

## INVESTIGASI XRD PADA INTERLOGAM $Ni_3Sn_2$ YANG DISINTESIS SECARA TERMOKIMIA: EFEK TEMPERATUR, WAKTU DAN pH HIDROTERMAL

### *XRD Investigation of Thermochemically Synthesised Intermetallic $Ni_3Sn_2$ Effect of Temperature, Time, and pH of Hydrothermal*

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#### ABSTRACT

X-ray diffraction studies of bulk structure of intermetallic nickel-tin ( $Ni_3Sn_2$ ) alloys that have been synthesised via a simple thermochemical method from non-organometallic precursor at low temperature were performed. Astoichiometric solution contains nickel chloride hexahydrate (3.6 mmol) in water and tin chloride dihydrate (2.4 mmol) in ethanol were mixed and homogenized at 323 K for 18 h, adjusted pH of 2-14 using NaOH solution, hydrothermal treatment at prescribed temperature of 423-523 K and time of hydrothermal of 6-72 h then finally reduced under  $H_2$  gas flow at 673 K for 1.5 h. The temperature of hydrothermal, length of hydrothermal, and adjusted pH before hydrothermal treatment were significantly affected towards the crystallinity and purity of the synthesised intermetallic  $Ni_3Sn_2$ . The best condition of the preparation of intermetallic  $Ni_3Sn_2$  with high crystallinity and purity is at 423 K, 24 h, and adjusted pH of 12.

**Keyword:** thermochemical method, hydrothermal, adjusted pH, intermetallic  $Ni_3Sn_2$

#### ABSTRAK

Studi secara sistematis menggunakan difraksi sinar-X pada senyawa interlogam nikel-timah ( $Ni_3Sn_2$ ) dibuat dengan metode termokimia yang sederhana dari bahan baku bukan organologam telah dilakukan. Larutan nikel klorida heksahidrat (3,6 mmol) dalam air dan larutan timah klorida dihidrat (2,4 mmol) dalam etanol dicampur dan dihomogenkan pada temperatur 323 K selama 18 jam. pH campuran divariasikan dari 2-12 dengan cara menambahkan larutan NaOH, kemudian dilakukan hidrotermal pada temperatur 423-523 K dan waktu hidrotermal 6-72 jam dan terakhir reduksi dengan gas  $H_2$  pada 673 K selama 1,5 jam. Pengaruh kondisi pembuatan seperti temperatur hidrotermal, lama waktu hidrotermal, dan penyesuaian pH larutan bahan baku sebelum hidrotermal berpengaruh secara signifikan terhadap kristalinitas dan kemurnian interlogam  $Ni_3Sn_2$  yang terbentuk. Kondisi terbaik pembuatan interlogam  $Ni_3Sn_2$  dengan kristalinitas dan kemurnian yang tinggi adalah 423 K, 24 jam, dan pH 12.

**Kata kunci:** metode termokimia, hidrotermal, penyesuaian pH, interlogam  $Ni_3Sn_2$

#### INTRODUCTION

Recently, bimetallic surfaces and alloy-based catalysts have been attractively investigated and applied for numerous reactions (Sachtler, and Van Santen, 1977). Their catalytic performances could be addressed to the having unique structures and catalytically active sites that provided a specificity in activity, selectivity, and stability

compared to the pure metal catalyst (Sachtler, and Van Santen, 1977; Arvela et al., 2005). Among of the interested bimetallic alloy is nickel-tin (Ni-Sn) which is well-known as an effective catalyst for cyclohexane dehydrogenation (Onda et al., 1998), partial hydrogenation (Onda et al., 2000), hydrogen production (Shabakaer et al., 2004), CO oxidation (Pengpanich et al., 2008), and

carbonylation (Liu et al., 1994), and steam reforming (Nikolla et al., 2006).

Developed synthesis method for Ni-Sn alloy such as arc-melting of the mixture of metallic powder (Onda et al., 2000), co-impregnation of metallic salts (Masai et al., 1975), surface reaction of organometallic tin on nickel (Agnelli et al., 1990), and chemical vapor deposition (Onda et al., 1998; Shabaker et al., 2004; Nikolla et al., 2006) have been reported previously. However, in these methods, a high temperature and an inert atmosphere (e.g. helium or argon) are required to form a crystalline Ni-Sn alloy and in some cases, the use of organometallic precursors is also needed (Onda et al., 2000; Shabaker et al., 2004; Nikolla et al., 2006; Agnelli et al., 1990). On the other hand, polyol mediated process in the presence of hydrazine or NaBH<sub>4</sub> as reducing agents has been alternated choice, since it could be applied at the relatively moderate temperature to form the crystalline Ni<sub>3</sub>Sn<sub>4</sub> alloy, but it was not active for catalyst (Henderson and Schaak, 2008). Although the studies on the syntheses and applications of Ni-Sn alloy have been reported previously, the development of the simple synthesis method with controllable size, dispersion, composition, and alloy structure are greatly desired. The altered methods were developed such dendrimetic route using bulk-organo template (Arther et al., 2010), polyol process assisted microwave irradiation (Cable and Schaak, 2005), or simultaneous co-condensation in organic solvent at 77 K using the chemical liquid deposition (CLD)

method (Cardenas et al., 2005). The later methods were also limited in practical application and produced a low stability of Ni-Sn alloys for catalytic application. Therefore, our proposed idea is to approach a simple method which highly active and highly selective of intermetallic nickel-tin alloys catalysts without any specific equipment and common conditions.

We have reported the utilisation of bulk and supported intermetallic Ni-Sn as catalyst for chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds into unsaturated alcohol (Rodiansono et al., 2012a; Rodiansono et al., 2012b) and selective hydrogenation of biomass-derived furfural into furfuryl alcohol with excellent activity and selectivity (Rodiansono et al., 2014). Most recently, we have reported the effect of ethylene glycol/H<sub>2</sub>O volume ratio on the formation of Ni<sub>3</sub>Sn<sub>2</sub> alloy species in Ni-Sn(1.5) (Saputra et al., 2014). In this present report, we continue to describe a thermochemical synthesis of bimetallic Ni-Sn alloys without organometallic tin precursor as starting materials and its characterisation. The intermetallic Ni-Sn with Ni/Sn molar ratio of 1.5 were synthesised and the effect of temperature of hydrothermal, length of hydrothermal, temperature of H<sub>2</sub> treatment, adjusted pH system, and XRD investigations were also investigated.

## EXPERIMENTAL SECTION

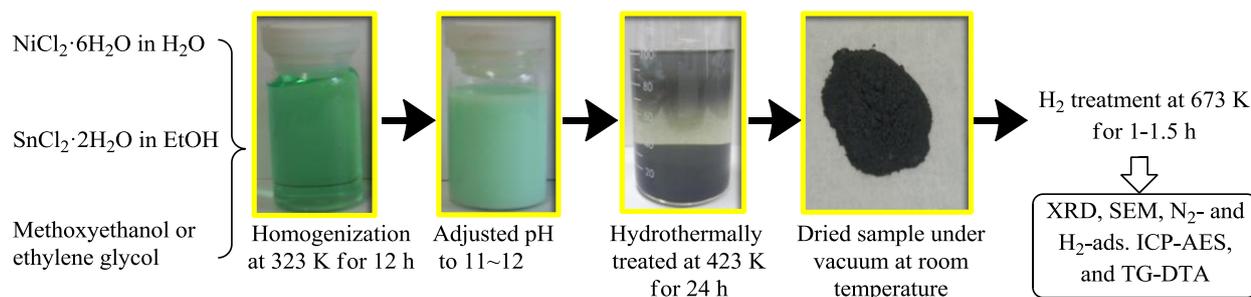
### Chemicals

All chemicals were used as received and purchased from WAKO Pure Chemical

unless otherwise stated nickel (II) chloride hexahydrate, 98%; tin (II) chloride dihydrate, 99.9%; aluminium hydroxide, ethanol, 99.5%; iso-propanol, 99.5%; ethylene glycol, 99.5%; and methoxy ethanol, 99.5%.

### Synthesis Ni-Sn alloys

A typical procedure of the synthesis of Ni-Sn alloy with Sn/Ni ratio of 1.5 had been reported elsewhere (Rodiansono et al., 2012a). The schematic diagram and photo images for the synthesis route of bulk intermetallic Ni-Sn are shown in **Figure 1**.



**Figure 1.** Schematic diagram and photo images for the synthetic route of Ni-Sn(x) alloy catalysts

### Characterizations

XRD measurements were recorded on a Mac Science M18XHF instrument using monochromatic CuK $\alpha$  radiation ( $\lambda = 0.15418$  nm). The XRD was operated at 40 kV and 200 mA with a step width of  $0.02^\circ$  and a scan speed of  $4^\circ \text{ min}^{-1}$  ( $\alpha_1 = 0.154057$  nm,  $\alpha_2 = 0.154433$  nm). ICP measurements were performed on an SPS 1800H plasma spectrometer of Seiko Instruments Inc. (Ni: 221.7162 nm and Sn: 189.898 nm). The BET surface area ( $S_{\text{BET}}$ ) and pore volume ( $V_p$ ) were measured using  $\text{N}_2$  physisorption at 77 K on a Belsorp Max (BEL Japan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the BET surface area via the BET equation. The pore volume was estimated to be the liquid volume of nitrogen at a relative

pressure of approximately 0.995 according to the Barrett–Joyner–Halenda (BJH) approach based on desorption data (Lowell et al., 2004). SEM images of the synthesised catalysts were taken on a JEOL JSM-610SEM after the samples were coated using a JEOL JTC-1600 autofine coater.

The  $\text{H}_2$  uptake was determined through irreversible  $\text{H}_2$  chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was treated at 673 K under  $\text{H}_2$  for 30 min. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. The  $\text{H}_2$  measurement was conducted at 273 K, and  $\text{H}_2$  uptake was calculated according to the method described in the literature (Bartholomew et al., 1980; Bartholomew and Panel, 1980).

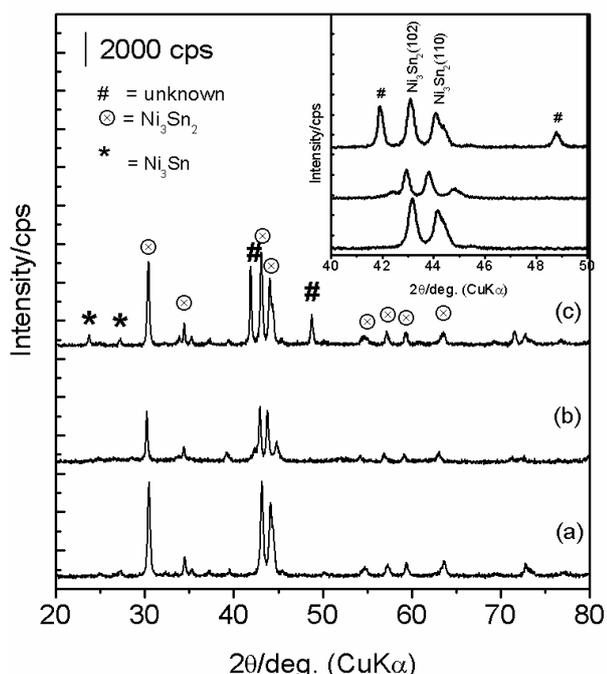
## RESULTS AND DISCUSSION

The bulk composition, BET specific surface area, maximum H<sub>2</sub>-uptake, and SEM images of synthesised intermetallic Ni<sub>3</sub>Sn<sub>2</sub> have already published elsewhere (Rodiansono et al., 2012a). We report here the XRD data of the synthesised intermetallic Ni<sub>3</sub>Sn<sub>2</sub>.

### Effect of hydrothermal temperature

The effect of hydrothermal temperature in the formation intermetallic Ni-Sn(1.5) was evaluated at 423-523 K and XRD patterns of the results are shown in

**Figure 2.**



**Figure 2.** XRD patterns of intermetallic Ni-Sn (1.5) that obtained at different hydrothermal temperature. (a) 423 K, (b) 473 K, and (c) 523 K.

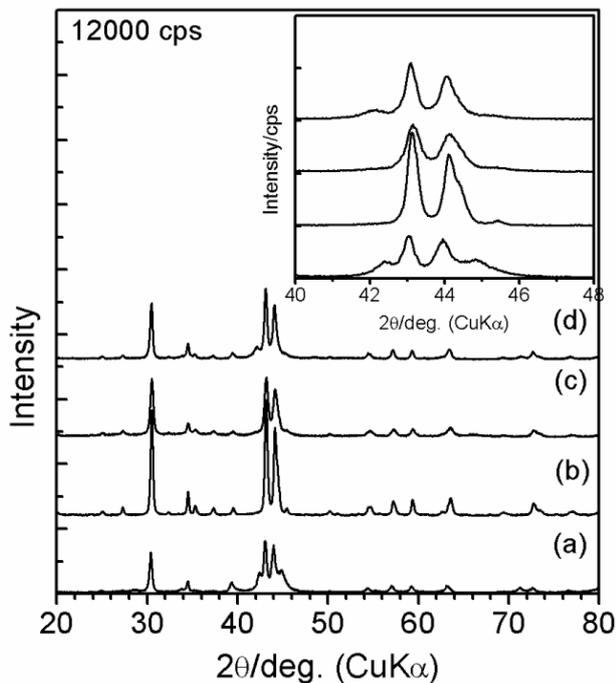
The formation of high crystalline Ni<sub>3</sub>Sn<sub>2</sub> alloy species after H<sub>2</sub> treatment at 673 K was clearly observed at temperature of hydrothermal of 423 K (**Figure 2a**). On the

other hand, at 473 K, the formation of Ni(111) metal species at 2θ of 44.8° as well as at temperature of 523 K (**Figure 2b,c**). In addition to temperature of 523 K, the formation of Ni<sub>3</sub>Sn alloy species and unknown Ni-Sn alloy phases were also observed at 2θ of 23.6°, 27.1° and 48°, respectively. As a conclusion, the best temperature of hydrothermal for the synthesis of intermetallic Ni<sub>3</sub>Sn<sub>2</sub> was 423 K that much lower than that of other methods previously reported (Onda et al., 1998; Onda et al., 2000; Shabaker et al., 2004).

### Effect of length of hydrothermal

The effect of length of hydrothermal in the formation bulk structure intermetallic Ni-Sn(1.5) was evaluated at the range of 6-72 h and XRD patterns of the results are shown in **Figure 3**.

According to profile of XRD pattern, it is clearly observed that high crystalline intermetallic Ni<sub>3</sub>Sn<sub>2</sub> can be achieved after hydrothermal for 24 h at 423 K. At 12 h, the formation of Ni(111) species and unknown phase at 2θ of 42.3° and 44.8°, respectively, were observed (**Figure 3a**). However, the longer time of hydrothermal to 48-72 h, reduced the crystallite sizes of Ni<sub>3</sub>Sn<sub>2</sub>(101) species at 2θ of 30.46° from 14 nm and 13 nm, respectively (**Figure 3c,d**), compared to that of 24 h of 19 nm (**Figure 3b**). The inset in **Figure 3** (the selected area of 2θ of 40-46°) also clearly evidenced the change of crystallite sizes of Ni<sub>3</sub>Sn<sub>2</sub> species due to the prolong time of hydrothermal.



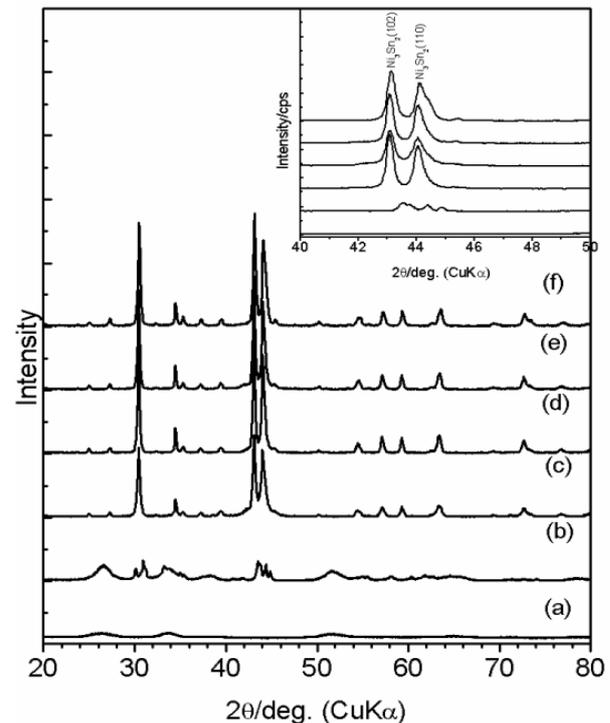
**Figure 3.** XRD patterns of intermetallic Ni-Sn(1.5) that obtained at different length of hydrothermal time. (a) 12 h, (b) 24 h, (c) 48 h, and (d) 72 h.

#### Effect of adjusted pH

Another important point of our synthetic procedure is the change of pH of precursor solution before hydrothermal treatment. The effect of adjusted pH in the formation intermetallic  $\text{Ni}_3\text{Sn}_2$  was evaluated at the range of 2-12 and XRD patterns of the results are shown in **Figure 4**.

The addition of alkaline solution is one of the important step as well as the hydrothermal treatment. We found that the formation of metal hydroxide would facilitate easily ethylene glycol or polyol to reduce it into metal species. Therefore, the presence of polyol is also important as well as the alkaline solution. XRD patterns evidenced that the formation of intermetallic  $\text{Ni}_3\text{Sn}_2$  are clearly observed after adjusted pH of 6 (**Figure 4c**). The intensity of diffraction peak

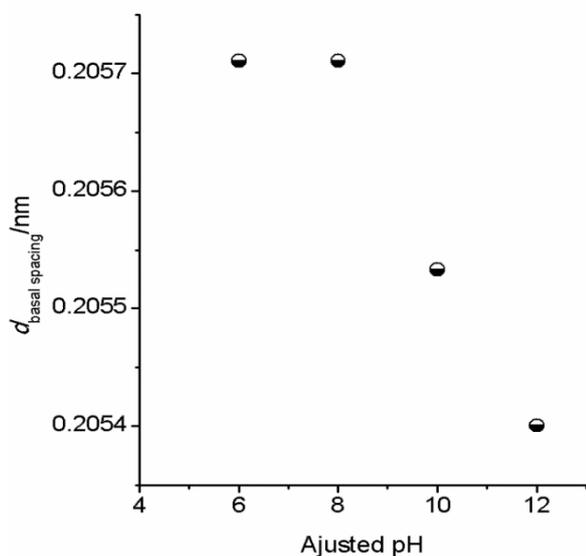
of  $\text{Ni}_3\text{Sn}_2$  species are almost similar for adjusted pH of 8-12 (**Figure 4d-f**). Therefore, we suggest that in order to obtain intermetallic  $\text{Ni}_3\text{Sn}_2$  with high crystallinity and purity, the adjusted pH of precursor solution is required at least at pH of 6.



**Figure 4.** XRD patterns of Ni-Sn(1.5) that obtained at different adjusted pH before hydrothermal process. (a) 2.0, (b) 4.0, (c) 6.0, (d) 8.0, (e) 10.0, and (f) 12.0.

According to XRD patterns of intermetallic  $\text{Ni}_3\text{Sn}_2$  as shown in **Figure 4**, we calculated the shifting of  $d$  basal spacing of  $\text{Ni}_3\text{Sn}_2(110)$  using Bragg's Law equation and the results are shown in **Figure 5**. The peak position of  $\text{Ni}_3\text{Sn}_2(110)$  shifted to lower degree and as a results the  $d$  value decreased as the increase of adjusted pH. We suggest that at concentrate alkaline, the metal hydroxide was completely formed as an important step for reducing by ethylene glycol or during  $\text{H}_2$  treatment rather than the formation of metal oxide. Our current results

are good agreement with the previous work as reported by Saputra et al. (Saputra et al., 2014).



**Figure 5.** Change of  $d_{\text{basal spacing}}$  (nm) of  $\text{Ni}_3\text{Sn}_2(110)$  as a function of adjusted pH.

## CONCLUSIONS

XRD investigation on the synthesised intermetallic  $\text{Ni}_3\text{Sn}_2$  systems those were prepared via a thermochemical method. The temperature of hydrothermal, length of hydrothermal treatment, and adjusted pH were found significantly affected to the formation of high crystalline intermetallic  $\text{Ni}_3\text{Sn}_2$ .

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