

MATERIALS AND METHODS

Materials

1. Reagents

- Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, Carlo, 99.5%) was distilled at 190°C under normal atmospheric pressure, prior to use. Pure ethylene glycol was collected and stored under molecular sieves in a dry bottle.

- Nickel hydroxide [$\text{Ni}(\text{OH})_2$, 66.4% as NiO] was obtained by precipitation method. The base (conc. NH_4OH) was added dropwise into 0.5 M nickel chloride solution with constant stirring until the precipitate occurred. The precipitate was filtered, washed with deionized water and dried in an oven at 110°C for 2 h.

All listed of the following chemicals were used as purchased without further purification

- Nickel nitrate hexahydrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Carlo, 99.0%]
- Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Ajax, 99.0%)
- Nickel acetate tetrahydrate [$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Across, 99.0%]
- Aluminium hydroxide hydrate [$\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$, Aldrich, 63.2% as Al_2O_3]
- Triethanolamine [$\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, Carlo, 98.0%]
- Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Carlo, 99.8%)
- n-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, Carlo, 99.5%)
- Iso-propanol [$(\text{CH}_3)_2\text{CHOH}$, Fluka, 99.8%]
- Nitric acid (HNO_3 , Lab scan, 70.0%)
- Ammonium hydroxide (NH_4OH , Merck, 25.0%)
- Dimethyl sulfoxide- d_6 [$(\text{CD}_3)_2\text{SO}$, Aldrich, 99.9%]

2. Instrumentation

- Electrospray Ionization Mass Spectrometer (Bruker Esquire mass spectrometer)
- ^1H - and ^{13}C -Nuclear Magnetic Resonance Spectrometer (INOVA VARIAN NMR Spectrometer 400 MHz)
- Thermogravimetric Analyzer (Perkin-Elmer TGA 7)
- Horizontal tube furnace (Lenton thermal designs)
- X-ray diffractometer (Philips P.W.1830)
- Fourier Transform Infrared Spectrophotometer (Perkin-Elmer 2000-FTIR)
- Scanning Electron Microscope (JEOL JSM-6301F)
- Surface Area and Porosimetry Analyzer (Micromeritics ASAP 2020 surface analyzer)
- pH meter (WTW, Inolab level1)

Methods

1. Preparation of nickel aluminate precursor by the One Pot Synthesis

The appropriate condition for synthesizing nickel aluminate precursor was studied. Aluminium hydroxide hydrate, $[\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}]$ (63.2% as Al_2O_3 16.10 g, 100 mmol), nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (29.07 g, 100 mmol), 3 mol equivalent of triethanolamine (TEA, 40.0 ml, 300 mmol), were loaded to a 250 ml round bottom flask in a presence of solvent (60 ml ethylene glycol, EG). The reaction mixture was heated with heating mantle to 140°C under continuous stirring as shown in Figure 8. During the reaction proceed; water was produced as a by-product, which was distilled off along with solvent (EG). Subsequent portion of EG (60 ml) was added and continuous heating until homogeneous solution took place. Further heating was applied in order to remove excess EG. Finally, the greenish viscosity product was obtained. The warm product was transferred to a dried bottom.

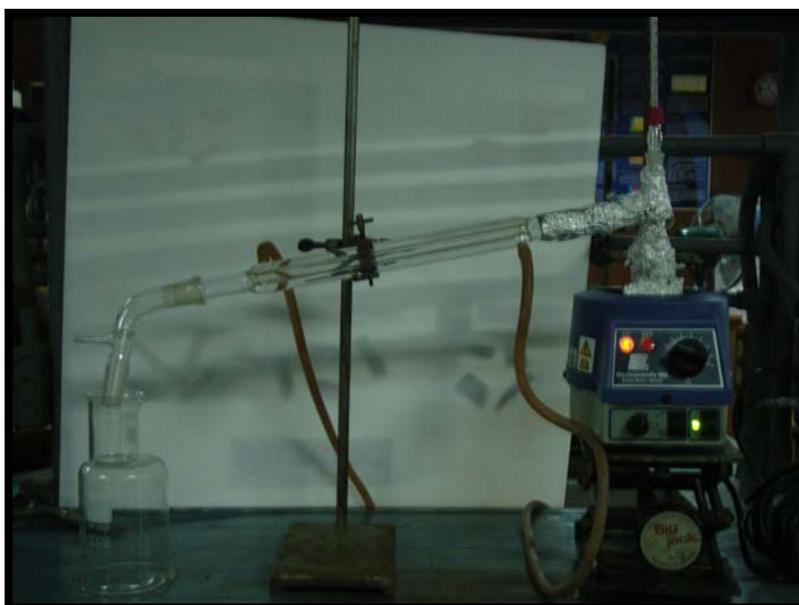


Figure 8 Apparatus set up for preparation of nickel aluminate precursor by the One Pot Synthesis

Attempt to prepare nickel aluminate precursor from other nickel (II) salts was also studied, using the same procedure as previously described. Various nickel(II) salts, such as nickel chloride hexahydrate [$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (23.770 g, 100 mmol)], nickel hydroxide [$\text{Ni}(\text{OH})_2$ (11.2 g, 100 mmol)] or nickel acetate tetrahydrate [$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (24.886 g, 100 mmol)] was mixed with $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ (63.2% as Al_2O_3 16.10 g, 100 mmol), TEA (40 ml, 300 mmol), and EG (60 ml) in a 250 ml round bottom flask. The reactions were performed at 140°C for approximately 7 h. The homogeneous products obtained were kept separately in a dried bottom. All precursor products obtained were characterized by ESI-MS, ^1H -, ^{13}C -NMR and FTIR.

2. Preparation of nickel aluminate spinel

2.1 Preparation of nickel aluminate spinel directly from nickel aluminate precursor.

The nickel aluminate precursor which obtained via the one pot synthesis was put in an alumina crucible and calcined in a horizontal tube furnace. Variations of the calcined conditions are presented in table 2. The calcination time for each temperature ranging from 500°C - 900°C is 5 h and for 1000°C; 2, 3, 4 and 5 h. Step of calcination temperature also carried out at 500°C for 5 h and held at 1000°C for 5 h. The obtained powder samples were ground in an alumina mortar and characterized by FTIR, XRD, SEM and BET.

Table 2 The calcined conditions of nickel aluminate precursor

Calcination temperature	Calcination time
500°C	5 h
600°C	5 h
700°C	5 h
800°C	5 h
900°C	5 h
1000°C	2, 3, 4 or 5 h
Step calcination at 500°C, 5 h and 1000°C, 5 h	

2.2 Preparation of nickel aluminate spinel via sol gel process.

The appropriate conditions for preparations of NiAl_2O_4 spinel via sol-gel process were studied by changing five processing parameters:

i) Spinel precursor sources.

Due to different nickel(II) salts were used as starting materials for synthesizing nickel aluminate precursors via one pot process. Two nickel aluminate precursor sources, designed as SPNO and SPAC, representing the nickel aluminate precursor obtained from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, respectively, were employed to study gel formation.

ii) Concentrations of precursors

A series of SPNO and SPAC alcoholic solution with various concentrations of 16.0, 20.0, 24.0, 28.0 and 32.0%(w/v) were prepared by weighting precursor 4.0, 5.0, 6.0, 7.0 and 8.0 g, respectively and the final volume of solution was 25.00 ml.

iii) Type of solvents.

The nickel aluminate precursor (SPNO and SPAC) were dissolved in alcohol: ethanol, n-propanol or iso-propanol.

iv) pH

Conc. HNO_3 and conc. NH_4OH were used to adjust pH values of alcoholic precursor solutions. The pH values studied were 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0.

v) Gelation temperatures

The gelation temperatures were investigated at room temperature ($\approx 30^\circ\text{C}$) and incubated at 60°C in an oven.

The block diagram of nickel aluminate spinel powders prepared via sol-gel method is briefly shown in Figure 9.

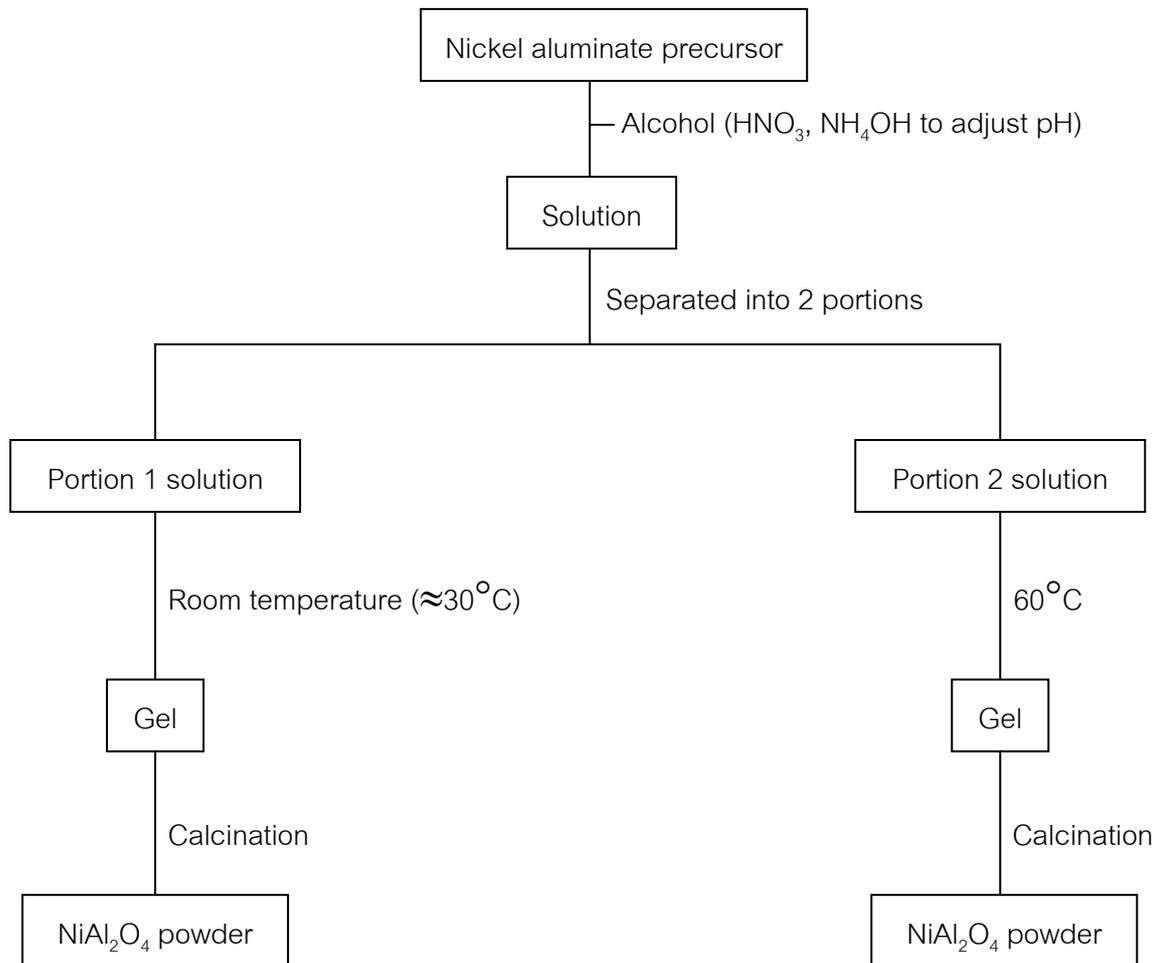


Figure 9 Block diagram of nickel aluminate spinel powders prepared via sol-gel method

Preparation solutions for sol-gel studied are described in detail in the following.

2.2.1 Studied the effect of concentration and spinel precursor source

4.0, 5.0, 6.0, 7.0 and 8.0 g of SPNO precursor in five separate 100 ml beakers, was dissolved with approximately 15.0 ml of ethanol and mixed with a vigorous stirring at room temperature until the precursor is completely dissolved. Each solution was transferred to 25 ml volumetric flask in which 1.00 ml of distilled water was

presented. The volume of alcoholic precursor solutions was adjusted to 25 ml by adding ethanol, resulting in a series of SPNO precursor solutions with concentrations of 16.0, 20.0, 24.0, 28.0 and 32.0%(w/v). pH measurement of these solutions was found to be 9.0. The 16.0, 20.0, 24.0, 28.0 and 32.0%(w/v) series of alcoholic precursor solutions were collected into dried vials and divided each solution into two half, the first half was kept at room temperature and the second half was incubated at 60°C in an oven. Finally, the duration time that used to form gel (gelation time) was noticed and recorded at room temperature and 60°C.

Series of 16.0, 20.0, 24.0, 28.0 and 32.0%(w/v) SPAc spinel precursor solutions in ethanol were prepared in the same procedure. The gelation times of all solutions were observed at both room temperature and 60°C. The pH of SPAc alcoholic precursor solutions obtained was 11.0.

2.2.2 Studied the effect of solvents

The same procedure as described in section 2.2.1 was repeated, but used n-propanol or iso-propanol to dissolve the precursors.

2.2.3 Studied the effect of pH

Firstly, strong acidic and basic solutions of alcohol (ethanol, n-propanol and iso-propanol) were prepared. Concentrate HNO₃ and/or conc. NH₄OH were added to alcohol until the pH range demonstrated in Table 3 was reached. All of these acidic and basic alcoholic solutions were used to dissolve and adjust the specific pH value of spinel precursor solutions throughout these experiments.

Series of alcoholic precursor solutions were prepared in the same procedure as described in section 2.2.1 or 2.2.2, but used strong acidic and basic

solutions of alcohol (ethanol, n-propanol and iso-propanol) as mentioned above to dissolve and adjust the specific pH value of spinel precursor solutions. For example, acidic ethanol pH around 0.40 - 0.60 was used to dissolve 4.0 g of SPNO precursor, resulting in 16.0%(w/v) of SPNO precursor solution with pH 6.0. For the other pH values (7.0, 8.0 and 10.0), use the list of solvent that has the pH values shown in Table 3.

All conditions studied for sol-gel formation are shown in Table 4.

The gel formation occurred at a particular condition was calcined in a furnace at 1000°C for 5 h and step heat treatment at 500°C for 5 h and held at 1000 °C for 5 h, resulted in a greenish blue powder. All powder products obtained were investigated by XRD and SEM.

Table 3 The pH values of solvents on the preparation of NiAl₂O₄ spinel via sol-gel process

Spinel precursor source	pH value of the obtained alcoholic precursor solution	pH range of solvent used for dissolving precursor		
		ethanol	n-propanol	iso-propanol
SPNO	6.0	0.40-0.60	0.20-0.30	0.20-0.30
	7.0	0.70-1.00	0.40-0.50	0.40-0.50
	8.0	1.10-1.30	0.60-0.70	0.60-0.70
	9.0	*	*	*
	10.0	13.30-13.40	12.70-12.80	12.50-12.60
SPAc	7.0	0.20-0.30	0.09-0.10	0.09-0.10
	8.0	0.40-0.60	0.20-0.30	0.20-0.30
	9.0	0.70-1.00	0.40-0.50	0.40-0.50
	10.0	1.10-1.30	0.60-0.70	0.60-0.70
	11.0	*	*	*

* = no addition of conc. HNO₃ and/or conc. NH₄OH