CATALYST FOR AUTOMOBILE EXHAUST EMISSION CONTROL

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RESEARCH VOTE NO: PJP/2005/PPA (2) – S117

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ABSTRACT

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(Keywords: Catalyst, CO Oxidation)

Tin (IV) oxide (SnO₂) has been identified as a potential catalyst for toxic gases treatment generated from vehicular and industrial activities. In this research, SnO₂ was used as a catalyst with the addition of cobalt (II) oxide and nickel (II) oxide as dopants. All the catalysts were prepared by modification of sol-gel method. The catalytic ability was tested towards the oxidation of carbon monoxide (CO) using SELOX. Two catalysts labeled as S1 calcined at 400 °C and S2 at 600 °C calcinations temperature gave a good catalytic ability towards CO oxidation. Both completed the CO oxidation to CO2 at 215 °C and 200 °C compared to the commercial catalyst, Pt/Al₂O₃ (T₁₀₀(CO)= 200 °C). Several techniques were used in this research to characterize the physical and chemical properties of the catalyst materials. The nitrogen adsorption analysis reveals that the best catalyst (S2) is in form of mesopore, open cylindrical in shaped with pore diameter of 10 nm. The FTIR analysis proved that increasing calcinations temperature enhanced the elimination of surface functional group like deformed mode and bridging hydroxyl. It is also cause the metal-oxygen vibration mode become sharper. The XRF analysis show that there are small differences (<5 %) between actual and experiment element composition percentage in the sample prepared. The SEM analysis illustrated the increment of particle size with the calcinations temperature due to agglomeration process. The XRD analysis shows the presence of SnO2 tetragonal and Co₂O₃ cubic phase which act as the active site in the catalytic oxidation. The existence of cobalt oxide (in a mixture of Co²⁺ and Co³⁺) expected to contribute the excellent oxidation of CO.

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ACKNOWLEDGEMENTS

Alhamdulillah, all praise to ALLAH for giving this opportunity to complete this research. I would like to thanks Y.Bhg. Prof. Dr. Mohamad Kadim B. Suaidi, Y.Bhg. Assoc. Prof. Dr. Hj. Su'aidi B. Dato' Safei, Y.Bhg. Assoc. Prof. Dr. Hanipah Bt. Hussin and KUTKM for giving this opportunity to conduct this research.

I would like to thanks the entire research group member, Mr. Mohd Haizal B. Mohd Husin (PPA), Y.Bhg. Assoc. Prof. Dr. Mohd. Ridzuan B. Nordin (PPA), Mr. Safarudin Gazali Herawan (FKM) and Mr. Muhamad Zahir B. Hassan (FKM) for their commitment and contribution in this research.

Special thanks to Y.Bhg. Prof. Dr. Wan Azelee B. Wan Abu Bakar (UTM), Y.Bhg. Assoc. Prof. Dr. Nor Aziah Bt. Buang (UTM), Y.Bhg. Assoc. Prof. Dr. Sh. Bee Bt. Abd. Hamid (Head of COMBICAT,UM) and also staff of PPA, UNIC and COMBICAT, UM.

Finally, my warmest and very specials thanks to my dearest son, Amirul Iman bin Imran Syakir for his understanding and support.

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1.0 INTRODUCTION

1.1 Background

The enormous increases in the environmental pollution are cause by exhaust emission which comes from automobile combustion engine. A toxic carbon monoxide gas has being recognized as the main pollutant. Over the past several years, the introduction of a catalytic converter was a breakthrough in the reduction of pollutant emission all over the world. The use of catalysts will definitely contribute to the production of clean automobile exhaust.

Platinum group catalysts currently represent the state of the art in the emission control catalyst technology. Anyway, these current catalysts are very limited and expensive. Also, the 'light off temperature' of these catalysts is still high before they can start to treat the exhaust gas pollutants.

One way to overcome this problem is to seek viable alternative materials for catalytic converter usage. Currently, the development of non-noble metal oxide exhaust emission catalyst is on demand due to low price, strategic importance and high availability. The catalytic activity of these catalysts also can be improved by mixing with another oxide element.

The purpose of this research is to introduce a non noble metal oxide based catalyst with high efficiency of catalytic activity performance as an alternative catalyst for automobile exhaust emission control.

1.2 Catalytic Converter Systems

Catalytic converter is a device fitted to the exhaust system of a motor vehicle in order to reduce toxic emissions from the engine. It converts the harmful exhaust products that cause air pollution to relatively harmless ones [1].

It does this by passing them over a mixture of catalysts coated on a metal or ceramic honeycomb (a structure that increases the surface area and therefore the amount of active catalyst with which the exhaust gases will come into contact) [1]. It is consisting of two major components [2]:

- a) the catalyst support system (substrate and washcoat)
- b) the catalyst (active material).



Figure 1: Commercial Catalytic Converter [3]

1.3 Mechanism for carbon monoxide (CO) oxidation

In general, most of the kinetic studies of CO oxidation suggest the Langmuir-Hinshelwood type of mechanism [4]:

 $CO (toxic) + S \leftrightarrow CO_{ads}$ $O_2 + S \leftrightarrow 2O_{ads}$ $CO_{ads} + O_{ads} \rightarrow CO_2 (non toxic) + 2S$

(where S is a surface site and ads is an adsorbed species)

1.4 Tin (IV) oxide as a catalyst

In the development of catalytic studies, tin (IV) oxide and compound containing tin (IV) oxide are being recognized these days as useful catalyst material. Tin (IV) oxide based material has been known for a long time to have good activity towards the CO/O₂ and CO/NO reactions [5].

However, tin (IV) oxide itself is not a promising catalyst. But, this may be modified substantially by the incorporation of heteroelement. Doping with some other metal oxides has produced product with potential performance as future materials in emission control system.

The advantages are the low price of the material, strategic importance, and low availability of the platinum group metals [6].

1.5 Research Objectives

This research was conducted to:

- a) Prepare a metal oxide based catalyst such as tin oxide, cobalt oxide and nickel oxide using sol-gel modification technique.
- b) Study the catalytic activity performance of the prepared samples towards the conversion of carbon monoxide gas (toxic) to carbon dioxide gas (nontoxic) in order to choose the best catalyst.
- c) Compare the catalytic activity performance of the best samples with the commercial catalyst, Pt/Al₂O₃.
- d) Obtain information and understand the catalytic behaviour of the best catalyst by characterize using various analytical techniques such as:
 - Nitrogen gas adsorption analysis
 - Fourier Transform Infrared Spectroscopy analysis (FTIR)
 - X-Ray Fluorescence analysis (XRF)
 - Scanning Electron Microscopy analysis (SEM)
 - X-Ray Diffraction analysis (XRD)

2.0 EXPERIMENTAL

2.1 Catalyst preparation

2.1.1 Preparation of tin (IV) oxide

Tin (IV) oxide was prepared via stannic chloride precipitation from aqueous solution with a 33 % w/w solution of NH_3 at a constant pH of 4 [7], at room temperature and under intensive stirring (refer Figure 2).



Figure 2: Diagram for Tin (IV) oxide synthesis [8]

The resultant gelatinous precipitate was washed until free of chloride ion (negative chloride test using AgNO₃ solutions) by repeated centrifuging and redispersing in triply distilled water. The solid gel was then allowed to dry at 80 °C for 24 hours. The white granular materials thus obtained was cracked with triply distilled water and then again dried at 80 °C. The materials were then manually ground into fine powder using a mortar.

2.1.2 Preparation of tin (IV) oxide sol

Tin (IV) oxide gel was obtained by ammonia precipitation method. Conversion to stable sol-gel modification was effected by peptisation using choline. The procedure is as followed:

Tin (IV) oxide was added in triply distilled water and choline with appropriate quantities and kept stirring until a clear brownish solution was obtained. If it is air dried at 80 °C for 24 hours, a brown glassy like solid was produced.

2.1.3 Preparation of sample Ni(II)/Co(II)-doped SnO₂

All the catalyst materials were prepared by sol-gel modification technique. The sample of nickel(II)/cobalt(II)-doped SnO₂ with appropriate quantities were dissolved in triply distilled water and left stirred for one hour.

The resulting clear dark yellow solutions were dried at 80 °C for 24 hours. The dried samples were then calcined at the temperature of 400 °C and 600 °C in muffler furnace for 17 hours. The calcined samples were then manually ground into fine powder using a mortar and undergo for catalytic activity screening and characterization.

2.2 Catalytic Activity Testing

Catalytic Activity data was obtained by using Continuous Fixed Bed Reactor (SELOX) at COMBICAT, University Malaya.

2.2.1 Introduction about SELOX

Selective oxidation of continuous catalytic reactor or commonly referred as 'SELOX' is a fixed bed tubular reactor. It comprises of two (2) hasteloy reactors in series (i.d.=0.5 ft, h=17 ft) that is suitable for operation at atmospheric up to 25 bar g pressure and temperature of up to 500 °C. Only 15 g of solid is needed to load up the reactor tube. The catalyst of small particle size (600-1000 micron) can be exposed to gaseous reactant mixture, which passes the catalyst bed in plug-flow mode. This means that the catalyst screening can be carried out under identical end-application conditions in a downsized mode.

The catalyst bed is situated in the central module. Heating is provided by an inner and an outer electrical heating element or rotational symmetry to ensure isothermicity of the reaction zones in the central ceramic module. Axial temperature profiles were controlled by thermocouples placed in each concentric ring of the reactor channels and it has been shown that the differences do not exceed 5 °C.

Different mass-flow controllers supply the different feed gases while the liquid feed is supplied by a pump and evaporated in the vaporizer to perform steam (gas phase). The mixing of steam and gases occurs after the vaporizer to ensure the mixture is homogenous mixture. For sampling the reactor channel effluent the outlets were connected individually to a set of port valve, which allow fast switching in the reactor channel for sequential analysis of the reaction products without interruption of the gas flow. To avoid condensation, polymerization or thermal decomposition of products all of these parts were installed inside an oven box heated to 150 °C while the feed lines to gas chromatography were covered by heating tape to avoid condensation of liquid products.

2.2.1.1 Operating Condition: SELOX Reactor

Phase Condition: Solid-Gas Phase

Mode: Plug flow continuous system

Max Pressure: 25 bar g

Max Temperature: 500 °C

Catalyst Loading: 10 mL (15 g)

- a) Material loaded consists of catalyst and inert
- b) Loaded volume within isothermal zone

Particle Size: 600-1000 micron

Inlet Gases:

- a) Oxygen –max 50 bar g, 0-200 ml/min
- b) Nitrogen –max 50 bar g, 0-400 ml/min
- c) Propane –at 7 bar g, 0-200 ml/min
- d) Propylene –at 8barg, 0-200ml/min
- e) CO/CO₂ -max 50 bar g, 0-200 ml/min

In CO oxidation, the only inlet gases use are carbon monoxide (CO) and air with calculated gas flow-rate. 4 % of CO is used as reactant to convert to CO₂ in presence of air, which is containing 96 %.

2.2.1.2 Reaction variables for Screening Reactor

If required, process variables can be changed

- a) Reactant composition
- b) Reactor temperature
- c) Reaction stabilization time
- d) Reactant flow rate



Figure 3: Parameter Screen

Figure 3 shows a parameter screen section. It is a section where the temperature of reactor (in red circle) and gas flow rate (blue circle) have been set up first into mass flow controller column according to the reactant uses before reaction started. In this case column CO gas and air/O₂ were used with 4 % CO and balance is air.



Figure 4: Feed Screen Section

In feed section, CO and air gases line are ready to have a reaction CO oxidation to produce CO₂. It can be observed in Figure 4 (pink circle) with total flow rate is 150 ml/min. It is a maximum total flow rate that has to be used for any reaction using SELOX reactor.

The start up reaction begins with nitrogen gas is purged about 30 minutes to diminish the contaminants inside reactor system and lines. Then only other gases use for reaction (such as CO oxidation process use CO) is open to flow. The reaction temperature in reactor system then is heat up according to operating condition needed.

Every one hour, sampling for analytics is taken. The online GC is used. This is to detect at what condition, CO gas is converted into CO₂ with percentage conversion (X %).



Figure 5: Process Overview Diagram for SELOX Reactor

The schematic diagram of SELOX reactor is as shown in Figure 5. The red block represents the reactor used in CO oxidation to CO₂. The catalyst is loading inside the reactor tube a solid phase. While the gases (CO and air) are flown from Gas Feed 1 line. Reaction will happen inside the red block and every one-hour sampling will be taken to analyze the conversion of CO to CO₂ using online GC.





Fixed Bed Reactor) Unit



Figure 7: SELOX Catalytic Reactor Unit



Figure 8: Analytical unit for qualitative and quantitative measurement

2.3 Characterization Techniques

Suitable analytical techniques must be employed to investigate the constitution of the active catalyst. Several techniques were used in this study to characterize the physical and chemical properties of the catalyst materials.

3.0 RESULT AND DISCUSSION

3.1 Catalytic Activity Testing

Catalytic activity testing was carried out to observe the complete oxidation CO to CO₂ by using Continuous Fixed Bed Reactor (SELOX) instrument. In CO oxidation, the only inlet gases use are carbon monoxide (CO) and air with calculated gas flow-rate. 4 % of CO is used as reactant in presence of 96 % air.

The temperature of testing condition was monitored by the temperature controller to get the light off temperature, CO oxidation= 5 %, (T_{10}) and the 100 % conversion temperature (T_{100}). The conversion of CO to CO₂ was analyzed using online GC (Agilent/6890N Network GC System).

Sample	Atomic Ratio	Тк (⁰С)	Tlo (°C)	T100 (°C)
Comm. Catalyst, Pt/Al ₂ O ₃ [8]			120	200
SnO ₂ [8]				342
Co(II)-doped SnO ₂ [8]	10.90	400	240	355
	10.70	600	260	320
Ni(II)/Co(II)-doped SnO ₂ (S1)	0 1/34 97/64 93	400	RT	215
	0.1,01,01,01,01,0	600	RT	230
Ni(II)/Co(II)-doped SnO ₂ (S2)	0 1/39 96/59 94	400	RT	230
	0.1,07770,0777	600	RT	200
Mn(II)/Co(II)-doped SnO ₂ [8]	0 1/29 97/69 93	400	RT	240
		600	205	250

Table 1: Data for catalytic activity towards CO oxidation of all sample prepared

T_K= calcinations temperature

RT= Room temperature (25 $^{\circ}$ C)

Catalytic activity testing for CO oxidation was carried out towards catalyst tabulated in the Table 1. Two samples show a good result as good as the commercial catalyst, Pt/Al₂O₃ (refer Figure 9) which are Ni(II)/Co(II)-doped SnO₂ or labeled as S1 and Ni(II)/Co(II)-doped SnO₂ labeled as S2. Both catalysts calcined at 400 °C and 600 °C give a complete CO oxidation (T₁₀₀) at 215 °C and 200 °C.



Figure 9: Percentage conversion of CO versus temperature over best prepared catalyst and commercial catalyst

3.2 Nitrogen Adsorption Analysis

3.2.1 Pore Texture Analysis by Nitrogen Adsorption-Desorption

BET procedure using nitrogen adsorption and desorption was used to analyze the surface area, pore size and pore size distribution. The adsorption and desorption was done using Sorptometric 1990 instrument. Approximately 20-50 mg sample was placed in a tube of known volume and heated to 413 K at rate 1 Kmin⁻¹ for degassed under vacuum for 5 hours. After outgassing, the sample was weighed again to determine the actual sample weight.

The sample tube was then placed in the analysis station, cooled in liquid nitrogen and a known amount of nitrogen gas was introduced into the cooled tube. After equilibrium, the pressure was measured and the sequence repeated with successive pulse of N₂. After the measurement completed, the gradually lowering nitrogen pressure will result in desorption of measurable quantities of nitrogen.

The use of sample prepared as a catalyst in catalytic system is effective only when it has a high surface area with optimum porosity. In this analysis, nonporous silica was used as a reference for the BET (Brunauer, Emmet and Teller) method.

3.2.2 Assessment of porosity of the S1 and S2

3.2.2.1 BET isotherm

Figure 10 and Table 2 shows the BET isotherm for S1 and S2 catalyst. Both S1 and S2 catalyst give similar isotherm curves which are a mixture of Type I and Type IV for 400 °C calcinations temperature. This type of isotherm shows the catalyst porosity in form of mesopore and micropore [9]. At this calcinations temperature, it is also show hysteresis loop type H1 which indicate the presence of open-ended cylindrical pore with a uniform size and shape [9].

Increasing calcinations temperature to 600 °C gives an isotherm curve Type IV which proves that the porosity for both catalysts start to shift to mesopore form [9]. The hysteresis loop is in type of H1 which is similar with previous calcinations temperature.





Comula	Calcination	Type of	Type of	Type of
Sample	Temperature (°C)	hysteresis	isotherm	porosity
	400	H1	I& IV	Meso &
S1	100	111	i di iv	micropore
	600	H1	IV	Mesopore
S2	400	H1	I & IV	Meso &
	100	111	1 d I v	micropore
	600	H1	IV	Mesopore

Table 2:	Type of	of porosi	ty for	S 1	and	S2
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3.2.2.2 Assessment of BET surface area (ABET), pore volume (V_P) and pore diameter (d) of the S1 and S2

The data of nitrogen adsorption analysis using BET method are shown in Table 3. At 400 °C calcination temperature, both S1 and S2 sample show a high surface area due to elimination of surface molecule in the material at lower temperature (<400 °C). Increasing calcinations temperature to 600 °C causes a decrement of the surface area. This is because of the agglomeration process that increases the catalyst particle size as prove by the SEM analysis.

The increment of calcinations temperature also indicate pore diameter to increase. The reason came from the transformation of porosity system starting the mixture of micro and meso to mesopore. This is due to sintering process to form a larger particle with higher crystalinity (as agree with SEM and XRD result) and at the same time reduces the pore volume, V_P [10].

Sample	Temp(°C)	А _{вет} (m²/g)	$V_p(cm^3/g)$	d(nm)	
S 1	400	1.46 x 10 ²	1.53 x 10 ⁻¹	4.2	
01	600	1.90 x 10 ¹	1.46 x 10 ⁻¹	8.3	
\$7	400	1.30 x 10 ²	1.41 x 10 ⁻¹	4.4	
52	600	$4.30 \ge 10^{1}$	1.11 x 10 ⁻¹	10.4	

Table 3: Data of N2 adsorption analysis using BET method

From this analysis, our best catalyst S2 calcined at 600 °C concluded to have an isotherm type IV (mesopore), open-ended cylindrical pore with a uniform size and shape and pore diameter around 10 nm. These surface conditions were expected to give an optimum active site for CO and O₂ adsorption at the catalyst surface. Even though calcinations at 400 °C give a higher surface area, but most of the catalyst surface is in micropore system. This is considering giving difficulty for gases to adsorp on the catalyst surface [11].

3.3 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

FT-IR spectra were recorded with a Bruker spectrometer model IFS 66v/s (made from Germany), using the technique of KBr pellets and working with a resolution of 4 cm⁻¹ in the middle range. Before analysis, air evacuation was performed under vacuum of 5 mbar for 15 minutes.

This analysis helps to identify the role of surface molecules in the catalytic performance of the sample prepared. It also provides information on the effect of calcinations temperature towards these surface molecules and also on the phase transformations of the catalyst.



Figure 11: FTIR diagram for S1 at 400 °C and 600 °C calcinations temperature

Calcination	Strecthing mode	A	Delection
Temperature (°C)	region (cm ⁻¹)	Assignment	Deduction
		OU	Surface water
	3445.6(m)	OH	molecules
	1619.8(w)	ОН	deformation mode
400	1384.4(w)	COO	Acetate
	1100.5(w)	ОН	Bridging
	(69.6)		Metal oxide
	008.0(m)	(Sn-O)	molecules
	24271(m)	OU	Surface water
	3437.1(m)	OH	molecules
	1623.6(w)	ОН	deformation mode
600	1383.7(w)	COO	Acetate
	1101.8(w)	ОН	Bridging
	665.5(s)	(6 - 0)	Metal oxide
	584.5(s)	(Sn-O)	molecules

Table 4: FTIR data of S1 catalyst

s-strong, m-medium, w-weak

FTIR diagram and data for S1 calcined at 400 °C and 600 °C were showed in Figure 11 and Table 4. The FTIR spectra at 400 °C illustrated a broad of OH stretching mode of coordinated and surface water molecules at 3750 cm⁻¹ to 2550 cm⁻¹ with a maximum at 3400 cm⁻¹. The corresponding water deformation mode for both 400 °C and 600 °C were observed at 1619.8 cm⁻¹ and 1623.6 cm⁻¹ respectively [12]. The bridging hydroxyls were observed at 1100.5 cm⁻¹ and 1101.8 cm⁻¹.

The sharp intensity band at 1384.4 cm⁻¹ and 1383.7 cm⁻¹ most probably due to the COO⁻ stretching mode from the material acetate based. In the region

between 668.6 cm⁻¹ to 584.5 cm⁻¹, the peak was assigned to metal oxide molecules stretching mode (Sn-O).

When the calcinations temperature increase, the surface hydroxyl stretching and deformation mode was decreased meanwhile the metal oxide peak increase. Increasing calcinations temperature gave high peak of metal oxide stretching mode due to the water molecules evaporated from the surface catalyst.



Figure 12: FTIR diagram for S2 at 400 °C and 600 °C calcinations temperature

Calcination	Strecthing mode	Assignment	Deduction
temperature (°C)	region (cm ⁻¹)	Assignment	Deduction
		OU	Surface water
	3436.5(m)	OH	molecules
	1630.8(w)	ОН	deformation mode
400	1384.1(w)	COO	Acetate
	1108.7(w)	ОН	Bridging
	665.3(s)	(Sn ())	Metal oxide
	582.0(s)	(511-0)	molecules
	3/35.5(m)	ОЧ	Surface water
	1600 Q()	OII	molecules
	1629.8(w)	OH	deformation mode
600	1384.4(w)	COO	Acetate
	1097.5(w)	OH	Bridging
	664.9(s)		Metal oxide
	576.1(s)	(Sn-O)	molecules

Table 5: FTIR data of S2 catalyst

s-strong, m-medium, w-weak

FTIR diagram and data for S2 calcined at 400 °C and 600 °C were showed in Figure 12 and Table 5. The trends are almost similar with the S1 catalyst. The OH stretching mode of coordinated and surface water molecules are found at 3750 cm⁻¹ to 2550 cm⁻¹ with a maximum at 3400 cm⁻¹. Two types of OH vibration mode for 400 °C and 600 °C are present at 1630.8 cm⁻¹ and 1629.8 cm⁻¹ (water OH deformation mode), 1108.7 cm⁻¹ and 1097.5 cm⁻¹ (bridging hydroxyl). The acetate stretching modes observed at 1384.1 cm⁻¹ and 1384.4 cm⁻¹ meanwhile the Sn-O peak observed at 665.3 cm⁻¹, 582.0 cm⁻¹ and 664.9 cm⁻¹, 576.1 cm⁻¹ for 400 °C and 600 °C calcinations temperature respectively. The catalyst studied usually comprise of small particle that bonded externally by surface hydroxyl groups through physical adsorption and by hydrogen bonded molecular water. With the increment of calcinations temperature, surface molecular water bands located at the region of 4000 cm⁻¹ to 1000 cm⁻¹ gradually diminish and the particle size increase as a result of condensation of hydroxyl group and lost water between particles [2],[13],[14].

Loss of the surface hydroxyl group results in the formation of Sn-O group as shown in the equation below [2]:

$$M-OH + OH-M \rightarrow M-O-M + H_2O$$

This observation was agreed with XRD analysis which is the crystallinity of the catalyst increase with the increment of calcinations temperature.

3.4 X-Ray Fluorescence (XRF) Analysis

The XRF analysis was performed using a Bruker x-ray flourescence model S4 Explorer (made from Germany) equipped with Spectra plus software for data acquisition and analysis. Data were acquired using x-ray generator using source operating at 1 KW at ambient temperature. The analysis was performed using semi-quantitative method. Samples were finely grinded using mortar and placed in the sample cup (40 mm diameter) installed with 6 µm mylar film at the bottom.

The x-ray was generated from x-ray tube and passed through the beryllium Oxide window slit before striking the sample. Then, the sample reflected the x-ray photon and the photon passed through the collimator before hit the synthetic multilayer crystal. The crystal was consisted of lithium fluoride and pentoerythrite elements. This crystal was used to diffract polychromatic x-ray beam coming from the sample into a monochromatic light-beam and then sent it to detector. Then, the detector converted the energy of the x-ray photon into a measurable energy form. XRF is an elemental analysis technique with unique capabilities including:

- a) highly accurate determinations for major elements and
- b) a broad elemental survey of the sample composition without standards.

In this study, XRF use to make comparison between actual and experiment element composition percentage in the sample prepared.

Sample	Element	XRF Result	Experiment
	Со	30.3	34.97
S1	Ni	0.249	0.10
	Sn	68.7	64.93
	Со	35.6	39.96
S2	Ni	0.273	0.10
	Sn	64.1	59.94

Table 6: Data of elemental percentage for S1 and S2

The results from Table 6 show that there are small differences (<5 %) between experiment result and XRF result.

3.5 Scanning Electron Microscopy Analysis (SEM)

SEM is a powerful tool to observe the textural and morphology of the sample using FEI model FESEM Quanta 2005 instrument (Made from Republic of Chezkolavaskia). The calcined samples were adhered to the aluminum stub using carbon conductive tape. The stub was then mounted on the stub holder and loaded into the chamber. The air evacuation in chamber was performed before analysis. Images were recorded with a Quanta 200 FEI microscope instrument.

The morphologies of S1 and S2 catalysts treated at 400 °C and 600 °C calcinations temperatures are shown in Figure 13 and Figure 14 with a 500 times magnification image (scale bar: 2 cm=50 μ m).





Figure 13: SEM micrographs of the S1

As illustrated, the primary particles of S1 (see Figure 13) calcined at 400 °C shows a variety of particle size within a range of 10–35 μ m. The structure was shown to be amorphous in the XRD analysis. Further calcination at 600 °C gave material with slightly larger particle size within the range 16–60 μ m with less degree of amorphous character in the material showed by the present of initial agglomerated structure in the micrograph [15].





Figure 14: SEM micrographs of the S2

S2 catalysts (see Figure 14) calcined at 400 °C also show a variety of particle size within a range of 15–42 μ m. The structure is shown to be amorphous and displays the mixture of irregular and bead in shape. Further calcination at 600 °C illustrates the enlargement of particle size within the range of 18–55 μ m. However, homogeneous dispersion between the base material and the dopants for both calcination temperatures showed an irregular and undefined shape of the particles.

3.6 X-Ray Diffraction Analysis XRD

The XRD diffractogram patterns for S1 and S2 at 400 °C and 600 °C calcination temperatures are shown in Figure 15 and Figure 16. The diffractogram data obtained from the XRD analysis were tabulated in Table 7 and Table 8. The phase changes for both samples, were obtained by comparing the 2 θ value of materials studied with the 2 θ value of phases from the Powder Diffractogram File [16].



Figure 15: The XRD diffractogram pattern of S1 at 400 °C and 600 °C calcinations temperature

Temperature (°C)	20 (°)	d/Å	d/Å(PDF)	Assignment
	26.48	3.36	3.35	SnO ₂ (t)
	34.01	2.63	2.64	$SnO_2(t)$
40000	37.06	2.42	2.44	Co ₃ O ₄ (c)
400°C	37.98	2.37	2.37	SnO ₂ (t)
	52.33	1.75	1.76	SnO ₂ (t)
	64.70	1.44	1.43, 1.42	$Co_3O_4(c), SnO_2(t)$
	26.63	3.34	3.35	SnO ₂ (t)
	33.79	2.65	2.64	$SnO_2(t)$
	36.70	2.45	2.44	Co ₃ O ₄ (c)
600°C	38.17	2.36	2.37	$SnO_2(t)$
	51.80	1.76	1.76	SnO ₂ (t)
	54.26	1.69	1.68	SnO ₂ (t)
	64.75	1.44	1.43, 1.42	$Co_3O_4(c), SnO_2(t)$

Table 7: Peak positions (2 θ) in the XRD patterns of S1

S1 catalyst (see Table 7) calcined at 400 °C shows the existence of tin oxide (SnO₂) tetragonal phase and cobalt oxide (Co₃O₄) cubic phase. All broad peaks indicate the amorphous nature of the material with small particles present. The peaks of SnO₂ were observed at $2\theta = 26.48$, 34.01, 37.98, 52.33 and 64.70° or at d values = 3.36, 2.63, 2.37, 1.75 and 1.44 Å [PDF d values = 3.35, 2.64, 2.37, 1.76 and 1.43 Å], Co₃O₄ at $2\theta = 37.06$ or at d values = 2.42 Å [PDF d values = 2.44 Å]. One Co₃O₄ peak was expected to be overlap with SnO₂ peak at $2\theta = 64.70$ or at d values = 1.44 Å [PDF d values = 1.42 Å]. Calcination at 600 °C, shows no phase changes except one new SnO₂ peak at $2\theta = 54.26°$ or at d value = 1.69 Å [PDF d value = 1.68 Å].



Figure 16: The XRD diffractogram pattern of S2 at 400 °C and 600 °C calcinations temperature

Temperature (°C)	20 (°)	d/Å	d/Å(PDF)	Assignment
400°C	27.06	3.29	3.35	SnO ₂ (t)
	33.40	2.68	2.64	$SnO_2(t)$
	37.01	2.43	2.44	Co ₃ O ₄ (c)
	38.44	2.34	2.37	$SnO_2(t)$
	51.27	1.78	1.76	$SnO_2(t)$
	64.31	1.45	1.43, 1.42	$Co_3O_4(c), SnO_2(t)$
600∘C	26.78	3.33	3.35	SnO ₂ (t)
	31.51	2.84	2.86	Co ₃ O ₄ (c)
	33.96	2.64	2.64	$SnO_2(t)$
	36.93	2.43	2.44	Co ₃ O ₄ (c)
	38.25	2.35	2.37	$SnO_2(t)$
	52.01	1.76	1.76	$SnO_2(t)$
	65.50	1.42	1.43, 1.42	$Co_3O_4(c), SnO_2(t)$

Table 8: Peak positions (20) in the XRD patterns of S2

For the S2 catalyst (see Table 8), calcination at 400 °C shows the same phase changes with the S1 catalyst at the same temperature. But at 600 °C calcination, new phase changes that occurred was identified as Co_3O_4 with cubic structure at 20 value = 31.51 ° or at d value = 2.84 Å [PDF d value = 2.86 Å].

In principle, XRD analysis gives information of phase changes and structure transformation of the samples. The catalytic activity testing showed that S2 catalyst calcined at 600 °C gave the best activity with $T_{100} = 200$ °C. The catalytic activity is good when the material observes cobalt oxide, Co₃O₄ (combination of CoO and Co₂O₃) peaks. In this case, both oxidation number of cobalt oxide, Co²⁺ and Co³⁺ (Co³⁺ > Co²⁺) expected to increase the catalytic activity [15]. As predictable, peak for second dopant (nickel oxide) could not be found due to the small ratio of nickel oxide used.

4.0 OVERALL CONCLUSION

In this research, all catalyst was prepared by using sol-gel modification technique. Tin (IV) oxide was used as a main catalyst. Unfortunately, tin (IV) oxide itself was not a promising catalyst. In order to improve the catalytic activity of the catalyst prepared, dopants such as nickel (II) oxide and cobalt (II) oxide was added.

Catalytic activity testing was carried out to investigate the ability of the catalyst to convert a toxic gas (carbon monoxide) to non toxic gas (carbon dioxide). This testing has been done in COMBICAT, UM using SELOX instrument. The data show some interesting result which is our S1 (calcined at 400 °C) and S2 (calcined at 600 °C) indicate a CO conversion slightly as good as commercial catalyst, Pt/Al₂O₃. Both samples give a T₁₀₀(CO) at 215 °C and 200 °C (Pt/Al₂O₃, T₁₀₀(CO)= 200 °C).

Since these materials are good with high activity, an in depth investigation into the properties of the catalyst was carried using various characterization techniques. Nitrogen adsorption analysis show both S1 and S2 catalyst porosity at 400 °C calcinations temperature are in form of mesopore and micropore and openended cylindrical pore with a uniform size and shape. Increasing calcinations temperature to 600 °C proves that the porosity for both catalysts start to shift to mesopore form.

Assessment of BET surface area (A_{BET}), pore volume (V_p) and pore diameter (d) for both S1 and S2 (calcined at 400 °C) indicate a high A_{BET}, low pore diameter and higher V_p . Increasing calcinations temperature to 600 °C causes a decrement of the A_{BET}, increment of pore diameter and reduces V_p . This is due to agglomeration process that increase the the catalyst particle size and the porosity system from mixture of micro and meso that change to mesopore.

FTIR analysis shows a similar trend for S1 and S2 catalysts. With the increment of calcinations temperature, surface molecular water bands located at the region of 4000 cm⁻¹ to 1000 cm⁻¹ gradually diminish and the particle size increase as a result of condensation of hydroxyl group and lost water between particles. Loss of the surface hydroxyl group results in the formation of Sn-O group.

XRF analysis used to make comparison between actual and experiment element composition percentage in the sample prepared. The results show that there are small differences (<5 %) between experiment result and XRF result.

SEM analysis was done to investigate the catalyst morphology. Both S1 and S2 catalyst indicate the growth of particle size with the increment of calcination temperature. As a result, it decreases the catalyst surface area. High surface area was expected to give more active site on the catalyst surface. However, from catalytic activity testing, S2 calcined at 600 °C give a better result. So, even though calcinations at 400 °C give a higher surface area, but most of the catalyst surface is in micropore system. This type of porosity system is considering giving difficulty for gases to adsorp on the catalyst surface.

XRD analysis gives information of phase changes and structure transformation of the samples. The catalytic activity testing showed that S2 catalyst calcined at 600 °C gave the best activity with $T_{100}(CO) = 200$ °C. The XRD diffractogram show the existence of SnO₂ tetragonal and Co₂O₃ cubic phase. The catalytic activity is good when the material observes cobalt oxide, Co₃O₄ (combination of CoO and Co₂O₃) peaks. In this case, both oxidation number of

As predictable, peak for second dopant (nickel oxide) could not be found due to the small ratio of nickel oxide used.

REFERENCES

- [1] <u>http://encyclopedia.farlex.com/catalytic+converter</u>
- [2] Nor Aziah Buang (2000), "Zirconia Based Catalysts for Environmental Emission Control: Synthesis, Characterization and Catalytic Activity." PhD Thesis. UTM.
- [3] <u>http://www.importcatalytic.com/</u>
- [4] Wan Azelee and Nor Aziah Buang (1995) "A Short Review on the Mechanism of Automobile Catalytic Reaction" *Buletin Kimia*. 10. 47-53.
- [5] Harrison P.G., Bailey C., Azelee W., (1999), Modified Tin (IV) Oxide (M/SnO₂: M= Cr, La, Pr, Nd, Sm, Gd) Catalysts for the Oxidation of Carbon Monoxide & Propane. *J. of Catal.* 186:147-159.
- [6] Wan Azelee (1995), Non-Noble Metal Environmental Catalyst: Synthesis, Characterisation and Catalytic Activity. Ph.D Thesis, University of Nottingham, U.K.
- [7] Livage, J. (1998) "Sol-Gel Synthesis of Heterogeneous Catalysts from Aqueous Solutions" *Catalysis Today*. 41. 3-19.
- [8] Imran Syakir Mohamad (2001). "Mangkin Berasaskan Oksida Timah (IV) Bagi Rawatan Emisi Gas Toksik Karbon Monoksida", Master Thesis, Universiti Teknologi Malaysia.
- [9] Leofanti G. et.al (1998) "Surface Area and Pore Texture of Catalyst" *Catalyst Today*. 41. 207-219.
- [10] Sterenson, S.A. et.al (1987) "Metal-support Interaction in Catalyst, Sintering and Redispersion" Van Nostrand Reinfold Company. New York.
- [11] Wan Azelee, Nor Aziah Buang and Harrison P.G. (1997) "Analisis Tekstur Liang bagi Oksida Komposit SnO₂-ZrO₂" *Malays. J. Anal. Sci.* 3(1). 143-155.
- [12] Wachs, I.E. (1996) "Surface Metal Oxide Species on Oxide Support: Supported Metal Oxide Catalyst" *Catalyst Today.* 27. 437-453

- [13] Harrison, P.G. (1993) "The Effect of Calcinations on Metal Oxide Oxidation Catalysts" *Catalysis Today*. 17. 483-491.
- [14] Valigi, M. et.al (1996) "Manganese Oxide-Zirconia Oxide Solid Solution: An X-Ray Diffraction, Raman Spectroscopy, Thermogravimetry and Magnetic Study." *Matter. Chem.* 6(3). 403-408.
- [15] Imran Syakir Mohamad, et.al. (2000) "Applications of XRD and SEM Techniques for Structure and Morphology Elucidation of Tin (IV) Oxide Based Catalyst" *Nuclear Science Journal of Malaysia*. 18(2). 30-41.
- [16] Powder Diffraction File, (1995), Inorganic Phases, International Centre for Diffraction Data, American Society of Testing Material