DEVELOPMENT OF TIN (IV) OXIDE BASED CATALYST FOR CARBON MONOXIDE EMISSION CONTROL

Imran Syakir Mohamad[1], Mohd Haizal Mohd Husin[1],
Safarudin Gazali Herawan[1], Muhamad Zahir bin Hassan[1],
Mohd. Ridzuan Nordin[2], Wan Azelee Wan Abu Bakar[3],
Nor Aziah Buang[3], Abdul Rahim Yacob[3]

[1]Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka,
Locked Bag 1752, Pejabat Pos Durian Tunggal,
76109 Durian Tunggal, Melaka, Malaysia.

[2]Centre for Graduate Studies, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia.

[3]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia,
81310 UTM Skudai, Johor Darul Takzim, Malaysia.

ABSTRACT

Tin (IV) oxide has been recognized as an alternative catalyst for carbon monoxide gas treatment generated from vehicular and industrial activities. Carbon monoxide is a poisonous gas produce from incomplete burning of hydrocarbon based fuel and emitted directly from vehicles tailpipes which can affect human health. In this research, tin (IV) oxide was used as a catalyst with the addition of cobalt (II) oxide and nickel (II) oxide as dopants, prepared by modification of sol-gel method. The catalytic ability was tested towards the oxidation of carbon monoxide using Continuous Fixed Bed Reactor (SELOX) instrument. Two catalysts, ECAT1-400 calcined at 400°C and ECAT2-600 calcined at 600°C gave a promising catalytic ability towards carbon monoxide oxidation. Both catalysts completed the carbon monoxide oxidation to carbon dioxide at 215°C and 200°C (commercial catalyst, Pt/Al_2O_3 at 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 prepared catalyst, ECAT2-600 is in form of mesopore, open cylindrical in shaped with pore diameter of 10nm. The x-ray diffraction analysis shows the presence of SnO_2 tetragonal and Co_3O_4 cubic phase which act as the active site in the catalytic oxidation. The existence of cobalt oxide (in a mixture of Co^{2+} and Co^{3+}) expected to contribute the excellent oxidation of carbon monoxide.

KEYWORDS: catalyst, carbon monoxide oxidation

1.0 INTRODUCTION

The enormous increases in the environmental pollution are cause by exhaust emission which comes from incomplete vehicle combustion engine. A toxic carbon monoxide (CO) gas has being recognized as the main pollutant (Surachai et.al., 2006). Incomplete combustion occurs at low air to fuel ratios in the vehicle engine mainly during starting engine when air supply is limited. Over the past several years, the introduction of a catalytic converter was a breakthrough in the reduction of pollutant emission all over the world (Martyn et.al.,2007). The use of catalysts will definitely contribute to the production of clean automobile exhaust (Martyn et.al.,2007), (James et.al., 2005).

Platinum group catalyst currently represents the state of the art in the emission control catalyst technology. However, these current catalysts are limited and very 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 (Kaspar et.al., 2003). 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.

In this research, we develop a non noble metal oxide based catalyst with high efficiency of catalytic activity performance as an alternative catalyst for carbon monoxide treatment emitted from vehicle emission. In this paper, our catalysts were prepared from tin (IV) oxide based meanwhile cobalt (II) oxide and nickel (II) oxide used as dopants. Two catalysts showed excellent carbon monoxide conversion as good as the commercial catalyst, Pt/Al_2O_3. Samples Ni(II)/Co(II)-doped SnO_2 (ECAT1-400) calcined at 400°C and Ni(II)/Co(II)-doped SnO_2 (ECAT2-600) calcined at 600°C gave a complete carbon monoxide oxidation (T_{100}) at 215°C and 200°C, respectively.

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 ammonia at a constant pH of 4 (Livage et.al., 1998), at room temperature and under intensive stirring. The resultant gelatinous precipitate was washed until free of chloride ion (negative chloride test using argentum nitrate 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 Ni(II)/Co(II)-doped SnO_2

All the catalyst materials were prepared by sol-gel modification technique. The sample of nickel(II)/cobalt(II)-doped SnO_2 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.

3.0 RESULT AND DISCUSSION

3.1 Catalytic Activity Testing

Catalytic activity testing was carried out to observe the complete oxidation carbon monoxide (CO) to carbon dioxide (CO_2) by using Continuous Fixed Bed Reactor (SELOX) instrument. In carbon monoxide oxidation, the only inlet gases use are carbon monoxide and air with calculated gas flow-rate. Four percent of carbon monoxide is used as reactant in presence of 96% of air.

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

TABLE 1
Data for catalytic activity towards carbon monoxide oxidation

Sample	Atomic Ratio	Code	T_K (°C)	T_{LO} (°C)	T_{100} (°C)
Commercial Catalyst, Pt/Al_2O_3 (Imran, 2001)				120	200
Tin (IV) oxide, SnO_2 (Imran, 2001)	100%				342
Co(II)-doped SnO_2 (Imran, 2001)	10:90		400	240	355
			600	260	320
Co(II)-doped SnO_2 (Imran, 2001)	40:60		400	130	310
			600	160	320
Ni(II)/Co(II)-doped SnO_2	0.1/34.97/64.93	ECAT1-400	400	RT	215
		ECAT1-600	600	RT	230
Ni(II)/Co(II)-doped SnO_2	0.1/39.96/59.94	ECAT2-400	400	RT	230
		ECAT2-600	600	RT	200

TK=calcinations temperature
RT=room temperature (25°C)

Catalytic activity testing for carbon monoxide oxidation was carried out towards catalyst tabulated in the Table 1. Two samples show a good result as good as the commercial catalyst, Pt/Al_2O_3 (refer Figure 1) which are Ni(II)/Co(II)-doped SnO_2 (ECAT1-400) and Ni(II)/Co(II)-doped SnO_2 (ECAT2-600). Both catalysts, ECAT1-400 calcined at 400°C and ECAT2-600 calcined at 600°C give a complete carbon monoxide oxidation (T_{100}) at 215°C and 200°C.

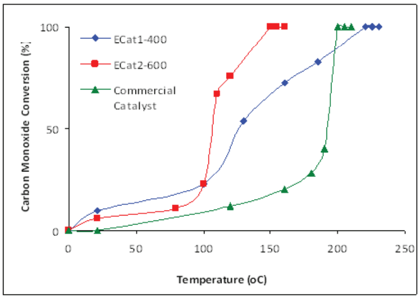

FIGURE 1
Percentage of carbon monoxide conversion versus temperature over ECAT1-400, ECAT2-600 and commercial catalyst

3.2 Nitrogen Adsorption Analysis

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, 20-50mg sample was placed in a tube of known volume and heated to 413K at rate 1Kmin^{-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 N_2. 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.

3.3 BET Isotherm

Figure 2 and Table 2 shows the BET isotherm for ECAT1 and ECAT2 catalyst. Both ECAT1 and ECAT2 calcined at 400°C and 600°C 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 (Leofanti et.al., 1998). 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 (Leofanti et.al., 1998).

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 (Leofanti et.al., 1998). The hysteresis loop is in type of H1 which is similar with previous calcinations temperature.

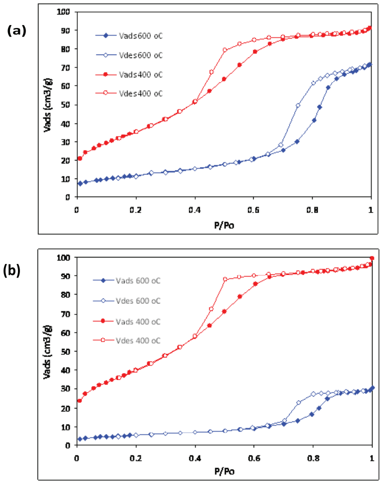

FIGURE 2
BET isotherm of (a) ECAT1 and (b) ECAT2 calcined at 400°C and 600°C

TABLE2
Type of porosity

Sample	Type of hysteresis	Type of isotherm	Type of porosity
ECAT1-400	H1	I & IV	Meso & micropore
ECAT1-600	H1	IV	Mesopore
ECAT2-400	H1	I & IV	Meso & micropore
ECAT2-600	H1	IV	Mesopore

3.4 Assessment of BET Surface Area (A_{BET}), Pore Volume (V_p) and Pore Diameter (d)

The data of nitrogen adsorption analysis using BET method are shown in Table 3. At 400°C calcination temperature, both ECAT1 and ECAT2 sample show a high surface area due to elimination of surface molecule in the material at lower temperature (less than 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.

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 XRD result) and at the same time reduces the pore volume, V_p (Sterenson et.al., 1987).

TABLE 3
Data of N_2 adsorption analysis using BET method

Sample	A_{BET} (m^2/g)	V_p(cm^3/g)	d(nm)
ECAT1-400	1.46×10^2	1.53×10^{-1}	4.20
ECAT1-600	1.90×10^1	1.46×10^{-1}	8.30
ECAT2-400	1.30×10^2	1.41×10^{-1}	4.40
ECAT2-600	4.30×10^1	1.11×10^{-1}	10.40

From this analysis, our best catalyst ECAT2-600 concluded to have an isotherm type IV (mesopore), open-ended cylindrical pore with a uniform size and shape and pore diameter around 10nm. These surface conditions were expected to give an optimum active site for CO and O_2 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 adsorb on the catalyst surface (Azelee et.al., 1997).

3.5 X-Ray Diffraction Analysis XRD

The XRD diffractogram patterns for ECAT1 and ECAT2 at 400°C and 600°C calcination temperatures are shown in Figure 3 and Figure 4. The diffractogram data obtained from the XRD analysis were tabulated in Table 4 and Table 5. The phase changes for both samples, were obtained by comparing the 2θ value of materials studied with the 2θ value of phases from the Powder Diffractogram File (Powder Diffraction File, 1995).

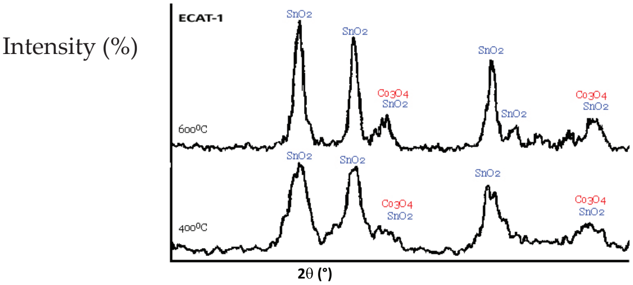

FIGURE 3
The XRD diffractogram pattern of ECAT1 calcined at 400°C and 600°C

TABLE 4
Peak positions (2θ) in the XRD patterns of ECAT1

Temperature (°C)	2θ (°)	d/Å	d/Å(PDF)	Assignment
400	26.48	3.36	3.35	SnO_2(t)
	34.01	2.63	2.64	SnO_2(t)
	37.06	2.42	2.44	Co_3O_4(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)
600	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_3O_4(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)

ECAT1 catalyst (see Table 1) calcined at 400°C shows the existence of tin oxide (SnO_2) tetragonal phase and cobalt oxide (Co_3O_4) cubic phase. All broad peaks indicate the amorphous nature of the material with small particles present. The peaks of SnO_2 were observed at 2θ = 26.48°, 34.01°, 37.98°, 52.33° and 64.70° or at d values = 3.36Å, 2.63Å, 2.37Å, 1.75Å and 1.44Å [PDF d values = 3.35Å, 2.64Å, 2.37Å, 1.76Å and 1.43Å], Co_3O_4 at 2θ = 37.06° or at d values = 2.42Å [PDF d values = 2.44Å]. One Co_3O_4 peak was expected to be overlap with SnO_2 peak at 2θ = 64.70° or at d values = 1.44Å [PDF d values = 1.42Å]. Calcination at 600°C, shows no phase changes except one new SnO_2 peak at 2θ = 54.26° or at d value = 1.69Å [PDF d value = 1.68Å].

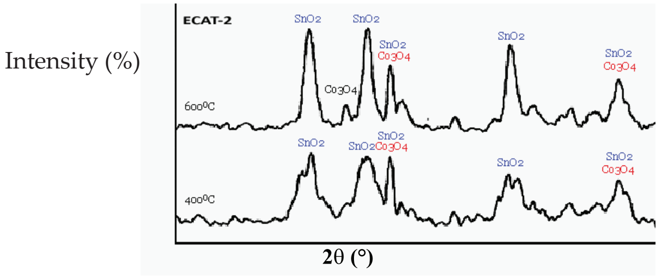

FIGURE 4
The XRD diffractogram pattern of ECAT2 calcined at 400°C and 600°C

TABLE 5
Peak positions (2θ) in the XRD patterns of ECAT2

Temperature (°C)	2θ (°)	d/Å	d/Å(PDF)	Assignment
400	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_3O_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	26.78	3.33	3.35	SnO_2(t)
	31.51	2.84	2.86	Co_3O_4(c)
	33.96	2.64	2.64	SnO_2(t)
	36.93	2.43	2.44	Co_3O_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)

For the ECAT2 catalyst (see Table 5), calcination at 400°C shows the same phase changes with the ECAT1 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 2θ value = 31.51° or at d value = 2.84Å [PDF d value = 2.86Å].

In principle, XRD analysis gives information of phase changes and structure transformation of the samples. The catalytic activity testing showed that ECAT2 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, Co_3O_4 (combination of CoO and Co_2O_3) peaks. In this case, both oxidation number of cobalt oxide, Co^{2+} and Co^{3+} ($Co^{3+} > Co^{2+}$) expected to increase the catalytic activity [11]. As predictable, peak for second dopant (nickel oxide) could not be found due to the small ratio of nickel oxide used.

4.0 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 ECAT1-400 (calcined at 400°C) and ECAT2-600 (calcined at 600°C) indicate a carbon monoxide conversion slightly as good as commercial catalyst, Pt/Al_2O_3. Both samples gave a T_{100}(CO) at 215°C and 200°C (Pt/Al_2O_3, T_{100}(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 ECAT1 and ECAT2 catalyst porosity at 400°C calcinations temperature are in form of mesopore and micropore and open-ended 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 ECAT1 and ECAT2 (calcined at 400°C) indicate a high surface area, low pore diameter and high pore volume. Increasing calcinations temperature to 600°C causes a decrement of the surface area, increment of pore diameter and reduces pore volume. This is due to agglomeration process that increases the catalyst particle size and the porosity system from mixture of micro and meso that change to mesopore.

XRD analysis gives information of phase changes and structure transformation of the samples. The catalytic activity testing showed that ECAT2-600 catalyst calcined at 600°C gave the best activity with T_{100}(CO)=200°C. The XRD diffractogram show the existence of SnO_2 tetragonal and Co_3O_4 cubic phase. The catalytic activity is good when the material observes cobalt oxide, Co_3O_4 (combination of CoO and Co_2O_3) peaks. In this case, both oxidation number of cobalt oxide, Co^{2+} and Co^{3+} ($Co^{3+} > Co^{2+}$) expected to increase the catalytic activity.

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