CATALYTIC OXIDATION OF VOLATILE COMPOUNDS GENERATED DURING FRYING PROCESS USING SUNFLOWER OIL

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ABSTRACT

CATALYTIC OXIDATION OF VOLATILE COMPOUNDS GENERATED DURING FRYING PROCESS USING SUNFLOWER OIL

The main goal of this 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 combustion of sunflower oil over modified single step sol-gel made Al_2O_3 supported metal and mixed metal oxides. All catalysts were tested at 170 ^{o}C and catalysts giving good activity among them were tested also at 195 ^{o}C. As a monometallic catalysts, Ni/Al_2O_3 (10, 25, 50 % Ni loaded), Ni/Al_2O_3 (50 % Ni loaded) derived from different Ni precursors, Mn/Al_2O_3 (50, 70 % Mn loaded) and as a bimetallic catalysts, $Ni-Mn_2O_3/Al_2O_3$ with Ni/Mn mass ratios of 20:56 and 23:66 catalysts were synthesized by a modified single step sol-gel method. In addition, in synthesizing step of bimetallic catalysts, the order of adding precursor was studied. The catalytic activities of all the catalysts were compared to 3% Pt/alumina. The combustion performances of pure Al_2O_3 and catalyst coated aluminum plates were also considered and volatile compound analysis was monitored by GC-MS and the amounts of CO and CO_2 generated during the combustion were calculated quantitatively from GC analyses.

The characterization of the samples was performed by XRD and BET techniques and it was observed that among the monometallic oxide catalysts, 50% Mn_xO_y/Al_2O_3 showed slightly better activity at 170 ^{o}C due to the its highly reducible oxide property. Among mixed metal/metal oxide catalysts, 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) was the catalyst demonstrated the highest catalytic activity at both temperatures. It seems to be due to the interaction between nickel and manganese oxide. In addition, the combustion was also carried out by using catalyst coated aluminum plates to observe if the best catalyst formulation found from the studies on the powder catalysts would be applicable for the self-cleaning metal plates used in the household ovens. In fact, the catalyst coated plates showed higher conversion at 170 ^{o}C in 1 h than that observed on the powder catalyst due to the elimination of internal mass transfer limitation.

ÖZET

AYÇİÇEK YAĞI KULLANILAN KIZARTMA İŞLEMİ ESNASINDA OLUŞAN UÇUCU BİLEŞENLERİN KATALİTİK OKSİDASYONU

Bu çalışmanın asıl amacı, ayçiçek yağının modifiye edilmiş tek basamaklı sol-gel yöntemiyle yapılan alumina destekli metal ve karışık metal oksit üzerindeki yanmasında; metal çeşidinin, metal oksit çeşidinin ve metal/oksit yüklemesinin sıcaklığa bağlı dönüşüm üzerindeki etkisini incelemektir. Tüm katalizörler 170 ^{o}C' de test edilmiştir ve aralarından iyi katalitik aktivite verenler 195 ^{o}C' de de test edilmiştir. Tek metalli katalizörler olarak, Ni/Al$_2$O$_3$ (10, 25, 50 % Ni yüklenmiş), farklı prekursörlerden elde edilmiş Ni/Al$_2$O$_3$ (50% yüklenmiş), Mn/Al$_2$O$_3$ (50, 70 % Mn yüklenmiş) ve çift metalli katalizörler olarak, Ni-Mn$_2$O$_3$/Al$_2$O$_3$ ve Ni: Mn kütle oranları 20:56 and 23:66 katalizörleri modifiye edilmiş tek basamaklı sol-gel yöntemiyle sentezlenmiştir. Ayrıca çift metalli katalizörlerin sentezi esnasında, eklenen prekursörün sırası da çalışılmıştır. Bunun yanında, sentezlenen tüm katalizörlerin katalitik aktiviteleri referans katalizör 3% Pt/alumina ile kıyaslanmıştır. Saf alumina ve kaplanmış aluminyum plakanın da yakma aktiviteleri göz önüne alınmıştır ve uçucu bileşen analizi GC-MS ile gözlemlenmiş ve CO ve CO$_2$ miktarları nicel olarak hesaplanmıştır.

Örneklerin karakterizasyonları XRD ve BET teknikleri kullanılarak yapılmıştır. Tek metalli katalizörler içinde, 50% Mn/Al$_2$O$_3$ büyük derecede indirgenebilir oksit özelliğinden ötürü 170 ^{o}C' de biraz daha iyi aktivite göstermiştir. Çift metalli katalizörler içinde, 20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (Önce nickel prekusörü eklendi), nikel ve manganez oksitin birlikte çalışma etkisinden dolayı her iki sıcaklıkta en yüksek aktiviteyi göstermiştir. Bunun yanında yakma işlemi, evlerdeki fırınlarda kullanılan kendi kendini temizleyen metal plakaların özelliğini gözlemlemek için kaplanmış aluminyum plaka kullanılarak yapılmıştır. Ayrıca, katalizör ile kaplı plakalar 170 ^{o}C ve 1 saatte dahili kütle transferinin eliminasyonundan dolayı, toz katalizörde gözlenenden daha fazla dönüşüm vermiştir.

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CHAPTER 1

INTRODUCTION

Througout the history, the urbanization and improvements in the technology have provided humans easiness in daily activities but this comfort and easy living style have caused some undesirable effects. For instance, this has led a rapid consumption of the natural resources and also caused an adverse change on the environment and also at the end of some processes, such as combustion used in heating homes, undesirable by-products are released, which caused health problems in short and long terms. Day by day, these problems together with increasing population and the accumulation of high amount of green house and toxic gases, such as CO_2 and NO_x, in the atmosphere have reached to a dangerous level for human beings. In this sense, most of volatile organic compounds (VOCs), which include over a thousand of different organic and inorganic molecules, contribute extensively to this problem. Since almost all the 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 addition, 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.

In terms of the main activities responsible for air pollution, the top polluting sources across Europe in 2008 included agriculture and fuel combustion by power plants, passenger and heavy-duty vehicles, and households. Agricultural activities alone caused 95 % of Europe's NH_3 emissions. However, the energy production and distribution sector remains a large source of air pollution, responsible for around 70 % of all European SO_x emissions and 21 % of total NO_x emissions and also, the road transport sector is a major source of air pollution. Heavy-duty vehicles are the single most important individual source of NO_x emission, while passenger cars are among the top sources of CO, NO_x and NMVOCs. Furthermore, another source of VOCs is vegetable oil usage. In several regions, it was a source use for smoking leaves, flowers; for consumption in salads; or for the manufacture of paint, edible, and medicinal seed,

and cooking oil. For example, deep-fat frying, a common cooking procedure, may be performed in a continuous or discontinuous manner. In repeated discontinuous frying — either at homes or restaurants — the vegetable oil remains hot for a long period of time, in contact with the surrounding air, in an ordinary cooking. Unfortunately, this type of cooking process is carried out with a relatively low rate of fresh-oil supply (i.e. turnover). In continuous frying, generally performed in industrial facilities for processing of fried and prefried foods, turnover is high because of the large amount of oil removed by the products during continuous cooking. The deterioration of deep-frying oil depends on a large number of factors; for example, frying frequency (discontinuous or continuous), turnover, the time in which the oil is hot, and type of oil. Besides, oil decomposition products, occurred during frying, are absorbed by fried foods and they affect not only the sensory and nutritional quality of these foods but also their shelf-life and some decomposition products are released into air. Some of these products cause lung, eye, skin irritation, premature death, heart and genetic diseases. In addition to these primary direct effects, air pollutants, released during the emission from a particular source, are subject to a range of atmospheric processes including atmospheric transport, mixing and chemical transformation, before exposure to humans. Air pollutants do not remain in the atmosphere forever. Depending on their physical‑chemical characteristics and factors, such as atmospheric conditions, they may be deposited back on Earth in such a way that pollutants can directly be washed out of the atmosphere by precipitation. As rain, snow, fog, dew, frost and hail, or by dry deposition, as gases or particulate matter, on the vegetation surfaces, such as crop or tree leaves. Eventaully, humans are directly and indirectly exposed to them. Particularly, nitrogen oxides (NO_x) and VOCs are potentially much more threatening for environment since the combination of these pollutants (VOC and NO_x) in the atmosphere cause acidic rain and also, photochemical smog in the ground level, where nitrogen oxides and VOCs react together to produce ozone and peroxy compounds in the presence of sunlight. Another pollutant is black carbon (BC), formed through the incomplete combustion of fossil fuels, biofuels and biomass. BC is an air pollutant harmful to health and also acts as a greenhouse gas by increasing atmospheric radiative absorption potential. At present, airborne particulate matter (PM), tropospheric (ground-level) ozone (O_3) and nitrogen dioxide (NO_2) are Europe's most problematic pollutants.

It's reported that methane, which is the lightest volatile organic compound, is almost 25 times more effective green house gas than its complete oxidation product,

carbon dioxide in 100 years period (Bunce, 1991). It's expected that reducing significant amount of methane concentration within a decade could give quick and significant results, than similar reductions in CO_2 emission. Thus, carbon oxides may be released to the environment with minimal environmental implications compared with 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 not generally 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 of years, while others can be consumed by atmospheric processes in a minute after they have been emitted. For instance, lifetime of carbon dioxide in air is estimated as 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 areas show differences due to atmospheric transportation and regional sources of these hazardous gases. Benzene level in the atmosphere, for example, might reach 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 long term effects, energy-holding potential in 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 apply national emission regulation 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 the reduction programs to reduce emissions from different types of mobile and stationary sources. In addition to applied national protection programs, international agreements and plans have been accepted around the world. Therefore, total emissions of VOCs, released from different types of emission sources, have been decreasing in European countries for last several years.

On this matter, there some methods, which are effective and economical in the reduction of volatile organic compounds (VOCs). However, as in many industrial

plants, process 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 the process and equipment modifications are generally used to minimize the volatilization or the formation of VOCs or to prevent the escape of these gases in which operation takes place in the process. The first is VOCs destruction method in which they are generally converted to carbon dioxide and water and the second one is VOCs recovery methods in which 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 VOCs. 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

(Source: Khan, 2000)

		VOC Concentration (ppm)	Temperature (^oF)	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

Among the control techniques, the condensation approach used for the recovery of VOCs is one of the efficient and safe alternatives. Unfortunately, it is applicable for high concentration of volatile organics, having 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. For instance, activated carbons, zeolites, silica gel and alumina are mostly used adsorbents 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 the recovery of expensive and unreacted raw material treatments. However, its efficiency reaches 95 % to 98 % when treating waste streams contain single compounds or relatively simple mixtures of compounds having concentration range from 10 to 10,000 ppm. Therefore, in adsorption methods-based on industrial process, are favorable for removal of low concentration of hydrocarbon vapors from gaseous stream. Also, VOCs molecular weights between 50 and 200 are more 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. Transport from gas stream to liquid solvent consists of the diffusion of gas components to the solvent and then their dissolution into the solvent. The absorbing liquids are generally chosen by their high capability to dissolve VOCs. Thus, any soluble VOCs will also be absorbed by the liquid phase. Absorption systems can treat waste stream gases containing very high concentrations of VOCs ranging from 500 to 5000 ppm but it may require a pretreatment of VOCs containing solvents.

Membrane separation in VOC reduction control technique is based on using a semipermeable 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 total destruction of VOCs is the most common and effective way in the reduction of volatile organic compounds emission. For instance, biological control system, based on the capability of certain microorganisms, transforms 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 destruction of VOCs, their efficiency may be low and may even form by-products more toxic than the original VOC compounds (Webster et al. 1996).

The 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 or air, produce carbon dioxide and water. Many odors and VOCs containing streams can be burned or oxidized by the 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 with 95% to 99% of VOCs destruction efficiencies. Thermal oxidizers have a 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 VOC in the vent stream. Thermal oxidizers can also be used for gas streams having VOC concentrations ranging from less than 10 ppm to very high concentrations, e.g. 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 of the broad applicability of this incineration technique, a large amount of fuel requirement for thermal oxidizers to heat the gas stream to necessary temperature introduces additional and expensive operating cost; large and heavy construction materials. Moreover, at high temperatures, undesirable by-products, such as nitrogen oxides, dibenzofurans and dioxins, can be formed in significant amounts.

In catalytic combustion emission control processes, waste gas stream and air are contacted over a catalyst 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 ^{o}F, is low because of the highly active catalysts. In the catalytic systems, VOC destruction efficiency changes with respect to catalysts volume per unit volume of processed gas, the reaction temperature, and VOC concentration and the composition in the waste stream. In addition, the catalytic system can be operated at low concentration of VOCs, such as 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 the poisoning effect, the catalyst used in the process may require to periodically 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 they are expensive and their availability in the world is limited. Therefore, it is important to use them at low concentrations in catalyst or ensure well dispersion on the 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 since they are cheaper than platinum group metals but they are less active than noble metals at low temperatures.

In this study, the emission of volatile organic compounds, generated during frying process, and also the splashed oil were eliminated using transition metal oxides supported nickel catalysts.The effect of the crystallite size of nickel, and the oxides, manganese oxides, in alumina support on the catalytic activity and also the product distribution was investigated at 170 ^{o}C and 195 ^{o}C operating temperatures (typical maximum operating temperature for the deep fryers) by using sunflower as the model vegetable oil.

This thesis contains five chapters. In chapter one, the emission control methods and also the aim of this thesis are introduced in addition to the general introduction for volatile organic compounds, their potential effects on both human health and environment and governments' VOCs reduction strategies. In chapter two, a literature survey on the properties of volatile organic compounds and their catalytic reduction 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 are presented and discussed. 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 led to stricter legislations on the release of air pollutants, particularly volatile organic gas emission, that is being involved in every part of our lives. Beside of being chemical products, they are the major contributors to photochemical smog 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 many attempts to give a more quantified definition for the term, volatile organic compounds, by refering them as organic compounds which are present in the atmosphere as gases, but would be liquids or solids under normal conditions of temperature and pressure. 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 gases 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, cooking activities, cleaning products, insulating and painting materials or they can be originated from industrial process, automobile exhausts and food outlets (barbecue or fastfood restaurants) that are mainly responsible for outdoor VOC pollution.

2.1.1. Volatile Organic Compounds (VOCs) from Food Outlets

Food outlets (barbecue or fastfood restaurants) vary in size and in the nature of the activities that occur in them. Typically they involve the following types of activities such as cooking food products for sale to the public (e.g. boiling, braising, roasting, frying, barbecuing etc.), cooking specific products such as barbecued chickens or wood-fired pizzas. The capacity of these businesses to manage air quality depends on their location and size. In very sensitive and adverse locations, even the smallest shops would face a real challenge to achieve adequate control. Large operations may need to resort to controls beyond the typical level to prevent or minimize unacceptable impacts on their neighbours. Studies on the exhaust emissions generated from barbecuing have revealed many unsaturated hydrocarbons, a form of VOCs that is highly reactive in the photochemical process. The estimated VOC emissions from a small barbecue shop are roughly equivalent to running a typical car for 20,000 km per year. Grease particles and aerosols can also be generated from the cooking process, and if not captured near the emission source, can impact on the surrounding environment. Barbecuing over charcoal has been shown to generate heavy organic compounds when the fats and greases drop onto the red-hot charcoal. Examples are polycyclic aromatic hydrocarbons (PAHs), benzene and toluene as air toxics.

The main air emission from food outlets is odour, primarily generated from the cooking process. Studies (including analysis of cooking fume emissions) have shown that many odorous hydrocarbons or VOCs (such as alkenes, aromatics, aldehydes and organic acids) are formed in the cooking process as breakdown products of natural fats and oils. The strength and offensiveness of the odours varies widely, depending on what is being cooked (e.g the type of meat) and the manner of cooking. For example, local tests show that emissions from charcoal roasting of chickens are three to ten times more odorous than emissions from gas-heated or electrically-heated roasting of chickens. Test showed emissions from 130 to 1300 odour units per bird cooked. However, aerosols of odorous materials, e.g. tiny organic liquid droplets in cooking fumes, can apparently increase odour strength. Moreover, similar to cigarette smoke, fumes from cooking oil contain lots of carcinogens, such as aromatic amines, polycyclic aromatic hydrocarbons (PAHs), nitro-polycyclic aromatic hydrocarbons. Several carcinogens, including polycyclic aromatic hydrocarbons (PAHs), aromatic amines and nitro-polycyclic

aromatic hydrocarbons, which are also found in cigarette smoke, can be found in the fumes from cooking oil used at homes. Animal studies have found that PAH can cause cancer in the epithelium of rat cervices. Cooking oil fumes have been suggested to increase the risk of lung cancer in oriental women by exposing them to mutagenic substances. In addition, fumes from cooking oils have been found to be genotoxic by several such short-term tests as the Ames test, sister chromatid exchange, and the SOS chromotest.

Food outlets also emit particulates in the form of oil and grease mist from deep frying and wok-type cooking, and from fats released during roasting and barbecuing. This is not only of potential nuisance to adjacent or nearby occupants (particularly sensitive land uses, such as schools, hospitals or residential areas), but also has associated odour and fallout issues.

2.2. Catalytic Oxidation of VOCs

Because of the complexity of components, cooking oil fumes and VOCs are notoriously difficult to treat using static method. Adsorption and washing are effective, while frequent maintenance is required. Therefore, volatile organic compounds (VOCs) can be oxidized by two oxidation methods; thermal and catalytic oxidations. While thermal oxidation is also an option, expensive equipment, high operating and maintenance cost and production of NO_x will offset the benefits of organics removal in addition to requiring high temperatures, typically above 700 ^{o}C. On the other hand, the catalytic oxidation operates at much lower temperatures; hence, avoiding the formation of toxic gases, such as NO_x, and particulates during the oxidation.

Cooking oil is mainly composed by saturated and unsaturated lipids and fats, which are sensitive to light and oxygen. When cooked, it will be oxidized and decomposed. Under the best scenario, a complete oxidation (i.e. combustion) on the catalysts will proceed in following way:

$$Oil + O_2 \rightarrow CO_2 + H_2O \tag{2.1}$$

With the progressive increased of production and usage of VOCs, their emission to the atmosphere should be treated to reduce the concentration at levels enforced 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, the catalytic combustion is one of the more frequently used type of elimination technology (Campesi et al., 2011) and especially preferred methd 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 shows better efficiency and produces no secondary pollution and also conserves the energy consumption.

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) dispersed on high surface area support materials, such as alumina (Al_2O_3), silica (SiO_2) and titania (TiO_2), have been intensively studied in the 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.

Several studies have been focused on finding the best catalyst formulation for VOC oxidation and also the improvement of the activity of the catalysts. Among many possible catalyst formulations, the hydrophobic catalysts have been found to be highly active for VOCs destruction at relatively low temperatures and be less sensitive to deactivation through surface concentration of water (Sharma et al., 1995).

The operating temperature of the catalyst is also crucial in a way that at higher temperatures, VOCs destruction is much more efficient but it can also accelerate catalyst deactivation; thus, reducing the catalyst activity. In catalytic oxidation, selection of a type of catalyst for the given hydrocarbon combustion reaction is very important. In this sense, two main types of catalysts become prominent: Noble metal catalysts and metal oxide supported catalysts.

2.3. Catalysts for VOCs Combustion

2.3.1. Noble Metal Catalysts

The activity of the combustion reactions at low temperatures and selectivity to the carbon dioxide and water formation is very high on noble metal catalysts (Spivey et al., 2004). For instance, McCabe et al. studied methanol

oxidation on various noble metal catalysts, such as rhodium (Rh), silver (Ag), copper (Cu), platinum (Pt) and palladium (Pd). Among these catalysts, platinum and palladium were found to have higher activity for methanol oxidation than the others (McCabe et al., 1986). In addition to McCabe research group, metals other than platinum and palladium were found to have lower activity for combustion because they undergo sintering, volatility losses (loss of metal components through volatilization) and irreversible oxidation at high temperatures (Prasad et al., 1984; Spivey et al., 2004).

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: $Pt/TiO_2 > Pd/TiO_2 >> Rh/TiO_2 \approx Ir/TiO_2 >> Au/TiO_2$.

In other studies, Pt catalysts were found to be more active as compared with Pd catalysts for the methanol oxidation. The low activity of the palladium catalysts was claimed to be due to the weak adsorption of oxygen on Pd crystallites (Gates et al., 1979; Sharma et al., 1995). Pt catalyst has higher activity for oxidation reaction and good stability; hence it is also commonly used as the best monometallic catalyst in the electrooxidation of methanol (Ferrin et al., 2009).

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 deteriorated and temporarily poisoned 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 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)

2.3.2. Metal Oxide Supported Catalysts

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

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 types of metals (Cu, Mn, Fe, V, Mo, Co, Ni, and 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).

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 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 Lindfors, 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^2g^{-1} and γ- Al_2O_3 50–250 m^2g^{-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).

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.

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 $CuOCeO_2/Al_2O_3$ 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.

Noureddini et al. (1999) studied liquid-phase catalytic oxidation of oleic acid with hydrogen peroxide in the presence of various transition metal/metal oxide catalysts. Unsupported catalysts used were tantalum, tungsten, molybdenum, zirconium, niobium, tungstic and tantalum oxides. Supported catalysts used were tantalum oxideon alumina and tungstic oxide on alumina and silica support. Tungstic oxide supported on silica is the most suitable catalyst for the oxidation of oleic acid with 85% of the starting oleic acid converted to the oxidation products in 60 min of reaction with high selectivity for azelaic acid. The smaller average pore diameter of alumina (135 Å) compared to the silica (250 Å) may have been responsible for the lower rate of reaction for the alumina-supported catalyst. Also alumina pellets tend to settle down in the bottom of the reactor vessel and create diffusion resistances which may result in slower reaction.

The household oven cleaning process is actually an issue for both customers and manufacturers. Traditional cleaning operations are today performed using suitable caustic detergents. An automated product has been implemented (usually known as the pyrolytic cleaning route) on high end products, in which organic remains are incinerated via high temperature (>500 ^{o}C) cycles, lasting from 1 to 3 h, and are there easily removed as dust such a feature implies additional design difficulties and the use of special materials, which result in severe safety and cost issues. Furthermore, the energy consumption related to the high temperature process is very elevated.

In light of these informations, Palmisano et al. (2009) aimed at developing oven walls with self-cleaning properties, via catalytically enhanced thermal oxidation of soiling material within the standard range of household oven, temperatures. Some

saturated fatty acids, e.g. myristic (tetradecanoic), palmitic (hexadecanoic) and stearic (octadecanoic) acids, were selected as single soiling compounds to investigate their thermal degradation behavior. $MnCr_2O_4$, $LaFeO_3$ and CeO_2 were chosen as oxidative catalysts. CeO_2 showed the best performance, followed by $LaFeO_3$ and $MnCr_2O_4$. However, the $MnCr_2O_4$ catalyst exhibited the best selectivity towards CO_2 (about 92%). Apart from the nature of the catalyst, a key parameter governing conversion seems to be the geometrical contact condition between the catalyst and soiling material, which was favoured by a highly corrugated catalyst surface. This was probably the reason why the more corrugated $MnCr_2O_4$ spinel layer ensured the best performance under real operating conditions. However, surface roughness may also lead to a scarce adhesion. This aspect requires an optimization trade-off.

Yang et al. (2005) studied low temperature catalytic oxidation of cooking oil fume by using a novel catalyst, based on MnO_2/CuO on different reaction parameters like different oil temperatures, catalyst temperatures and contact times. They decleared that the average initial oil concentrations in the fumes was increased by increasing the oil temperature. They also concluded that holding catalyst temperature constant percentage of oil removal is increasing with increasing contact and decreasing with decreasing oil temperature since at high temperatures removing of oil is more difficult than that from lower temperature oil. This could be explained that under high temperature, the oil decomposed and the complexity of fumes were increased. For instance, prolonged contact time also gave more favorable results. When the contact time was 1.59 s and the catalyst temperature was 300 ^{o}C, the oil fume removal is close to 90%, if the contact time is prolonged to 3.18 s, 96% removal could be achieved at 200 ^{o}C. Moreover, it was observed that as the catalyst temperature increased the organic removal also went up.

In other study, combustion of volatile organic compounds (VOCs), such as propyl alcohol, toluene and cyclohexane, were studied by using $La_{1-x}Sr_xCoO_3$ (x= 0, 0.2) as perovskite catalysts. (Huang et al 2007). Toluene was chosen as the model molecule to investigate the catalytic activities of perovskites for single VOC. The conversion was over 99% with $La_{0.8}Sr_{0.2}CoO_3$ as the catalyst when temperature was 235°C. At this temperature with $LaCoO_3$ as the catalyst, by comparison, the conversion rate for the oxidation of toluene was only 80%. A temperature of 340 ^{o}C was needed for 99% toluene to be converted on $LaCoO_3$. To evaluate the catalytic activities of perovskites for mixed VOCs, the mixture of toluene, cyclohexane and propyl alcohol

was tested. It was observed that, compared to $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$ was more active in oxidizing VOCs. This catalyst was synthesized via partial substitution of strontium (Sr) for lanthanum (La) at the A-sites of $LaCoO_3$. The substitution modifies the surface structure of the catalyst by, for example, greatly increasing the oxygen vacancies in the surface regions, which resulted in the higher catalytic activity of $La_{0.8}Sr_{0.2}CoO_3$ as compared to $LaCoO_3$.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

In this study, pure Al_2O_3, Ni/Al_2O_3, Mn_2O_3/Al_2O_3 and $Ni-Mn_2O_3/Al_2O_3$ with various ratios and also Pt/Al_2O_3 catalyst as a reference catalyst (Pt loading of 3 wt %) were synthesized via impregnation and the modified single step sol-gel method. In the synthesis of Pt/Al_2O_3catalysts, dihydrogen hexachloroplatinate (IV) hexahydrate was used as a precursor for platinum. In addition, for the synthesis of Ni/Al_2O_3 catalysts nickel (II) acetate monohydrate (Alfa Aesar) and nickel (II) chloride hexahydrate (Sigma) were used as a precursor for nickel; manganese (II) nitrate tetrahydrate (Merck) was used as a precursor for manganese oxide, respectively. For all types of the catalysts, aluminum isopropoxide (Alfa Aesar) was used as a precursor for alumina. Deionized water (DIW) as a solvent and nitric acid (HNO_3) as a peptizer in the sol-gel method were used. Commercial sunflower oil (from Tansas Inc.) was used without further treatment. 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	MolecularWeight (g/mol)	Purity (%)
Aluminum isopropoxide	$Al(OCH(CH_3)_2)_3$	204.24	98
Nickel (II) acetate monohydrate	$Ni(CH_3COO)_2.1H_2O$	194.69	99
Nickel (II) chloride hexahydrate	$NiCl_2.6H_2O$	237.69	99
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 Figure 3.1;

-Preparation of catalysts;

-Characterization of catalysts;

-Testing of catalysts in the experimental set-up

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│        └───────────────────────────────┘         │
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│     │    Characterization of catalysts   │        │
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│  │ Testing of catalysts in the experimental set-up │
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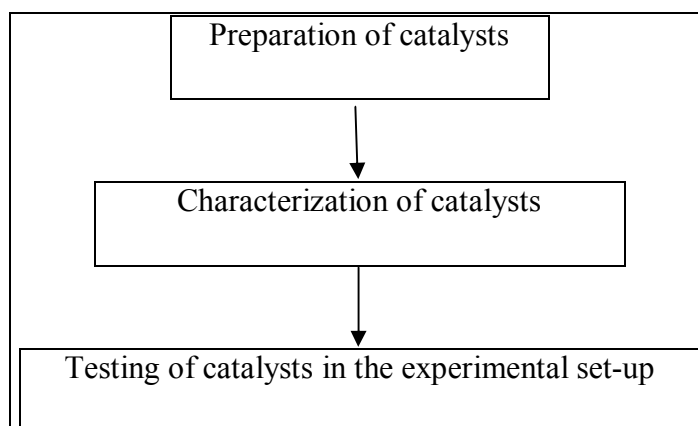
Figure 3.1. Experimental Procedure

3.2.1. Preparation of Catalysts

Platinum supported on alumina catalyst was prepared via incipient wetness impregnation method as seen in Fig. 3.2. As a starting point, to prepare alumina, necessary amount of alumina isopropoxide (AIP) was added to water at 85 ºC and mixed 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 for 6 h using a heating

rate of 10 °C /min. Finally, the 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 the surface of alumina powder is saturated with water. Therefore, by considering the appropriate loading of platinum on alumina, platinic acid was dissolved in the amount of water found earlier. Finally, Pt containing solution was impregnated to alumina powder and dried at 120 °C for 6 h then calcined at 500 °C for 6 h before any activity testing. For catalytic combustion of sunflower oil, 3% Pt/Al$_2$O$_3$ was first used.
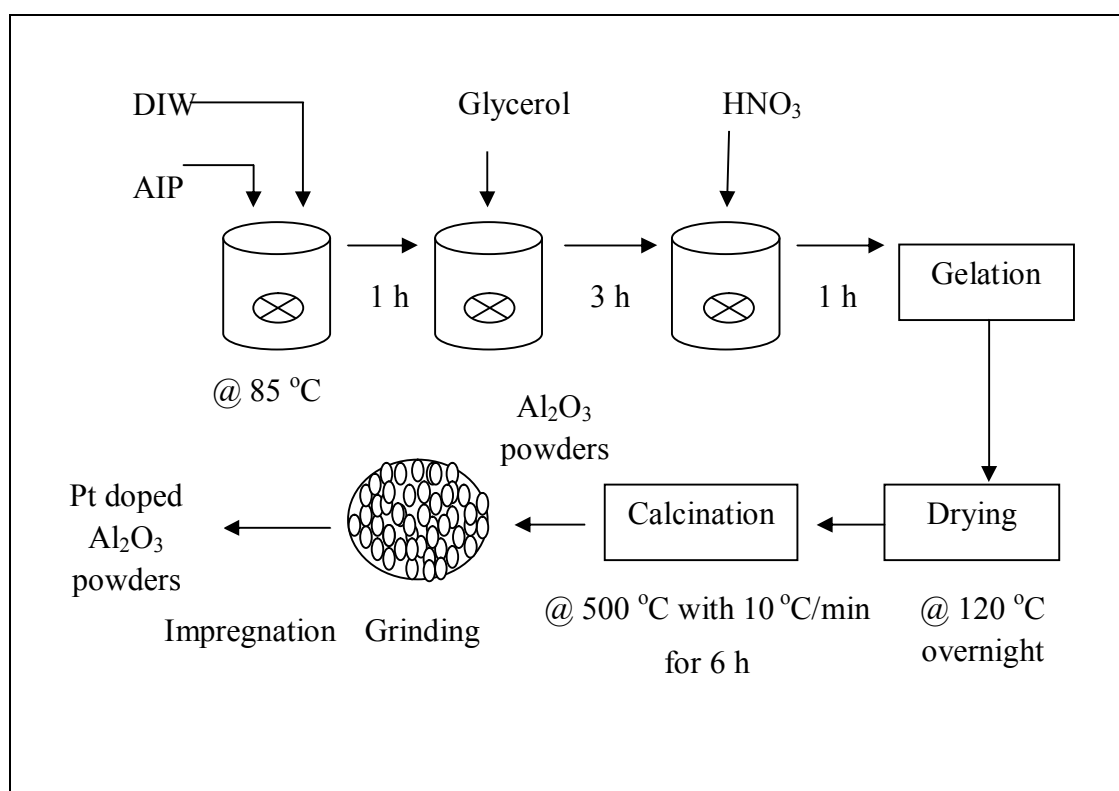
Figure 3.2. Experimental procedure for the preparation of alumina supported Pt catalyst

Nickel manganese oxide on alumina (Ni/Mn$_2$O$_3$/Al$_2$O$_3$) catalysts, 20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ and 23% Ni/66% Mn$_2$O$_3$ /Al$_2$O$_3$, were synthesized via modified single step sol-gel procedure. In Figure 3.3, experimental procedure for the synthesis of Ni-Mn$_2$O$_3$/Al$_2$O$_3$ catalyst is shown. First of all, AIP and water were mixed at 85 °C and stirred for 1 hour for the hydrolysis. Then, HNO$_3$ was added at the same temperature and kept stirred for 1 hour for peptization, and then, a needed amount of nickel (II) acetate monohydrate and manganese (II) nitrate tetrahydrate were dissolved in deionized water separately and added to alumina sol prepared as before. After that, the

separate solutions were added to prepared alumina sol in one step and mixed together. When gelation occurred, gels were dried at 120 ºC for 16 h and calcined at 500 ºC for 5 h, with a heating rate of 10 ºC /min. Finally, the catalysts were ground and sieved to 60 mesh (250 μm) size. Moreover, 50% Ni/Al$_2$O$_3$ which was prepared using nickel (II) acetate monohydrate and nickel (II) chloride hexahydrate precursors, and Mn$_2$O$_3$/Al$_2$O$_3$, alumina sol was prepared by the same procedure and then the appropriate amount of the metal precursor was added into the sol for each catalyst. The gels were dried at 120 ºC for 16 h, then calcined at 500 ºC for 5 h, and finally sieved to 250 μm (60 mesh) before their usage in combustion reaction.
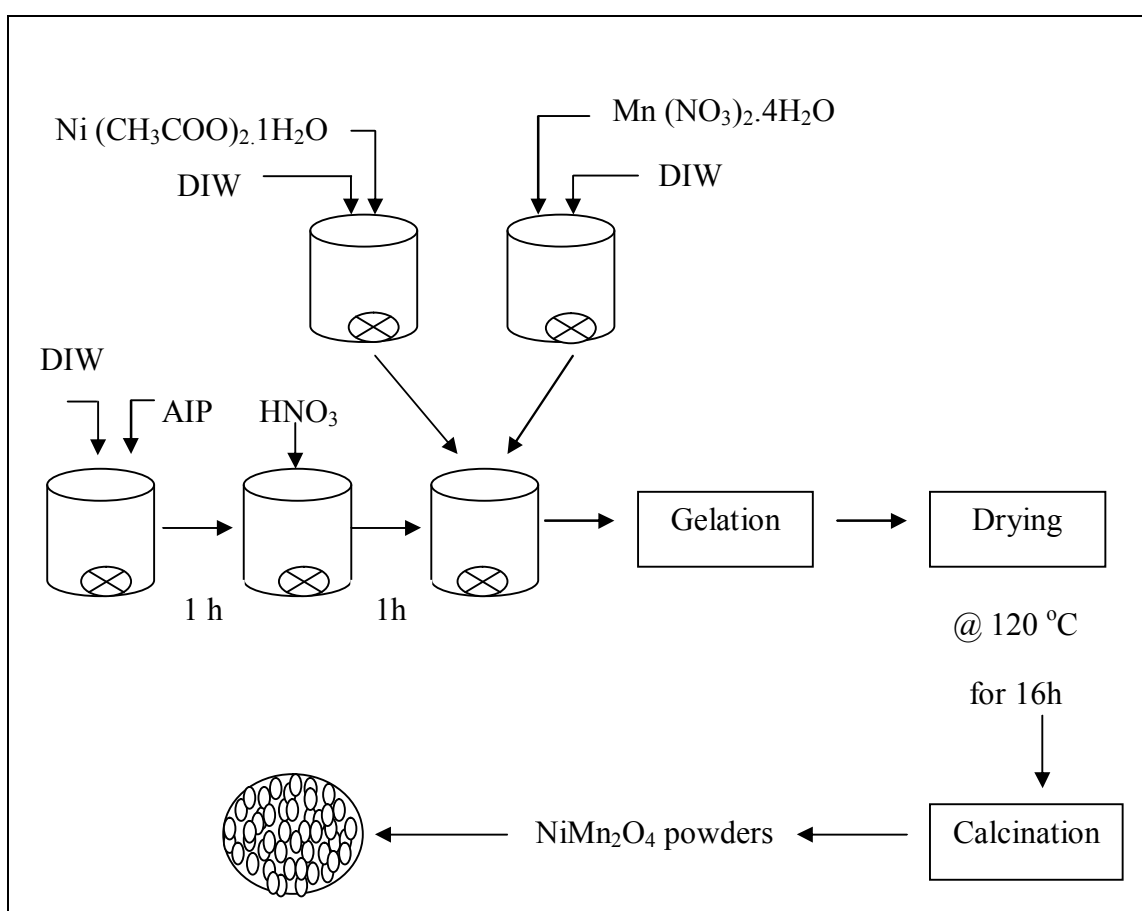

Figure 3.3. Experimental procedure for the preparation of Ni-Mn$_2$O$_3$/ Al$_2$O$_3$ catalysts

3.2.2. Characterization of the Materials

In the characterization of the catalysts, X-ray diffraction (XRD) and BET were used. In order to determine the crystalline phases and the average crystallite sizes of the

catalysts, XRD patterns were determined using a Philips Xpert Pro X-ray diffractometer. BET surface areas of the selected catalysts were determined by using Micromeritics Gemini analyzer at the scan mode at 77 K of liquid N_2. At the end of the combustion process, the compositions of the combustion products released during reaction were analyzed on a HP-5MS column which has 30 m length, inner diameter of 0.25 cm using a gas chromatography (Agilent 6890N) equipped with a mass spectrometry detector.

3.2.3. Experimental Setup and Catalysts Testing

3.2.3.1. Experimental Instruments

The catalytic oxidation of sunflower oil was performed in a beaker operated as a batch reactor at atmospheric pressure and the two diffrent temperature of 170 ^{o}C and 195 ^{o}C. In order to avoid flow of air stream during the catalyst testing step, small beakers containing the catalyst powder were placed in a larger beaker with heating oil and the whole system was placed over the heater with magnetic stirrer. Furthermore, K type-thermocouple immersed in heating oil in the beaker was used to monitor the temperature of the reactor.

3.2.3.2. Catalyst Testing

Figure 3.4 demonstrates a schematic of the experimental setup used in the sunflower oil oxidation. Product composition released during the combustion was analyzed by using GC-MS. Oil bath was used to keep the temperature constant. Moreover, sunflower oil impregnated catalyst powder was located at the bottom of the beaker to avoide external mass transfer limitation of air.

In the evaluation of prepared catalysts, 0.1 gr of the catalyst was added into the beaker and then necessary amount of sunflower oil was added slowly until reaching the surface saturation of powder at which impregnation of the catalyst was completed. Then, the reactor was set to a temperature that the experiment would be carried out. After 1 h, the mass changes of the oil impregnated catalyst were measured and the conversions based on mass were calculated. Besides, by following the same method,

combustion reactions were carried out in headspace vial for 1 h to determine the gas phase product distribution. For this, 0.5 ml volatiles were pulled from the vial and then analyzed in GC-MS.
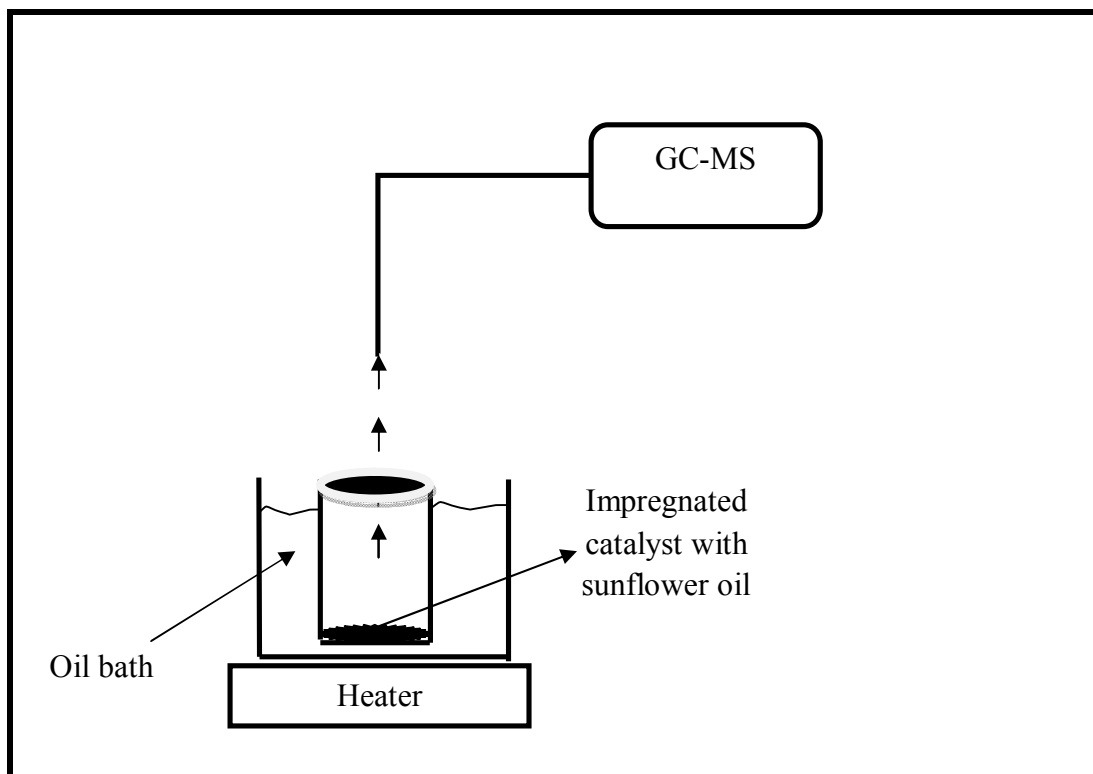
Figure 3.4. Experimental set-up of sunflower oil combustion

3.2.4. Catalyst Coated Plate Preparation Procedure

To investigate the applicability of the catalyst formulation to the household appliances, such as oven, the catalyst coated aluminum plate was prepared. For this purpose, two different catalysts, 50 % Ni/Al_2O_3 and 20% $Ni/56\%$ Mn_2O_3/Al_2O_3 (First Ni precursor added), showing the highest activity found during the testing step was coated on aluminum plates using dip coating method.

Figure 3.5. Catalyst coated plate preparation procedure

Figure 3.5. demonstrates catalyst coated plate preparation procedure. The same procedure was applied until ''sol'' part. After that Al plate was dipped into solution. After drying and calcination steps coated plate was obtained.

CHAPTER 4

RESULTS AND DISCUSSION

The oxidation of sunflower oil was studied over single metal oxide and mixed oxide supported metal catalysts with various metal ratios and t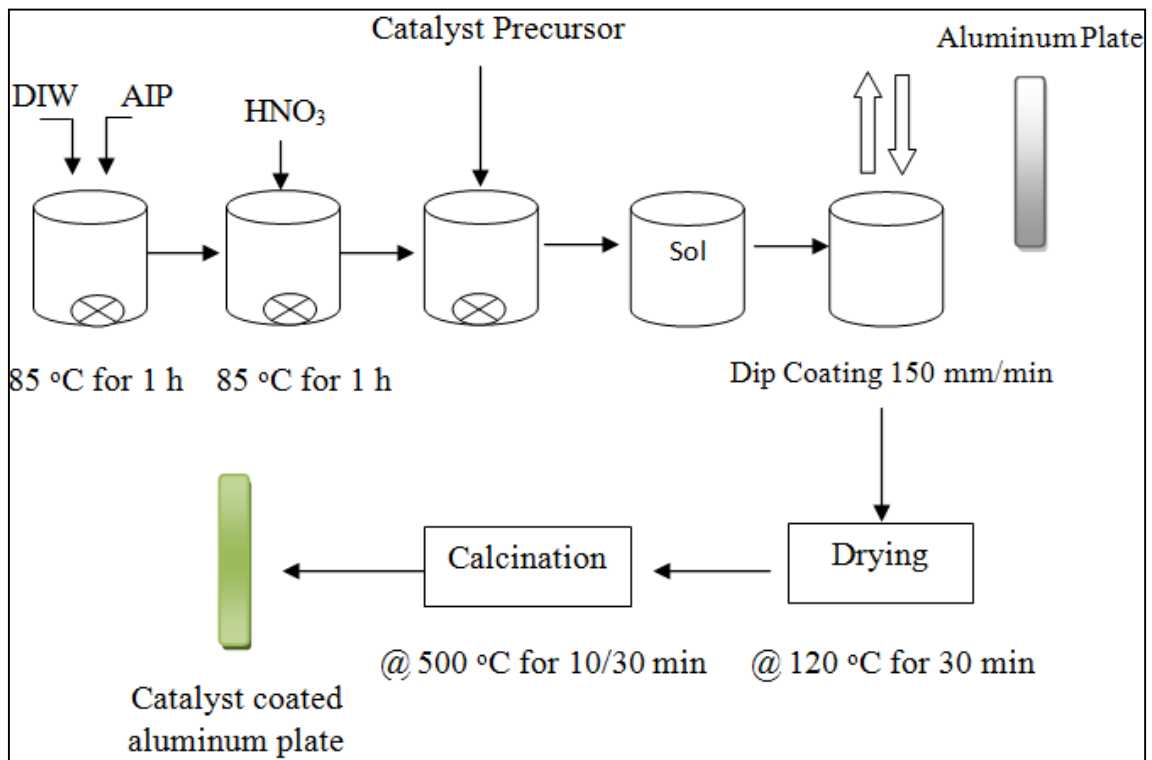he loadings, prepared by using a modified sol-gel method, which allows one to control the chemical reactions; hence, indirectly tailoring the textural and chemical properties of the catalyst. The most effective catalysts for the sunflower oil combustion were selected by considering low temperature at which high conversion, such as >80%, was obtained. Furhermore, alumina was selected as the support material since alumina was the most widely used stable support material for commercial applications. Notable features of alumina supports are their ability to highly disperse the active metal and metal oxide active phases and good mechanical properties.

All the catalysts were tested in a batch reactor system containingcatalyst impregnated with necessary amount of sunflower oil which was approximately 35 mg. The catalytic oxidation of sunflower oil was performed at two different temperatures of 170 ^{o}C and 195 ^{o}C. Prior to the catalytic tests, all the catalysts were activated under the dry air flow at 500 ^{o}C for 2 h. For all combustion steps, each run was repeated 4 times under the same reaction conditions to find out the uncertainities in the conversions.

Table 4.1. Operating conditions for sunflower oil combustion

Operating parameters	Operating value
Reaction temperature	170 ^{o}C and 195 ^{o}C
Reaction time	1 h
Amount of catalyst	≈ 0.1 g
Amount of oil	≈ 0.0350 g

4.1. Blank Test

To observe if there is an oil oxidation/vaporization, 'blank test', i.e. in the absence of the catalyst, was tested in the batch reactor containing only 0.035 g sunflower oil. Results showed that total oil conversion increased with increasing temperature. As seen in Table 4.2, blank test conversions were 10.7% and 33.32% at 170 $^{\circ}$C and 195 $^{\circ}$C, respectively. Based on the GC-MS analyses, the product distribution seems to range from free fatty acids, alcohols, aldehydes to water. The GC-MS chromatograms obtained for blank tests at 170 $^{\circ}$C and 195 $^{\circ}$C are shown in Figures 4.1 and 4.2.

Table 4.2. Sunflower oil conversion of blank test with experimental errors

	Sunflower Oil Conversion (%)	
	170 $^{\circ}$C	195 $^{\circ}$C
Sunflower oil without catalyst	10.7 (±0.99)	33.32 (±1.26)
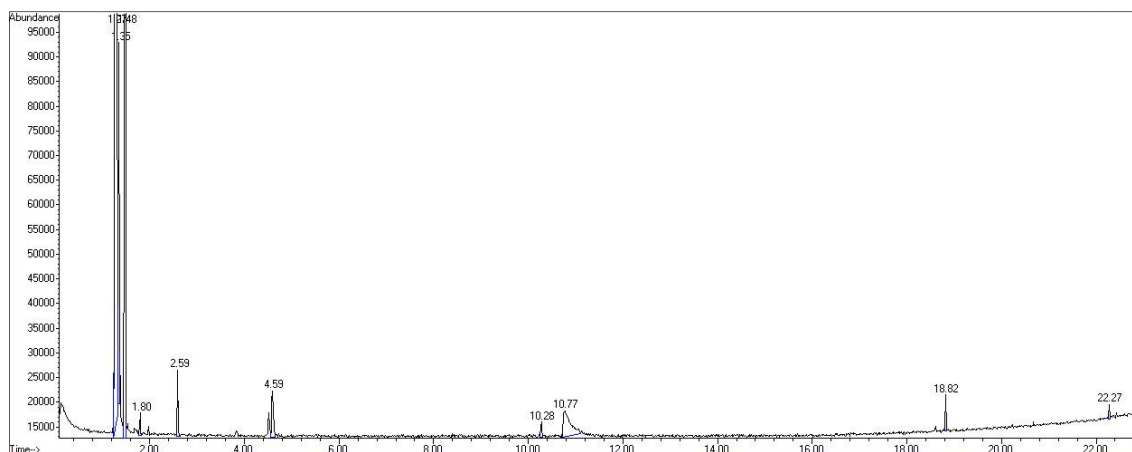
Figure 4.1. GC-MS chromatogram of blank test of sunflower oil at 170 $^{\circ}$C

As seen in the figure above, at 170 $^{\circ}$C, acetaldehyde + butane, pentane and trans-2-methylcyclopentanol are observed at 1.35, 1.483 and 4.593 min, respectively while at 10.774, 18.817 and 22.274 min, 1, 2, 3, 4-butanetetrol, trans, trans- 2, 4-decadienal and n-hexadecanoic acid (palmitic acid) being similar to the study by Katragadda et al.. Chang et al. also reported that dienaldehydes were by-products of peroxidation of

polyunsaturated lipids and commonly found in many foods or food-products. Cancer Institute (NCI) and NTP have expressed great concern on the potential genotoxicity and carcinogenicity of dienaldehydes. Trans, trans-2, 4-decadienal (tt-DDE or 2, 4-De), a specific type of dienaldehyde, is abundant in heated oils and has been associated with lung adenocarcinoma development. Previous studies on dienaldehydes have focused on their genotoxic or carcinogenic effects in the gastrointestinal tract. Moreover, acute (short-term) exposure to acetaldehyde results in effects including irritation of the eyes, skin (EPA) and respiratory tract and hexanal cause sensory irritation and other health concerns (Chang et al). So, these products must be removed from coking oils or their volatile products.
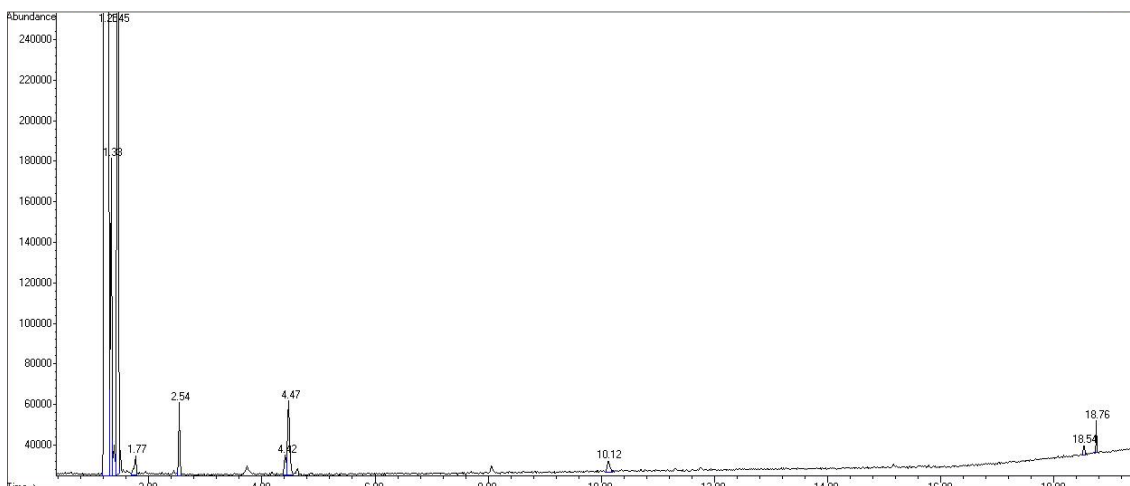

Figure 4.2. GC-MS chromatogram of blank test of sunflower oil at 195 ^{o}C

As seen in the figure above, at 1.35, 1.483 and 4.47 min, acetaldehyde + butane, pentane, and hexanal were again observed and also different isomers of 2, 4-decadienal were detected at 18.54 and 18.755. Volatile organic compounds, obtained using only sunflower oil heated at 195 ^{o}C, have higher peak areas than that of sunflower oil heated at 170 ^{o}C. This is plausible since the conversion at 195 ^{o}C was higher than that at 170 ^{o}C.

Previous studies in literature show that the noble metal catalysts, in particular Pt and Pd catalysts, are mostly used and desirable catalysts since they have high activity at relatively low temperatures, such as 100-200 ^{o}C, and show high selectivity for the formation of carbon dioxide and water, with lower partial oxidation products.

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). Similarly, the studies conducted in Assoc. Prof. Seker's research group showed that 3% Pt/Al_2O_3 had the highest catalytic activity among the noble metal catalysts for the combustion of ethanol. Hence, in this study, for the sunflower oil combustion, 3% platinum on sol-gel made alumina was also selected as the reference catalyst.

Table 4.3. Sunflower oil conversion on 3% Pt/Al_2O_3 catalyst

Catalysts	Sunflower Oil Conversion (%)	
	170 ^{o}C	195 ^{o}C
3% Pt/Al_2O_3	79.06 ($\pm$1.06)	100

The results show that by using 3% Pt/Al_2O_3, 79.06 % conversion was achieved at 170 ^{o}C whereas 100 % conversion was reached at 195 ^{o}C. Although precious metals are highly active catalysts for the oxidation of various VOCs, their high costs hinder their practical usage. So, the studies have been focused on supported metal oxide and base metal catalysts.

4.2. Catalytic Performance of Single Component Metal Catalysts in Sunflower Oil Combustion

4.2.1. Loading Effect of Mn: 50% Mn/Al_2O_3 vs. 70% Mn/Al_2O_3

From previous studies, the conversion of propane being non-halogenated VOC was achieved more easily on reducible transition metal oxides, such as Mn oxides. Manganese oxides (MnO_2, Mn_2O_3 and Mn_3O_4) were found previously to be very active and stable catalysts for the combustion of organic compounds in the temperature range of 100-500 ^{o}C (Baldi et al. 1998) and also Mn_2O_3/γ-Al_2O_3 catalyst was active for halogenated VOCs, such as dichloroethane, and 100% was achieved at 427 ^{o}C (Tseng et al. 2010). In addition, manganese-based catalysts have also attracted a great attention

due to high activity towards total oxidation reactions, low cost, low toxicity and its highly reducible oxide property.

In this study, the activities of the single step sol-gel made Mn_xO_y/Al_2O_3 catalysts in two different loadings were investigated in the combustion of sunflower oil. Beside of manganese oxide catalysts, the mixed oxides of Ni and Mn_2O_3 on alumina were synthesized by using the same single step sol-gel method to explore the effect of each metal/metal oxide on the activity and product distribution. Combustion results for two different temperatures are given in Table 4.4;

Table 4.4. Sunflower oil conversion on Mn/Al_2O_3 catalysts with experimental errors

Catalysts	Sunflower Oil Conversion (%)	
	170 ^{o}C	195 ^{o}C
50% Mn_xO_y/Al_2O_3	42.92 ($\pm$1.01)	51.9 ($\pm$3.21)
70% Mn_xO_y/Al_2O_3	37.99 ($\pm$2.29)	52.48 ($\pm$1.47)

For both catalysts, the conversions were increased approximately 10% by increasing temperature. At 170 ^{o}C and 195 ^{o}C, the conversions on all the catalysts were ~10% different but at 170 ^{o}C, the conversion on 50% Mn/Al_2O_3 was slightly higher that on 70% Mn/Al_2O_3. Also, at 195 ^{o}C, the conversion was the same within the experimental uncertainty regardless of the loading of Mn_xO_y. This may be due to that during the synthesis of the materials, for high manganese oxide loading, manganese oxide crystallites may be occluded in the alumina matrices; hence, hindering the accessibility of the oxygen gas and oil to the manganese oxide sites.

To find out the main reason behind the difference in conversion vs. temperature behavior observed among the catalysts with varying Mn_xO_y loadings, XRD characterization method was used.
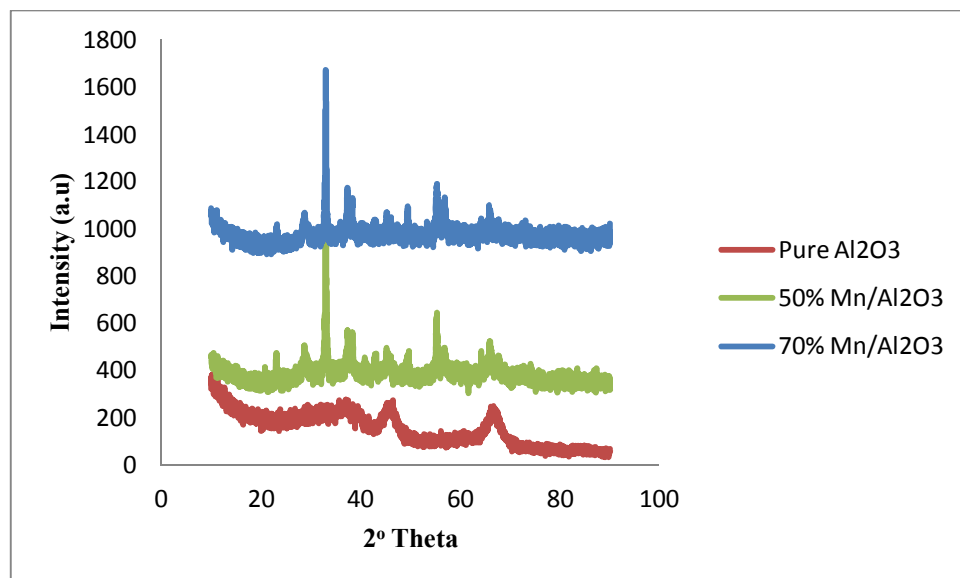
Figure 4.3. XRD patterns of Pure Al_2O_3 and different weight loadings of Mn/Al_2O_3 catalysts

Figure 4.3 shows XRD patterns of pure Al_2O_3, 50% Mn/Al_2O_3 and 70% Mn/Al_2O_3 before using them in activity tests. At 37.44, 46.03 and 67.76 of 2Θ angles, alumina peaks are seen. At 23.21, 32.95, 38.20, 55.33, 49.37, 55.4, 65.96 of 2Θ angles, Mn_2O_3 peaks and at 28.71, 37.37, 43.10, 56.65 of 2Θ angles, MnO_2 peaks are seen on Mn/Al_2O_3 catalysts for both loadings. Besides, it is a well known that for manganese oxide catalysts, there is a wide range of stoichiometries and crystalline phases because Mn atoms are found in various oxidation states at different temperatures and different loadings. In the studies considering the activity of alumina supported manganese oxide catalysts with different loadings, for instance, Rezaei et al. reported that increasing Mn loading from 1% to 20% on alumina resulted in decrease in BET surface area and pore volume, which is similar to what was found in this study and also catalysts at lower loadings up to 10% were mostly composed of Mn_2O_3 while a mixture of MnO_2 and Mn_2O_3 were present in catalysts with loadings higher than 10%. It was shown that the fraction of MnO_2 and oxidation state of Mn increased with increase of Mn loading. Reed et al. also reported that higher loadings of Mn on silica are more active in oxidation of acetone by ozone due to their lower oxidation state and higher oxygen delivery ability of adjacent Mn sites in catalysts with higher loadings but Einaga et al. have reported that lower loadings of Mn on alumina are more favorable in catalytic ozonation of benzene due to higher dispersion of Mn. In this part of the study, surface area measurements comfirmed that why the catalysts showed similar conversions. BET surface area and pore volume of both catalysts are similar; for example,. $BET_{50\%}$

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$_{Mn/Al2O3}$= 119 m^2/g, BET$_{70\% Mn/Al2O3}$= 104 m^2/g and pore volume 50% Mn/Al$_2$O$_3$= 0.148 cm^3/g, pore volume 70% Mn/Al$_2$O$_3$= 0.132 cm^3/g and also crystallite size of Mn$_2$O$_3$ phases at 32.947 of 2Θ angle are 45.5 nm for 50% Mn/Al$_2$O$_3$ and 54.2 nm for 50% Mn/Al$_2$O$_3$; hence, confirming similar conversions observed on these catalysts.

4.2.2. Metal Precursor Effect for 50 % Ni/Al$_2$O$_3$

50 % Ni/Al$_2$O$_3$ was chosen as the main catalyst for comparing the effects of the nickel precursors and the different nickel loadings on the activity of 50%Ni/Al$_2$O$_3$. The catalyst was prepared using two different precursors, nickel (II) acetate monohydrate and nickel (II) chloride hexahydrate. Nickel was selected instead of noble metal catalysts because of its lower cost and higher availability of Ni. Besides, Ni has been widely investigated due to its known activity in cleavage of C−C, O−H, and C−H bonds. The combustions performance of Ni/Al$_2$O$_3$ catalysts as a function of Ni precursors are given in Table 4.5.

Table 4.5. Sunflower oil conversion on Ni/Al$_2$O$_3$ catalysts with experimental errors

Catalysts	Sunflower Oil Conversion (%) at 170 ^{o}C
50 % Ni/Al$_2$O$_3$ (NiCl$_2$.6H$_2$O)	26.7 (±0.73)
50 % Ni/Al$_2$O$_3$ (Ni(CH$_3$COO)$_2$.1H$_2$O)	35.16 (±0.33)

Both catalysts, listed in Table 4.5, were tested in sunflower oil combustion under the same operating conditions. At the same temperature, 50 % Ni/Al$_2$O$_3$ prepared from nickel (II) acetate monohydrate showed ~10% higher conversion. The reason may be due to the nickel dispersion on Ni/Al$_2$O$_3$ catalysts resulted in by the presence of the different anion introduced by the nickel precursors during the preparation. Ni/Al$_2$O$_3$ prepared by nickel acetate possesses high Ni dispersion; hence, indicating small nickel crystallite size. Nickel chloride derived Ni/Al$_2$O$_3$ catalysts had large Ni crystallite sizes (i.e. low Ni dispersion); thus, resulting in low conversion. This low dispersion finding is similar to the studies conducted on nickel catalysts (Wu et al.).

The specific surface areas of 'fresh' catalysts (before using them in the reactions) were measured using BET method. Table 4.6 shows the BET surface areas of two catalysts prepared with different precursors.

Table 4.6. Surface area measurements of 50 % Ni/Al$_2$O$_3$ derived form NiCl$_2$.6H$_2$O) and 50 % Ni/Al$_2$O$_3$ derived from (Ni(CH$_3$COO)$_2$.1H$_2$O)

Catalysts	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average pore diameter (A)
50 % Ni/Al$_2$O$_3$ (NiCl$_2$.6H$_2$O)	226.3	0.214	37.8
50 % Ni/Al$_2$O$_3$ (Ni(CH$_3$COO)$_2$.1H$_2$O)	302.3	0.4072	53.9

Surface area measurements confirmed the activity behaviors of catalysts seem to be due to that the most active catalyst, which is 50 % Ni/Al$_2$O$_3$ derived from (Ni (CH$_3$COO)$_2$.1H$_2$O), has higher specific surface area. Besides, Figure 4.4 shows XRD patterns of both 50 % Ni/Al$_2$O$_3$ derived form NiCl$_2$.6H$_2$O and 50 % Ni/Al$_2$O$_3$ derived from Ni (CH$_3$COO)$_2$.1H$_2$O. As seen in the figure, 50 % Ni/Al$_2$O$_3$ derived from (Ni (CH$_3$COO)$_2$.1H$_2$O) and pure Al$_2$O$_3$ show similar XRD pattern, which means that Ni crystallite size is less than 5 nm. This is plausible since XRD method is not sensitive to crystallite sizes below 3-5 nm. Conversely, XRD pattern of 50 % Ni/Al$_2$O$_3$ derived from (NiCl$_2$.6H$_2$O) showed peaks licated at 37.40, 43.3 and 63.17 of 2Θ angles corresponding to NiO crystalline phase. It is known that chloride ions results in sintering of the nickel metal, i.e. formation of larger crystallites, in the presence of chloride ions and also the degree of formation of metallic Ni affects the activity of the nickel based catalysts (Wu et al.). Therefore, the low conversion observed on the catalysts made by nickel chloride precursor seems to be due to the presence of large NiO crystallites and also the formation of NiO phase instead of metallic Ni. At this point, it is not clear which one is the controlling the activity of the catalysts made using chloride precursor.
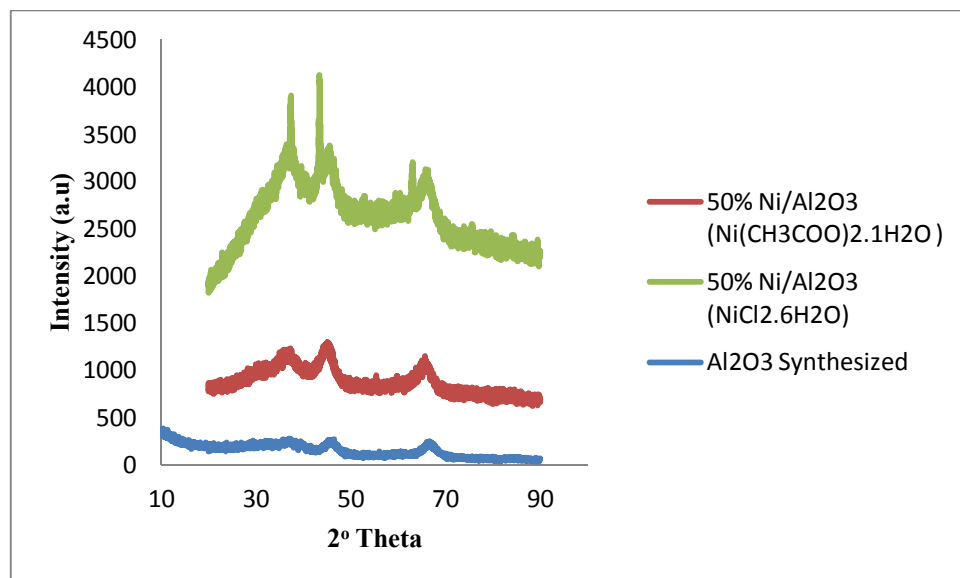
Figure 4.4. XRD patterns of 50 % Ni/Al$_2$O$_3$ (NiCl$_2$.6H$_2$O), 50 % Ni/Al$_2$O$_3$ (Ni (CH$_3$COO)$_2$.1H$_2$O) and pure Al$_2$O$_3$

4.2.3. Comparison of Ni/Al$_2$O$_3$ Catalysts Prepared Different Metal Loadings on Pure Alumina

Different Ni metal loadings on alumina were prepared using nickel (II) acetate monohydrate precursor since it showed higher conversion activity. Catalytic behavior of all the catalysts at 170 ^{o}C is as follows;

Table 4.7. Sunflower oil conversion on Ni/Al$_2$O$_3$ catalysts prepared different metal loadings and Pure Al$_2$O$_3$

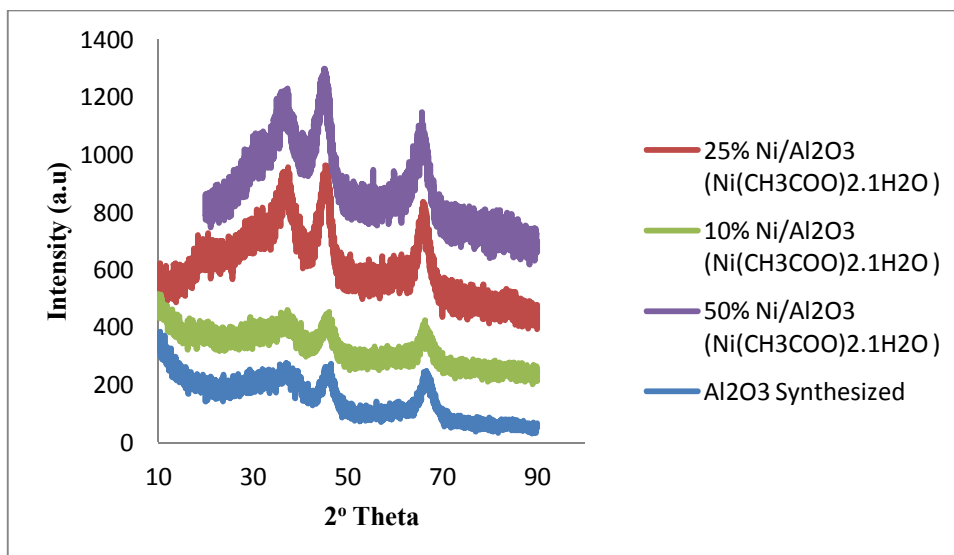| Catalysts	Sunflower Oil Conversion (%) at 170 ^{o}C
50 % Ni/Al$_2$O$_3$	35.16 (±0.33)
25 % Ni/Al$_2$O$_3$	36.21 (±1.59)
10 % Ni/Al$_2$O$_3$	32.33 (±1.59)
Pure Al$_2$O$_3$	31.72 (±0.68)

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Figure 4.5. XRD patterns of Ni/Al$_2$O$_3$ catalysts with different metal loadings and pure Al$_2$O$_3$

As seen in the figure above, Ni loaded alumina for Ni loadings and also pure alumina show similar XRD patterns, which means that Ni crystallite size is less than 5 nm. This is plausible since XRD method is not sensitive to crystallite sizes below 3-5 nm. In other words, this indicates that on fresh catalysts (i.e. unused) nickel was highly dispersed on alumina support regardless of the Ni loading. Moreover, it is well known that the catalytic activity increases with increasing the number of available "active" sites at the surface. But increasing Ni loading while keeping the crystallite size as small as possible, such as less than 5 nm, seems not to provide additional active sites; hence, not resulting in an increased conversion as Ni loading was increased. This result might be due to the occlusion (i.e. trapping in closed pores) of some Ni and/or NiO crystallites in the alumina structure occurred during the sol-gel preparation; hence resulting in inaccessible Ni and/or NiO crystallites. Ni loaded alumina catalysts are less active than that of the Mn loaded alumina catalysts at 170 $^{\circ}$C. For 25 % Ni/Al$_2$O$_3$ catalysts, which showed slightly better catalytic activity among the alumina supported nickel catalytsts, when the temprerature increased from 170 $^{\circ}$C to 195 $^{\circ}$C, the conversion increased from 36.21% ($\pm$1.59) to 70.04% ($\pm$1.99) on 25 % Ni/Al$_2$O$_3$ whereas the conversion was 51.9% ($\pm$3.21) on 50% Mn/Al$_2$O$_3$ and 52.48% ($\pm$1.47) on 70% Mn/Al$_2$O$_3$ at 195 $^{\circ}$C. It may be due to Mn atoms are found in various oxidation states at different temperature ranges which means that the decrease in the catalyst activity may be resulted from the increased crystallization of amorphous phase that sintering causes, and/or specific

surface area lose. Because it is reported that higher catalyst surface area leads to increase in catalytic activity of MnO_x (Cadus et al., 2006).

4.3. Catalytic Performance of Ni-Mn$_2$O$_3$/Al$_2$O$_3$ Catalysts in Sunflower Oil Combustion

After combustion experiments of sunflower oil by using different metal loadings of Ni/Al$_2$O$_3$ and Mn/Al$_2$O$_3$ catalysts, Ni-Mn$_2$O$_3$/Al$_2$O$_3$ catalysts were also synthesized using the same single step sol-gel method to study the effect of metal loading and the order of adding metal precursor on the activity of the catalysts.

Table 4.8. Sunflower oil conversion on Ni-Mn$_2$O$_3$/Al$_2$O$_3$ catalysts with different metal loadings and the order of adding metal precursor

Catalysts	Sunflower Oil Conversion (%)	
	170 ^{o}C	195 ^{o}C
23% Ni/66% Mn$_2$O$_3$/Al$_2$O$_3$ (First Mn precursor added)	43.75 ($\pm$0.76)	86.19 ($\pm$2.54)
20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Mn precursor added)	47.49 ($\pm$3.03)	68.17 ($\pm$3.34)
20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Ni precursor added)	59.6 ($\pm$3.11)	91.61 ($\pm$0.64)

All the catalysts, listed in Table 4.8, were tested in sunflower oil combustion under the same operating conditions used in testing Pt/Al$_2$O$_3$ catalyst. The activity of the mixed metal/metal oxide catalysts was evaluated. Among the all synthesized catalysts, the highest conversions were obtained using Ni/MnO$_x$/Al$_2$O$_3$ catalysts, especially at 195 ^{o}C. For instance, 20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Ni precursor added) catalyst have the highest activity at both temperatures among all the catalysts; in fact, the conversion increased from 59.6% ($\pm$3.11) at 170 ^{o}C to 91.61% ($\pm$0.64) 195 ^{o}C. The reason why the mixed metal/metal oxide catalysts showed higher activity may be due to the formation of the NiMnO$_3$ and Ni$_6$MnO$_8$ mixed oxides phases in addition to the formation of Mn$_2$O$_3$ phase at 500 ^{o}C of calcination temperature (Morales et al.). Furhermore, 20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Ni precursor added) catalyst showed higher activity when compared to 20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Mn precursor

added). The effect of order of precursors added during the preparation of the catalysts may be explained in such a way that based on the catalyst characterization results, the surface of Ni metal particles was partially covered with MnO_x, and the interaction between Ni metal and MnO_x can play an important role on the enhancement of the catalytic activity and the suppression of coke deposition (Koike et al.). Thus, one may expect to obtain nickel metals covered with MnO_x when nickel precursor added first.
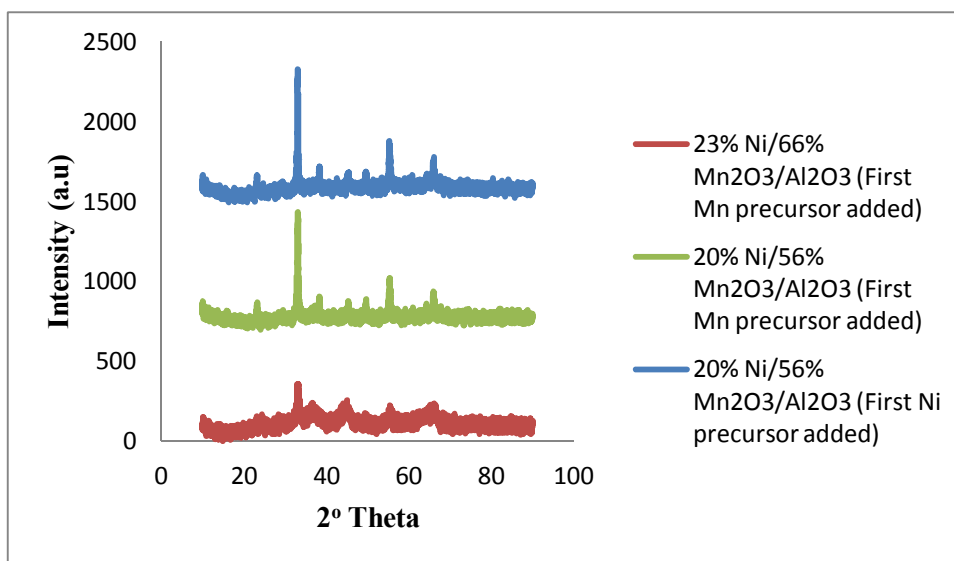

Figure 4.6. XRD patterns of Ni-Mn_2O_3/Al_2O_3 catalysts with different metal loadings and order of adding precursor

In the XRD pattern of 23% Ni/66% Mn_2O_3/Al_2O_3 (First Mn precursor added) catalyst, at 36.46, 45.001, 66.195 of 2Θ angles, alumina peaks are seen and at 33.24, 55.56 of 2Θ angles, Mn_2O_3 are seen. When compared to other two catalysts, 23% Ni/66% Mn_2O_3/Al_2O_3 (First Mn precursor added) catalyst showed the least activity 43.75% (±0.76) at 170 $^{\circ}C$. Since excess MnO_x addition decreased the catalytic activity by decreasing the number of the surface Ni atoms (Koike et al.). However, when the temperature was increased to 195 $^{\circ}C$, conversion increased to 86.19% (±2.54). This could be due to increased availability of surface oxygen of MnO_x crystalline phase. In the literature, the combinations of MnO_x with other oxides deposited on a high surface area supports used in oxidation processes are known to exhibit improved catalytic activity as compared to a single component catalyst (Cadus et al., 2006). In order to understand of activity behavior of the corresponding catalysts, crystallite size of Mn_2O_3 and MnO_2 were investigated.

Table 4.9. Crystallite Size of Fresh Catalysts

Catalysts	Crystallite Size of Mn_2O_3 (nm)	Crystallite Size of MnO_2 (nm)
23% Ni/66% Mn_2O_3/Al_2O_3 (First Mn pre.)	20.7	XRD amorphous
20% Ni/56% Mn_2O_3/Al_2O_3 (First Mn pre.)	38.2	53.6
20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni pre.)	44.3	68.9

From table above for better conversion both Mn_2O_3 and MnO_2 phases are necessary with big crystallite size.

4.4. Reusability of the Selected Catalysts at 170 ^{o}C

In addition to high catalytic activity, the catalysts must also comprise important features like high stability in severe conditions, ability to be reused several times and should have high tolerance against deactivation.

On this matter, four different catalysts were chosen in terms of their activities to investigate their reusability performance in combustion of sunflower oil. 25 % Ni/Al_2O_3, 50% Mn/Al_2O_3, 23% Ni/66% Mn_2O_3/Al_2O_3, (First Mn precursor added), 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) were the catalysts selected. The conversions over them after 6 times used were 25.24%, 21.44%, 28.12% and 29.76%, respectively. The combustion performance of selected catalysts is as follows;

Table 4.10. Sunflower oil conversion of selected catalysts

Catalyst	Sunflower Oil Conversion (%) at 170 °C					
	1st use	2nd use	3rd use	4th use	5th use	6th use
25 % Ni/Al$_2$O$_3$	36.21	32.63	31.36	29.72	29.28	25.24
50% Mn/Al$_2$O$_3$	42.92	40.19	33.8	31.73	22.53	21.44
23% Ni/66% Mn$_2$O$_3$/Al$_2$O$_3$ (First Mn precursor added)	43.75	33.6	33.06	32.86	31.39	28.12
20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Ni precursor added)	59.6	39.09	36.41	32.39	31.26	29.76

To understand the activity loses of the selected catalysts listed in Table 4.9, usage number at 170 °C was plotted as a function of conversion as seen in Fig. 4.7.
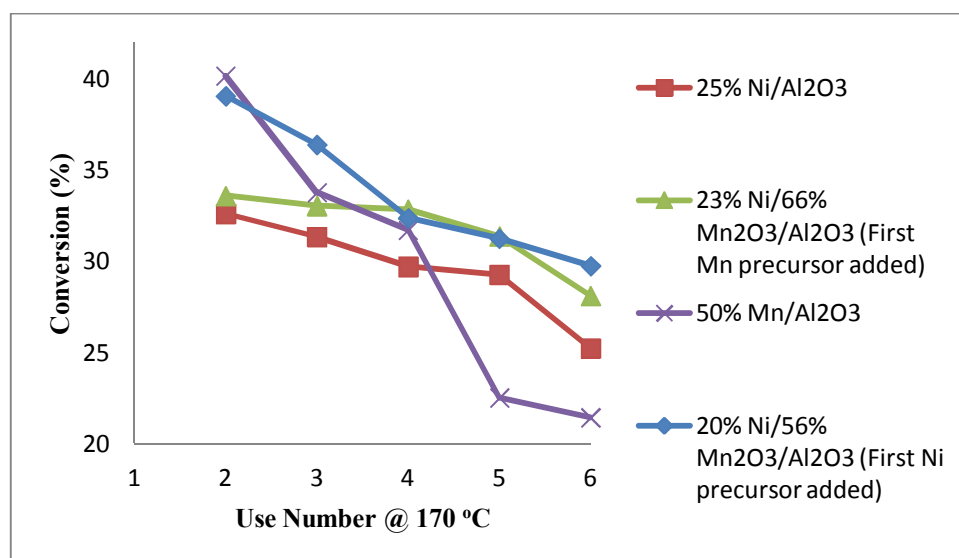

Figure 4.7. Conversion as a function of use number at 170 °C

To summarize, 20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Ni precursor added) catalyst showed better activity (29.76 at 170 °C) after six times used.
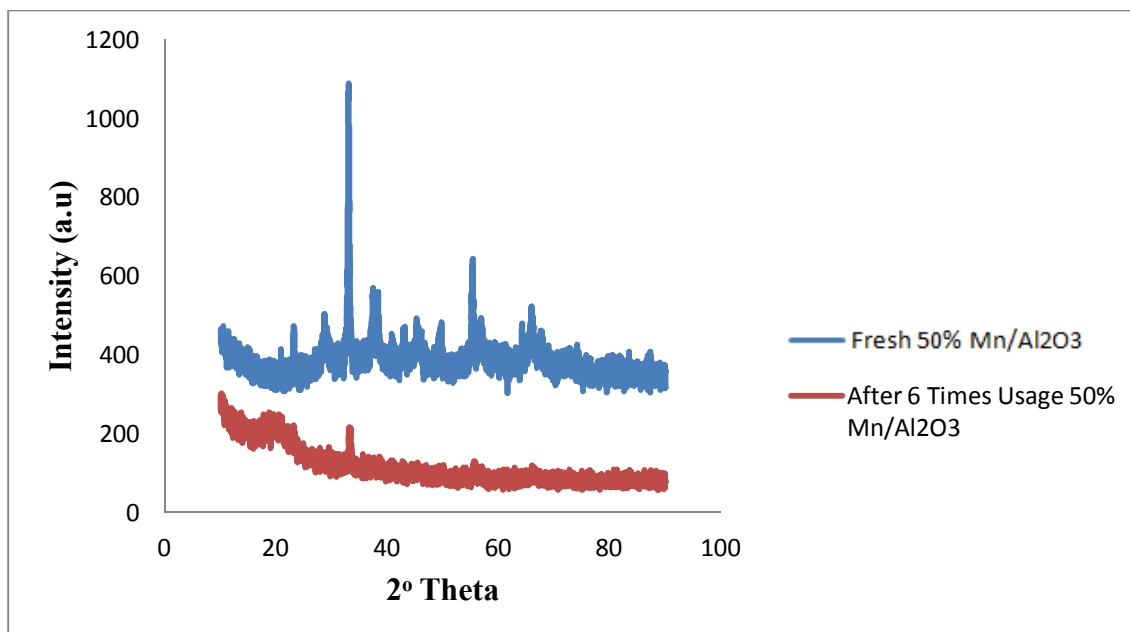
Figure 4.8. XRD patterns of fresh and 6 times used 50% Mn/Al$_2$O$_3$ catalysts at 170 ^{o}C

Figure 4.8 shows XRD patterns of the fresh and 6 times used 50%Mn/Al$_2$O$_3$ catalyst. For the catalyst used for 6 times, at 33.34 of 2Θ angle, Mn$_2$O$_3$ peak is seen and also at 55.56 of 2Θ angle Mn$_2$O$_3$ is hardly distinguished from backround noise, but a peak appeared at 19.55 of 2Θ angle, related to the carbon of possibly carbonaceous deposit . Interestingly, it is seen that other peaks observed on fresh catalyst disappeared; hence, indicating the redispersion, i.e. decrease of the crystallite size, of the manganese oxide crystallites. Besides, the catalytic activity of 50% Mn/Al$_2$O$_3$ decreased too when compared to other catalysts because total mass of each catalyst after six times used increased from 0.1 g (fresh catalyst) to 0.18 g because of by products left on the catalyst, such as hydrocarbons, water, even coke (or carbonaceous materials) and after 6 times usage crystallite size of Mn$_2$O$_3$ decreased from 45.5 nm to 29.3 nm. As mentioned in part 4.3, the crystallite size of Mn$_2$O$_3$ must be large for obtaining the high conversion.

4.5. Product Distribution of Combustion of Sunflower Oil

Emissions of volatile organic compounds, including aldehydes, hydrocarbons, dienes or other volatiles commonly formed during edible oil degradation, create unpleasant flavour; reduce the shelf-life of edible oils and may further cause health problems related to heating of cooking oils, such as coconut oil, olive oil or sunflower

oil. So, home cooking has to be considered as an indoor pollution problem. Catalytic combustion seems to be a promising approach to eliminate this problem but the product distribution during the catalytic combustion must not cause additional problems. The synthesized catalyst showed the best combustion activity at 170 ^{o}C and 195 ^{o}C in 1 h was 20% Ni/56% Mn_2O_3/Al_2O_3. Thus, the combustion products released during combustion on this catalyst carried out in a headspace vial was monitored by GC-MS and shown in Figure 4.9 and 4.10.

Figure 4.9. GC-MS chromatogram of combustion of sunflower oil by using 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) at 170 ^{o}C for 1 h
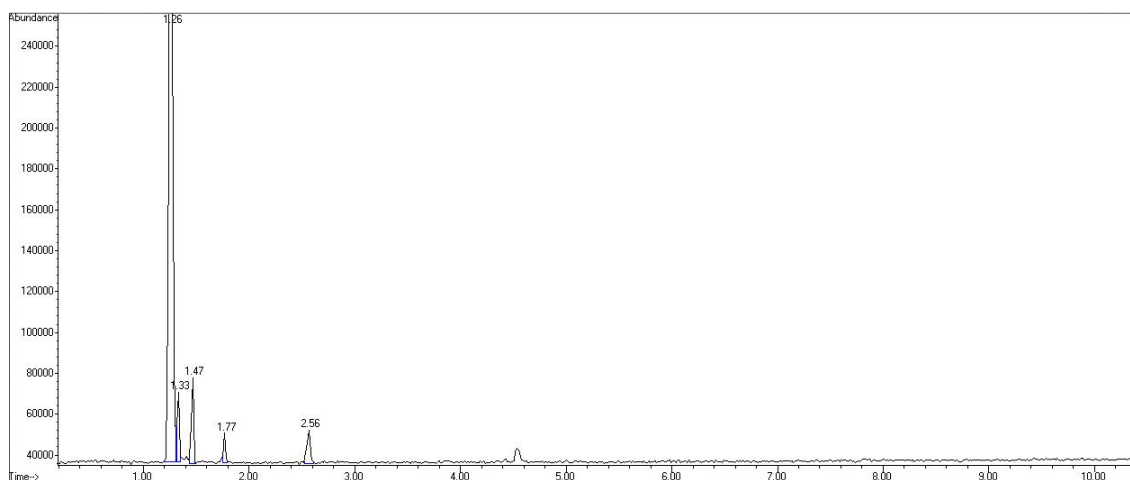

Figure 4.10. GC-MS chromatogram of combustion of sunflower oil by using 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) at 195 ^{o}C for 1 h

As seen in the figure 4.9, the combustion product formed at at 170 ^{o}C are O_2, N_2, CO, CO_2, H_2O and also organic compounds, butane, pentane, butanal and pentanal,

which were observed at 1.26, 1.33, 1.47, 1.77, 2.56 min of analysis times, respectively. After the 10 min, there were no compounds detected. Furthermore, the same combustion step was performed at 195 ^{o}C for 1 h. As seen in figure 4.10, O_2, N_2, CO, CO_2, H_2O and also butane, pentane, butanal were again observed, at 1.26, 1.33, 1.47 and 1.77 min but at 195 ^{o}C of the reaction temperature, pentanal at 2.56 min was not detected. When combustion products injected to GC for second time for both temperatures, all peaks were observed invariably. In fact, the compounds released during the blank tests, such as 2, 4-decadienal, acetaldehyde and hexanal, mentioned in section 4.1 of this thesis was not detected. This could come from the instrument set-up itself but it needs to be clearified.

The combustion was also carried out on 20% Ni/56% Mn_2O_3/Al_2O_3 (First Mn precursor added) catalyst at both temperatures. The products released during combustion was monitored by GC-MS and shown in figures 4.11 and 4.12.
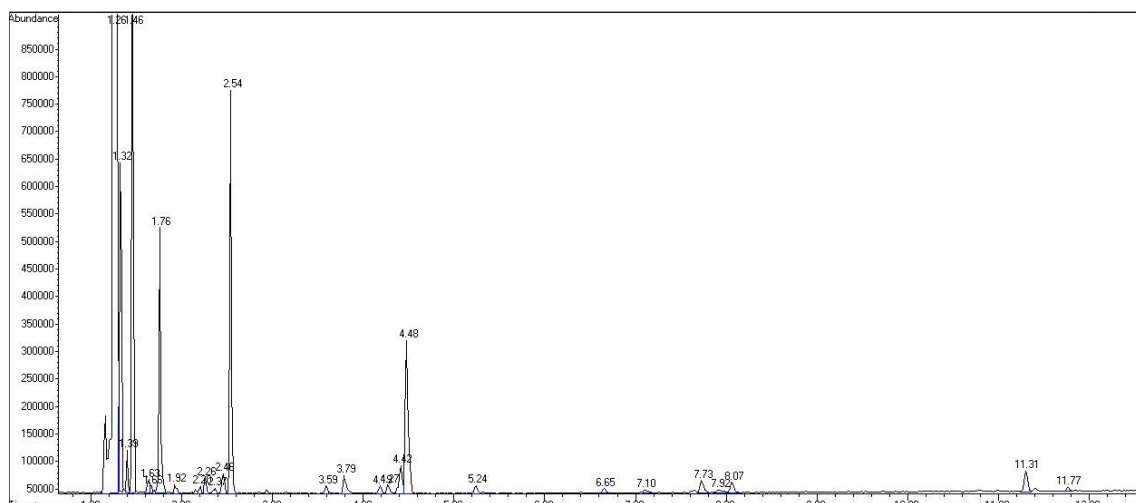

Figure 4.11. GC-MS chromatogram of combustion of sunflower oil by using 20% Ni/56% Mn_2O_3/Al_2O_3 (First Mn precursor added) at 170 ^{o}C for 1 h
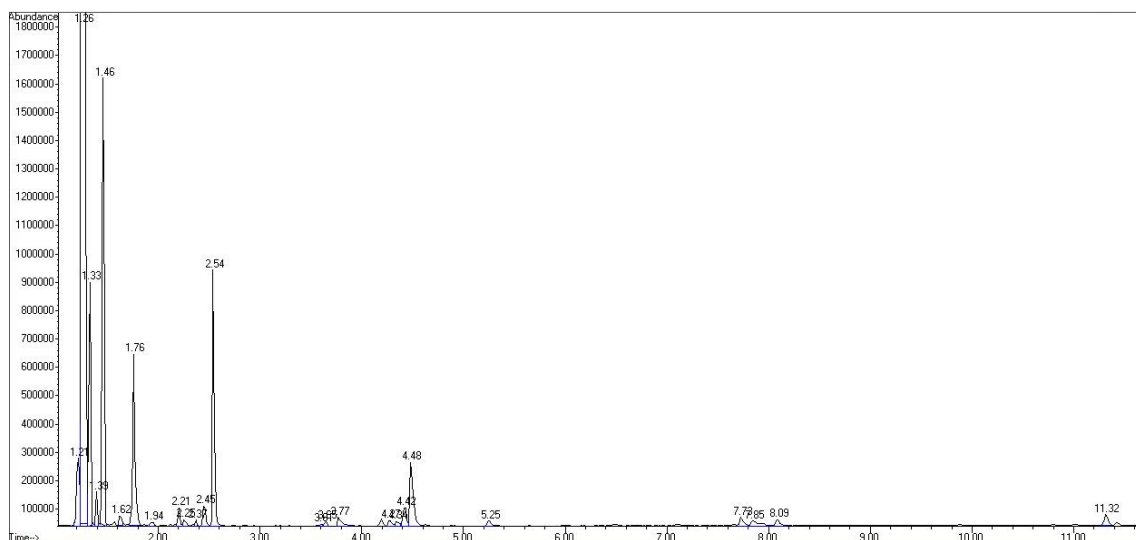
Figure 4.12. GC-MS chromatogram of combustion of sunflower oil by using
20% Ni/56% Mn_2O_3/Al_2O_3 (First Mn precursor added) at 195 ^{o}C
for 1 h

As seen in the figures, at 170 ^{o}C, O_2, N_2, CO, CO_2, H_2O and also acetaldehyde + butane, pentane, butanal, pentanal, octane, hexanal, 2-pentylfuran being similar to the study of DuPuy et al. are observed at 1.26, 1.33, 1.47, 1.77, 2.54, 4.43, 4.48 and 11.32 min, respectively. Similarly, all the inorganic and organic compounds observed at 170 ^{o}C were also determined at 195 ^{o}C with almost similar or higher peak areas and in addition, at 2.21 min, benzene was clearly seen. When combustion products injected second time for both temperatures, the number of peaks decreased. But, O_2, N_2, CO, CO_2, H_2O and also acetaldehyde + butane, pentane, butanal, pentanal, octane, hexanal, 2-pentylfuran and benzene were still observed.

The combustion product analysis was also carried out for 3 % Pt/Al_2O_3 as a reference catalyst and shown in Fig. 4.13. As seen in the figure, at 195 ^{o}C, the first peak included O_2, N_2, CO, CO_2, H_2O and also butane, pentane, hexane and heptane, were eluted at 1.24, 1.32, 1.44, 1.75 and 2.52, respectively. Additionally, the peak areas of air, butane and pentane obtained using 3 % Pt/Al_2O_3 are higher than those of 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added). Especially, the peak area of the first peak is 8.2 times larger.
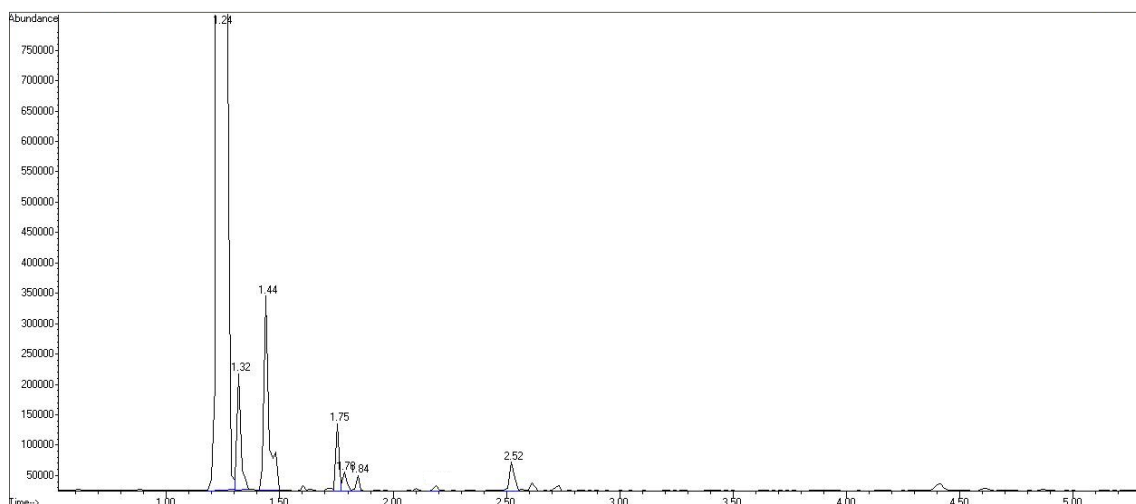
Figure 4.13. GC-MS chromatogram of combustion of sunflower oil by using 3 % Pt/Al$_2$O$_3$ at 195 $^{\circ}$C for 1 h

The same combustion procedure was applied for pure Al$_2$O$_3$ and the results showed that volatile compounds released include CO, CO$_2$ and excessive amount of n-hexadecanoic acid. In the analysis of coated aluminum plate, CO, CO$_2$ were detected at the end of the reaction. All volatiles released after 1 h were shown in table 4.11

Table 4.11. Released Volatiles as a result of Combustion and/or Oxidation Processes at 170 $^{\circ}$C and 195 $^{\circ}$C

Catalysts / Volatiles	Blank	Pure Al$_2$O$_3$	20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Ni pre.)	20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Mn pre.)	3% Pt/Al$_2$O$_3$ (Used for only 195 $^{\circ}$C)	20% Ni/56% Mn$_2$O$_3$/Al$_2$O$_3$ (First Ni pre.) coated Al Plate (195 $^{\circ}$C)
N$_2$+O$_2$+CO+CO$_2$+H$_2$O	(N$_2$+O$_2$+H$_2$O)	✔	✔	✔	(N$_2$+O$_2$+CO$_2$+H$_2$O)	✔
Acetaldehyde	✔			✔		
Butane	✔	✔	✔	✔	✔	
Pentane	✔	✔	✔	✔	✔	✔
Butanal	✔		✔	✔		✔
Pentanal	✔		✔ (Absent at 195 $^{\circ}$C)	✔		✔
2,4-decadienal	✔					
Hexanal	✔ (Present at 195 $^{\circ}$C)			✔		
Octane				✔		
2-pentylfuran				✔		
Benzene				✔ (Present at 195 $^{\circ}$C)		
n-hexadecanoic acid	✔	✔ (Excessive)				

In blank test, CO and CO$_2$ were not detected because in this test only vaporization was observed. Except for 3 % Pt/Al$_2$O$_3$, all combustion activities generated

CO. In addition to this, the analysis of pure Al_2O_3 combustion products included excessive amount of n-hexadecanoic acid. Because pure Al_2O_3 has acidic nature and this resulted in hydrolysis of triglycerides to fatty acids. Besides 3 % Pt/Al_2O_3 did not generate CO because of its high combustion activity towards volatile compounds. The red symbols refers to volatiles resulted from bulk oil inside the catalyst pores. This red symbols referring volatiles also were observed in the blank test with higher peak areas. But there was an exception, when 20% Ni/56% Mn_2O_3/Al_2O_3 (First Mn precursor added) was used octane, 2-pentylfuran and benzene being unfavorable compounds were also generated.

4.6. Plate Coating

After the tests of sunflower oil combustion on powder catalysts in the batch reactor, the reaction was also performed on catalyst coated aluminum plates because plate reactors for oil combustion is more suitable for practical applications, such as ovens. In addition, mass transfer limitations observed on powder catalysts can be prevented by using catalyst coated plates; specifically internal mass transfer limitations are eliminated on plate reactors. So, the catalyst coated aluminum plates were prepared by dip-coating method and also using the most active catalysts formulations, such as 50% Ni/Al_2O_3 ($Ni(CH_3COO)_2.1H_2O$) and 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added). 50% and 67% conversions were reached on 50% Ni/Al_2O_3 ($Ni(CH_3COO)_2.1H_2O$) and 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) at 170 ^oC in 1 h, respectively. After two hours of reaction, 50% Ni/Al_2O_3 coated plate reached 83% conversion and 20% Ni/56% Mn_2O_3/Al_2O_3 coated plate reached 100% of conversion at 170˚C.

4.6.1. GC-TCD Results of Selected Catalysts related to CO and CO_2

For all the combustion tests, CO and CO_2, detected using GC-MS except for 3% Pt/Al_2O_3, were further quantitatively analyzed by GC-TCD. As seen from the figure 4.14, CO and CO_2, eluted at 2.585 and 8.054 min, with the peaks areas of 3.467 and 17872.2, are observed on 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) at 195 ^oC for 1 h whereas on 3% Pt/Al_2O_3, the peak area of CO_2 increased to 25637.8 and CO

peak was not observed as seen in Figure 4.15. Also, on 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) coated aluminum plate at 195 ^{o}C for 1 h, CO and CO_2 were detected at 1486.3 and 2879.4 min of elution times but their amounts were lower than that obtained on the corresponding powder catalysts. This could be due to the lower amount of oil used during tests of the catalyst coated aluminum plate.

Figure 4.14. GC-TCD chromatogram of combustion of sunflower oil by using 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) at 195 ^{o}C for 1 h

Figure 4.15. GC-TCD chromatogram of combustion of sunflower oil by using 3% Pt/Al_2O_3 at 195 ^{o}C for 1 h

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Figure 4.16. GC-TCD chromatogram of combustion of sunflower oil by using 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) coated Al plate at 195 ^{o}C for 1 h

As a result, from the amount of CO and CO_2 calculated quantitatively, it was found that 20 cc headspace vial contained 2.14% CO and 9.8% CO_2 when 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) was used and 14.06% CO_2 when 3% Pt/Al_2O_3 was used at 195 ^{o}C for 1 h of the reaction time.

CHAPTER 5

CONCLUSION

In this study, sunflower oil combustion was investigated over metal and metal oxide type of catalysts and their loadings on the conversion of sunflower oil as a function of temperature over single step sol-gel made Al_2O_3 supported metal or mixed metal oxides. The combustion performance of catalysts was evaluated at two different temperatures selected as 170 ^{o}C and 195 ^{o}C.

Initially, sunflower oil combustion was carried out on 3% Pt/Al_2O_3 and the conversion increased from 79% to 100% by increasing temperature. Among Mn loaded catalysts, 50% Mn/Al_2O_3 showed slightly better conversion when compared to 70% Mn/Al_2O_3 confirmed by incread surface area, but when temperature was increased. conversios increased approximately 10%. Besides, nickel (II) acetate monohydrate precursor was found to be better nickel precursor than Nickel (II) chloride hexahydrate to obtain highly active catalysts. Because nickel (II) acetate precursor provided better Ni and/or NiO dispersion, i.e. small Ni and/or NiO crystallites, but nickel (II) chloride precursor resulted in sintering of NiO crystallites; hence, resulting in formation of larger crystallites because of residual chloride ions. All the Ni loadings derived from nickel (II) acetate showed almost similar conversions; hence, indicating possibility of occlusion of Ni crystallites in alumina.

Next, in the investigation of mixed metal/metal oxide catalysts, 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added), showed the highest activity at both temperatures; e.g. conversion increased from 59.6% to 91.6% when temperature was increased from 170 to 195 ^{o}C and also coke deposition was observed and for high conversion. both Mn_2O_3 and MnO_2 phases are necessary. Besides, bigger crystallite size resulted in higher conversion. Pure Al_2O_3 also was active in sunflower oil combustion. Moreover, its acidic nature caused hydrolysis of triglycerides; hence, resulting in formation of fatty acids, such as palmitic acid. 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni precursor added) showed the highest activity at 170 ^{o}C among selected catalysts after six times of usage. At the end of 6 times usage, carbonaceous materials were found to be deposited on the catalyst surface that caused the decrease of conversion.

CO_2 and CO were observed on 20% Ni/56% Mn_2O_3/Al_2O_3 (First Ni pre.), 20% Ni/56% Mn_2O_3/Al_2O_3 (First Mn pre.), pure Al_2O_3 and coated Al plate. On all the catalysts, some volatiles, such as butane, pentane, were generated from the bulk oil inside the pores. CO_2 were the only combustion product on 3% Pt/Al_2O_3. As an exception, 20% Ni/56% Mn_2O_3/Al_2O_3 (First Mn precursor added) generated octane, 2-pentylfuran and benzene being undesired volatile compounds. Catalyst coated plate showed higher conversion due to the elimination of internal mass transfer limitations.

This study shows that Ni and Mn_xO_y based catalysts are as highly active as the noble metal catalysts but still they need improvement in the design of their formulation.

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