APPLICATION OF X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY TECHNIQUES FOR STRUCTURE AND MORPHOLOGY ELUCIDATION OF TIN (IV) OXIDE BASED CATALYST.

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ABSTRACT

X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used to investigate the structure and morphology of tin (IV) oxide based catalyst. The catalysts of Co(II)-doped SnO_2 and Ni(II)/Co(II)-doped SnO_2 were prepared using sol-gel modification technique. The XRD results of the studied samples showed the existence of tetragonal SnO_2 phase, CoO cubic phase, Co_3O_4 cubic phase and Co_2SnO_4 cubic phase for the 400 °C, 600 °C, 800 °C and 1000 °C calcination temperatures. Furthermore, the SEM analysis results illustrate the enlargement of particle size with the increment of calcination temperatures and all the studied samples displayed the mixture of irregular and bead in shape.

ABSTRAK

Teknik pembelauan sinar-X (XRD) dan mikroskopi imbasan elektron (SEM) digunakan untuk mengkaji struktur dan morfologi mangkin berasaskan oksida timah (IV). Mangkin Co(II)-dop SnO_2 dan Ni(II)/Co(II)-dop SnO_2 disediakan menggunakan kaedah modifikasi sol-gel. Pencirian XRD ke atas sampel yang dikaji menunjukkan kehadiran fasa SnO_2 tetragonal, fasa CoO kubik, fasa Co_3O_4 kubik dan fasa Co_2SnO_4

kubik untuk suhu pengkalsinan 400 °C, 600 °C, 800 °C dan 1000 °C. Manakala, analisis SEM pula menggambarkan peningkatan saiz partikel yang berkadaran dengan peningkatan suhu pengkalsinan dan semua sampel yang dikaji memperlihatkan zarah berbentuk campuran tidak sekata dan butiran kecil.

INTRODUCTION

Reducing pollution of the earth atmosphere from noxious gases such as NO_x, HC and CO has been an important study and discussion elsewhere. Therefore, the development in catalytic technologies will help in improving the quality of the atmosphere from the noxious gases especially in the production of the catalytic converter that helps to purify industrial and automobile exhausts emission [1].

Platinum group catalysts currently represent the state of the art in internal combustion engine emission technologies [2]. However, there are significant advantages to be gained from the development of non-noble metal exhaust emission catalyst. The advantages are the low price of the material, strategic importance, and low availability of the platinum group metals [2, 3].

In the development of catalytic studies, tin (IV) oxide and compound containing tin (IV) oxide are being recognised these days as useful catalyst material. Tin (IV) oxide based material have been known for a long time to have good activity towards the CO/O_2 and CO/NO reactions [4].

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. In this paper, dopants such as Co(II) and Ni(II) were used. The catalytic activity testing for the Co(II)-doped SnO_2 (30:70) material calcined at 400 °C, 600 °C, 800 °C and 1000 °C gave 100 % conversion of CO to CO_2, T_{100} = 175 °C, 180 °C, 250 °C and 390 °C. The oxidation catalytic of CO for the Ni(II)/Co(II)-doped SnO_2 (0.1:29.97:69.93) material calcined at 400 °C, 800 °C and 1000 °C gave T_{100} = 220 °C, 260 °C and 390 °C. Meanwhile, the calcination at 600 °C of this material showed the best and optimum catalytic activity with T_{100} = 150 °C.

Research has been carried out to investigate the structures and morphologies of tin (IV) oxide based catalysts using the X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

MATERIALS AND METHODS

Catalyst preparation

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, at room temperature and under intensive stirring. The resultant gelatinous precipitate was washed until free of chloride ion (negative chloride test using $AgNO_3$ solutions) by repeated centrifuging and redispersing in triply distilled water. The solid gel was then allowed to dry at 120 °C for 24 hours. The white granular materials thus obtained was cracked with triply distilled water and then again dried at 120 °C. The materials were then manually ground into fine powder using a mortar.

Preparation of tin (IV) oxide sol

Tin (IV) oxide gel was obtained by ammonia precipitation method. Conversion to stable sol-gel modification is 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 120 °C for 24 hours, a brown glassy like solid is produced.

Preparation of samples Co(II)-doped SnO_2 and Ni(II)/Co(II)-doped SnO_2

All the catalyst materials were prepared by sol-gel modification technique. The samples of cobalt (II)-doped SnO_2 (Co:Sn atomic ratio 30:70) and nickel (II)/ cobalt

(II)-doped SnO_2 (Ni:Co:Sn atomic ratio 0.1:29.97:69.93) with appropriate quantities were dissolved in triply distilled water and left stirred for one hour.

The resulting clear dark yellow solutions were dried at 120 °C for 24 hours. The dried samples were then calcined at the temperature of 400 °C, 600 °C, 800 °C and 1000 °C in muffler furnace for 17 hours. The calcined samples were then manually ground into fine powder using a mortar and characterised with X-ray diffraction and scanning electron microscopy analytical techniques.

Characterisation

X-Ray Diffraction (XRD)

Calcined samples were analysed by the Diffractometer D5000 Siemens Kristalloflex with Cu-Kα radiation (λ: 1.540560 Å). The 2θ angular regions from 10° to 70° were scanned. The X-ray diffraction diffractogram patterns of the samples were then interpreted using the Powder Diffraction File (PDF) [5].

Scanning Electron Microscopy (SEM)

A Philip XL 40 scanning electron microscopy was used to obtain the morphologies of tin (IV) oxide based catalysts. Filament current was set at an accelerating voltage of 10 KeV.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis (XRD)

The XRD diffractogram patterns for Co(II)-doped SnO_2 and Ni(II)/Co(II)-doped SnO_2 at various calcination temperatures are shown in Figure 1 and Figure 2. The diffractogram data obtained from the XRD analysis were tabulated in Table 1 and Table 2. The phase changes for both samples, Co(II)-doped SnO_2 and Ni(II)/Co(II)-doped SnO_2 at various calcination temperatures were obtained by comparing the 2θ

value of materials studied with the 2θ value of phases from the Powder Diffractogram File [5].

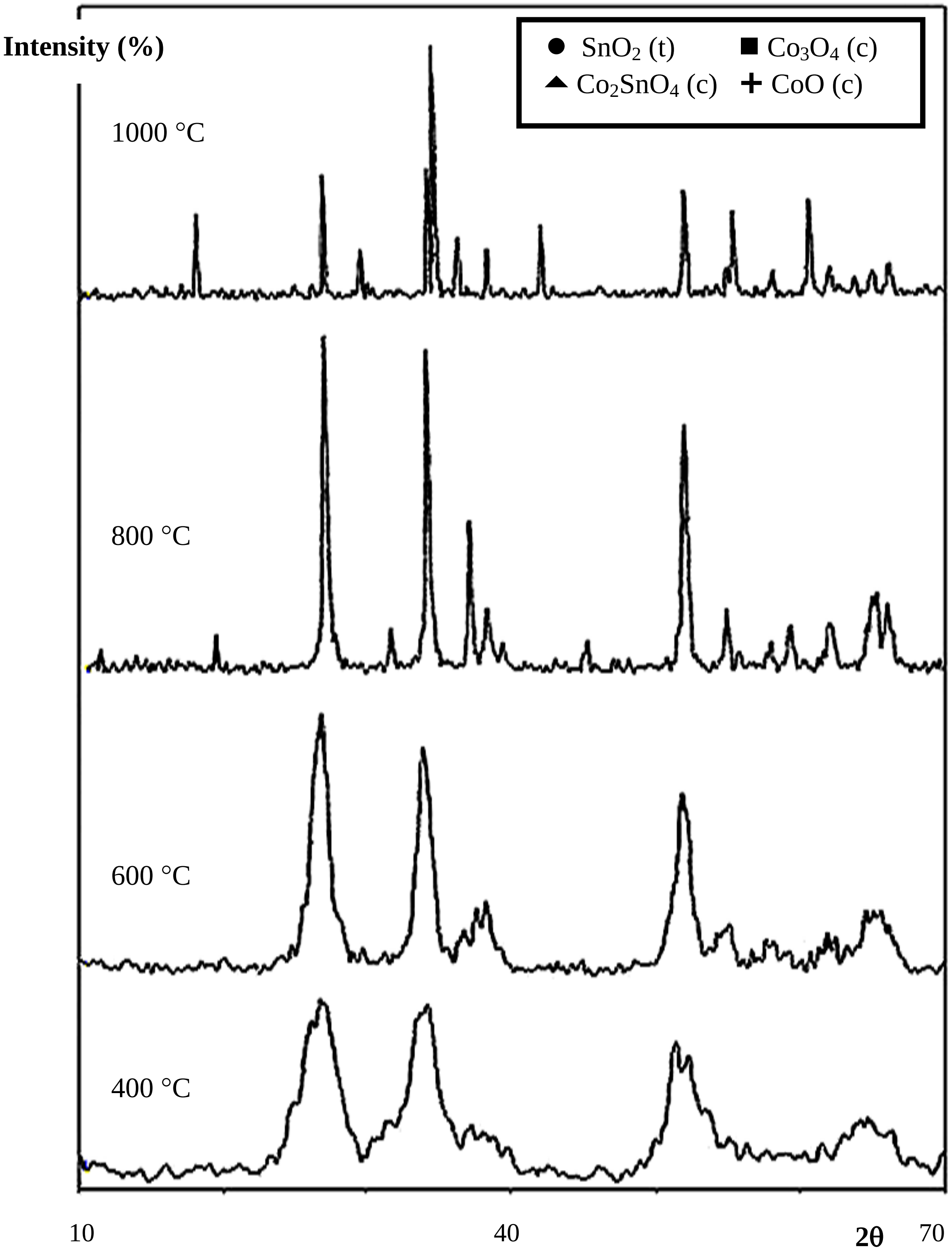


Figure 1: The XRD diffractogram pattern of Co(II)-doped SnO_2 (30:70) calcined at various temperatures.

Table 1: Peak positions (2θ) in the XRD patterns of Co(II)-doped SnO_2 (30:70)

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, 2.62	SnO_2(t), CoO(c)
	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, 2.62	SnO_2(t), CoO(c)
	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)
800	19.02	4.66	4.67	Co_3O_4(c)
	26.75	3.33	3.35	SnO_2(t)
	31.28	2.86	2.86	Co_3O_4(c)
	34.01	2.63	2.64, 2.62, 2.61	SnO_2(t), CoO(c), Co_2SnO_4(c)
	36.93	2.43	2.44	Co_3O_4(c)
	38.04	2.36	2.37	SnO_2(t)
	39.14	2.30	2.31	SnO_2(t)
	44.99	2.01	2.02	Co_3O_4(c)
	51.97	1.76	1.76	SnO_2(t)
	54.87	1.67	1.68	SnO_2(t)
	57.98	1.59	1.59	SnO_2(t)
	59.38	1.56	1.56	Co_3O_4(c)
	62.00	1.50	1.50	SnO_2(t)
	65.42	1.43	1.43	Co_3O_4(c)
	66.03	1.41	1.42	SnO_2(t)
1000	17.93	4.94	4.99	Co_2SnO_4(c)
	26.77	3.33	3.35	SnO_2(t)
	29.38	3.04	3.06	Co_2SnO_4(c)
	34.09	2.63	2.64	SnO_2(t)
	34.55	2.59	2.62, 2.61	CoO(c), Co_2SnO_4(c)
	36.18	2.48	2.49	Co_2SnO_4(c)
	38.10	2.36	2.37	SnO_2(t)
	41.94	2.15	2.16	Co_2SnO_4(c)
	51.97	1.76	1.76	SnO_2(t)
	55.35	1.66	1.66	Co_2SnO_4(c)
	58.16	1.58	1.59	SnO_2(t)
	60.63	1.53	1.53	Co_2SnO_4(c)
	62.13	1.49	1.50	SnO_2(t)
	64.99	1.43	1.44	SnO_2(t)
	66.27	1.41	1.42	SnO_2(t)

t: tetragonal, c: cubic

Co(II)-doped SnO_2 catalyst (see Table 1) calcined at 400 °C shows the existence of tin oxide (SnO_2) tetragonal phase and cobalt oxide (Co_3O_4 and CoO) cubic phase. All broad peaks indicate the amorphous nature of the material with small particles present. The peaks of SnO_2 are observed at 2θ = 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], Co_3O_4 at 2θ = 37.06 and 64.70 ° or at d values = 2.42 and 1.44 Å [PDF d values = 2.44 and 1.42 Å] and CoO peak is found overlapped with SnO_2 peak at 2θ = 34.01 ° or at d value = 2.63 Å [PDF d value = 2.62 Å]. Calcination at 600 °C, shows no phase changes except one new SnO_2 peak at 2θ = 54.26 ° or at d value = 1.69 Å [PDF d value = 1.68 Å].

Further increment of temperature at 800 °C reveals new peaks of tetragonal structure SnO_2 at 2θ values = 39.14, 57.98 and 62.00 ° or at d values = 2.30, 1.59 and 1.50 Å [PDF d values = 2.31, 1.59 and 1.50 Å] and cubic structure of Co_3O_4 at 2θ values = 19.02, 31.28, 44.99 and 59.38 ° or at d values = 4.66, 2.86, 2.01 and 1.56 Å [PDF d value = 4.67, 2.86, 2.02 and 1.56 Å]. A ternary compound of Co_2SnO_4 with cubic structure phase is expected to overlap with the SnO_2 and CoO peak at 2θ value = 34.01 ° or at d value = 2.63 Å [PDF d value = 2.61 Å].

The calcination at 1000 °C shows the existence of Co_2SnO_4 with cubic structure 2θ values = 17.93, 29.38, 34.55, 36.18, 41.94, 55.35 and 60.63 ° or at d values = 4.94, 3.04, 2.59, 2.48, 2.15, 1.66 and 1.53 Å [PDF d values = 4.99, 3.06, 2.61, 2.49, 2.16, 1.66 and 1.53 Å]. Meanwhile, a new SnO_2 peak is found at 2θ value = 64.99 ° or at d value = 1.41 Å [PDF d value = 1.44 Å]. A CoO peak is expected to overlaped with Co_2SnO_4 peak at 2θ value = 34.55 ° or at d value = 2.59 Å [PDF d value = 2.62 Å]. In other word, the peak at 2θ value ≈ 34.00 ° shows a high intensity mainly due to the overlapping of SnO_2, CoO and Co_2SnO_4 phases in that area. XRD diffractogram shows that no Co_3O_4 peak is found at this calcination temperature.

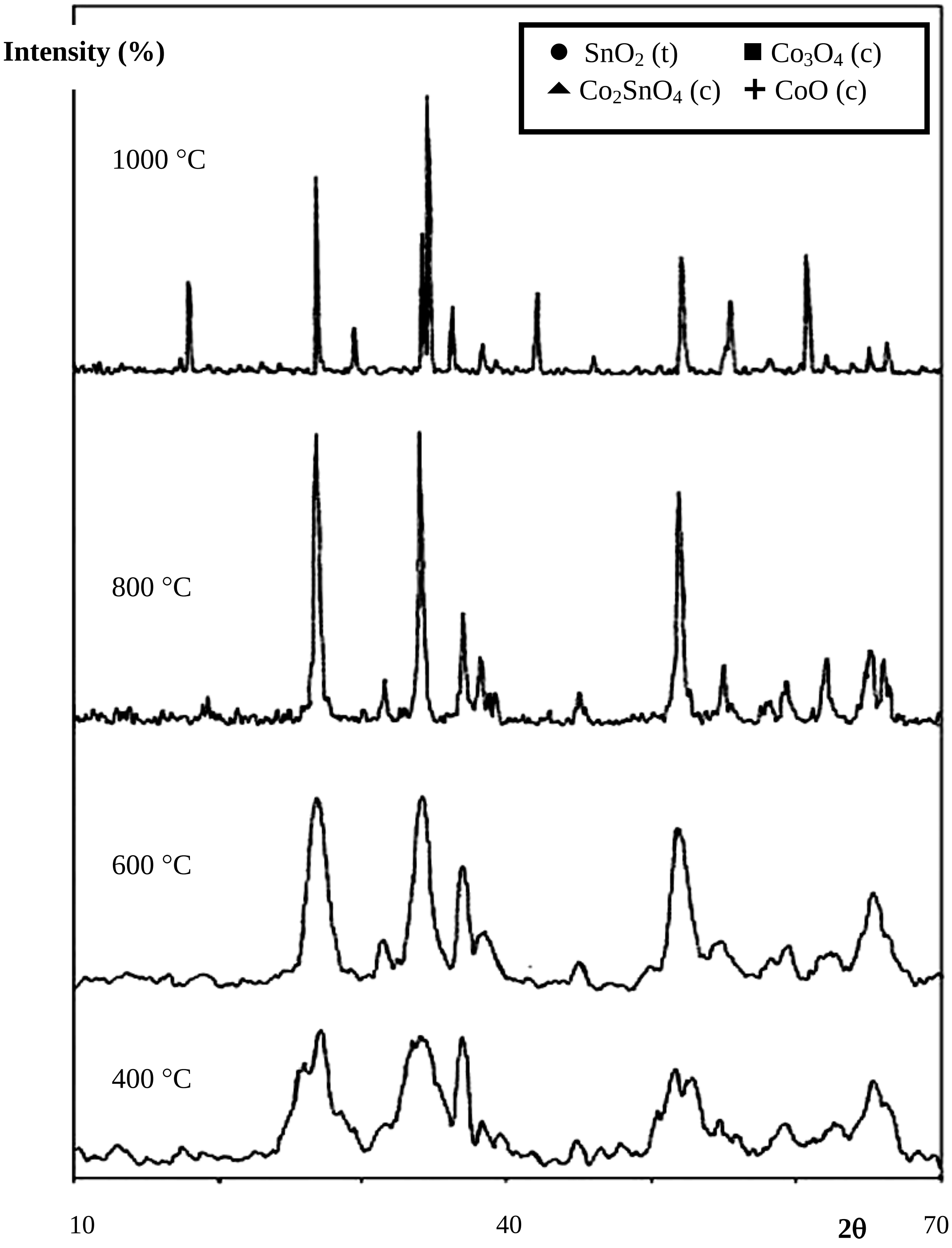


Figure 2: The XRD diffractogram pattern of Ni(II)/Co(II)-doped SnO_2 (0.1:29.97:69.93) calcined at various temperatures.

Table 2: Peak positions (2θ) in the XRD patterns of Ni/Co(II)-doped SnO_2 (0.1:29.97:69.93)

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, 2.62	SnO_2(t), CoO(c)
	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)
	34.32	2.61	2.62	CoO(c)
	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)
	58.49	1.58	1.61	CoO(c)
	65.50	1.42	1.43, 1.42	Co_3O_4(c), SnO_2(t)
800	26.77	3.33	3.35	SnO_2(t)
	31.40	2.85	2.86	Co_3O_4(c)
	34.01	2.63	2.64, 2.62, 2.61	SnO_2(t), CoO(c), Co_2SnO_4(c)
	36.89	2.43	2.44	Co_3O_4(c)
	38.04	2.36	2.37	SnO_2(t)
	39.14	2.30	2.31	SnO_2(t)
	44.93	2.02	2.02	Co_3O_4(c)
	51.94	1.76	1.76	SnO_2(t)
	54.93	1.67	1.68	SnO_2(t)
	59.32	1.56	1.56	Co_3O_4(c)
	62.13	1.49	1.50	SnO_2(t)
	65.05	1.43	1.43	Co_3O_4(c)
	66.09	1.41	1.42	SnO_2(t)
1000	17.87	4.96	4.99	Co_2SnO_4(c)
	26.72	3.33	3.35	SnO_2(t)
	29.31	3.05	3.06	Co_2SnO_4(c)
	34.04	2.63	2.64	SnO_2(t)
	34.51	2.60	2.62, 2.61	CoO(c), Co_2SnO_4(c)
	36.09	2.49	2.49	Co_2SnO_4(c)
	38.04	2.36	2.37	SnO_2(t)
	41.91	2.15	2.16	Co_2SnO_4(c)
	51.95	1.76	1.76	SnO_2(t)
	55.24	1.66	1.66	Co_2SnO_4(c)
	60.63	1.53	1.53	Co_2SnO_4(c)
	64.87	1.44	1.44	SnO_2(t)
	66.03	1.41	1.42	SnO_2(t)

t: tetragonal, c: cubic

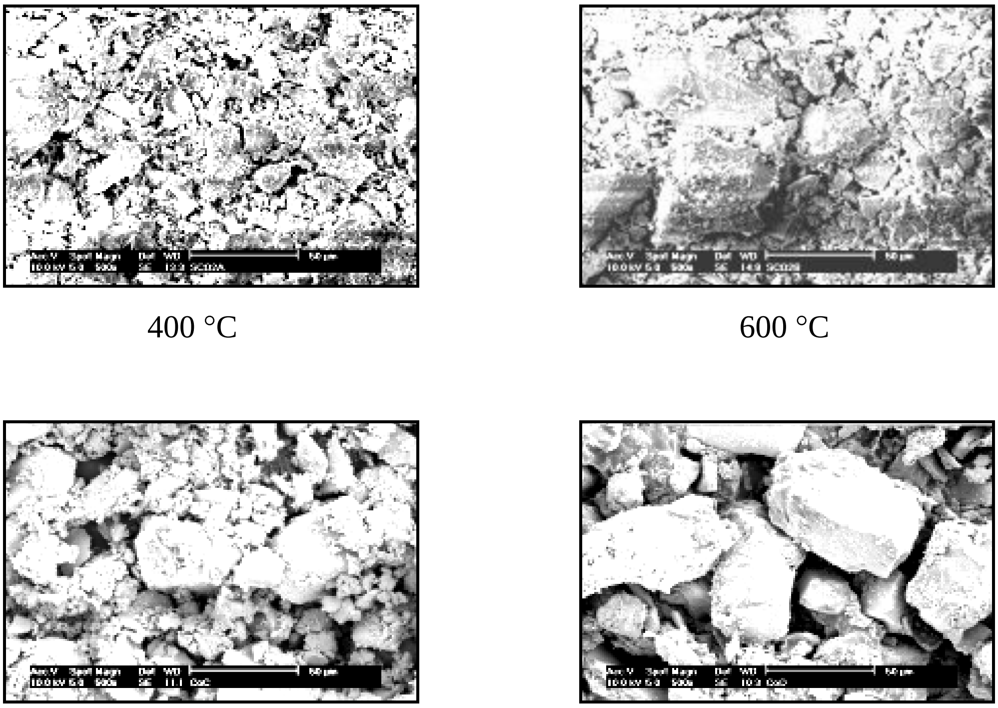
For the Ni(II)/Co(II)-doped SnO_2 catalyst (see Table 2), calcination at 400 °C shows the same phase changes with the Co(II)-doped SnO_2 catalyst at the same temperature. But at 600 °C calcination, phase changes that occurred is identified as Co_3O_4 with cubic structure at 2θ value = 31.51 ° or at d value = 2.84 Å [PDF d value = 2.86 Å] and together with the cubic structure of CoO at 2θ values = 34.32 and 58.49 ° or at d values = 2.61 and 1.58 Å [PDF d values = 2.62 and 1.61 Å].

Further increment of temperatures at 800 °C and 1000 °C shows similar phase changes compared to Co(II)-doped SnO_2 catalyst at the same calcination temperatures. The increment of calcination temperature from 800 °C to 1000 °C reveals the existence of ternary compound, Co_2SnO_4 with cubic structure at 2θ values = 19.87, 29.31, 34.51, 36.09, 41.91, 55.24 and 60.63 ° or at d values = 4.96, 3.05, 2.60, 2.49, 2.15, 1.66 and 1.53 Å [PDF d values = 4.99, 3.06, 2.61, 2.49, 2.16, 1.66 and 1.53 Å].

In principle, XRD analysis gives an information of phase changes and structure transformation of the samples. Furthermore, at higher calcination temperature the diffractogram patterns of each material shows narrow peaks with higher intensity which indicates the formation of crystalline properties in the material [6]. The catalytic activity testing showed that Ni(II)/Co(II)-doped SnO_2 catalyst calcined at 600 °C gave the best activity with T_{100} = 150 °C. The catalytic activity is good when the material observes both cobalt oxide (CoO and Co_3O_4) peaks. In this case, both oxidation number of cobalt oxide, Co^{2+} and Co^{3+} ($Co^{3+} > Co^{2+}$) will increase the catalytic activity. However, the efficiency of the catalyst reduces at 800 °C calcination. This phenomenon is probably due to the increment of cobalt oxide with oxidation number +2. Meanwhile, calcination at 1000 °C gave the worst catalytic activity because of the existence of ternary compound, Co_2SnO_4. As expected, peak for second dopant (nickel oxide) could not be found due to the small ratio of nickel oxide used.

Scanning Electron Microscopy Analysis (SEM)

The morphologies of Co(II)-doped SnO_2 and Ni(II)/Co(II)-doped SnO_2 catalysts treated at various temperatures are shown in Figure 3 and Figure 4 with a 500 times magnification image (scale bar: 2 cm = 50 μm).



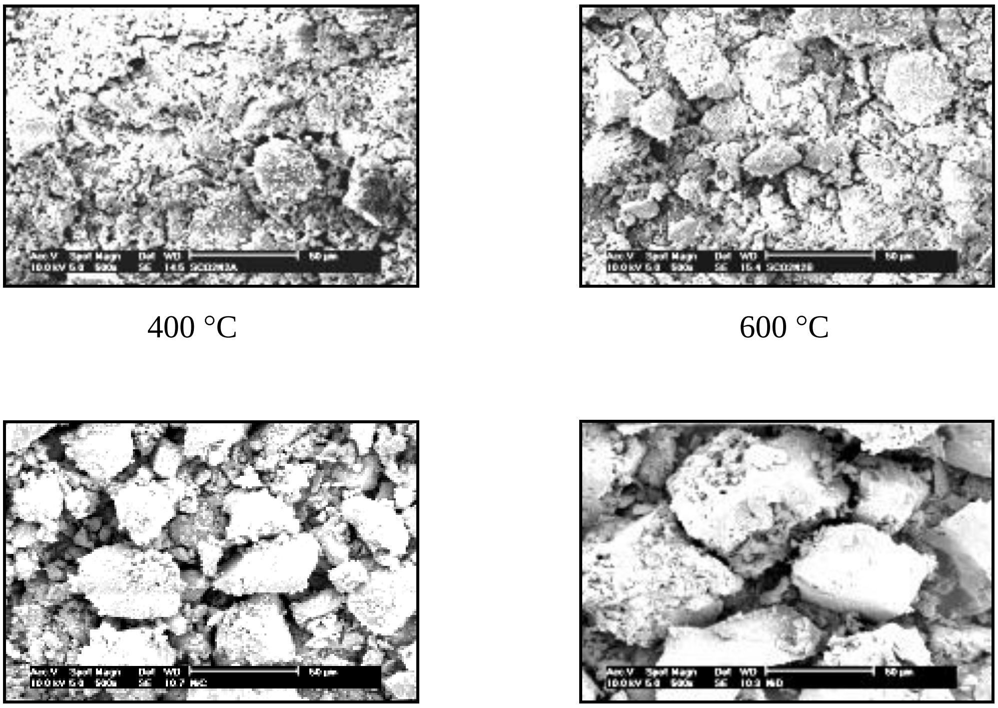
400 °C 600 °C

800 °C 1000 °C

Figure 3: SEM micrographs of the Co(II)-doped SnO_2 calcined at various calcination temperatures (scale bar: 2 cm = 50 μm; magnification: 500 times)

As illustrated, the primary particles of Co(II)-doped SnO_2 (see Figure 3) calcined at 400 °C show a variety of particle size within a range of 8 – 40 μm. 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 15 – 65 μm with less degree of amorphous character in the material showed by the present of initial agglomerated structure in the micrograph.

At 800 °C, the particle size started to grow within the range of 20 – 80 μm which may possibly due to the agglomeration process towards the formation of secondary particles [7]. However, 1000 °C calcination revealed transformation of primary particles into secondary particles with average size within 25 – 100 μm. It is illustrated that the shape of the particles is slightly slimmer with clear and sharp edges which is possibly due to higher degree of crystallinity in the material. This observation is in good agreement with the presence of narrow and high intensity peaks in XRD diffractogram pattern.



400 °C

600 °C

800 °C

1000 °C

Figure 4: SEM micrographs of the Ni(II)/Co(II)-doped SnO_2 calcined at various calcination temperatures (scale bar: 2 cm = 50 μm; magnification: 500 times).

Ni(II)/Co(II)-doped SnO_2 catalysts (see Figure 4) calcined at 400 °C also show a variety of particle size within a range of 12 – 40 μm. The structure is shown to be amorphous and displays the mixture of irregular and bead in shape. Further calcination at 600 °C illustrate the enlargement of particle size within the range of 17 – 50 μm. However, homogeneous dispersion between the base material and the dopants for both calcination temperatures showed an irregular and undefined shape of the particles. At 800 °C, the particle size is within the range of 20 – 75 μm. This observation indicates the growth of particles and promoted the agglomeration of primary particles. At 1000 °C, the micrograph shows that sintering process results in a larger size compared to other calcination temperatures. The particles with average size within 35 – 100 μm was observed.

CONCLUSION

Sample Ni(II)/Co(II)-doped SnO_2 calcined at 600 °C showed the best and optimum activity towards carbon monoxide conversion. The structural study showed that both oxidation number of cobalt oxide (CoO and Co_3O_4) with cubic structure, Co^{2+} and Co^{3+} ($Co^{3+} > Co^{2+}$) observed in the materials will increase the catalytic activity. Meanwhile, the morphology study at this temperature gave material with slightly larger particle size within the range 17 – 50 μm with less degree of amorphous character in the material showed by the presence of initial agglomerated structure in the micrograph.

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REFERENCES

1. Husselbee W. R., (1984), Automobile Emission Control. Reston Publishing Company Inc., New York. 337-356.

2. Azelee W., (1995), Non-Noble Metal Environmental Catalyst: Synthesis, Characterisation and Catalytic Activity. Ph. D Thesis, University of Nottingham, U.K.

3. Ahmad M. T., (1996), Beberapa Bahan Oksida Novel Berasaskan Timah: Analisis Struktur & Tekstur Liang. B. Sc Thesis, Universiti Teknologi Malaysia.

4. Harrison P.G., Bailey C., Azelee W., (1999), Modified Tin (IV) Oxide (M/SnO_2: M= Cr, La, Pr, Nd, Sm, Gd) Catalysts for the Oxidation of Carbon Monoxide & Propane. *J. of Catal.* **186**:147-159.

5. Powder Diffraction File, (1995), Inorganic Phases, International Centre for Diffraction Data, American Society of Testing Material.

6. Matan K., Zhao D., Goldfard D., Azelee W., Daniell D., Harisson P. G., (1995), *J. Phys. Chem.*, **99**, 9966.

7. Aziah N., (2000), Zirconia Based Catalysts for Environmental Emission Control: Synthesis, Characterisation and Catalytic Activity. Ph. D Thesis, Universiti Teknologi Malaysia.