other Pt loadings. Therefore, the three times used Pt catalysts were analyzed using XRD to better understand the reason why 3%Pt had the highest activity while 1 and 2% Pt catalysts showed similar activities. As seen in Figure 4.4, Pt diffraction lines located at 39.67 and 46.28 of 2Θ angles are clearly seen on the used 1% and 2% Pt catalysts whereas there is no diffraction lines corresponding to Pt metal on the used 3% Pt catalyst. This indicates that based on XRD, Pt crystallites on 3% Pt catalyst did not sinter during the ethanol combustion reaction; hence, staying below than 5 nm but the average crystallite sizes of the used 1% and 2% Pt catalysts became ~4.98 and 14.15 nm, respectively. One should notice that the occlusion of Pt crystallites inside the pores might have happened during the synthesis as well. Therefore, 1% and 2% seem to show similar behavior although the average crystallite size of 2%Pt is 2.84 times bigger than that of 1% Pt; hence, resulting in the equal number of total available surface sites on both catalysts and this seems to give the same conversion vs. temperature plot on both catalysts.

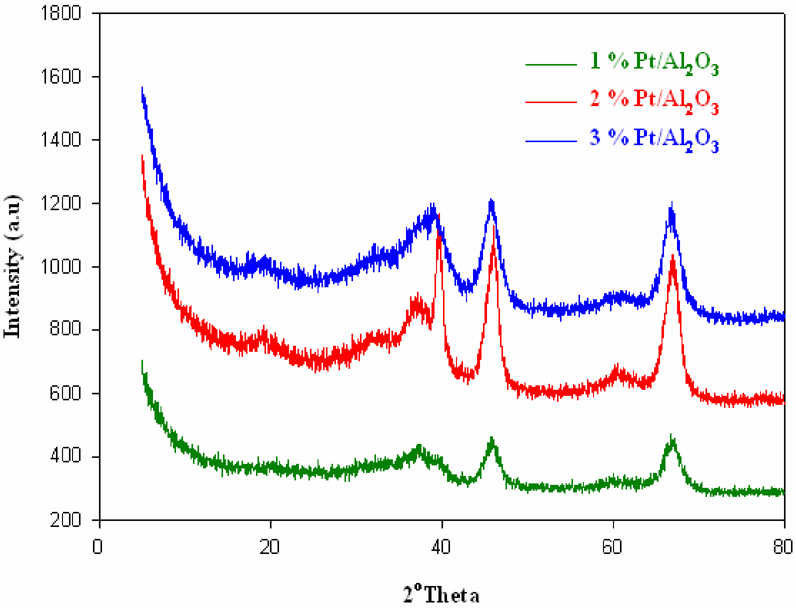

Figure 4.4. XRD pattern of Pt/Al_2O_3 catalysts after reactions

Although precious metals among the highly active catalysts for the oxidation of various VOCs, due to their high costs, the studies have focused on supported and unsupported metal oxide catalysts.

4.3. Catalytic Behavior of $CuO-Mn_2O_3/Al_2O_3$ on Ethanol Combustion

Copper and manganese oxides widely used and economic metal oxides yielding comparable activities in the oxidation of VOCs. Moreover, the mixed oxide of copper and manganese, known as hopcalite catalyst, shows high activity for ethanol and carbon monoxide oxidation as compared to single oxides of CuO/Al_2O_3 and Mn_2O_3/Al_2O_3 due to the formation of copper manganese oxide ($CuMn_2O_4$) phase (Hutchings et al., 2009). In light of these characteristic, in this study, the activity of the sol-gel made $CuO-Mn_2O_3/Al_2O_3$ catalysts were investigated in the ethanol and CO oxidation. Beside of copper manganese oxide catalysts, single phase of CuO and Mn_2O_3 on alumina were synthesized by the same single step sol-gel method to explore the effect of each metal oxide on the activity of the catalysts.

Table 4.3. Copper manganese oxide catalysts with different ratios and loadings

Catalysts	**Molar metal ratio (Cu/Mn)**	**Metal Loading (wt %)**	**Cu (wt %)**	**Mn (wt %)**
$CuO-Mn_2O_3/Al_2O_3$	1	50	25.096	24.904
		70	35.134	34.866
		90	45.173	44.827
$CuO-Mn_2O_3/Al_2O_3$	5	50	41.720	8.280
		70	58.408	11.592
		90	75.095	14.904
$CuO-Mn_2O_3/Al_2O_3$	12	50	46.181	3.819
		70	64.653	5.347
		90	83.126	6.874
CuO/Al_2O_3	0	70	70	0
Mn_2O_3/Al_2O_3	0	70	0	70

All the catalysts, listed in Table 4.3, were tested in ethanol combustion under the same operating conditions used in testing Pt catalysts. Keeping the operation conditions and metal molar ratio (Cu/Mn) constant, the activity of the mixed oxide catalysts were evaluated as a function of total metal oxide loadings.

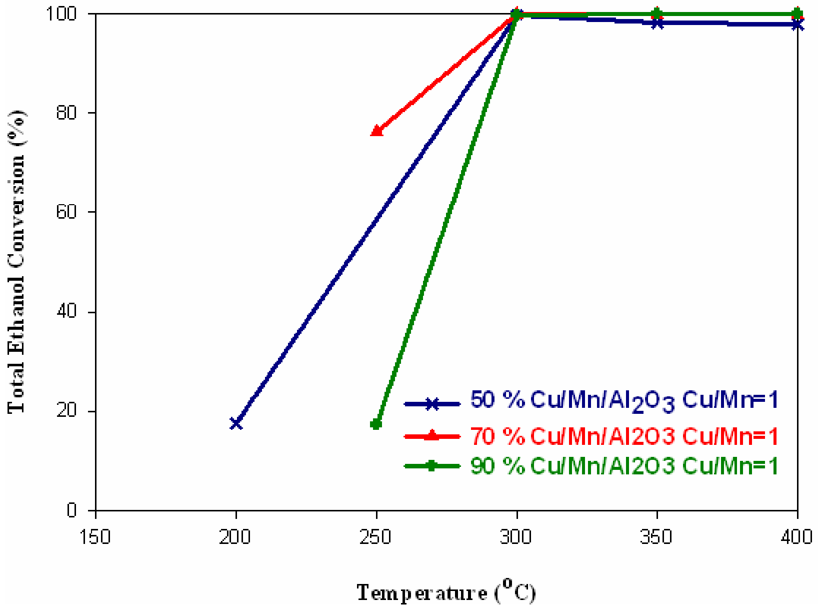

Figure 4.5. Effect of different weight loadings of $CuO-Mn_2O_3/Al_2O_3$ (Cu/Mn=1:1) on total ethanol conversion at various temperatures (Inlet Conc.=1500 ppm, SV=12000 h^{-1})

First, copper manganese oxide catalysts (for Cu/Mn=1:1) with various total oxide loadings were tested in a fixed bed reactor with an inlet concentration of ~1500 ppm ethanol. Figure 4.5 shows the total ethanol conversion as a function of temperature. Above 300 °C, all the catalysts show high conversion, ~99%. However, as the reaction temperature decreases, total ethanol conversion decreases in such a way that the total ethanol conversion over the catalyst (for Cu/Mn=1:1) with 70 % loading is ~76 % at 250 °C while other catalysts have lower activities at this temperature as seen in Figure 4.5.

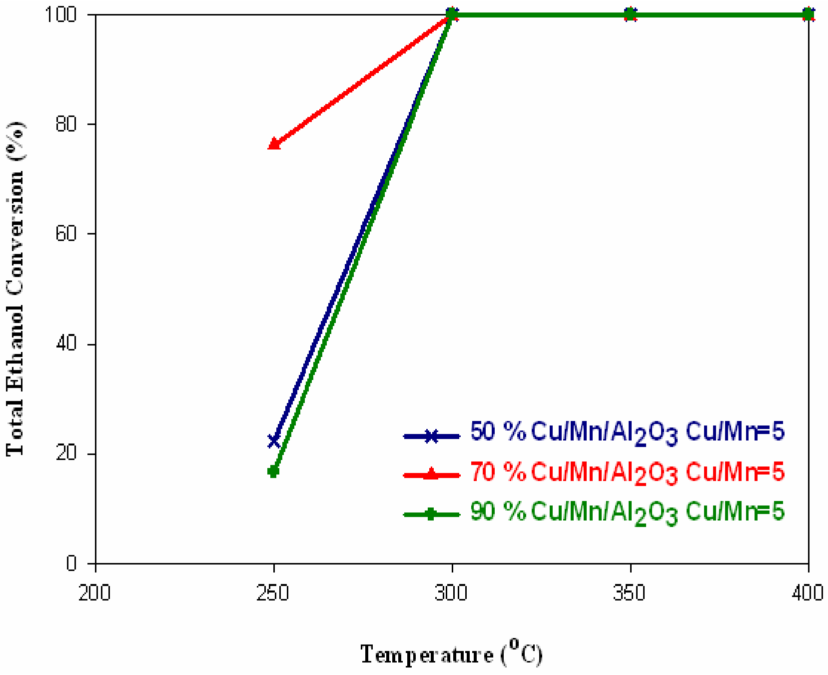

Figure 4.6. Effect of different weight loadings of CuO-Mn_2O_3/Al_2O_3 (Cu/Mn=5:1) on total ethanol conversion at various temperatures (Inlet Conc.=1500 ppm, SV=12000 h^{-1})

In addition, the catalytic activities of CuO-Mn_2O_3/Al_2O_3 (with Cu/Mn=5) catalysts for varying total oxide (Cu and Mn) loadings were shown as a function of the reaction temperatures in Figure 4.6. Similar to the catalysts (Cu/Mn=1:1), ethanol was almost completely converted to CO_2 at the temperatures above 300 °C. However, at 250 °C, the catalysts with 50 % and 90 % total oxide loadings exhibited almost the same conversion while 70 % loading showed the highest conversion activity.

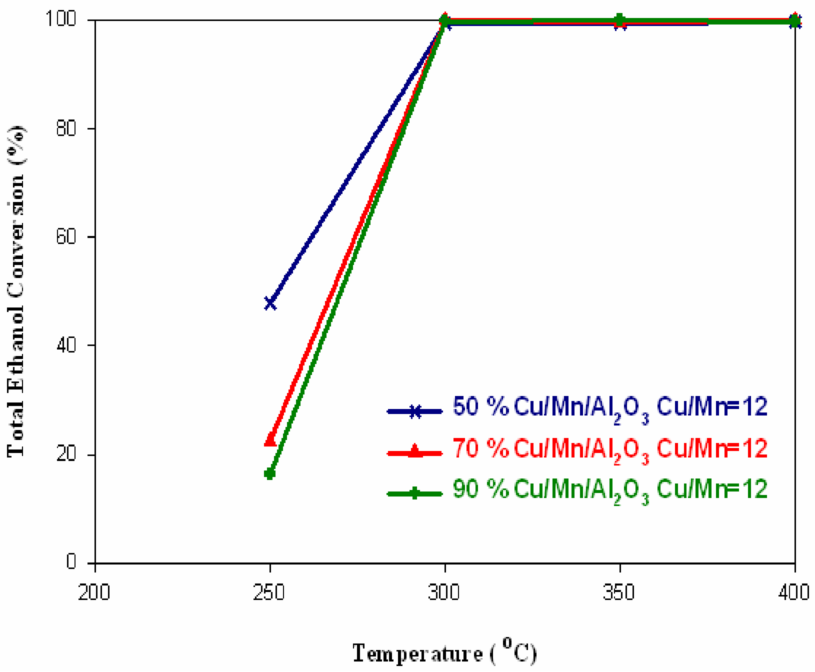

Figure 4.7. Effect of different weight loadings of CuO-Mn_2O_3/Al_2O_3 (Cu/Mn=12:1) on total ethanol conversion at various temperatures (Inlet Conc.=1500 ppm, SV=12000 h^{-1})

Similar to other Cu/Mn molar ratio, 70 % loading showed higher conversion activity for Cu/Mn=12:1 catalyst, too. However, as seen in Figure 4.7, when Cu:Mn molar ratio increased to 12, 70 % catalysts did not show high conversion as observed with Cu/Mn=1:1 and 5:1; in fact, yielding only 22 % of ethanol conversion at 250 ^{o}C. The low catalytic activity of copper manganese mixed oxide catalysts may be resulted from ethanol adsorption at lower temperatures. It is possible that when the surface exposed to a mixture of ethanol and oxygen, clean catalyst surface becomes covered with ethanol, just because, ethanol requires a single vacant adsorption site while oxygen requires two adjacent sites. Therefore, the dissociation of oxygen molecules on the surface may probably be harder than ethanol adsorption on the surface. Hence, ethanol coverage will result in activity decreasing on the surface. However, in the case of various reaction temperatures, catalytic behavior of copper manganese oxides can be understood clearly by the analysis of catalysts in terms of phase composition and specific surface area of each sample. It is a well known characteristic of manganese oxide catalysts that they have a wide range of stoichiometries and crystalline phases because Mn atoms are found in various oxidation states at different temperature ranges. Therefore, by changing metal molar ratio, phase composition responsible for the high catalytic activity, will also show differences at different reaction temperatures. Thus, it would be meaningful if the catalysts were tested in-situ using XPS to detect the exact oxidation state of metals during the reaction.

4.3.1. Deactivation of $CuO-Mn_2O_3/Al_2O_3$ Catalysts

After the catalysts were used, it was observed that activity decrease occurred for the catalyst at the same temperature. Figure 4.8 demonstrate ethanol conversion differences for the fresh and used 70 wt% $CuO-Mn_2O_3/Al_2O_3$ (Cu/Mn =1:1) catalyst. In the first usage of the catalyst, it yielded 76 % conversion at 250 °C, but after a while, more than second time usage, the same catalyst showed lower activity, yielding 35 % ethanol conversion at the same reaction temperature and conditions.

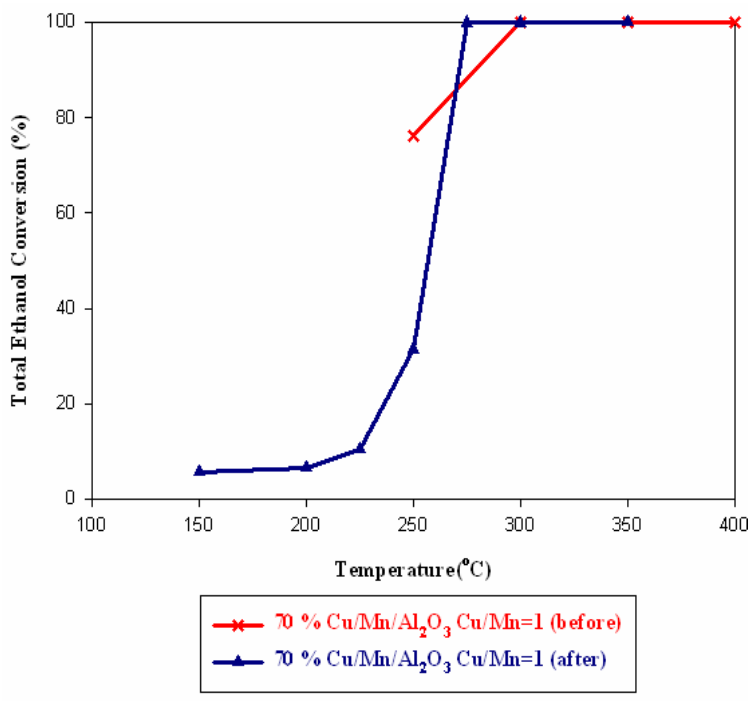

Figure 4.8. Deactivation of 70 wt % $CuO-Mn_2O_3/Al_2O_3$ (Cu/Mn=1:1) catalyst before and after reaction

In literature, the activity decrease of hopcalite materials was discussed by many researchers. According to Hutchings and coworkers (2009), the activity of hopcalite materials is mainly affected by two factors; namely surface area and the phase composition. It was observed that change of the oxidation states from Cu^{+2} to Cu^{+} and from Mn^{+3} to M^{+4} resulted in activity decrease in hopcalite catalysts. In addition, sintering, which is resulted from crystallization of amorphous hopcalite catalysts, leads to the decrease of the surface area; thus lowering of the catalytic activity (Taylor et al., 1997). Beside the sintering effect, the rapid deactivation of hopcalite catalysts is favored by the presence of moisture (Njagi et al., 2010). Maier et al. (2006) investigated the sol-gel derived $Cu_{20}Mn_{80}O_x$ and found that it was active for the oxidation of CO at room temperature in dry air. However, under humid air, they observed that the catalyst deactivation occurred within a few minutes. In addition, Hoflund and co-workers (1995) investigated the relation between CO_2 and the catalyst decay on gold catalysts and discussed the carbon species formed during the reaction and retained on the surface. By taking into account this, to figure out the main reasons, which cause the deactivation, one of the catalysts used in this study was analyzed with FT-IR.

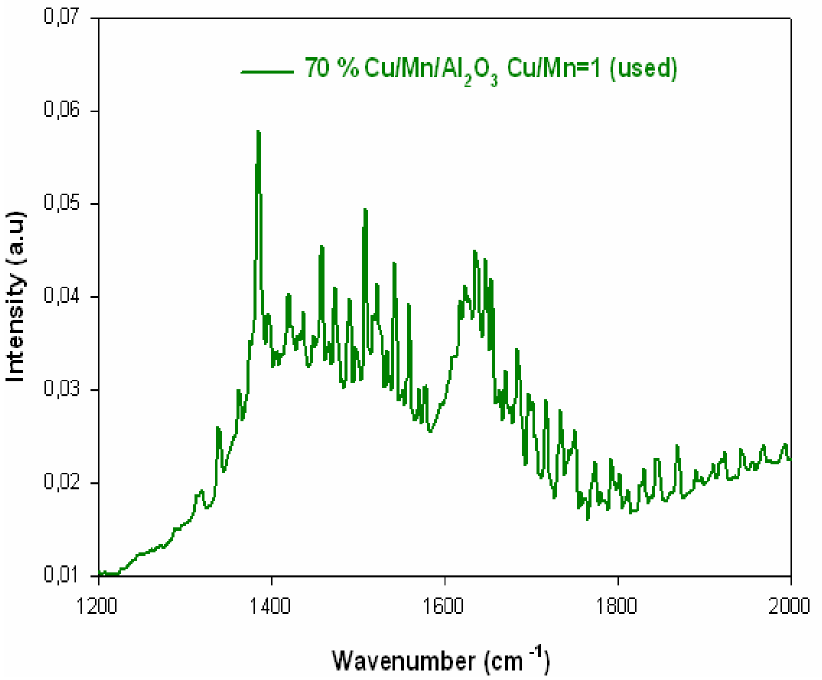

Figure 4.9. FT-IR spectra of used $Cu/Mn/Al_2O_3$ (Cu/Mn=1:1) catalysts.

By looking at the peaks, located between1200 and 1800 cm^{-1} in FT-IR spectra, it can be said that carbonaceous species occurred on the $Cu/Mn/Al_2O_3$ (Cu/Mn=1:1) catalysts. According to literature studies, the peaks located at around 1340-1363, 1418-1421 and 1484-1488 cm^{-1} are attributed to monodentate carbonates (Solis, 2010), whereas the peaks located at 1550-1565 and 1632-1639 cm^{-1} are generally attributed to bidentate carbonates. However, by considering experimental conditions, carbon dioxide in air and/or reaction by-products must be adsorbed on catalysts surface and resulted in the activity decrease.

Since the results obtained from the FT-IR spectra confirm the CO_2 adsorption on catalyst surface, new catalysts were synthesized. Depending on the results obtained before, 70 % loading for the various catalysts was selected. The new 'fresh' catalysts were tested at the same reaction conditions for total ethanol oxidation. Before using catalysts in the reaction system, the preparation route to synthesize the catalyst was the same as explained in material and methods section. Thus, after the preparation of the catalysts, they calcined at 500 °C for 2 h in an air stream and then reaction was carried out at the high temperatures and then the reaction temperature was lowered.

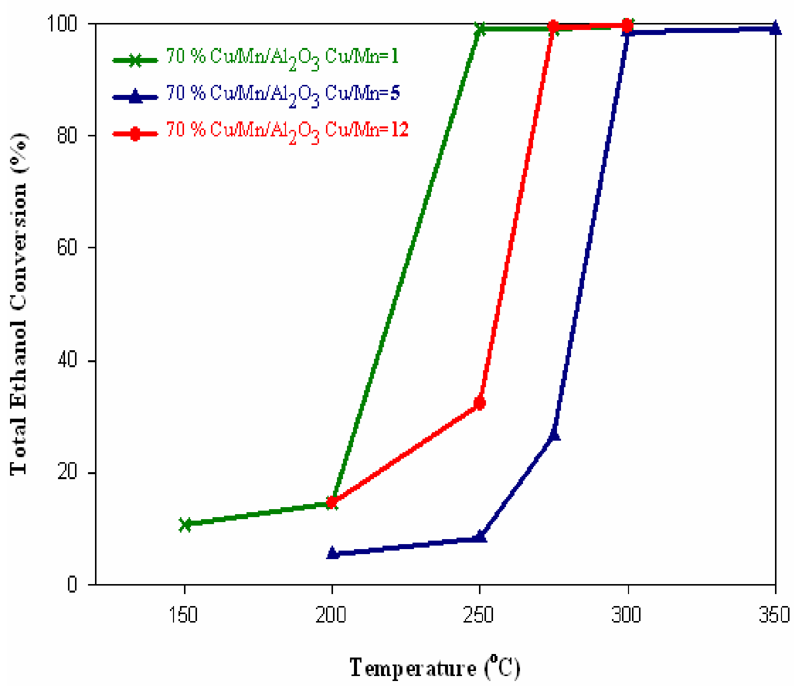

Figure 4.10. 70 % weight loading of varied molar ratios of CuO-Mn_2O_3/Al_2O_3 catalysts

Figure 4.10 demonstrate the catalysts activity of 70 % loading for Cu/Mn =1:1, 5:1 and 12:1 in the total ethanol conversion with respect to various reaction temperatures. In the comparison of the catalysts, Cu/Mn=1:1 catalyst is the most active one that yields almost 99 % ethanol conversion at 250 °C while the others convert less than 40 % ethanol . The activity of catalysts coincide with the results that observed before, for the Cu/Mn =1:1 and 12 (70 %) catalysts within the experimental error. However, Cu/Mn =5:1 (70 %) catalyst showed highly different result at 250 °C as compared to one conducted before. Although the same preparation method was applied, the decrease in the catalyst activity may be due to the increased crystallization of amorphous phase, and/or specific surface area lose. In addition, it may result from the formation and/or absence of species that was responsible for the high activity. In the evaluation of Cu/Mn=1:1 catalysts, the high activity can be explained by the presence of Cu^{+2} and Mn^{+3} oxidation states which is reported to be responsible for the high activity for the catalysts (Li, 2009). To explain the oxidation states of the working catalysts, it is necessary to have additional characterization techniques, such as X-ray photoelectron spectroscopy (XPS). In addition to oxidation states of Cu and Mn, the catalytic behavior can be related to the existence of a mixed oxide phase in the catalysts.

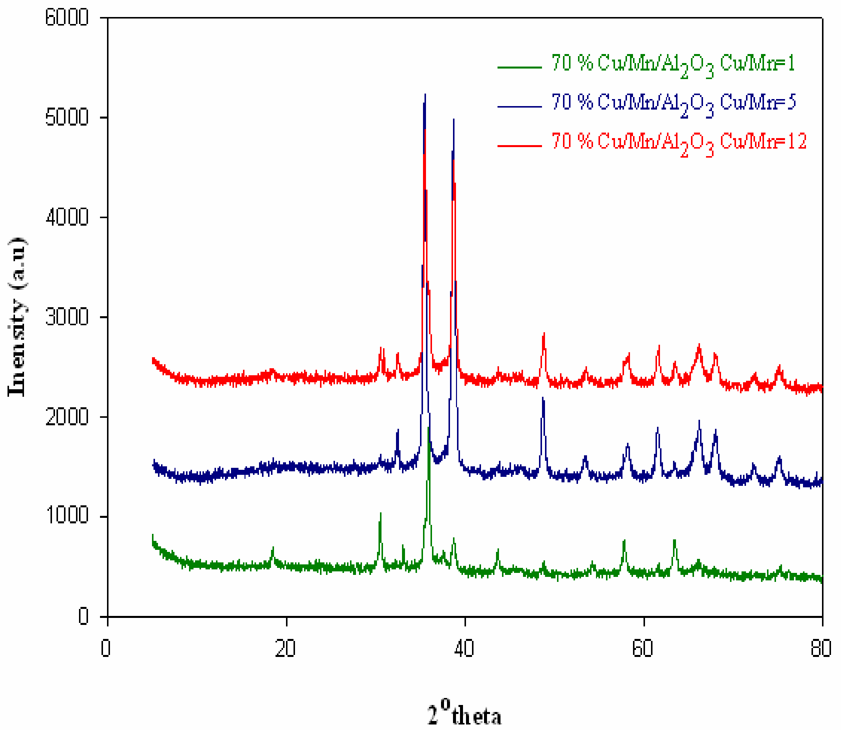

Figure 4.11. XRD pattern of different metal ratio of 70 % $CuO-Mn_2O_3/Al_2O_3$ catalysts

In order to examine the reason behind the activity differences, the phase composition of various synthesized oxides was analyzed with XRD measurements. In Figure 4.11, the diffraction pattern of each fresh (not used in reaction) catalysts were exhibited, but the differences in phase composition can be clearly understood from the figures given in the appendix section. According to X-ray patterns of the samples, Cu/Mn=1:1 catalyst mainly consists of $Cu_{1.5}Mn_{1.5}O_4$ and CuO phases. This result is in accordance with the study, in which catalyst activity was related with the existence of $Cu_{1.5}Mn_{1.5}O_4$ phase by Cadus et al. (2006). In addition, Hutchings et al. (2009) synthesized a catalyst by co-precipitation with a molar ratio Cu:Mn=1/1, and calcined at 500 °C. As found in this thesis study, they reported that $CuMn_xO_y$ mixed phase and

CuO was responsible for the high activity. Therefore, at this point, the activity of 70 % CuO-Mn_2O_3/Al_2O_3 (Cu/Mn=1:1) was due to the presence of the $Cu_{1.5}Mn_{1.5}O_4$ phase which is responsible for the high activity of catalysts.

To analyze the catalyst activity in terms of surface area, the specific surface areas of 'fresh' catalysts (before using them at any reaction) were measured using BET analysis method. Table 4.4 shows the BET surface areas of various molar ratios of (70%) Cu/Mn/Al_2O_3 catalysts.

Table 4.4. BET surface area of (70 % wt) CuO-Mn_2O_3/Al_2O_3 catalyst

Catalyst Type (70 % wt)	**Cu:Mn molar ratio**	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Avarage pore diameter (A)**
CuO-Mn_2O_3/Al_2O_3	1:1	92.35	0.0088	54.9384
CuO-Mn_2O_3/Al_2O_3	1:5	78.39	0.0076	45.6538
CuO-Mn_2O_3/Al_2O_3	1:12	79.97	0.1395	52.9843

Surface area measurements confirmed the activity behaviors of catalysts that the most active catalyst, which is CuO-Mn_2O_3/Al_2O_3 Cu/Mn=1:1, has the highest surface area while CuO-Mn_2O_3/Al_2O_3 Cu/Mn=5:1 and 12:1, have the comparable surface areas. This is in agreement with Hutchings et al. who pointed out that the surface area was of importance for the catalytic performance of copper manganese oxides. In comparison of Cu/Mn=5:1 and Cu/Mn=12:1 catalysts, 70 wt% CuO-Mn_2O_3/Al_2O_3 Cu/Mn=12:1 is more active than the other one. This may be resulted from existence of small copper manganese oxide crystallite phase not detectable by XRD.

In conclusion, for the ethanol oxidation reaction, 70 wt% CuO-Mn_2O_3/Al_2O_3 Cu/Mn=1:1 catalysts prepared by the single step sol-gel method showed the highest catalytic performance in metal oxide catalysts due to existence of $Cu_{1.5}Mn_{1.5}O_4$ phase. In addition, a high catalyst surface area provides better dispersion that enables the catalyst to convert ethanol to CO_2. For Cu-Mn mixed oxide catalysts (70 wt%), carbon dioxide was observed above 250 ^oC (gas phase products are showed in Table A.1 in Appendix A) and also, any formation of partial oxidation products, such as acetaldehyde, was not detected.

Importance of the presence of the catalyst on the ethanol conversion may illustrated easily as seen in Figure 4.12 below.

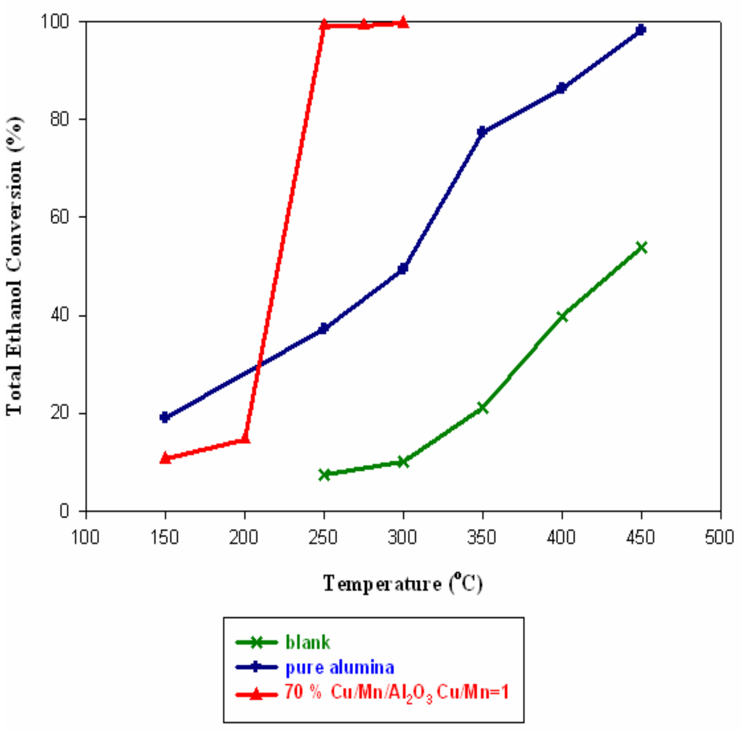

Figure 4.12. Effect of blank and pure alumina catalyst

As seen in Figure 4.12, the gas phase reaction of ethanol was below 10 % conversion at 250 °C and reaction over pure alumina exhibited around 30 % at the same temperature. However, presence of Cu/Mn (70 wt %) on alumina significantly increased the conversion such that ~99 % ethanol conversion achieved at the same temperature, indicating that Cu/Mn catalyst was responsible in obtaining high ethanol combustion. Hence, $CuO-Mn_2O_3/Al_2O_3$ (70 wt %) is found to be highly active catalyst in the combustion of ethanol.

4.4. Effect of Single Composition of CuO/Al_2O_3 and Mn_2O_3/Al_2O_3 Catalysts on Ethanol Oxidation

It is known that combination of MnO_x with other oxides, such as a high surface area support, exhibit different catalytic activity as compared to a single component catalyst (Cadus et al., 2006). It has a great impact on its bulk and surface structure and well dispersion of MnO_x on the support surface leads to significant increases in catalytic activity. In addition, the supported manganese oxide could be reduced at a lower temperature than bulk Mn_2O_3. By considering all of these, the synergy between the copper manganese mixed oxide catalysts and single oxides of CuO and Mn_2O_3 were investigated in terms of catalyst activity as a function of various temperatures.

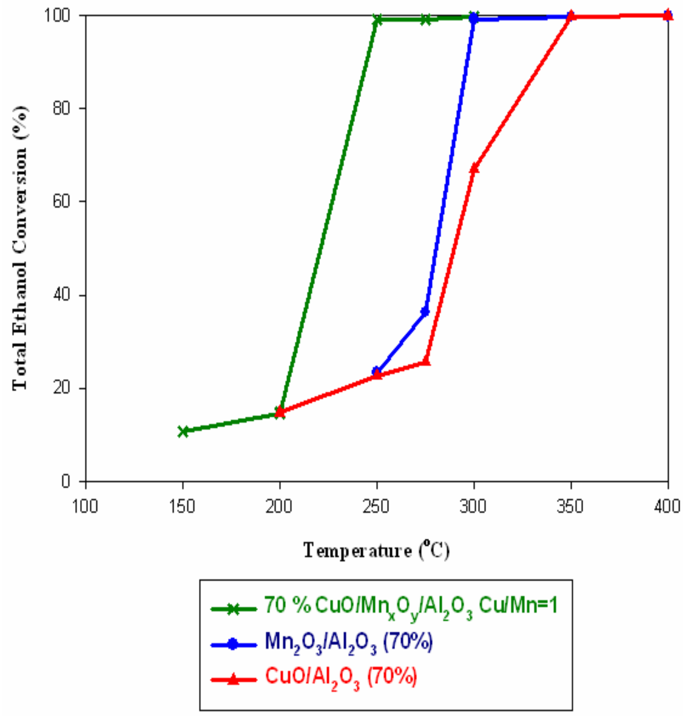

Figure 4.13. The activities of Mn_2O_3 and CuO single oxides on alumina

Figure 4.13 indicates that the complete conversion of ethanol over Mn_2O_3/Al_2O_3 occurred at 300 °C, while it was at 350 °C on CuO/Al_2O_3. However, ethanol oxidation on pure alumina has also a reasonable contribution on the catalyst activity because at 300 °C, nearly 50 % of ethanol was converted by pure alumina. When the activity of single oxide of CuO and Mn_2O_3 on alumina was compared to 70 wt % CuO-Mn_2O_3/Al_2O_3 (Cu:Mn=1) mixed oxide catalyst, the combination of copper and manganese oxide result in a significant increase in the oxidation of ethanol. Although single phase of copper and manganese oxides can only convert 20 % of ethanol, copper manganese oxide (70 wt %, Cu:Mn=1), is highly active even at 250 °C; yielding almost 99 % ethanol conversion. Therefore, the results obtained in this study confirm that the combination of MnO_x with other oxides deposited on high surface area support exhibit a high catalytic activity as compared to a single component of the catalysts in the oxidation of ethanol.

Activity differences observed between CuO/Al_2O_3 and Mn_2O_3/Al_2O_3 catalysts could be explained by surface areas. In addition, it is reported that higher catalyst surface area leads to increase in catalytic activity of MnO_x (Cadus et al., 2006). Moreover, Marion et al. (1990) reported that low Cu loading on Al_2O_3 led to better dispersed ionic Cu, while high loading of Cu on alumina result in poorly dispersed CuO with more covalent character. They concluded that ionic character of Cu resulted in high catalytic activity for methane combustion. Furthermore, Fortunato et al. (2001) approved that, the catalysts with lower Cu^+ concentration was more active than the sample with a high content of univalent copper. Therefore, it is important to determine the oxidation states of species and the surface area of the catalysts. Comparison of BET surface areas of fresh CuO/Al_2O_3 and Mn_2O_3/Al_2O_3 is shown in Table 4.5.

Table 4.5. BET surface area of CuO/Al_2O_3 and Mn_2O_3/Al_2O_3 catalysts

Catalyst Type (70 % wt)	BET Surface Area
Mn_2O_3/Al_2O_3	83.92 m^2/g
CuO/Al_2O_3	79.81 m^2/g
Pure Al_2O_3	350 m^2/g

4.5. Effect of Pd-Mn_2O_3/Al_2O_3 Bimetallic Catalyst on Ethanol Combustion

It is known that to use noble metal catalysts in industry are costly and show less resistant to poisoning. It may be possible to lower the amounts of noble metals and improve the catalyst activity by combining noble metals and metal oxides. It was reported that in methanol/formaldehyde combustion, addition of 0.1 % Pd to 18.2 wt % Mn/Al_2O_3 catalysts decreased the light off temperature from 220 ^oC to 90 ^oC; thus increasing the activity (Galvan et al., 2004). In addition, to lower the deactivation of the catalysts in the presence of moisture, Maier et al. (2010) investigated the effect of platinum and palladium addition to hopcalite catalysts and found that the addition of palladium is proved to have positive effect. However, in their study, they observed that 0.5 wt % Pt did not improve water resistance of active hopcalite catalysts.

In this study, the effect of different loading of palladium metal, prepared by a single step sol-gel method, on the manganese oxide catalytic activity was investigated as a function of temperature for the total ethanol conversion.

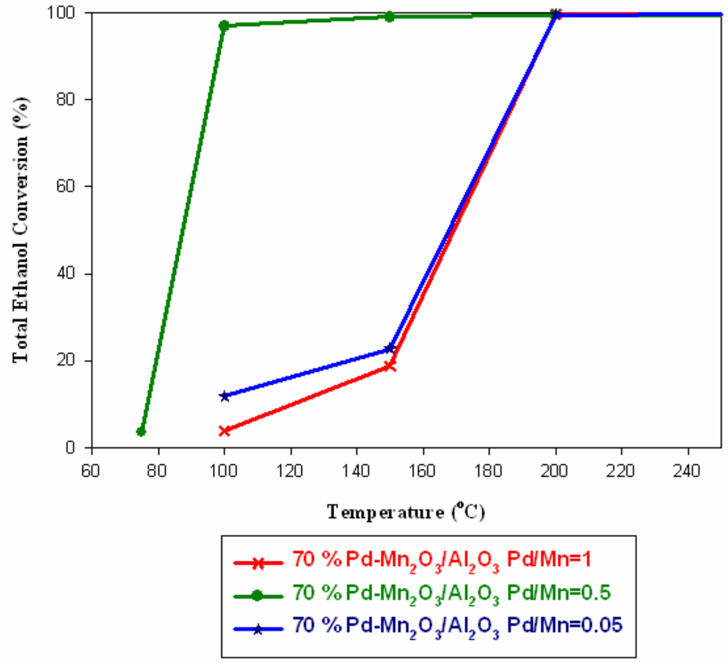

Figure 4.14. Effect of Pd addition on ethanol combustion

As observed before, ~99% ethanol conversion was obtained over Mn_2O_3/Al_2O_3 catalysts at 300 C. However, as shown in Figure 4.14, palladium addition to Mn_2O_3/Al_2O_3 improved metal oxide catalytic activity and the best activity was achieved over Pd loaded catalysts having Pd/Mn molar ratio of 0.5. To understand why the Pd:Mn=0.5 showed significant difference than the catalysts having different molar ratio, XRD patterns of samples were taken.

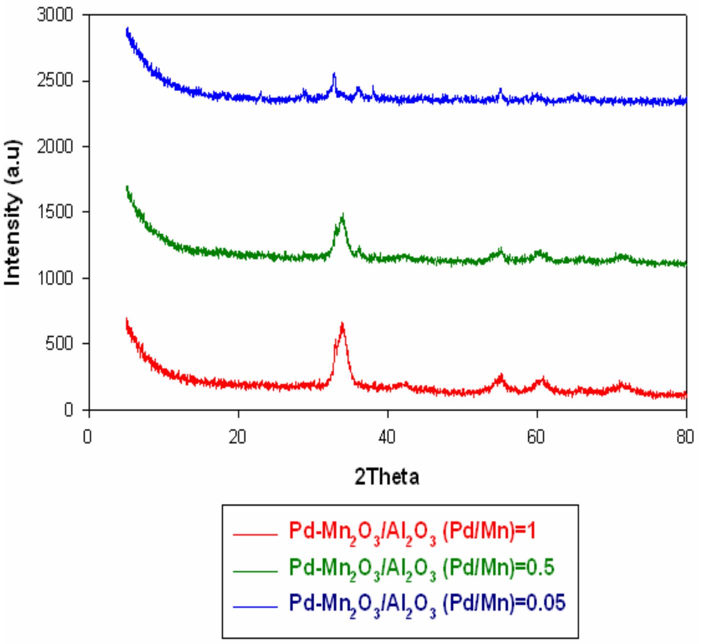

Figure 4.15. XRD pattern of used Pd- Mn_2O_3/Al_2O_3 catalysts

Figure 4.15 shows different metal loaded Pd-Mn_2O_3/Al_2O_3 catalysts. It was analyzed that all diffraction lines correspond to Mn_2O_3 crystallites located at 32.93 and 55.14 of 2Θ angles. The activity of the bimetallic catalysts was explained by the synergy between supported manganese and palladium phases (Galvan et al., 2004). They also associated this activity with the ability of manganese oxide to release oxygen. They claimed that this released oxygen molecule facilitated the formation of the PdO phase and then a fraction of this PdO reduced to Pd and that provided sites for the decomposition of organics. However, PdO crystallite formation was only observed at 34.13 and 55.15 of 2Θ angles over Pd:Mn=1 catalysts (Other related peaks are shown in Figure A.11 in Appendix A). Therefore, to explain activity differences clearly, further studies must be carried out. It was reported that, the existence of oxygen vacancies may improve the catalytic performance of the catalysts. In other words, it is important to determine the oxygen vacancies responsible for the improvement of catalyst activity using temperature programmed desorption (TPD) and temperature programmed reaction (TPR) techniques. In general, two types of desorption peaks, namely surface and bulk oxygen, are observed. A combustible molecule may adsorb on the surface oxygen vacancies or it may use the oxygen in the catalyst bulk. In conclusion, by determining the oxygen vacancies, its contribution to catalyst activity and morphology can be understood clearly. Unfortunately, these techniques are not currently available in out institute.

4.6. Carbon Monoxide Oxidation

In carbon monoxide oxidation, 0.5 vol % CO was tested over 70 wt% Cu/Mn/Al_2O_3 ($(Cu/Mn)_{molar}$=1, 5, and 12) mixed oxides and 0.5 % Pd loaded alumina catalysts. Between 150-450 °C, their product analyses were done by a gas chromatograph-mass spectrometry. A small amount of carbon dioxide formation was observed. However, the conversion of CO to CO_2 was not quantitatively obtained due to the difficulties in separation of CO and small amount of CO_2 in the GC column.

As widely reported in literature, the activity of the hopcalite catalysts in CO oxidation is strongly depend on the redox couple of $Cu^{+2}+Mn^{+3}=Cu^{+}+Mn^{+4}$. In addition, amorphous $CuMn_2O_4$ phase is important parameter to have high activity. By considering all of these, it could be said that some CO_2 observation on Cu-Mn mixed oxides might be resulted from enrichment of Cu^{+} and Mn^{+4} on the surface or crystallization of the $CuMn_xO_y$ phase. However, to tell the main the reason, further study is needed.

CHAPTER 5

CONCLUSION

In this study, ethanol and carbon monoxide oxidation was investigated over different types and weight loadings of metal and metal oxide xerogel catalysts. Based on the converted amount of ethanol and/or carbon monoxide, each catalysts performance was determined at various temperatures.

In ethanol oxidation, it was observed that increasing Pt loading resulted in increasing conversion of ethanol. Among Pt loading used in this study, 3 wt % Pt loading in Pt/Al_2O_3 showed that highest activity in such a way that it yielded almost 96 % ethanol conversion at 75 ^oC. In contrast, for the mixed metal oxide catalysts, 70 % loading for $CuO-Mn_2O_3/Al_2O_3$ with Cu/Mn molar ratio of 1 exhibited the high catalytic activity due to presence of copper manganese oxide phase. It converted almost 99 % of ethanol at 250 ^oC while this conversion was obtained at higher temperatures for the metal oxide catalysts with other loadings and Cu/Mn ratios due to absence of $Cu_{1.5}Mn_{1.5}O_4$ phase. Products analyzed by a GC-MS were CO_2 for all the catalysts at high temperatures while ethanol and small amount of ethyl acetate were measured at low temperatures. XRD and BET analyses showed that a small crystallite size and a high surface area were important parameters to obtain highly active catalyst most probably due to the accessibility to active sites on the catalysts surface. In addition, according to FT-IR analyses, it was found that the deactivation which resulted in decreasing activity, occurred on $CuO-Mn_2O_3/Al_2O_3$ catalyst surface due to the presence of carbonaceous species most probably formed by carbon dioxide.

To figure out the effect of adding Cu and/or Mn on catalyst activity, mixed oxides and single oxides of copper and manganese were compared. It was observed that prepared $CuO-Mn_2O_3/Al_2O_3$ mixed oxide exhibited higher catalytic activity than Mn_2O_3/Al_2O_3 and CuO/Al_2O_3 single oxides due to the formation of a $Cu_{1.5}Mn_{1.5}O_4$ mixed phase. Moreover, palladium addition was investigated over Mn_2O_3/Al_2O_3 (70 wt %) catalysts to study possible improvement of the catalysts activity in the presence of noble metal addition. Results indicated that, addition of Pd ($(Pd/Mn)_{molar}=0,5$) enhanced the activity of metal oxide catalyst.

High conversion catalysts, which were tested in ethanol combustion, were used in CO oxidation. However, results were only able to demonstrate the presence of some amount of combustion product, such as carbon dioxide, between 150 and 450 ^{o}C.

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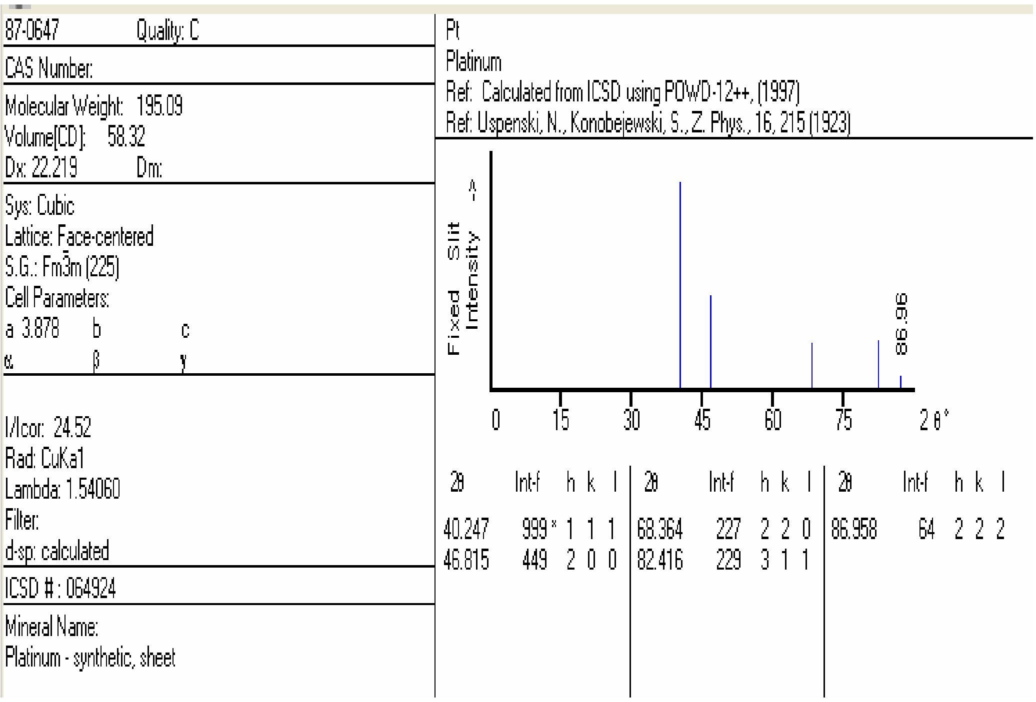
APPENDIX A

XRD PATTERN OF CATALYSTS



87-0647 Quality: C

CAS Number:

Molecular Weight: 195.09
Volume[CD]: 58.32
Dx: 22.219 Dm:

Sys: Cubic
Lattice: Face-centered
S.G.: Fm$\bar{3}$m (225)
Cell Parameters:
a 3.878 b c
α β γ

I/Icor: 24.52
Rad: CuKa1
Lambda: 1.54060
Filter:
d-sp: calculated

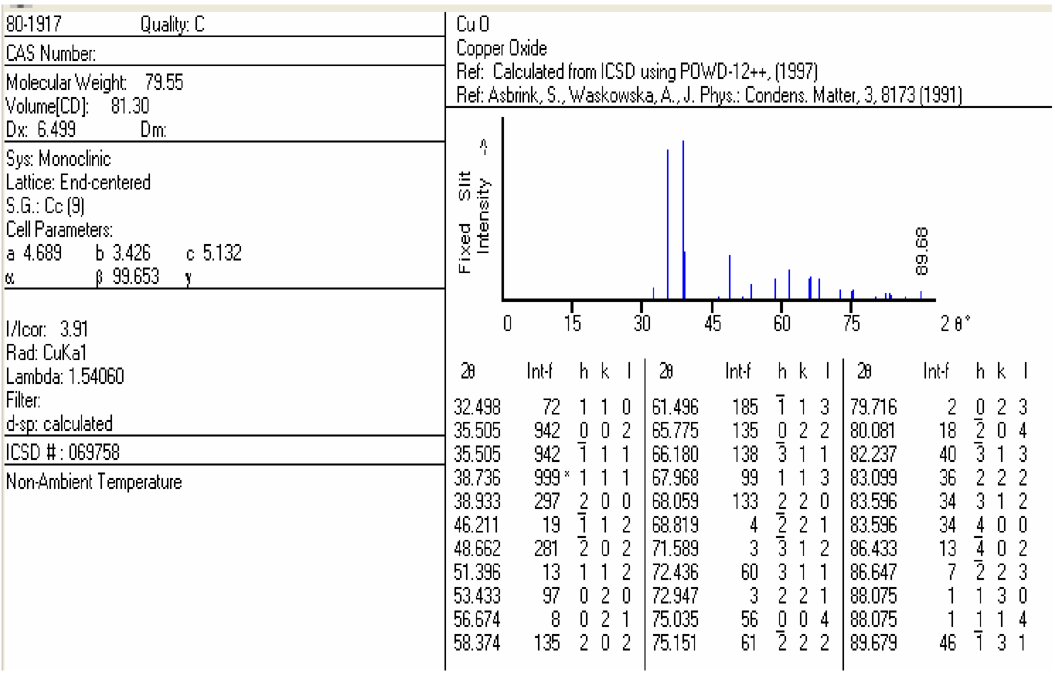
ICSD # : 064924

Mineral Name:
Platinum - synthetic, sheet

Pt
Platinum
Ref: Calculated from ICSD using POWD-12++, (1997)
Ref: Uspenski, N., Konobejewski, S., Z. Phys., 16, 215 (1923)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
40.247	999 *	1	1	1	68.364	227	2	2	0	86.958	64	2	2	2
46.815	449	2	0	0	82.416	229	3	1	1					

Figure A.1. Powder diffraction data of Platinum (Ref.No: 87-0647)



80-1917 Quality: C

CAS Number:

Molecular Weight: 79.55
Volume[CD]: 81.30
Dx: 6.499 Dm:

Sys: Monoclinic
Lattice: End-centered
S.G.: Cc (9)
Cell Parameters:
a 4.689 b 3.426 c 5.132
α β 99.653 γ

I/Icor: 3.91
Rad: CuKa1
Lambda: 1.54060
Filter:
d-sp: calculated

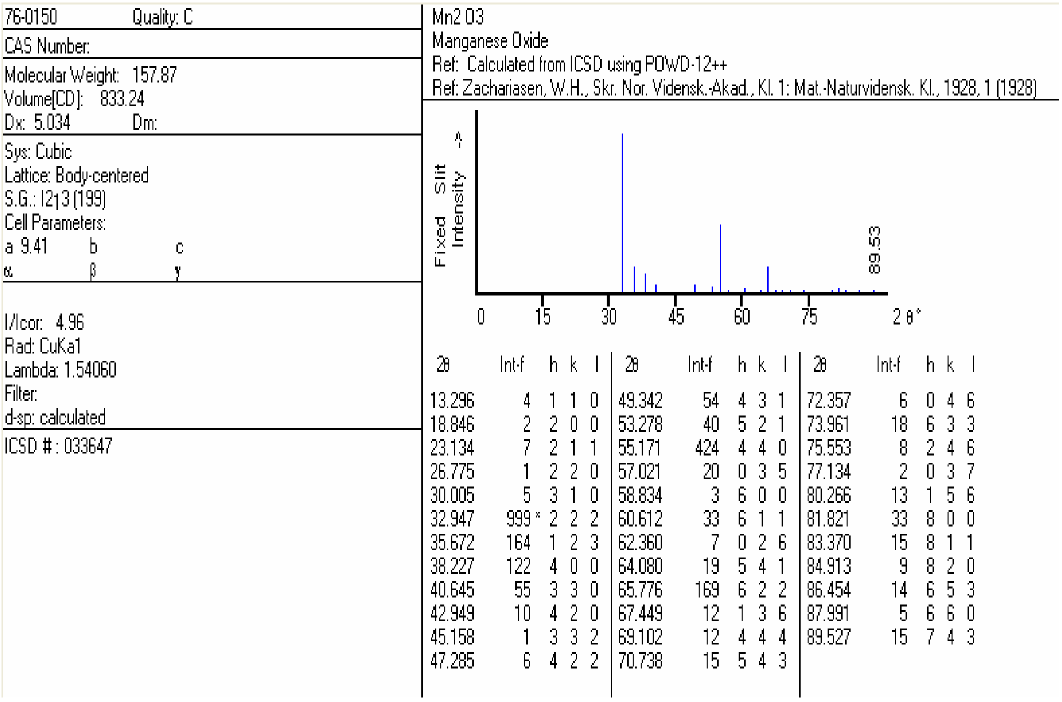
ICSD # : 069758

Non-Ambient Temperature

Cu O
Copper Oxide
Ref: Calculated from ICSD using POWD-12++, (1997)
Ref: Asbrink, S., Waskowska, A., J. Phys.: Condens. Matter, 3, 8173 (1991)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
32.498	72	1	1	0	61.496	185	$\bar{1}$	1	3	79.716	2	0	2	3
35.505	942	0	0	2	65.775	135	0	2	2	80.081	18	$\bar{2}$	0	4
35.505	942	$\bar{1}$	1	1	66.180	138	$\bar{3}$	1	1	82.237	40	$\bar{3}$	1	3
38.736	999 *	1	1	1	67.968	99	1	1	3	83.099	36	2	2	2
38.933	297	2	0	0	68.059	133	2	2	0	83.596	34	3	1	2
46.211	19	$\bar{1}$	1	2	68.819	4	$\bar{2}$	2	1	83.596	34	4	0	0
48.662	281	$\bar{2}$	0	2	71.589	3	$\bar{3}$	1	2	86.433	13	$\bar{4}$	0	2
51.396	13	1	1	2	72.436	60	3	1	1	86.647	7	$\bar{2}$	2	3
53.433	97	0	2	0	72.947	3	2	2	1	88.075	1	1	3	0
56.674	8	0	2	1	75.035	56	0	0	4	88.075	1	1	1	4
58.374	135	2	0	2	75.151	61	$\bar{2}$	2	2	89.679	46	$\bar{1}$	3	1

Figure A.2. Powder diffraction data of copper oxide (Ref.No: 80-1917)



76-0150 Quality: C

CAS Number:

Molecular Weight: 157.87
Volume[CD]: 833.24
Dx: 5.034 Dm:

Sys: Cubic
Lattice: Body-centered
S.G.: I2₁3 (199)
Cell Parameters:
a 9.41 b c
α β γ

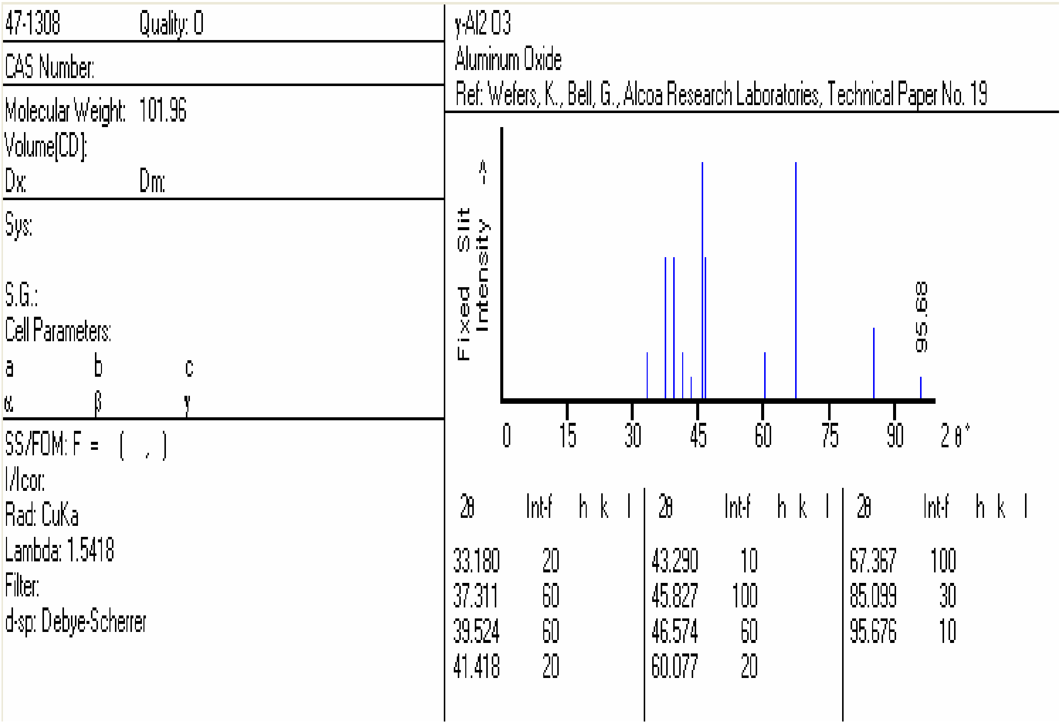
I/Icor: 4.96
Rad: CuKa1
Lambda: 1.54060
Filter:
d-sp: calculated

ICSD # : 033647

Mn2 O3
Manganese Oxide
Ref: Calculated from ICSD using POWD-12++
Ref: Zachariasen, W.H., Skr. Nor. Vidensk.-Akad., Kl. 1: Mat.-Naturvidensk. Kl., 1928, 1 (1928)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
13.296	4	1	1	0	49.342	54	4	3	1	72.357	6	0	4	6
18.846	2	2	0	0	53.278	40	5	2	1	73.961	18	6	3	3
23.134	7	2	1	1	55.171	424	4	4	0	75.553	8	2	4	6
26.775	1	2	2	0	57.021	20	0	3	5	77.134	2	0	3	7
30.005	5	3	1	0	58.834	3	6	0	0	80.266	13	1	5	6
32.947	999 *	2	2	2	60.612	33	6	1	1	81.821	33	8	0	0
35.672	164	1	2	3	62.360	7	0	2	6	83.370	15	8	1	1
38.227	122	4	0	0	64.080	19	5	4	1	84.913	9	8	2	0
40.645	55	3	3	0	65.776	169	6	2	2	86.454	14	6	5	3
42.949	10	4	2	0	67.449	12	1	3	6	87.991	5	6	6	0
45.158	1	3	3	2	69.102	12	4	4	4	89.527	15	7	4	3
47.285	6	4	2	2	70.738	15	5	4	3					

Figure A.3. Powder diffraction data of manganese oxide (Ref.No: 76-0150)



47-1308 Quality: O

CAS Number:

Molecular Weight: 101.96
Volume[CD]:
Dx: Dm:

Sys:

S.G.:
Cell Parameters:
a b c
α β γ

SS/FOM: F = (,)
I/Icor:
Rad: CuKa
Lambda: 1.5418
Filter:
d-sp: Debye-Scherrer

γ-Al2 O3
Aluminum Oxide
Ref: Wefers, K., Bell, G., Alcoa Research Laboratories, Technical Paper No. 19

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
33.180	20				43.290	10				67.367	100			
37.311	60				45.827	100				85.099	30			
39.524	60				46.574	60				95.676	10			
41.418	20				60.077	20								

Figure A.4. Powder diffracion data of Aluminum Oxide (Ref.No: 47-1308)

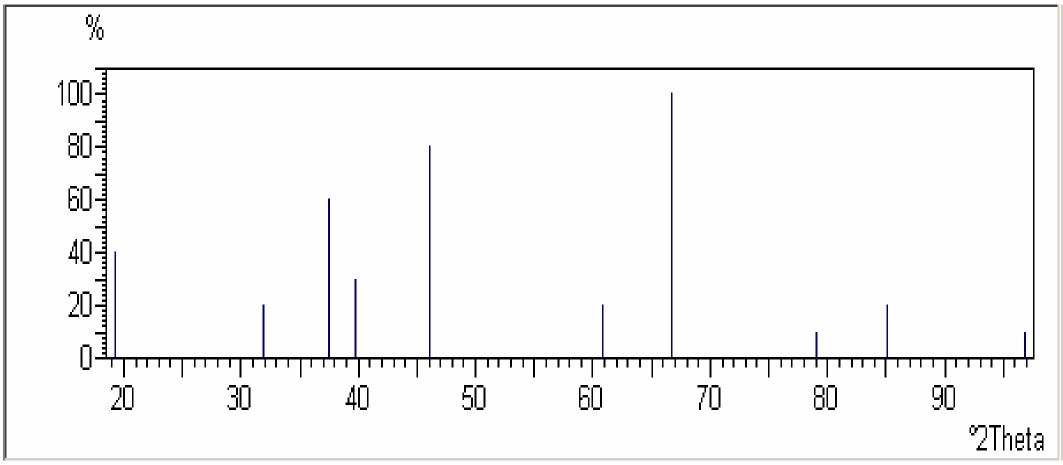


Figure A.5. Shematic of diffraction pattern of Al_2O_3 (Ref.No: 04-0875)

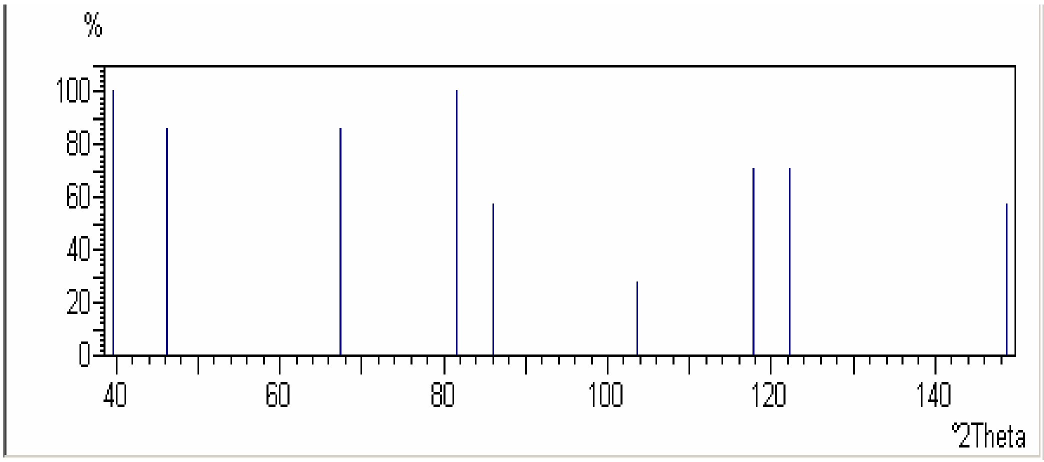


Figure A.6. Shematic of diffraction pattern of Pt (Ref.No: 01-1190)

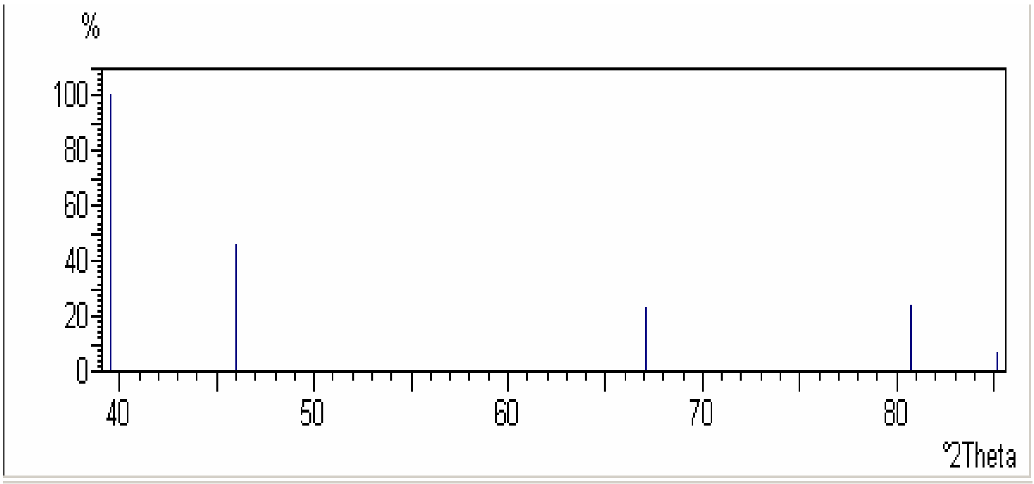


Figure A.7. Shematic of diffraction pattern of Pt (Ref.No: 87-0636)

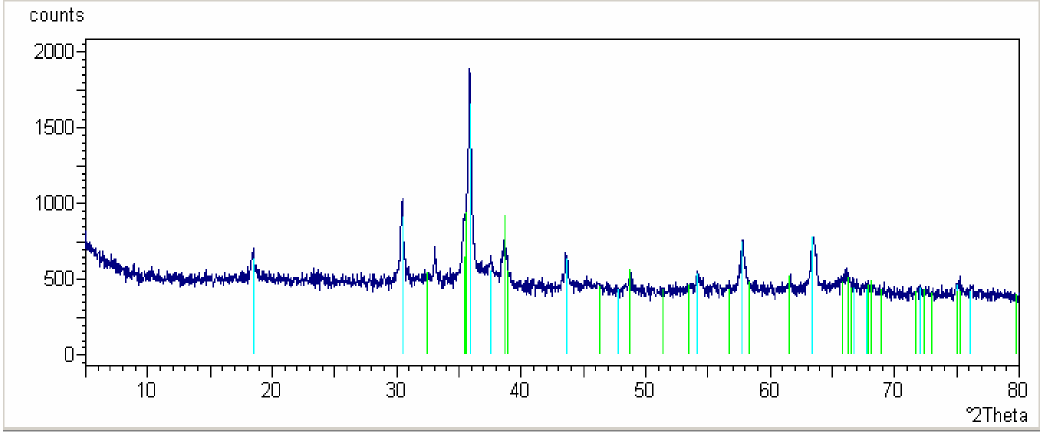


Figure A.8. 70% CuO-Mn_2O_3/Al_2O_3 Cu/Mn=1 peaks in blue: Copper Manganese oxide (Ref.No: 70-0262); in green: Copper oxide (Ref.No: 48-1548)

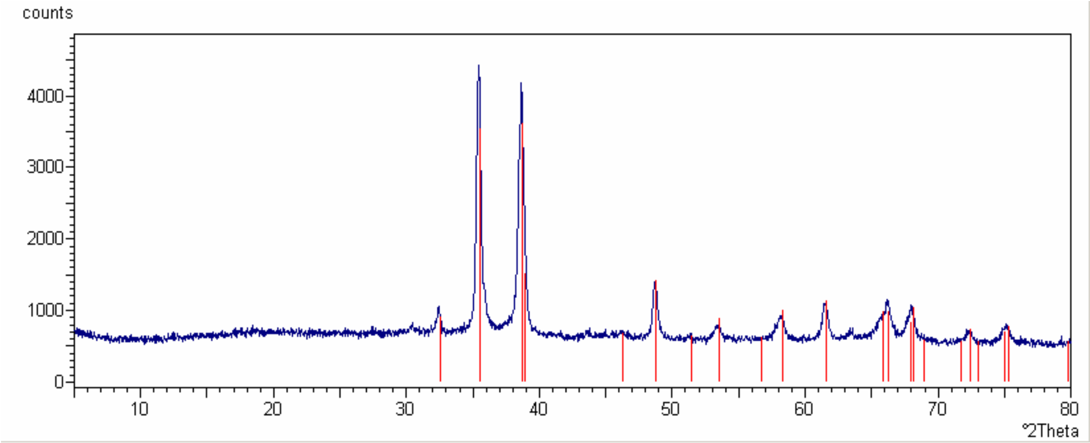


Figure A.9. 70% CuO-Mn_2O_3/Al_2O_3 Cu/Mn=5 peaks in red: Copper oxide (Ref.No: 72-0629)

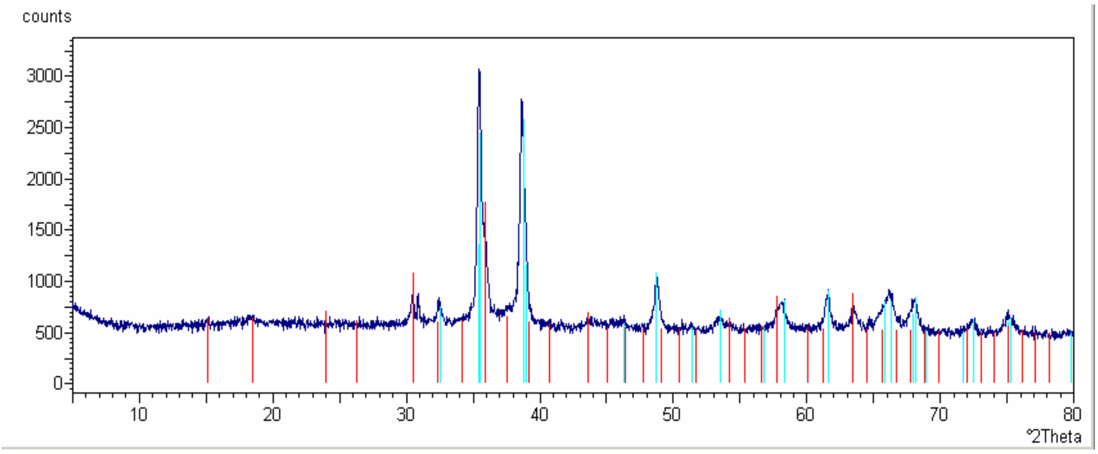
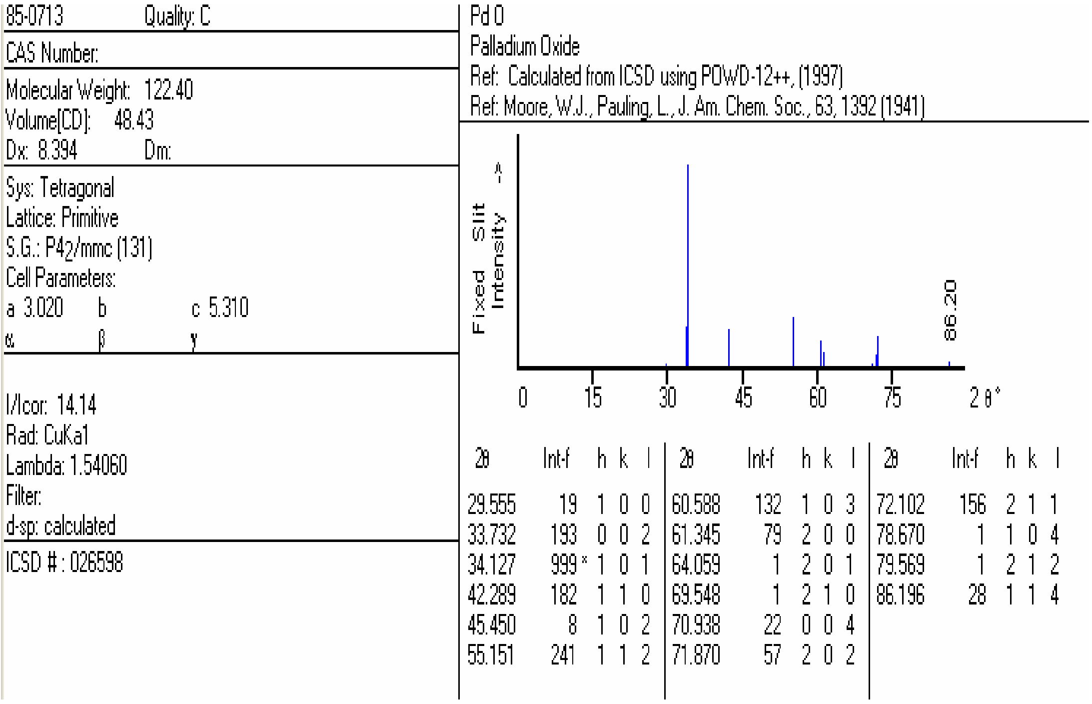


Figure A.10. 70% CuO-Mn_2O_3/Al_2O_3 Cu/Mn=12 peaks in red: Copper manganese oxide (Ref.No: 70-0261); peaks in blue: Copper oxide (Ref:80-1268))



85-0713 Quality: C
CAS Number:
Molecular Weight: 122.40
Volume[CD]: 48.43
Dx: 8.394 Dm:
Sys: Tetragonal
Lattice: Primitive
S.G.: $P4_2/mmc$ (131)
Cell Parameters:
a 3.020 b c 5.310
α β γ

I/Icor: 14.14
Rad: CuKa1
Lambda: 1.54060
Filter:
d-sp: calculated
ICSD # : 026598

Pd O
Palladium Oxide
Ref: Calculated from ICSD using POWD-12++, (1997)
Ref: Moore, W.J., Pauling, L., J. Am. Chem. Soc., 63, 1392 (1941)

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
29.555	19	1	0	0	60.588	132	1	0	3	72.102	156	2	1	1
33.732	193	0	0	2	61.345	79	2	0	0	78.670	1	1	0	4
34.127	999 *	1	0	1	64.059	1	2	0	1	79.569	1	2	1	2
42.289	182	1	1	0	69.548	1	2	1	0	86.196	28	1	1	4
45.450	8	1	0	2	70.938	22	0	0	4					
55.151	241	1	1	2	71.870	57	2	0	2					

Figure A.11. Powder diffraction data of Palladium Oxide (Ref.No: 85-0713)

Table A.1. Types of Catalyts' Products at Varying Operating Temperatures

Catalyst Type	REACTION TEMPERATURES (^{0}C)									
	450	400	350	300	250	200	150	100	75	50
1% Pt/Al_2O_3	■	■	■	■	■	■	■	▲	▲	▲
2% Pt/Al_2O_3	■	■	■	■	■	■	■▲	■▲	▲●	▲●
3% Pt/Al_2O_3	■	■	■	■	■	■	■	■	■▲●	■▲●
70 % Cu/Mn/ Al_2O_3 Cu/Mn=1	■	■	■	■	■	▲●	▲			
70 % Cu/Mn/ Al_2O_3 Cu/Mn=5	■	■	■	■	▲	▲●	▲			
70 % Cu/Mn/ Al_2O_3 Cu/Mn=12	■	■	■	■	■▲●	▲	▲			
Blank	■▲	■▲	▲	▲	▲	▲	▲			
Pure Alumina	■	▲★●■	▲★●■	▲★●						

▲ Ethanol ■ Carbon dioxide ● Ethyl acetate ★Ethyl ether