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# Phosphorous Poisoning and Characterization of Al<sub>2</sub>O<sub>3</sub> Based Support Material

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<p>Purpose of this thesis project was to study the effect of phosphorus poisoning on Al<sub>2</sub>O<sub>3</sub> based support material. Al<sub>2</sub>O<sub>3</sub> is widely used as a support material in natural gas oxidation catalysts as a part of support material. The work was done in the Mass and Heat Transfer process Laboratory, University of Oulu as a part of a larger project that focuses on catalyst poisoning in more detail.</p> <p>The first part of the study was consisted of poisoning monolith samples by gaseous phase under three different phosphorus feed concentrations. The second part of the project focused on characterization of the poisoned samples. Techniques used for characterization were physisorption analyses, field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD).</p> <p>It was found that phosphorus changes the specific surface area of the support material. Total BET surface area and pore volume were lower in the phosphorus-poisoned samples compared to the fresh sample. It was also found that these changes are related to the amount of phosphorus available in the feed during poisoning. In addition, phosphorus accumulation in the inlets of the samples was much larger than the phosphorus accumulation in the sample outlets. It was also found that phosphorus binds chemically with Al<sub>2</sub>O<sub>3</sub> based support forming AlPO<sub>4</sub>.</p> <p>The results of this project can be utilized in further understanding of phosphorus-induced catalyst deactivation. It will help developing catalysts that are more resistant to phosphorus.</p>	
Keywords	Natural Gas Oxidation Catalyst, Phosphorous poisoning, catalyst deactivation, aluminium oxide, automotive catalytic converter

## List of Abbreviations

BET	Brunauer-Emmet-Teller theory
BJH	Barrett-Joyner-Halenda theory
DOC	Diesel Oxidation Catalyst
EDS	Energy Dispersive X-ray Spectrometer
EDTA	Ethylene diamine tetraacetic Acid
EC	European Commission
EU	European Union
FESEM	Field Emission Scanning Electron Microscopy
HC	Hydrocarbon
PGM	Platinum Group Metal
PM	Particulate Matter
NGOC	Natural Gas Oxidation Catalyst
SCR	Selective Catalytic Reduction
SOF	Soluble Organic Fraction
TEM	Transmission Electron Microscopy
TWC	Three-way Catalyst
XRD	X-ray Diffraction
ZDDP	Zinc Dialkyldithiophosphate

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## 1. Introduction

Since 1970's, air pollution has been one of Europe's most important political concerns (European Commission, 2013). Despite major success in reducing air pollutant emission over several decades, it continues to be one of Europe's key environmental challenges (Guerreiro et al., 2013). One of the major air pollution contributors is transport sector. According to a report published in 2012 by European Environment Agency, in 2010 transport sector alone contributed to all most 30 % of total major air pollution in 32 member states (European Environment Agency, 2012). All fossil and bio-fuel driven vehicles emit exhaust gases that has a negative impact on both human health and environment (Guerreiro et al., 2013; Amann et al., 2011; Fattah et al., 2013). Automobile exhaust gases mainly include carbon monoxide (CO), unburned hydrocarbons (HC), hydrogen (H<sub>2</sub>), particulate matter (PM) and nitrogen oxides (NO<sub>x</sub>) (Štěpánka et al., 2009). European Commission took several steps to improve the situation by passing new legislations targeting problem sectors in order to improve air quality among member states. Regulation Euro 5 and Euro 6 set new exhaust gas emission standards for the transport sector. In addition to setting lower emission standards, the EU also changed its policy regarding the use of fossil fuel. Directive 2009/28/EC sets a target that by 2020, 20 % of total energy demand and 10 % of energy demand in transport sector shall come from a renewable source. With that, the use and production of bio-diesel and bio fuel derived from biomass has increased significantly (Mittelbach, 1996; Festel et al., 2013).

Among fossil fuels, natural gas has a lower emission during combustion (Engerera and Hornb, 2010; Hajbabaie et al., 2013; Bielaczyc et al., 2014). In Asia and Latin America, natural gas vehicles are widespread (Engerera and Hornb, 2010). Lean-burn natural gas engines emit less NO<sub>x</sub> and particulates compared to both gasoline and diesel fueled vehicles (Bielaczyc et al., 2014; Ma et al., 2007). One of the drawbacks could be the presence of unburned methane in the exhaust (Mowerya et al., 1999; Gélin et al., 2003). Currently methane is not under any legislation but has a high global warming potential of 72 over 20 years time period<sup>1</sup> (IPCC, 2014). However, unburned methane can be converted to less harmful form (CO<sub>2</sub> and H<sub>2</sub>O) using an oxidation catalyst. In

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<sup>1</sup> Global Warming Potential (GWP) is an index based on the ratio of the radiative forcing of an equal emission of a particular gas and CO<sub>2</sub> (other reference gases can be used too), integrated either over all time or up to an arbitrarily determined time horizon (Lee et al., 2004). In this example, CH<sub>4</sub> has a GWP of 72 over 20 years time period means that, CH<sub>4</sub> will trap 72 times more heat in atmosphere than the same amount of CO<sub>2</sub> in a time span of 20 years.

recent years, some European states decided to foster natural gas by developing incentives (e.g. tax reduction) for environmental purposes. This could prove effective to improve air quality as technology for using natural gas in conventional engines is quite advanced (Engerera and Hornb, 2010).

Catalysis has been in use to control automotive air pollution since 1970. With the increasing number of automobiles and tightening of emission standards, the need for developing more durable and efficient catalysts has increased dramatically (Greening, 2001). Catalysts are used to convert harmful gases found in vehicle exhaust into less harmful gases (e.g. CO to CO<sub>2</sub> as well as NO<sub>x</sub> to N<sub>2</sub>) (Heck and Farrauto, 2001).

It is important to take catalytic deactivation in to consideration while designing any catalyst. In exhaust converters, catalytic deactivation is caused primarily by poisoning and thermal degradation (Koltsakis and Stamatelos, 1997; Ramanathan and Oh, 2013). While deactivation is inevitable, it is possible to delay it by developing a catalyst that has better thermal and poison resistance. The economical and environmental benefit of a more durable catalyst is undeniable. Exhaust feed might contain poisons such as sulfur (S) originating from fuel and phosphorus (P), zinc (Zn), calcium (Ca), and magnesium (Mg) originating from lubricants (Shelef and McCabe, 2000). Beside developing a poison resistant catalyst, an overall advancement of engine system, exhaust gas after treatment and more efficient fuel is also necessary in order to control deactivation (Wallington et al., 2006).

The challenge is mainly targeted to the academy researchers as well as to the catalytic material and system development companies to make a more durable and efficient catalyst. The key is to understand the complete reactions and overall dynamics of the effect of poisoning on different catalyst components. A typical automotive oxidation catalyst contains precious metals palladium (Pd), platinum (Pt) and a support material such as aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) or cerium oxide (CeO<sub>2</sub>) (Galisteo et al., 2004). In addition, there are a number of various other materials to make the catalyst active, durable and stable (Kröger, 2007; Zotin et al., 2005). Despite the huge number of studies conducted on the effect of poisoning on the components of oxidation catalyst, the mechanism of the process remains yet to be discovered. The purpose of this thesis project was to study the effect of phosphorus poisoning on Al<sub>2</sub>O<sub>3</sub> based support material without the precious metal on a mesoscopic level using several characterization techniques. This is a part of a larger project that focuses on catalyst poisoning in more detail.

Laboratory scale gaseous poisoning of monolithic samples was conducted with three different molar concentrations of phosphorous. To study and determine the effect of phosphorous, several characterization techniques were used. Since the studied sample did not contain precious metals, activity tests were not carried out.

## 2. Automotive Exhaust Gas Components and Their Impacts

Typically, motor vehicles use liquid fossil and bio-fuels as the energy source. In the ideal condition, following overall reaction takes place in the combustion chamber of a vehicle (Heck and Farrauto, 2001):



In real engines that is not the case. The combustion of the fuels results into emission of several gases which are considered to have a negative impact on the both environment and human health. The exhaust gas from motor vehicles is generally composed of carbon dioxides ( $\text{CO}_2$ ), carbon monoxides (CO), nitrogen oxides ( $\text{NO}_x$ ), hydro carbons (HC) and particulate matter (PM). Ozone ( $\text{O}_3$ ) might also be present as a secondary by product. Depending on the source and composition of fuel, a significant amount of sulfur oxides ( $\text{SO}_x$ ) are also emitted (Walsh, 2011).

$\text{CO}_2$  is the principal component of all carbon based fuel emission; fossil fuels and bio-fuels for example. Anthropogenic carbon dioxide emission is the main contributor to global warming (Ghommem et al., 2012). According to the International Transport Forum, 23 % of total global  $\text{CO}_2$  emission comes from transport sector (International transport forum, 2010). There is yet to discover an effective and efficient technology to break down  $\text{CO}_2$  to its core elements. But so far energy efficiency, energy conservation and switching to renewable energy have been considered as the main strategy in order to reduce  $\text{CO}_2$  emission. Current  $\text{CO}_2$  emission standard set by European Commission is 130 g/km and a goal of 95 g/km is set to achieve by 2015 (EC, 2009).

CO is produced as an exhaust gas when fuel is not completely burnt. CO poses a serious health risk to humans even with small exposure. CO binds with haemoglobin instantaneously but has such an extremely low dissociation rate that it is virtually irreversible (Varma et al., 2009). The occupational exposure limit for CO in Finland is 30 ppm TWA (Time Weighted Average)<sup>2</sup> (Spectra gases Inc., 2005). According to Euro 6

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<sup>2</sup> A time-weighted average is used to calculate a workers daily exposure to a hazardous substance (such as chemicals, dusts, fumes, mists, gases, or vapors) or agent (such as occupational noise), averaged to an 8-hour workday, taking into account the average levels of the sub-

regulation, the emission limit for CO in passenger cars with diesel engine is 0.50 g/km and 1 g/km for gasoline and natural gas engine (EC, 2007).

NO<sub>x</sub> refers to the combination of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). In the motor vehicles, NO<sub>x</sub> is produced mainly due to high temperature in combustion chamber (Christodoulou and Megaritis, 2013). The effect of NO<sub>x</sub> is rather explicit on environment. They are one of the main culprits responsible for acid deposition and acid rains and tropospheric ozone formation (Sutton et al., 2011). NO<sub>x</sub> also has adverse effect on human respiratory system and increase the susceptibility of respiratory infections (Kampa and Castanas, 2008). Euro 6 emission standard for NO<sub>x</sub> in passenger cars is 0.08 g/km for diesel engine and 0.06 g/km for gasoline and natural gas engine respectively (EC, 2007).

HCs are found in exhaust gas when the fuel is not burnt completely. HC reacts with NO<sub>x</sub> in the presence of sunlight forming for example ground-level ozone and smog. Ground-level ozone can cause eye irritation and lung damage. For gasoline and natural gas engine the emission limit for HC is 0.10 g/km (EC, 2007).

Particulate matters (PM) are exclusive to diesel engine emission. They have the widest range of adverse effects on human health, ecology, visibility, climate change and the environment (Maricq, 2007). Depending on the nature of PM, they can either absorb light (elemental carbon) or reflect light (sulfur aerosol) causing opposite effects on climate (Jacobson, 2009). A complete knowledge on the role of PM is rather complex and yet not fully understood. In addition they have a number of adverse effects on human, especially on cardiovascular system (Martinelli et al., 2013). The European emission standard (Euro) for PM in passenger cars with diesel engine as well as with gasoline and natural gas engine is 0.005 g/km. PM limit set for gasoline and natural gas engines is only applicable on a lean-burn direct-injection gasoline vehicle (EC, 2007).

Table 1 gives Euro 5 and 6 vehicle emission standards for EU member states.

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stance or agent and the time spent in the area (Office of Water Program, Sacramento State, 2012)

Table 1. Emission limit standard for vehicle exhaust in Europe (Dieselnet, 2014; EC, 2007)

Stage	Date	CO	HC	HC+NO <sub>x</sub>	NO <sub>x</sub>	PM	Particle Number
		g/km					/km
<b>(Diesel)</b>							
<b>Euro 5a</b>	2009.09	0.50	-	0.23	0.18	0.005	-
<b>Euro 5b</b>	2011.09	0.50	-	0.23	0.18	0.005	6.0×10 <sup>11</sup>
<b>Euro 6</b>	2014.09	0.50	-	0.17	0.08	0.005	6.0×10 <sup>11</sup>
<b>(Gasoline/ Natural Gas)</b>							
<b>Euro 5</b>	2009.09	1.0	0.10	-	0.06	0.005	-
<b>Euro 6</b>	2014.09	1.0	0.10	-	0.06	0.005	6.0×10 <sup>11</sup>

### 3. Automotive Exhaust Catalyst

Automotive exhaust catalysts came to the US market in 1975 (Kasper et al., 2003; Shelef and McCabe, 2000). Following its success at catalyzing vehicle exhaust gases, Europe adopted the automotive catalyst in 1986 (Shelef and McCabe, 2000). The first catalytic converters were meant for and capable of treating only HC and CO emissions (Heck and Farrauto, 2001). In 1980s, stricter NO<sub>x</sub> emission standards were followed by the development of three-way converters (TWC). Three-way converters are capable of catalyzing three sets of reactions at the same time: reduction of NO<sub>x</sub> and oxidation of CO and HC (Gandhi et al., 2003). Three-way converters (TWC) are used for treating exhaust gases from gasoline engines and natural gas engines in the stoichiometric conditions. Diesel oxidation catalyst (DOC) and natural gas oxidation catalyst (NGOC) are used to treat exhaust gases from diesel engines and lean natural gas engines respectively. They are designed to oxidize CO and un-burnt HCs. In the diesel fuelled vehicles, the exhaust treatment system now contains particulate filters (PF), selective catalytic reduction (SCR) or NO<sub>x</sub> storage and reduction catalyst (Twigg, 2006). As mentioned earlier, lean-burn natural gas-fuelled engines have very low emission of NO<sub>x</sub> and PM. Because of this reason, oxidation catalyst alone is in many cases enough in this type of engines (Engerera and Hornb, 2010).

Automotive catalysts have a ceramic or metallic structure in the form of monoliths. In the vehicle applications, ceramic catalytic converters are the most used. However, metallic monoliths are also common. In some applications, metal monolith is actually preferable than ceramic due to the fact that metals have higher heat capacity than the ceramic, thus reducing the time taken for the catalyst to achieve desired reaction temperature. The geometry of the monolith used should be such that it provides a high surface area with a low pressure drop. In this study, metallic monolith catalytic converter structure was used. A support material with a high surface area such as  $\text{Al}_2\text{O}_3$  is then spread over the monolith. To stabilize the support material against the varying temperatures and gas compositions, the additional support material as well as promoters such as lanthanum (La), barium (Ba) or silicon oxides ( $\text{SiO}_2$ ) are also used. The catalytic active compounds (e.g. Pd and Pt) are then dispersed to the support material in varying proportion to enable the whole system to catalyze the intended reactions such as oxidation and reduction (Heck and Farrauto, 2001; Ziaei-Azad et al., 2011; G lin et al., 2003).



**Figure 1. Typical structure of a metallic monolithic catalyst by DinexEcocat Oy**

### 3.1 Natural Gas Oxidation Catalyst (NGOC)

Natural gas oxidation catalysts (NGOC) are installed in lean-burn natural gas driven vehicles to treat exhaust gases. The emission from natural gas vehicles (NGV) highly depends on the composition of the fuel. Typically natural gas (NG) is composed of up

to 90 volume % methane. Primary emissions from a NGV is unburned methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), water vapor (H<sub>2</sub>O), oxides of sulfur (SO<sub>x</sub>), oxides of nitrogen (NO<sub>x</sub>) and carbon monoxide (CO) (Gélin et al., 2003; Klingstedt et al., 2001; Hajbabaei et al., 2013). Table 2 shows the typical composition of lean-burn NGV exhaust gases.

**Table 2. Composition of lean-burn natural gas engine exhaust gas (Gélin et al., 2003; Mowerya et al., 1999)**

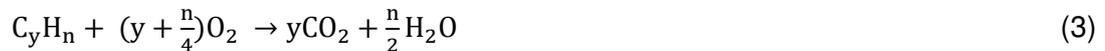
<b>CH<sub>4</sub></b> <b>(ppm)</b>	<b>H<sub>2</sub>O</b> <b>(vol- %)</b>	<b>CO<sub>2</sub></b> <b>(vol- %)</b>	<b>O<sub>2</sub></b> <b>(vol- %)</b>	<b>SO<sub>x</sub></b> <b>(ppm)</b>	<b>NO<sub>x</sub></b>	<b>CO</b>
<b>500-1000</b>	10-15	15	8	1	Not Available	Not Available

Unburned methane is the most problematic emission gas among all other exhaust components due to its high stability. NGOC catalytically oxidizes methane and carbon monoxide. The main reaction products are carbon dioxide and water (Mowerya et al., 1999). Primary oxidation reactions in natural gas oxidation catalyst are as follows:

Oxidation of CO:



Oxidation of HC:



The operating temperature of NGOC is less than 500-550 ° C. Therefore, thermal stability of the catalyst is not a big concern. It is more important for the catalytic converter to be highly active at a low temperature and to be resistant to poison such as sulfur (Gélin et al., 2003). It has been noted that palladium (Pd) is the most active methane oxidation catalyst (Mowerya et al., 1999). However, palladium is very sensitive to water and sulfur-containing compounds, which may cause severe deactivation phenomena (Gélin et al., 2003). To solve the problem, commercial NGOC contains a high loading of palladium (Pd) along with lower platinum (Pt) loading dispersed into support material such as Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> (Lampert et al., 1997; Gélin et al., 2003). Platinum is added due its resistance to sulfur poisoning even though its catalytic ability is much lower than that of palladium (Lampert et al., 1997).

### 3.2 Diesel Oxidation Catalyst (DOC)

Diesel oxidation catalysts (DOC) are used to treat exhaust gas from diesel fueled vehicles. DOC catalytically oxidizes hydrocarbons (HC), carbon monoxide (CO), nitrogen monoxide (NO), aldehydes, soluble organic fraction (SOF), and odorous compounds (Zelenka et al., 1996; Kröger, 2007; Wiebenga et al., 2012). Composition of diesel engine exhaust gases is given in Table 3.

**Table 3. Compositions of diesel fuel vehicle exhaust gases (Roduit et al., 1998; Kröger, 2007)**

<b>CO</b> <b>(ppm)</b>	<b>HC</b> <b>(ppm)</b>	<b>NO<sub>x</sub></b> <b>(ppm)</b>	<b>H<sub>2</sub>O</b> <b>(vol- %)</b>	<b>CO<sub>2</sub></b> <b>(vol- %)</b>	<b>O<sub>2</sub></b> <b>(vol- %)</b>	<b>SO<sub>2</sub></b> <b>(ppm)</b>	<b>Particles</b> <b>(wt- %)</b>	<b>N<sub>2</sub></b> <b></b>
<b>490</b>	30	1135	4-5	7.1	10.5	30	<0.02	Balance

DOC operates at relatively low temperatures. Moreover, nitrogen monoxide (NO) oxidation to nitrogen dioxide (NO<sub>2</sub>) is a very important step in removing NO<sub>x</sub>. Due to these reasons, platinum (Pt) is used as a catalyst in DOC. But the major drawback of Pt is poor durability (Wiebenga et al., 2012). Commercial DOC manufacturers have solved this problem by adding low amount of palladium (Pd) loading with higher platinum (Pt) loading (Wiebenga et al., 2012). The noble metals are dispersed in support material such as zeolite, CeO<sub>2</sub> etc (Kröger, 2007).

### 3.3 Three-way Catalytic Converter (TWC)

Three-way converters are typically used to treat the exhaust produced by a gasoline fueled spark-ignition engine. Primary emissions from gasoline engines are CO, HCs and NO<sub>x</sub>. As the name suggests, three-way converter converts all three of the pollutants simultaneously into less harmful gases (Heck and Farrauto, 2001). Catalytic oxidation of CO and HCs are favored under lean conditions and the reduction of NO<sub>x</sub> takes place under rich conditions (Lox and Engler, 1997).

In a TWC, cerium (CeO<sub>2</sub>) -based oxides with a doping of zirconium (ZrO<sub>2</sub>) oxide or aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) are used as the support material. CeO<sub>2</sub> has an excellent oxygen storage capacity while ZrO<sub>2</sub> aids the mobility of bulk O<sub>2</sub> diffusion from CeO<sub>2</sub> (Kröger, 2007).

Gasoline is composed mainly of different hydrocarbon chains. In ideal condition, gasoline burns in oxygen to produce heat and CO<sub>2</sub>. However, in reality that is seldom the case. It is more than regular to have incomplete combustions of gasoline that leads to several exhaust components beside CO<sub>2</sub>. Table 4 gives the composition of typical gasoline exhaust.

**Table 4. Composition of gasoline engine exhaust gases (Heck and Farrauto, 2001)**

<b>CO</b> (vol- %)	<b>HC</b> (ppm)	<b>NO<sub>x</sub></b> (ppm)	<b>H<sub>2</sub></b> (vol- %)	<b>H<sub>2</sub>O</b> (vol- %)	<b>CO<sub>2</sub></b> (vol- %)	<b>O<sub>2</sub></b> (vol- %)	<b>N<sub>2</sub></b>
<b>0.5</b>	350	900	0.17	10	10	0.5	Balance

Three-way automotive converters catalyze the following sets of equation (Heck and Farrauto, 2001)

Oxidation of CO:



Oxidation of HC:



Reduction of NO<sub>x</sub>:



In addition to the reactions mentioned above, there is several other reactions take place in a three-way converter.

#### 4. Catalyst Deactivation Mechanism

Catalyst deactivation refers to the loss of catalytic activity and/ or selectivity over time (Bartholomew, 2001). Deactivation is a complex phenomenon and might involve more than one process. The time for total catalytic deactivation varies from seconds to years, depending on the type of catalyst and the design of the system it is used in. However, total deactivation of catalyst is not avoidable. Once the catalyst is deactivated, regeneration is very difficult. Therefore, it is of extreme economical importance to understand the deactivation process in order to develop a better catalyst. Most effective way to delay catalytic failure is to prevent deactivation itself.

Deactivation can be caused by mechanical, chemical or/and thermal process (Bartholomew, 2001). Despite the complex nature, deactivation mechanisms can be classified in the following categories:

**Table 5. Catalyst Deactivation Mechanism (Bartholomew, 2001)**

Type	Mechanism	Description
Chemical	Poisoning	Blocking of the reaction active site on the catalytic surface due to strong chemisorptions.
	Vapour formation	Production of volatile compounds due to the reaction between catalytic phase and the gas.
	Reactions: Vapour-solid and solid-solid	Formation of inactive phase as a result of reactions between vapour, support or promoter with catalytic site.
Mechanical	Fouling	Physical deposition of species from gas or fluid onto the catalyst surface or pores.
	Attrition/crushing	Depletion of catalytic material or internal surface area due to abrasion or mechanically-induced crushing

		of the catalyst.
Thermal	Thermal degradation	Loss of catalytic surface, support surface area and active phase-support reactions due to thermal degradation.

In the automotive converters, chemical and thermal aging is the main reason for catalyst deactivation (Koltsakis and Stamatelos, 1997).

#### 4.1 Poisoning

Poisoning is the loss of activity due to the strong chemisorption on the active sites of a catalyst due to the presence of impurities (poisons) in the feed stream (Forzatti and Lietti, 1999). It is often accompanied by a relatively high and varying operating temperature. In automotive catalysts, poisons can contaminate both the support material and precious metal by blocking the active sites. It results in a reduction of catalytically active surface thus decreasing the reaction rates and diminishing catalyst activity. It should be noted that inhibitors are different than poisons. Their interactions with active site are weak and reversible (Forzatti and Lietti, 1999).

Poisons alter the catalytic activity by different methods. It can simply block the active sites (geometric effect) or alter the adsorptivity of other species by electronic effect. Poison can also modify the chemical nature of the active site or form a new compound (reconstruction) altering catalyst performance (Forzatti and Lietti, 1999). Whether a species acts as a poison or not, depends on its adsorptive strength compared to that of the other competing species present on the feed (Bartholomew, 2001).

Poisons can be classified as selective or non-selective (Bartholomew, 2001; Forzatti and Lietti, 1999). In non-selective poisoning, the substrate surface is uniform to the poison and the chemisorptions happen consistently all over it. As a result, net activity of the surface is a liner function of the total amount of poisons adsorbed. Selective poisoning is not so straight forward. There exists some distribution of characteristics over the surface (eg. Acid strength) that makes the interactions quite complex. In this particular scenario, poison will be adsorbed in the most active sites first leading to various relationships between the amounts of poisons chemisorbed and the total catalytic activity (Bartholomew, 2001).

Another way of classifying poisoning is based on their reversibility. If regeneration is possible after poisoning takes place, it is reversible. If the changes are permanent and cannot be reversed, it is irreversible. The interaction of a poison with active site is strong and often irreversible (Butt and Peterson, 1988; Bartholomew, 2001; Andersson et al., 2007). Only a small amount of poison present in the feed may cause poisoning (Forzatti and Lietti, 1999). In case of automotive catalyst poisoning, the damages are often irreversible and regeneration is quite difficult (van Kooten et al., 2000).

The most typical oil and fuel derived-impurities found in a vehicle-aged catalytic converter are S, P, Zn, Ca and Mg; S and P being the principal poisons. The major poison in the first generation catalytic converter was lead (Pb). In modern days, gasoline has either a very low concentration of lead or is practically 100 % lead free (López Granados et al., 2006). This particular improvement has ruled out lead as a major cause of poisoning in three-way converters. Iron (Fe) can also cause poisoning in platinum (Pt) group metals (Kalantar et al., 2004). Fe is assumed to be derived from the corrosion and wear of the metal engine components (Galisteo et al., 2004). Other impurities that might originate from engine parts are chromium (Cr), nickel (Ni) and copper (Cu) (Angelidis and Sklavounos, 1995; Galisteo et al., 2004).

Catalytic deactivation of automotive converters by poisoning is a widely studied topic. Each of the poisons responsible has been thoroughly studied for quite a long time now. Due to the immense importance and complex nature of this topic, it is still an interesting field for researchers. Despite countless number of experiments and studies carried out on this matter, full chemical and physical mechanism of poisoning is still unknown. In automotive catalysts, thermal deactivation happens often simultaneously with poisoning. Independent and combined effect of these two mechanisms remains yet to be fully discovered (Albersa et al., 2001)

#### 4.1.1 Phosphorus Poisoning

Historically, the main source of phosphorus poisoning in vehicle aged exhaust catalyst is lubrication oil (Kröger et al., 2006). Zinc dialkyldithiophosphate is a common phosphorus-containing compound found in lubrication oil (Burkinshaw et al., 2012).

Zinc dialkyldithiophosphate or ZDDP as it is commercially known, is the most used anti-wear, antioxidant and corrosion inhibiting additive in various fields of industry (Burkinshaw et al., 2012; Rudnick, 2010). The molecular structure of ZDDP has been presented in Figure 2 and the typical characteristics for ZDDP in Table 6. For more

than 50 years, it has been used as a low cost multi-functional additive in engine lubrication oils, transmission fluids, hydraulic fluids, gear oils, greases and other lubricant application (Rudnick, 2010).

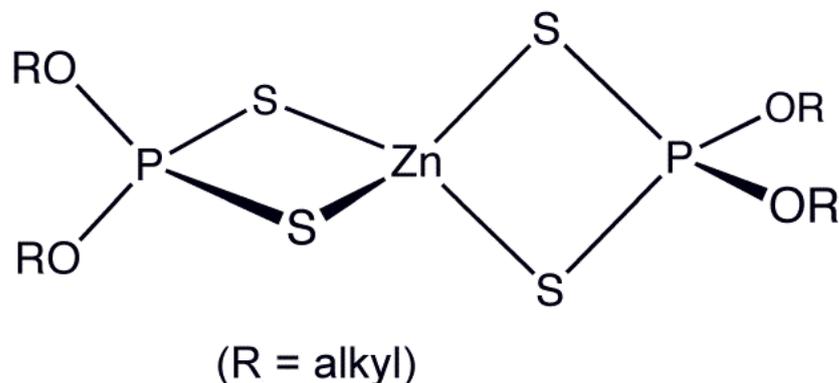


Figure 2. Molecular structure of ZDDP (Rudnick, 2010)

Table 6. General characteristics of ZDDP (Research Institute of Petroleum Industry, 2002)

Characteristics	Approximate value
Density (g/ml) at 15.5° C	1.09
Viscosity (c.st) at 100 ° C	10.3
Sulfur content (wt- %)	19
Phosphorous content (wt- %)	10
Zinc content (wt- %)	11
pH	5-6

In the mechanical parts of engines, lubricants are used to protect the metal parts from wear and corrosion. When two metal surfaces are rubbed together, the frictional heat produced cause ZDDP to interact with the surface chemically and form a strong anti-wear film along the metal parts. The composition and thickness of the film is multi-fold and directly proportional to the temperature and the extent of surface contacts. The complexity of this process is outside the scope of this thesis. In general, it can be said that the film is composed of various layers of ZDDP degradation products. The composition of the layers is temperature-dependent (Rudnick, 2010). In an automotive catalyst, ZDDP is the primary source of phosphorous (P) and zinc (Zn) poisoning (Kumar et al., 2004). The question might be asked; that why despite a higher concentration of sulfur (S) in ZDDP, phosphorous (P) is the prominent poison rooted from it. One possible speculation is the absorbance of disulfide into the metal surface. However, the answer is beyond the scope of this particular study.

The impact of phosphorus poisoning in automotive catalysts is multidimensional. Chemical composition of phosphorus compounds found in catalytic converters depends on several variables such as the chemical structure of oil and oil additives, how old the oil used is and the overall condition of the engine (Xu et al., 2004). It has been reported that the catalytic activity decreases linearly with the increasing amount of phosphorus accumulated on the catalyst surface (Caracciolo and Spearot, 1976). Studies indicate that, phosphorous content as low as 0.4 wt % can induce poisoning in automotive catalyst (Joy et al., 1985). Current phosphorus content of lubricants is about 0.08 - 0.15 wt % (Bunting et al., 2005). A possible way to prolong catalyst life is to use lubricants with lower phosphorus content (Kalantar et al., 2004).

Phosphorus forms an over-layer of different phosphate compounds on the surface of the catalyst. The over-layer is basically a mixture of Ca, Zn and Mg phosphates on the support (Rokosz et al., 2001). These compounds have a very stable structure on the catalyst surface (Andersson et al., 2007). A formation of glassy and amorphous phosphorus-containing layer blocking active sites has also been observed (Klimczak et al., 2010). Ca and Mg have been reported to resist phosphorus poisoning in the automotive catalyst. In a study conducted by Ueda et al. (1994), it was found that by using Ca and Mg sulphonates as oil additives, phosphorus poisoning of the oxygen sensor and the catalyst can be prevented to some degree.

In addition to forming a phosphate-containing over-layer, phosphate forms bonds and compounds directly with the support components (Kröger et al., 2004). The result is the formation of for example aluminum ( $\text{AlPO}_4$ ) and cerium phosphate ( $\text{CePO}_4$ ) (Rokosz et al., 2001; Kröger et al., 2004). In an aged diesel catalyst, the interaction of  $\text{PO}_4$  with  $\text{Al}_2\text{O}_3$  is believed to be partially responsible for the deactivation (Galisteo et al., 2004). One can only speculate that this is also the case with natural gas oxidation catalyst since they share the similar structure. Formation of  $\text{CePO}_4$  weakens the oxygen storage and release capacity of CeO (Larese et al., 2003).

Phosphorus has been detected mostly in the front part of the catalyst. This has been associated with the declining catalytic activity and loss of surface area in the forward section of the converter (Angove and Cant, 2000).

#### 4.1.1.1 Regeneration Techniques for Phosphorous-Poisoned Catalyst

Catalyst reactivation is quite a difficult task. Often poison-induced changes are irreversible and therefore it is easier to prevent the deactivation itself rather than regeneration (Bartholomew, 2001). In case of phosphorus poisoning, several methods have

been experimented with. The most successful cases have been reported to be treatment with organic acids. Galisteo et al. (2005) reported that citric acid was able to remove a huge portion of phosphorus and most of sulfur accumulation from the catalyst. Oxalic acid was also found to be quite efficient in removing accumulated phosphorus from catalysts (Christou et al., 2007; Rokosz et al., 2001). Catalytic activities were found to be dramatically improved after a wash with oxalic acid (Rokosz et al., 2001). Angelidis and Sklavounos, (1995) have reported that acetic acid can revive a catalyst poisoned with P, S, Ca, Pb, Zn and Fe. EDTA (Ethylene diamine tetraacetic acid) was found to be quite effective in regenerating catalytic activity lost due to Zn, Ca, Pb, Mn, Cu, Ni, S and Fe. EDTA, however was not effective for a phosphorous-poisoned catalyst (Christou et al., 2007).

#### 4.2 Thermal Deactivation

Typically thermal deactivation results from loss of catalytic surface area due to any or all of the following phenomena (Bartholomew, 2001):

1. crystallite growth of the catalytic phase
2. loss of support area due to support collapse and loss of catalytic surface area due to pore collapse on crystallites of the active phase
3. chemical transformations of catalytic phases to non-catalytic phases

First two of the phenomena mentioned above are called sintering. Sintering is usually observed when the reaction temperature is higher than 500° C and is accelerated in the presence of water vapor (Bartholomew, 2001). It is not so serious of a problem for NGOC since the exhaust temperature is in the range of 500° C - 550° C. However, thermal aging cannot be fully excluded due to the temperature range and presence of water vapor in the exhaust stream. In DOCs, the exhaust gas temperature might vary from 100° C to 700° C depending on the load (Galisteo et al., 2004).

Sintering involves a complex chemical and physical mechanism that makes the understanding of the whole process a difficult task. The ultimate result is the reduction of total surface area of both support material and precious metal. Sintering takes place in both supported and unsupported metal catalyst. In unsupported catalyst, the sintering is induced by agglomeration and coalescence of small metal crystallites into larger ones lessening the surface-to-volume ratio. In supported catalyst (i.e. monolithic oxidation catalyst) the process is much more complicated (Forzatti and Lietti, 1999). So far

three models have been proposed to explain sintering in the supported metal catalyst: atomic migration model, crystallite migration model and in very high temperature vapor migration model. In atomic migration model, metal atoms detach from crystallite, migrate over the support surface and ultimately are captured by larger crystallites. In the crystallite migration model, the whole crystallite migrates over the support surface followed by collision and coalescence. All three models are rather simplified theories ignoring the possibility of simultaneous occurrence (Bartholomew, 2001).

Thermal degradation plays quite a crucial role in the deactivation risk of the catalyst. Chemical phase transformation and sintering decreases the total active area available for catalytic reaction by inducing structural change in the support and catalytic material. These changes might lead to the encapsulation of active metal particles (Butt and Peterson, 1988; Lassi, 2003). Sintering is often irreversible (Bartholomew, 2001).

#### 4.3 Mechanical Deactivation

Mechanical deactivation can be caused by a number of processes: crushing due to a load, attrition, size reduction or erosion due to high fluid velocity. Commercial catalysts are rather vulnerable to mechanical failure and the result might be catastrophic (Bartholomew, 2001). In automotive catalysts, this particular form of deactivation might be caused by high temperature. Since converters do not have any moving parts; strain, fatigue, decompression, buckling and fracture can be ruled out as the basis of mechanical failure. In automotive catalyst, there are two sources that can cause high temperature. The first source is the operating condition of the engine. The second source is misfire. In this case, non-combusted fuel-air mixture enters the catalyst chamber and goes through a catalytic combustion. The reaction is exothermic and is capable of producing a very high temperature. At 1200° C, the metal foil softens and starts to shrink. The melting begins when the temperature reaches 1400° C. At this point, the damage is beyond recovery and the catalyst is ruined (Mooney, 2005). Metallic structure is better at enduring heat than a ceramic structure (Laurikko, 1995).

In a monolithic automotive catalyst, the back pressure of the exhaust gas might grow due to the crushing of the structure. If it goes unnoticed, the local rise in temperature might lead to thermal deactivation and even to the melting of the honey-comb (Laurikko, 1995).

## 5. Experimental Materials and Procedures

The experiments and analyses have been conducted at the University of Oulu in the Mass and Heat Transfer Process Laboratory.

### 5.1 Catalyst

For this thesis project, metallic monolith catalysts provided by Dinex Ecocat Oy with  $\text{Al}_2\text{O}_3$  based support without any precious metals was used. The cell density of the monoliths was 300 cpsi and the weight about 1.50 g. The monoliths were wrapped into a cylinder with a diameter of 1cm and with a length of 3.8 cm (see Figure 3).



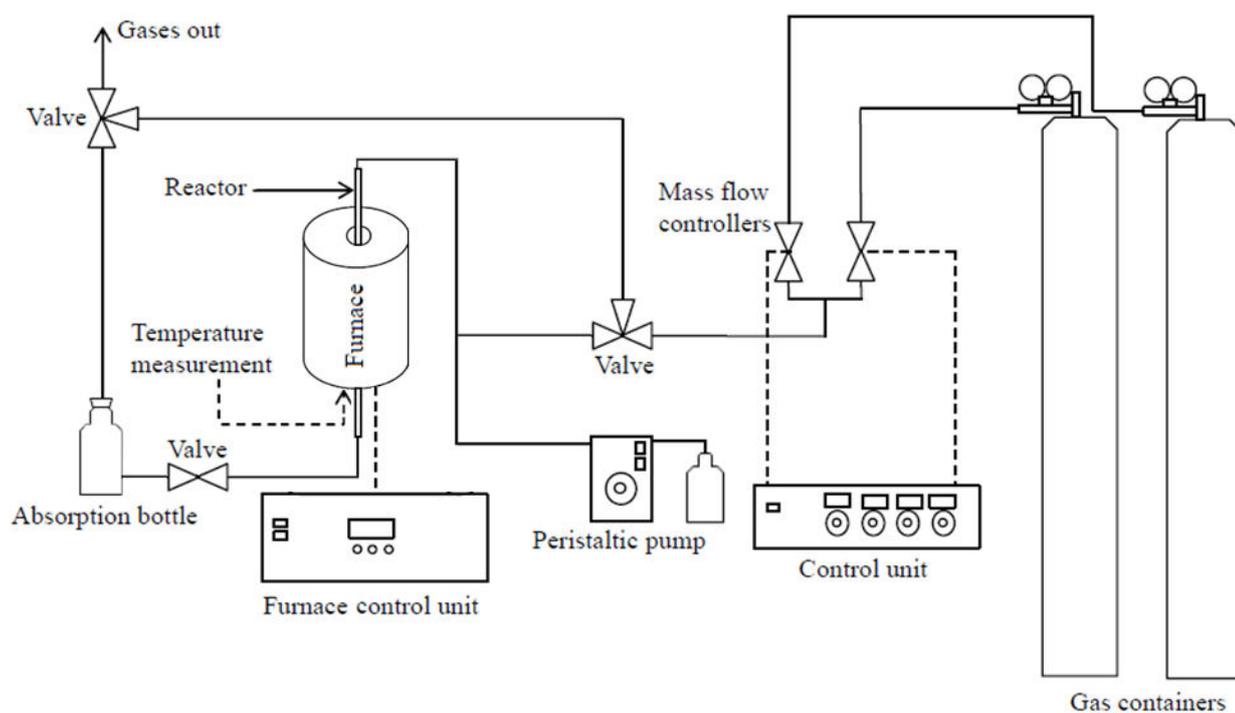
**Figure 3. Photograph of a monolith sample used in the poisoning**

### 5.2 Gaseous Phosphorus Poisoning Procedure

The experiment was carried out by poisoning three sets of samples with three different concentration of phosphorus feed: 0.065 M, 0.13 M and 0.20 M. ammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) was used as a source of phosphorus. Under experimental conditions the solution is gaseous. A total of 4 samples were poisoned with each concentration of phosphorus, resulting in a total of 12 phosphorus-poisoned samples. The whole poisoning was carried out in gaseous phase using a laboratory scale vertical flow reactor.

The monolith sample was placed into a quartz reactor with an inner diameter of 1 cm and a length of 70 cm. The reactor was then placed into a vertical tube furnace. The reactor flow was controlled by using mass flow controller. The phosphorus feed was

supplied by a peristaltic pump. A schematic diagram of the experimental setting is given in Figure 4.



**Figure 4- Laboratory set up for gaseous phosphorus poisoning (Avila, 2011)**

The poisoning temperature was set at 400° C to avoid any thermal deactivation. Feed gas volume was kept constant during the entire procedure at 1000 ml/min. During heating and cooling, the gas composition was 90 volume % N<sub>2</sub> and 10 volume % air. During poisoning, composition of the feed was: 80 volume % N<sub>2</sub>, 10 volume % air and 10 volume % phosphorus solution which correspond to 0.065 ml/min liquid feed. The total poisoning time was 5 hours with gas hourly space velocity of 20000/h (GHSV). The phosphorus poisoning procedure is illustrated in Figure 5.

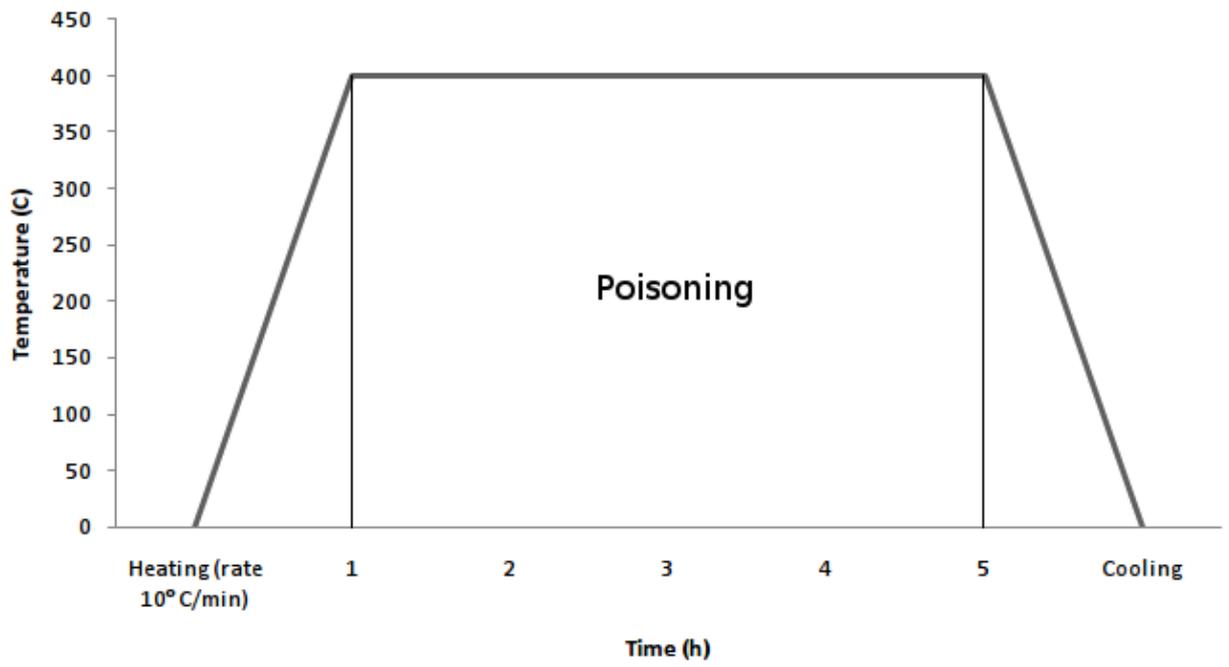


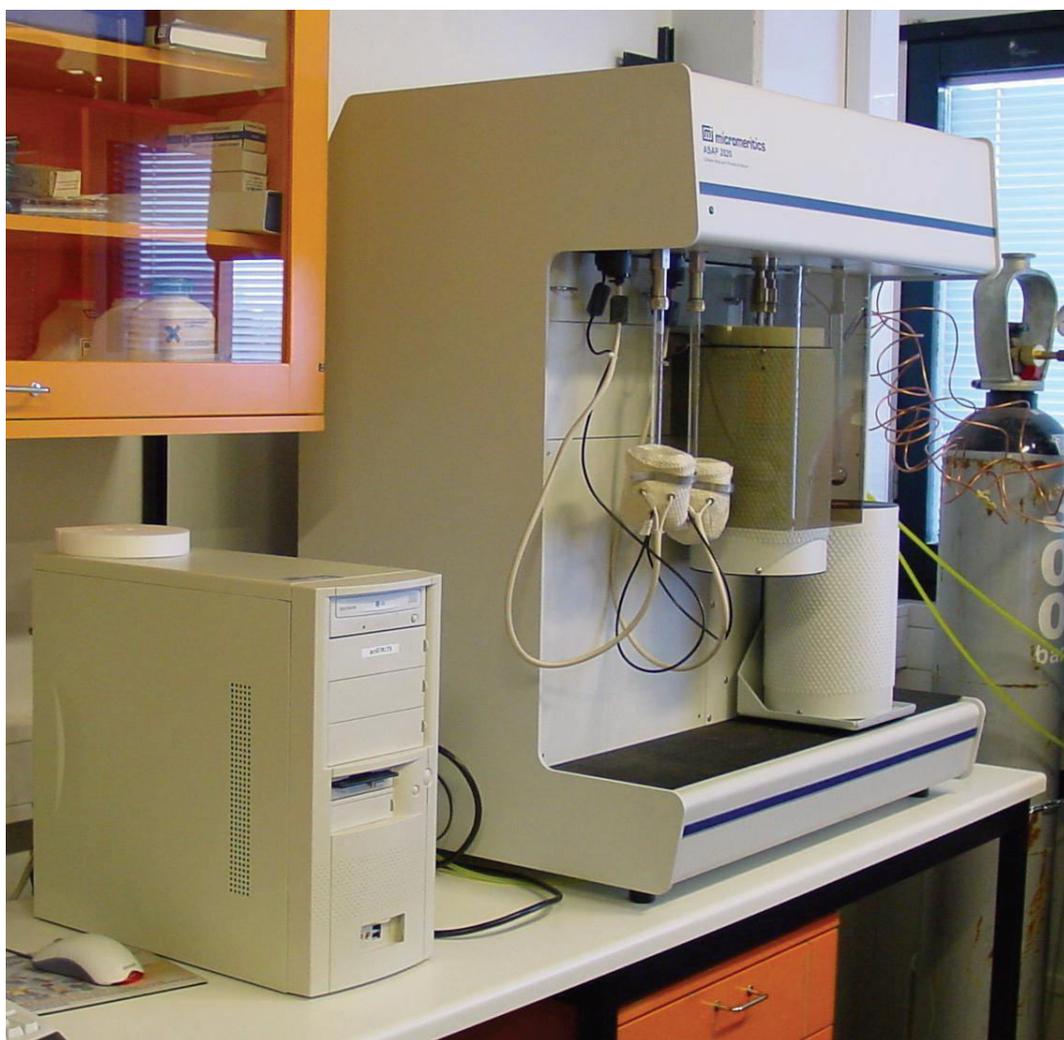
Figure 5. Phosphorus poisoning: temperature over time

### 5.3 Catalyst Characterization Techniques

In this project, poisoned samples were analyzed using following techniques: physisorption analysis, X-ray diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM).

#### 5.3.1 Physisorption Analysis

To characterize the catalysts before and after poisoning, physisorption measurements were carried out with a Micromeritics ASAP 2020 device (Figure 6). Brunauer, Emmett and Teller (BET) theory was used to calculate the specific surface area. The calculations were carried out assuming that the pores had a cylindrical shape and by using N<sub>2</sub> adsorption isotherms at  $-196^{\circ}\text{C}$ . To evaluate the total pore volume (ml/g) and average pore size (nm) of the specimens, Barrett-Joyner-Halenda (BJH) theory was used. For calculations, desorption isotherms at  $-196^{\circ}\text{C}$  were used.



**Figure 6. Micromeritics ASAP 2020 used for physisorption analysis (Kröger, 2007)**

### 5.3.2 Field Emission Scanning Electron Microscopy

A Field Emission Scanning Electron Microscope (FESEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS) was used to determine the phosphorus content in the surface of poisoned samples. Before measurement, the samples were coated with carbon. The  $\text{Al}_2\text{O}_3$  based support was studied in two different physical forms. In the first form, the support was scratched from the metal foil, crushed into a homogenous powdered sample and studied with a scanning microscope Zeiss ULTRA plus FESEM. In the second analysis, inlet and outlet parts of the poisoned monolith were studied with Zeiss Sigma FESEM.

### 5.3.3 X-Ray Diffraction

X-ray diffraction (XRD) was used to identify phosphorus compounds in the poisoned catalyst samples. The X-ray diffraction diagrams were recorded from the catalyst powders on a plastic sample holder with a Siemens D5000 using  $\text{Cu K}\alpha$  radiation at  $0.040^\circ$  intervals in the range of  $15^\circ \leq 2\theta \leq 90^\circ$  with 4 s count accumulation per step. Diffraction patterns were assigned using a PDF database supplied by International Centre for Diffraction Data (PDF-2 Powder Diffraction File Database).

## 6. Results

In this section, results from each of the analysis techniques used will be summarized and interpreted in terms of phosphorus induced poisoning.

### 6.1 FESEM-EDS Analysis

EDS was used to measure the accumulated weight percent of phosphorus in each sample at three or four random points and sometimes selected areas. The results of powdered and foil samples are summarized in the next section.

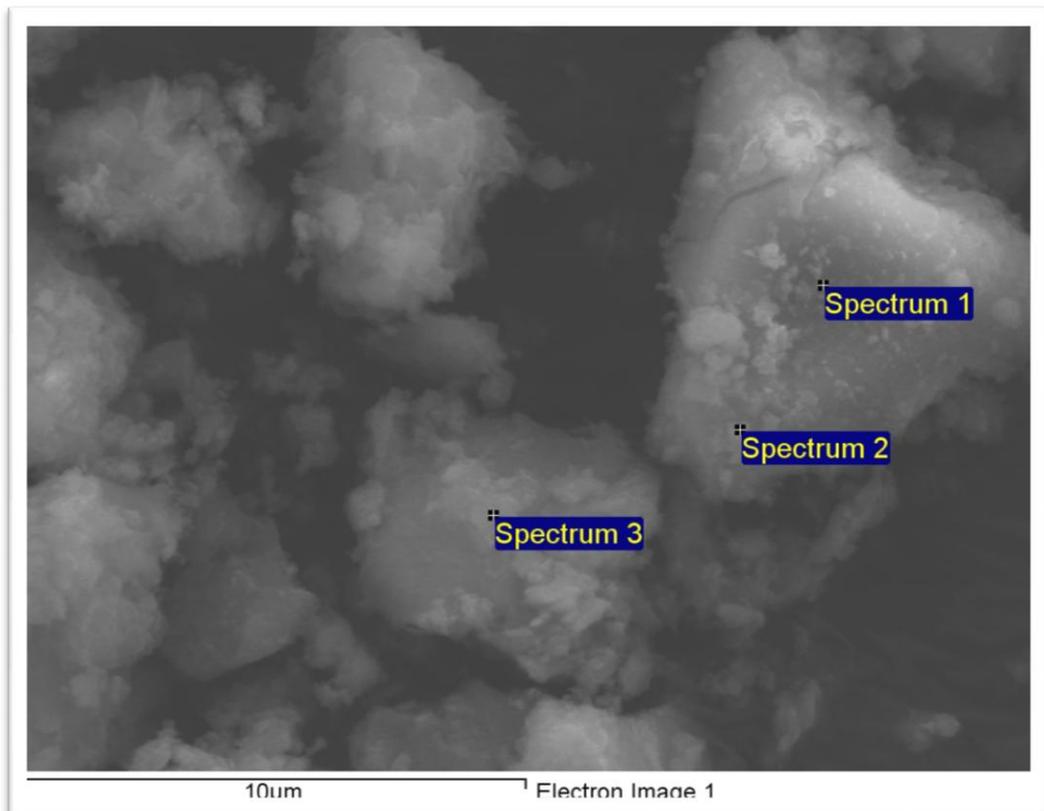
#### 6.1.1 FESEM-EDS Results of The Powdered Samples

Fresh sample was analyzed to be used as a reference. As we can see from Table 7, fresh sample only contains Aluminum (Al) and Oxygen (O).

**Table 7-EDS analysis of the fresh sample**

<b>Spectrum</b>	<b>O (wt %)</b>	<b>Al (wt %)</b>
<b>Spectrum 1</b>	47.63	52.37
<b>Spectrum 2</b>	48.00	52.00
<b>Spectrum 3</b>	47.54	52.46
<b>Spectrum 4</b>	43.61	56.39

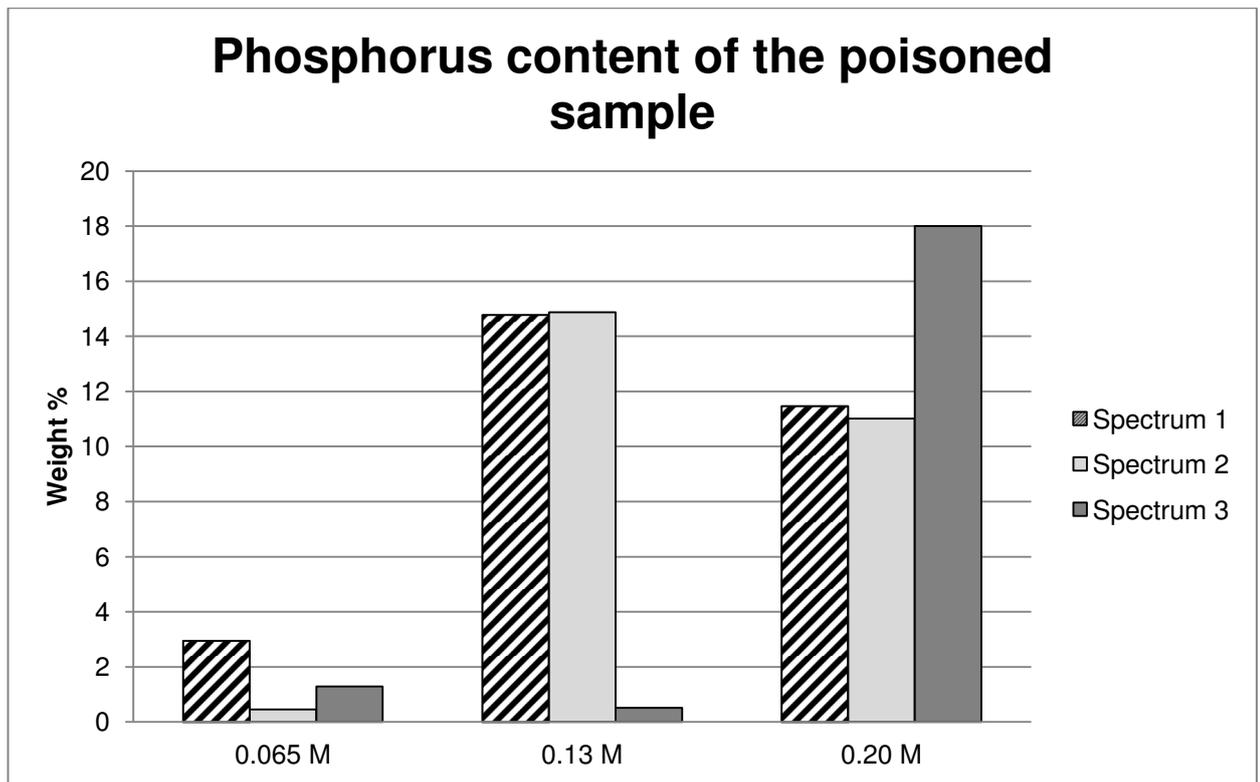
Figure 7 is a photograph of 0.13 M phosphorus poisoned sample taken during analysis.



**Figure 7. FESEM image of the 0.13M phosphorus poisoned sample**

Points marked as Spectrum 1, 2 and 3 are the points the measurements were taken from. All samples were analyzed in similar way. Points were picked randomly.

Phosphorus content of the poisoned samples is shown in Figure 8 below.

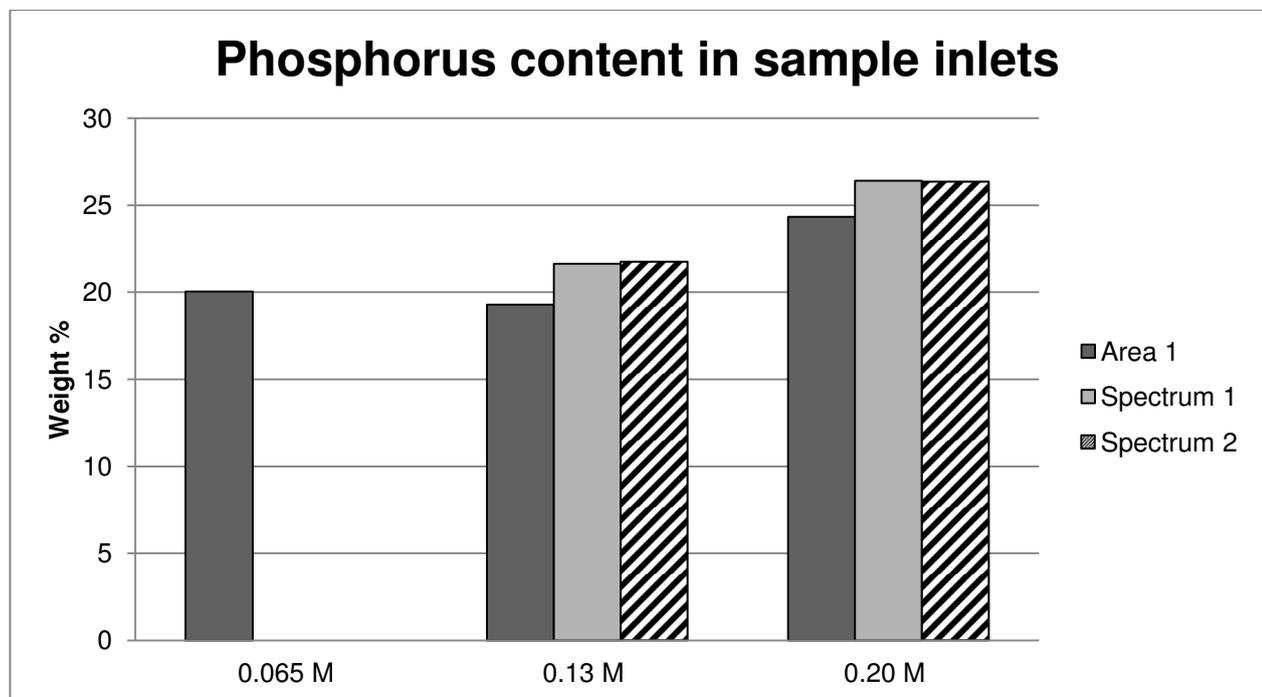


**Figure 8. Phosphorus content of the poisoned samples in wt %. Measurements have been made in powder form.**

Figure 8 shows the measured phosphorus content in each spectra. It can be seen that the phosphorus content of the powder specimens was not homogenous. In all three samples, the difference in phosphorus content between spectra is quite large. For example, in the 0.13 M phosphorus-poisoned sample, the difference between spectrum 2 and spectrum 3 is more than 95 %. Similarly in the 0.065 M phosphorus-poisoned sample, the difference between Spectrum 1 and Spectrum 2 is about 84 %. In the 0.20 M phosphorus-poisoned sample, the difference between Spectrum 2 and Spectrum 3 is 35 %. Since the spatial differences in the powder samples were so large, it was decided to do a second series of FESEM analysis using inlet and outlet parts of the monolith samples separately.

### 6.1.2 FESEM Results of the Foil Samples

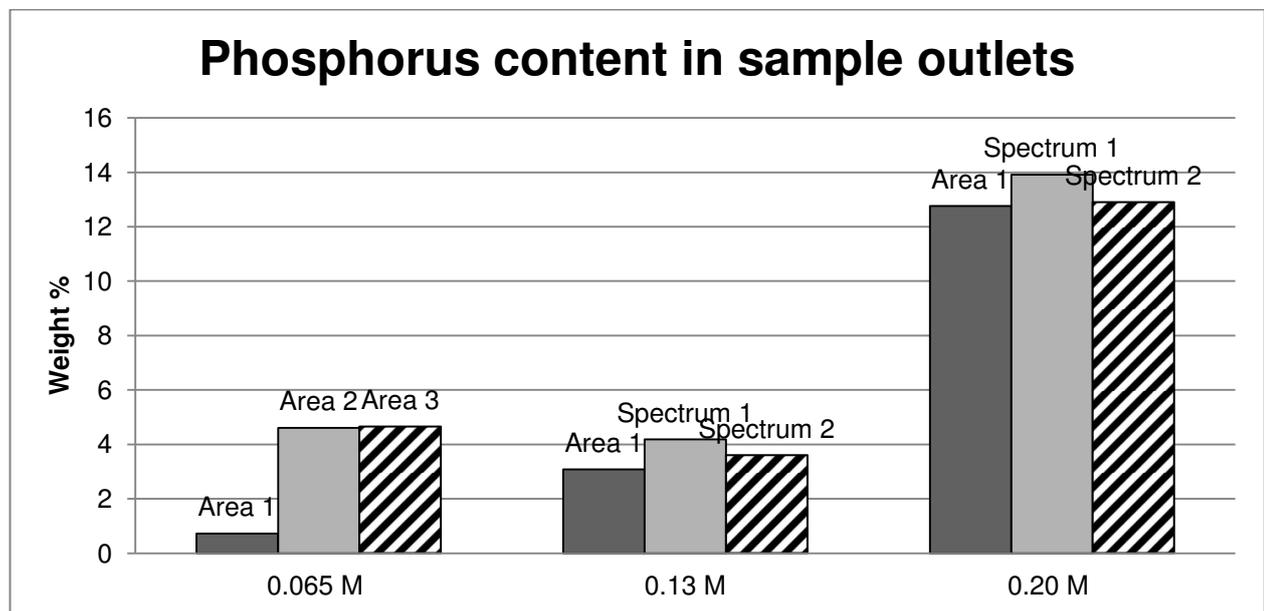
The analysis results for inlets of all three samples are represented graphically in Figure 9. Due to the charging effect, it was only possible to take measurement at a single point of the 0.065 M phosphorus-poisoned sample. From Figure 9 it can be seen that, at the inlet of the 0.13 M and 0.20 M phosphorus poisoned samples, the weight percent of accumulated phosphorus was almost homogenous. On the basis of this observation, it can be assumed true for the 0.065 M phosphorus-poisoned sample as well. Figure 9 also shows a possible positive correlation between the phosphorus feed concentration and the accumulation during poisoning. The 0.20 M phosphorus-poisoned sample has the most phosphorus accumulation during poisoning at the inlet with an average of 25 weight- % while the 0.065 M phosphorus-poisoned sample has the least phosphorus accumulation; 20 weight- %.



**Figure 9. Phosphorus content in weight- % in the sample inlets. Measurements have been made using foil samples.**

Figure 10 shows the phosphorus contamination in sample outlets part. Due to the charging effect, it was not possible to take point measurements for the 0.065 M outlet. As Figure 10 also shows, three area measurements were taken. From Figure 10, it is evident that in outlets, there is only a slight difference in the amount of phosphorus contamination between the 0.065 M and the 0.13 M phosphorus-poisoned sample. The

0.065 M sample has 3.27 weight- % and 0.13 M has 3.62 weight- % phosphorus accumulations on average. However, 0.20 M sample shows quite a large spike; an average of 19 weight- % phosphorus accumulation. The data available in this case is not sufficient enough to draw any exclusive numerical conclusion regarding the relationship between phosphorus feed concentration and amount of phosphorus detected in the outlet of the poisoned catalyst. Unlike the inlet parts, the outlet parts show less homogeneity in the phosphorus content.



**Figure 10. Phosphorus content in weight- % in the sample outlets. Measurements have been made using foil samples.**

In addition, Figure 11 clearly shows that there is a huge difference in phosphorus content between the inlet and the outlet of the poisoned monolith sample. It can be concluded from the figures that, most of the phosphorus accumulation occurs in the inlet of the catalyst. As the amount of phosphorus increases in the feed stream, accumulation in inlets increases.

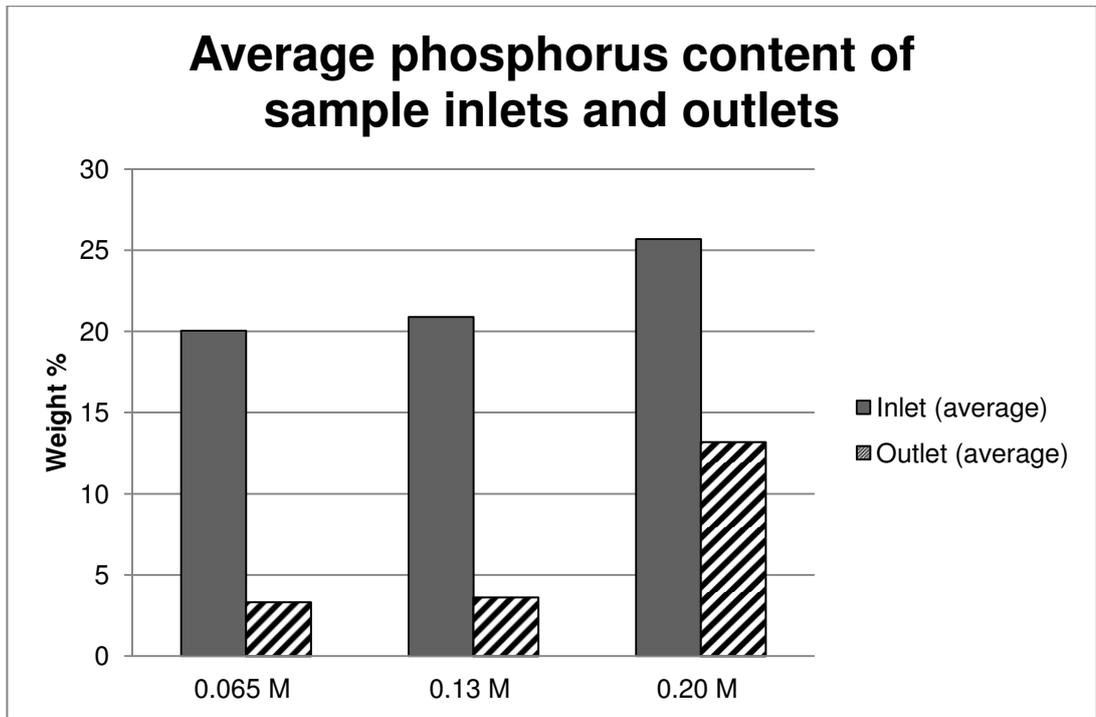
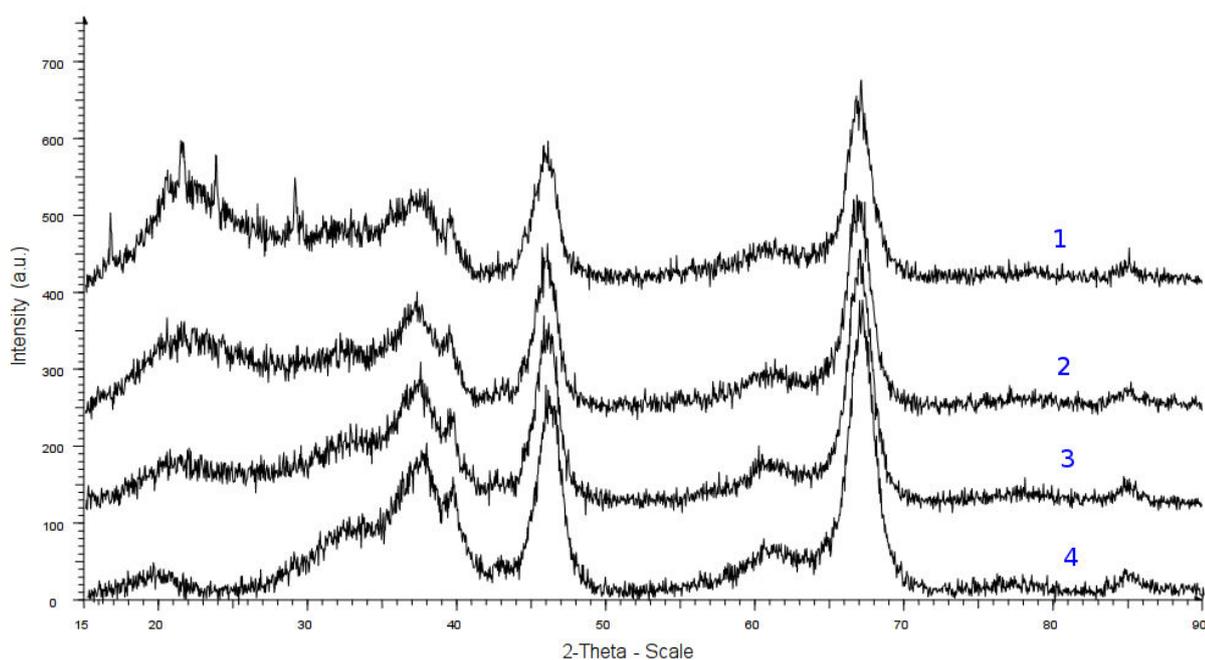


Figure 11. Average phosphorus content of the poisoned sample inlets and outlets

## 6.2 XRD Analysis Results

The XRD diffractogram of all poisoned and fresh samples is given in Figure 12. It can be seen from the diffractogram that, only the 0.20M phosphorus-poisoned sample (marked as 1) has a different peak at  $2\theta \sim 22, 25$  and  $30$ . Using the EVA analyzer, one possible match was found for the peaks. It was matched to EVA database number 00-050-0054 which corresponds to aluminum phosphate ( $\text{AlPO}_4$ ) crystals. From this result, it can be concluded that phosphorus chemically interacts with the alumina based support to form aluminum phosphate ( $\text{AlPO}_4$ ).



**Figure 12. XRD diffractogram of (1) 0.20 M, (2) 0.13 M, (3) 0.065 M phosphorous-poisoned and (4) fresh samples**

## 6.3 Physisorption Analysis

As a result of phosphorus poisoning, significant change in specific surface area of  $\text{Al}_2\text{O}_3$  based support was observed. The BET analysis clearly shows that there exist a relationship between the amount of phosphorus content in the feed and the total reduction of specific surface area of the samples. Figure 13 sums up the effect of phosphorus content on the support. The specific area reduced almost linearly as the phosphorus content in the feed stream increased. The BET surface area was reduced to all most 43 % compared to that of the fresh sample when the phosphorus content in the feed was the 0.20 M. In case of the 0.065 M and the 0.13 M phosphorus feed, the re-

duction in the specific surface area compared to that of the fresh sample was 27 % and 39 % respectively. The linear dependency cannot be confirmed based on this result only. The outcomes are elaborated in the Table 8 below.

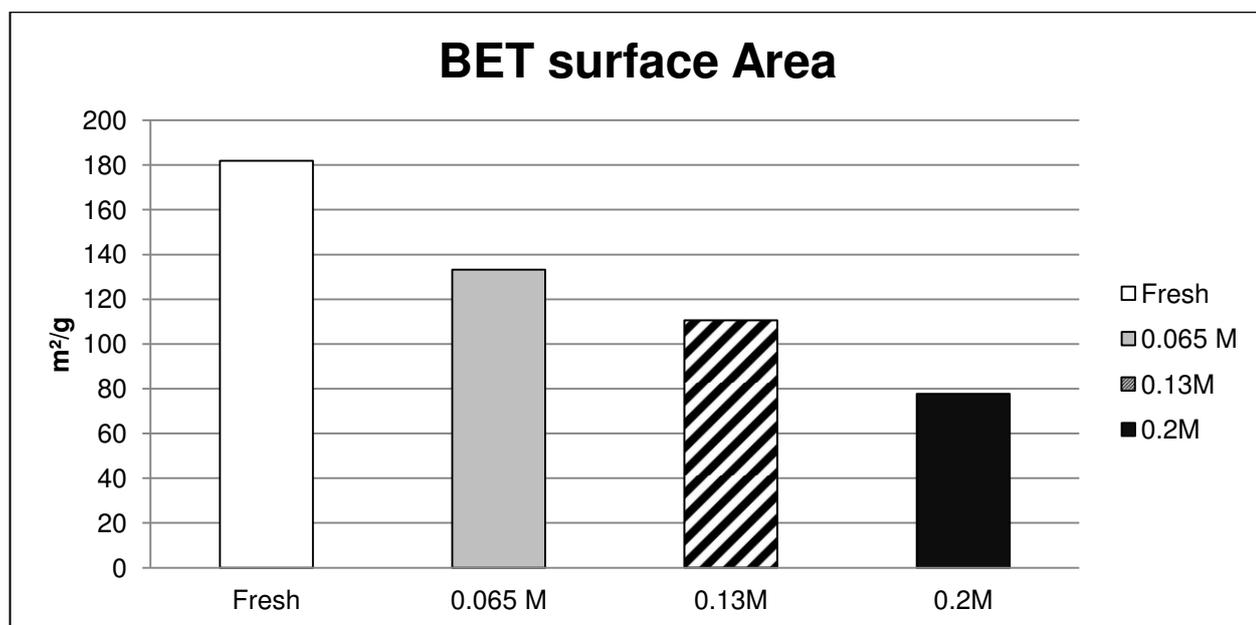
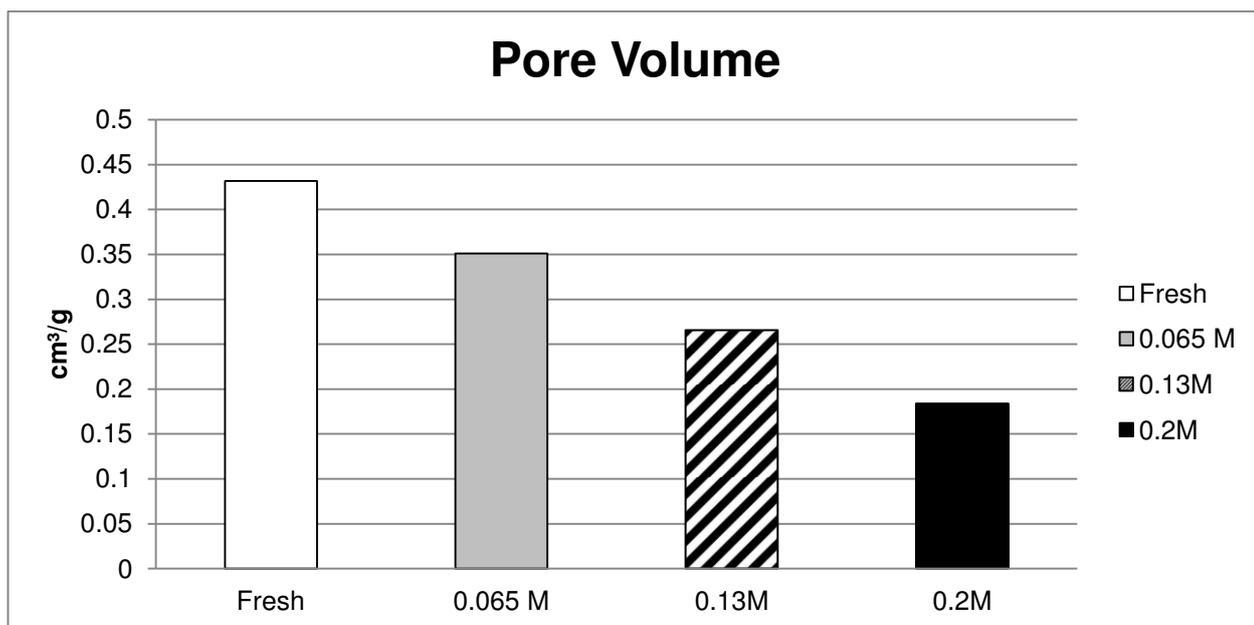


Figure 13. Specific surface areas of the fresh sample and the 0.065 M, 0.13 M and 0.20 M phosphorus-poisoned samples

Table 8. Summary of the effect of phosphorus poisoning on the specific surface area of the Al<sub>2</sub>O<sub>3</sub> based support

Sample	BET surface Area (m <sup>2</sup> /g)	Reduction compared to fresh sample (%)	Area compared to fresh sample (%)
Fresh	182		
0.065 M	133	27	73
0.13 M	111	39	61
0.20 M	78	57	43

Similar effect was observed on pore volumes. Figure 14 shows the total pore volume against the phosphorus concentration of the feed. The 0.065 M and 0.13 M phosphorus poisoned samples had 19 % and 39 % less pore volume than the fresh sample. The 0.20 M phosphorus poisoned sample had the least amount of pore volume; 57 % less than the fresh sample.



**Figure 14. Pore volumes of fresh sample and 0.065 M, 0.13 M and 0.20 M phosphorus poisoned samples**

When physisorption results are compared with FESEM results, it becomes apparent that higher phosphorus content of the samples corresponds to lower BET surface area and pore volume. For example, the 0.20 M phosphorus-poisoned sample had the most phosphorus accumulation both in inlets and outlets. It also had the smallest BET surface area and pore volume. Similarly, 0.065 M phosphorus poisoned sample had the least amount of phosphorus content in both inlets and outlets. It lost the least amount of BET surface area and pore volume when compared with other samples. It can therefore be concluded that, phosphorus accumulation is inversely correlated to BET surface area and pore volume.

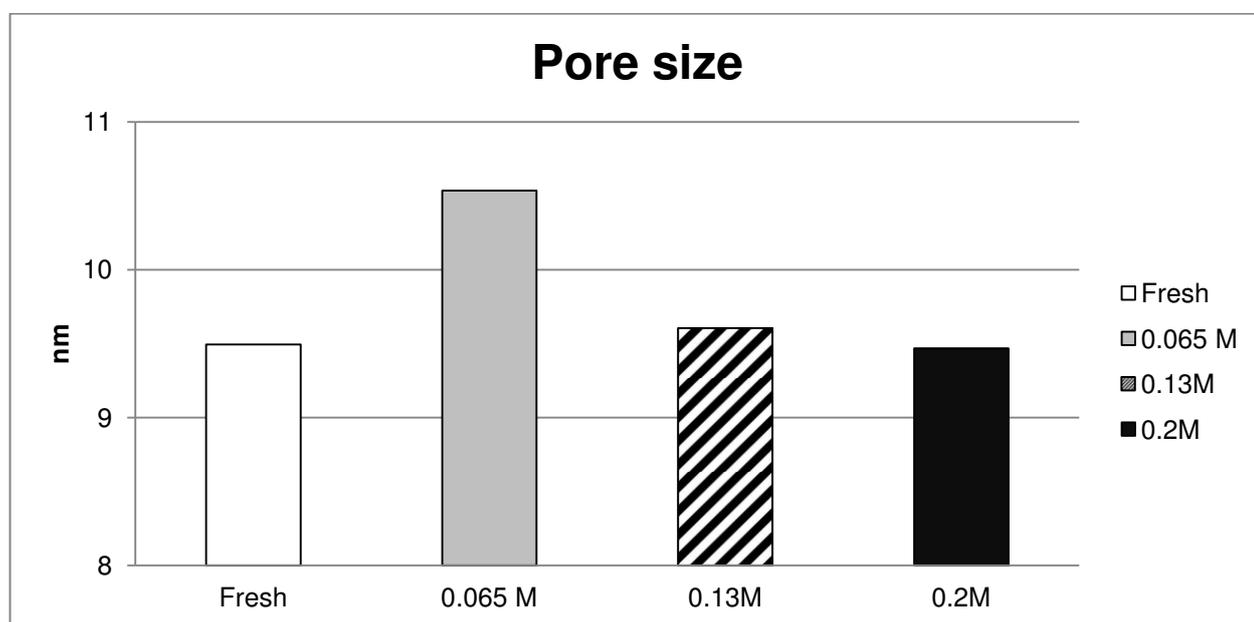
No changes in pore size suggest the lack of sintering. The result is consistent with the fact that the poisoning temperature was below thermal deactivation which is 400° C.

A further break down of the results is shown in Table 9.

**Table 9. Summary of the effect of phosphorus poisoning on the pore volume of the Al<sub>2</sub>O<sub>3</sub> based support**

Sample	Pore Volume (cm <sup>3</sup> /g)	Reduction compared to fresh sample (%)	Volume compared to fresh sample (%)
<b>Fresh</b>	0.43		
<b>0.065 M</b>	0.35	19	81
<b>0.13 M</b>	0.27	39	61
<b>0.20 M</b>	0.18	57	43

As for pore sizes, no noticeable change could be found. Table 10 illustrates the result.



**Figure 15. Summary of the effect of phosphorus poisoning on pore size of Al<sub>2</sub>O<sub>3</sub> based support**

**Table 10. Summary of the effect of phosphorus poisoning on the specific surface area, pore volume and pore size of the Al<sub>2</sub>O<sub>3</sub> based support**

Sample	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (%)
<b>Fresh</b>	182	0.43	
<b>0.065 M</b>	133	0.35	27
<b>0.13 M</b>	111	0.27	39
<b>0.20 M</b>	78	0.18	57

## 7. Summary

The aim of this thesis project was to investigate the effect of phosphorus poisoning on the  $\text{Al}_2\text{O}_3$  based support. By using different characterization techniques following conclusions were drawn.

FESEM-EDS results suggest that phosphorus accumulation on support is not even. Most of the poison accumulates on the inlets of the catalysts. The detected level of phosphorus increases with the increasing feed concentration of phosphorus. For the 0.065 M, 0.13 M and 0.20 M phosphorus poisoned samples, the measured average phosphorus contents in the inlets were 20 %, 21 % and 26 %, respectively.

XRD analysis sheds some light on the chemical nature of phosphorus poisoning. The formation of  $\text{AlPO}_4$  was detected on the alumina surface. Change in chemical composition of a catalyst support alters the surface chemistry, therefore changing the dynamics of the possible surface reactions. Together these results offer great insight on the physio-chemical changes induced by phosphorus poisoning in the  $\text{Al}_2\text{O}_3$  based support.

Physisorption analysis indicates that, phosphorus accumulation lessens the total specific surface area and pore volume of the support material. The effect worsens with increasing amount of phosphorus content in the feed. The 0.065 M, 0.13 M and 0.20 M phosphorus poisoned samples had 27 %, 39 % and 57 % less specific surface area compared to the fresh samples respectively. Together with the FESEM results, this suggests that, more phosphorus content in the feed causes more phosphorus accumulation and more specific area loss in the sample. Unvarying pore size suggests the lack of sintering. This result is consistent with the poisoning temperature 400° C. Thermal deactivation occurs above 500° C.

The conclusions and findings of this thesis project can be utilized in further investigating the effect of phosphorus poisoning on NGOCs. The catalyst used in this particular project did not contain any precious metals. Elaborated studies can be done on a catalyst containing precious metal and a comparison will help understanding the nature of phosphorus poisoning on different components of a catalyst. Overall, outcomes of this project will help to design better catalysts with more poison resistance.

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