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Full Paper

Nickel-aluminium complex: a simple and effective precursor for nickel aluminate ($NiAl_2O_4$) spinel

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Abstract: A reaction of aluminium hydroxide, nickel nitrate and triethanolamine in ethylene glycol provided, in one step, a simple and effective nickel-aluminium complex precursor for $NiAl_2O_4$ spinel. On the basis of ^{1}H-, ^{13}C-NMR spectroscopy, and mass spectrometry, the possible structure of the complex was proposed as a trimetallic double alkoxide consisting of two four-coordinate TEA-Al (alumatrane) moieties linked via a bridging TEA group enfolding the Ni^{2+} cation. Transformation of the nickel-aluminium complex to pure spinel occurred when the complex precursor was pyrolysed at 1000°C for 5 h. The BET surface area of the pyrolysed product was found to be 31 m^2/g. In addition, the morphology of the powder product was examined by SEM.

Keywords: nickel complex, nickel aluminate, spinel, one-pot process

Introduction

Nickel aluminate spinel ($NiAl_2O_4$) has received attention as a catalyst solid support due to its stability, strong resistance to acids and alkalis, and high melting point [1]. The ceramic material possesses a unique structure consisting of grains, grain boundaries, surfaces and pores, making it suitable for use as catalyst support when its microstructures are controlled [2].

Recently, the development of $NiAl_2O_4$ for advanced applications, especially as a solid support for metal catalysts, has been carried out. Salagre et al. studied the synthesis of $NiAl_2O_4$ for use as nickel catalyst support for the hydrodechlorogenation of 1,2,4-trichlorobenzene in the gas phase [1]. Rodeghiero et al. reported the transformation of Ni/Al layered double hydroxides to Ni/Al_2O_3 and $Ni/NiAl_2O_4$ composites which have found utility as methanation catalysts in the treatment of carbon monoxide rich gases [3]. Jin et al. focused on a new looping material based on the addition of the new binder, $NiAl_2O_4$, and applied it to chemical looping combustion [4]. Cesteros et al. discussed the effect of preparation conditions for nickel aluminium hydroxide gels and calcination temperatures on the final structure of the $NiAl_2O_4$. The obtained spinel may be consequently used in catalytic system of hydrogenation reactions and in preparation of more resistant reduced catalysts [5]. Joo and co-workers observed the effect of calcination temperatures on the catalytic activity and the stability of Ni/Al_2O_3 catalysts for CH_4 dry reforming [6]. However, for producing advanced ceramics, chemical routes offer many advantages over traditional methods, including control of homogeneity and purity of product, processing at lower temperatures, and control of the size, shape and distribution of the ceramic particles. Moreover, chemical techniques are often used for producing thin films and fibres [7-8].

Up to now, various synthetic routes for spinel have been reported, such as co-precipitation of hydroxides, sol-gel formation method, and solid-solid reaction [9-11]. However, the cost of starting materials, the homogeneity and purity, including processing temperatures are the most important disadvantages for these synthetic routes. A wide variety of inexpensive preceramic polymers derived directly from metal hydroxides and oxides has been therefore developed. One of the simple and straight- forward methods is the "oxide one-pot synthesis (OOPS)" process [12]. This method was applied to prepare $MgAl_2O_4$ spinel [13].

Recently, Laobuthee et al. studied the ceramic oxide of magnesium aluminate ($MgAl_2O_4$) spinel prepared via OOPS process for use as a humidity sensing material [14-16]. The obtained $MgAl_2O_4$ exhibited a similar performance compared to those prepared by other methods. The humidity responses of the spinel exhibited good linear relationship between the logarithm of resistance and the relative humidity (RH). The considerably high sensitivity and reproducibility of this spinel was also observed [14-16].

Due to the advantages of one-pot process as mentioned above and $NiAl_2O_4$ also having the same structure as $MgAl_2O_4$, in this research work the nickel-aluminium complex precursor of $NiAl_2O_4$ was then synthesised by the same procedure as the OOPS process. In our study, nickel nitrate was, however, employed as starting material in place of nickel oxide for preparing the nickel-aluminium complex.

Materials and Methods

Materials

Aluminium hydroxide hydrate, $[Al(OH)_3.xH_2O]$ and nickel nitrate, $[Ni(NO_3)_2.6H_2O]$ were purchased from Aldrich Chemical Co. Inc (USA) and Carlo Erba (Barcelona), respectively. They were used as received. Ethylene glycol $[HOCH_2CH_2OH]$ was purchased from Carlo Erba (Barcelona), and distilled prior to use. Triethanolamine [TEA, $N(CH_2CH_2OH)_3$, 98% purity] was obtained from Carlo Erba (Barcelona) and used as received.

Instrumental

The complex precursor was characterised by ^{1}H- and ^{13}C-NMR (INOVA VARIAN NMR Spectrometer 400 MHz). The NMR spectrometer operating in the quadrature mode was used to obtain ^{1}H- and ^{13}C-NMR spectra. Typical ^{1}H-NMR spectrum consisted of 16 transients of 23,954 data points over a 6.39 kHz bandwidth using a 3.2 μs at 45° pulse. Typical ^{13}C-NMR spectrum consisted of 25,600 transients of 30,144 data points over a 25.16 kHz bandwidth using a 7.25 μs at 45° pulse. Deuterated dimethylsulfoxide (DMSO-d_6) was used as solvent for the complex precursor. Mass spectrum was obtained from ESI-MS (Bruker Esquire mass spectrometer). Methanol was used as a solvent to prepare a complex solution for MS measurement. The mass range of a complex was set from m/z 100 to 1000. The decomposition phenomena and weight loss of the complex was studied by thermogravimetric analysis (TGA) (Perkin-Elmer TGA 7). A sample (10 mg) was heated at a rate of 5°C/min in N_2 (20 psi) from 27-1000°C. The TGA balance flow meter was set at 20 psi N_2, while the purge flow meter was adjusted at 20 psi of synthetic air.

The pyrolysed sample was characterised by X-ray diffraction (XRD) (Phillips P.W.1830 diffractometer). The powder sample was spread on double-sided sticky tape and mounted on glass microscope slides. Diffraction patterns were recorded over a range of 2θ angles from 15 to 80° and the crystalline phase was identified from the Joint Committee on Powder Diffraction Standards (JCPDS) file No. 10-0339 [1-2, 5]. Fourier Transform infrared spectra of $NiAl_2O_4$ were obtained on a Perkin-Elmer 2000-FTIR. Potassium bromide (KBr), powdered with an agate mortar and pestle, was used as non-absorbing media. Samples (0.3-0.5 wt%) were rigorously mixed with the KBr powder to prepare pellet specimens for identifying the spinel phase. Scanning electron micrographs (SEM) were obtained with a JEOL JSM-6301F scanning microscope operating at an acceleration voltage of 20 kV, a work distance of 15 mm and magnification values in 10,000x to identify the powder sample microstructures. Samples were mounted on alumina stubs using a liquid carbon paste and then sputter coated with Au to avoid particle charging. The Brunauer-Emmett-Teller (BET) surface area was calculated from the nitrogen adsorption isotherms at 77 K using a Micromeritics ASAP 2020 surface analyser and a value of 0.162 nm^2 for the cross-section of the nitrogen molecule. Samples were degassed at 350°C under high vacuum for 20 h before measurement.

Methods

The nickel-aluminium complex for $NiAl_2O_4$ spinel was prepared via one pot process as follows. Aluminium hydroxide hydrate, [$Al(OH)_3.xH_2O$ (63.2% as Al_2O_3 16.10 g, 100 mmol)], nickel nitrate hydrate [$Ni(NO_3)_2.6H_2O$ (29.07 g, 100 mmol)], 3 mol equivalent of triethanolamine (TEA, 40.0 ml, 300 mmol) and 60 ml of ethylene glycol (EG) as solvent, were added into a round bottomed flask. The mixture was then heated to 140°C to distill off EG and the water by-product produced during the reaction. The reaction mixture was continuously distilled for approximately 7 h. The homogeneous products obtained were characterised by ESI-MS, TGA, ^{1}H- and ^{13}C-NMR.

The nickel-aluminium complex was pyrolyzed in the horizontal tube furnace at 500°C for 5 h and then 1000°C for 5 h. The product was ground in an alumina mortar and then characterised by XRD, BET, and SEM.

Results and Discussion

In this present work, nickel nitrate was used instead of nickel oxide because it was easily dissolved in solvent as compared to nickel oxide. The reaction temperature for preparing the complex was consequently decreased to 140° C. The reaction of $Al(OH)_3$, $Ni(NO_3)_2$, and TEA was complete in 7 h resulting in a clear and black-green color solution. The product solution became a black-green viscous product when EG was removed. The product showed a good solubility in water and alcohols, such as, ethanol, n-propanol, and iso-propanol.

The structure of nickel-aluminium complex was determined by electrospray ionization (ESI) technique. The major peak as the protonated parent ion appeared at m/z = 554. The possible structure of product was proposed to be a trimetallic species, consisting of one TEA ligand per metal center (Figure 1). To minimise the charge separation for the most stable structure of the dipositive cation complex, it was assumed that the Ni^{2+} ion is enfolded by the third TEA, whose oxygen and nitrogen atoms can donate electrons to complex with the nickel ion as shown in Figure 1 [13-15].

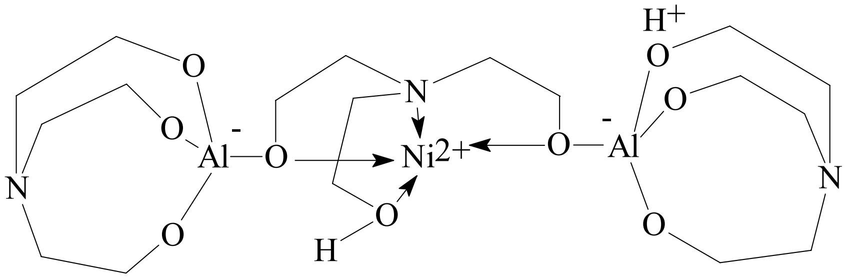

Figure 1. The proposed structure of nickel-aluminium complex (m/z =554)

The ^1H-NMR result for the nickel-aluminium complex is presented in Table 1. It was found that the peaks for methylene groups adjacent to oxygen and nitrogen atoms, occurred at chemical shifts of 3.452 ppm (triplet), and 2.637 ppm (triplet), respectively. Both peak positions shift 0.08 and 0.15 ppm respectively to downfield position compared to the free TEA.

Table 1. ^1H-NMR peak positions and assignments for nickel complex precursor

Peak position (ppm)	**Assignment**
2.49 (t)	$N(C\mathbf{H_2}CH_2OH)_3$, free TEA
3.37 (t)	$N(CH_2C\mathbf{H_2}OH)_3$, free TEA
4.45 (br)	OH of TEA either coordinated to Ni^{2+} or free TEA
2.64 (t)	$NC\mathbf{H_2}CH_2OAl$
3.45 (t)	$NCH_2C\mathbf{H_2}OAl$

The ^{13}C-NMR spectrum of the nickel-aluminium complex consists of four different peaks. The peaks at 54.759 and 59.646 ppm are assigned to the carbons of ethyleneoxy groups bound to Al while the peaks at 59.867 and 60.914 ppm are the most probable positions for the bridging TEA ligand (Table 2).

Table 2. ^{13}C-NMR peak positions and assignments for nickel complex precursor

Peak position (ppm)	Assignment
54.31	$N(\mathbf{C}H_2CH_2OH)_3$, free TEA
54.76	$N\mathbf{C}H_2CH_2OAl$
59.87	Bridging $N\mathbf{C}H_2CH_2O$
59.65	$NCH_2\mathbf{C}H_2OAl$
60.91	Bridging $NCH_2\mathbf{C}H_2O$
63.45	$N(CH_2CH_2OH)_3$, free TEA

The results also showed that it is not easy to distinguish between the free ethyleneoxy and the bridging groups. It might be due to the fact that the carbon peak (and proton) positions of the free ethyleneoxy group are close to those of the two bridging groups. However, the retained free TEA could be burned out during the pyrolysis.

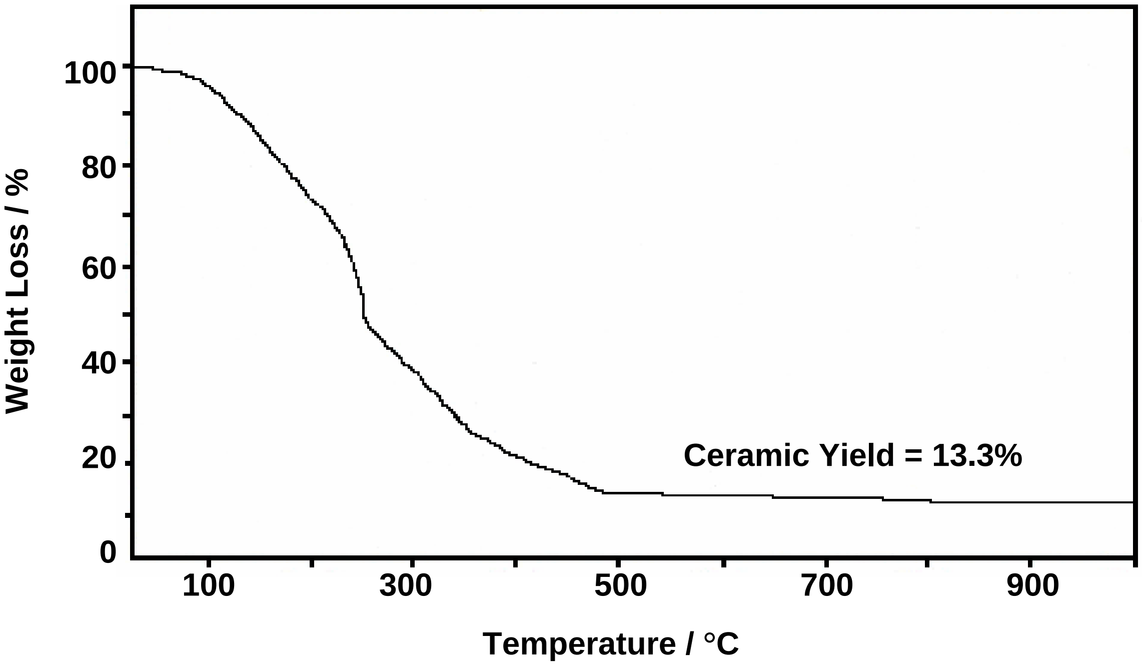

Figure 2. TGA thermogram of nickel-aluminate complex

To obtain $NiAl_2O_4$, the nickel-aluminium complex was then studied by TGA. The thermogram (Figure 2) shows three regions of mass loss. The first mass loss occurring between 100° and 250°C involved the decomposition of the organic ligand. In this step, volatiles and char were generated [13-15]. The char obtained was then oxidised during continuous heating from 250° to 500°C as shown in the region of second mass loss (Figure 2). The final mass loss occurred at 500-800°C. It should be noted that in the final mass loss, some $NiCO_3$ was formed. The formation of $NiCO_3$ during ligand decomposition could be confirmed by the FTIR result which shows a broad peak of low intensity and broad peak at approximately 1508 cm^{-1} (Figure 3).

After pyrolysing the complex at 500°C for 5 h and then at 1000°C for another 5 h, the obtained product had a blue colour. As the nickel-aluminium complex was a highly viscous liquid, the decomposition products, such as CO, CO_2, H_2O and volatile hydrocarbons produced during the pyrolysis of the complex were difficult to escape and retained in the resulting product. Consequently, a gas-filled and foam-like structure was obtained [13-15].

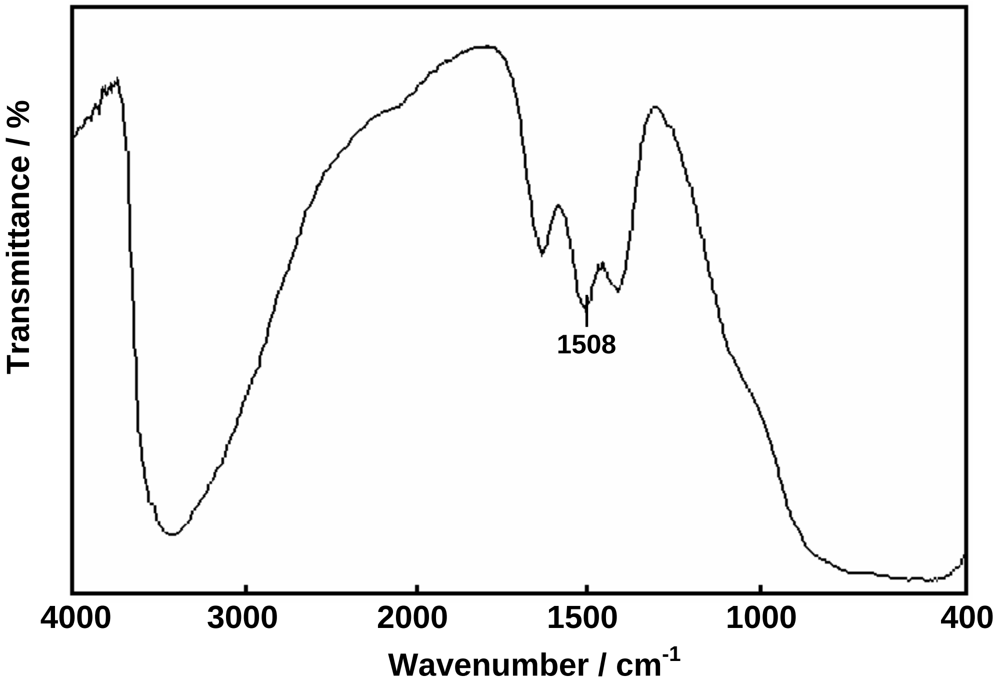

Figure 3. FTIR spectrum of the spinel precursor pyrolysed at 600°C for 5 h

Figure 4 shows the powder X-ray diffraction pattern of the $NiAl_2O_4$ obtained by calcination at 500°C for 5 h and then at 1000°C for another 5 h. All peak positions were identified by comparing with JCPDS file No. 10-0339. The major peaks for spinel were the *hkl* reflection of 311, 400 and 440. The diffraction peaks in Figure 4 indicate the phase purity of the $NiAl_2O_4$ spinel.

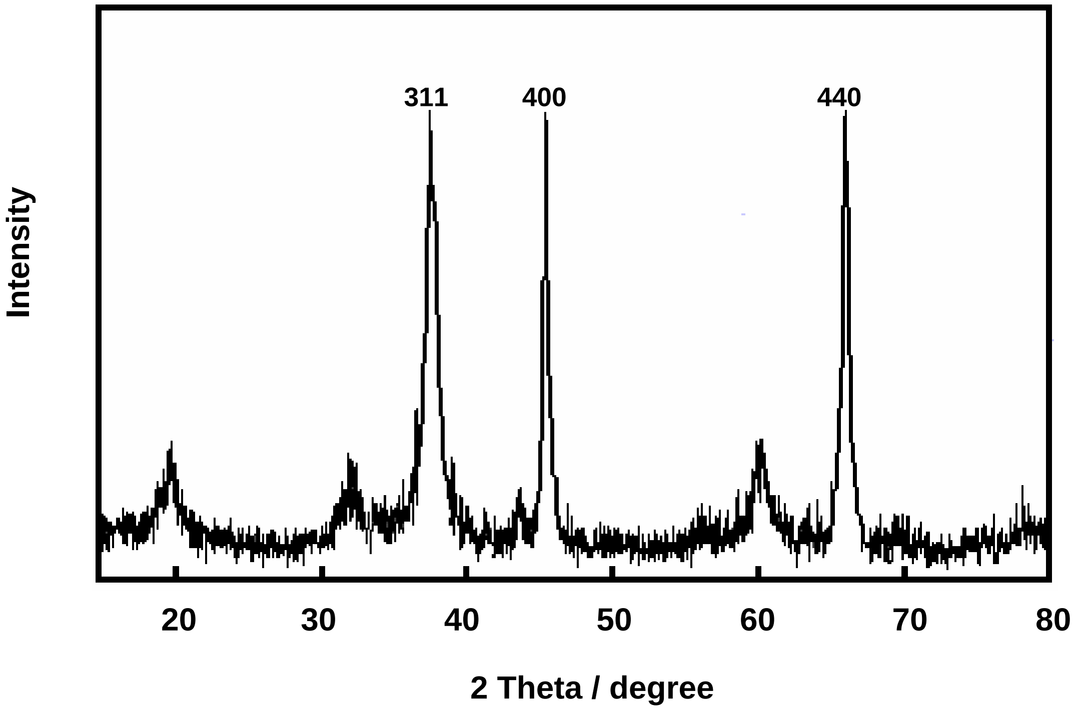

Figure 4. Powder X-ray diffraction pattern of the $NiAl_2O_4$

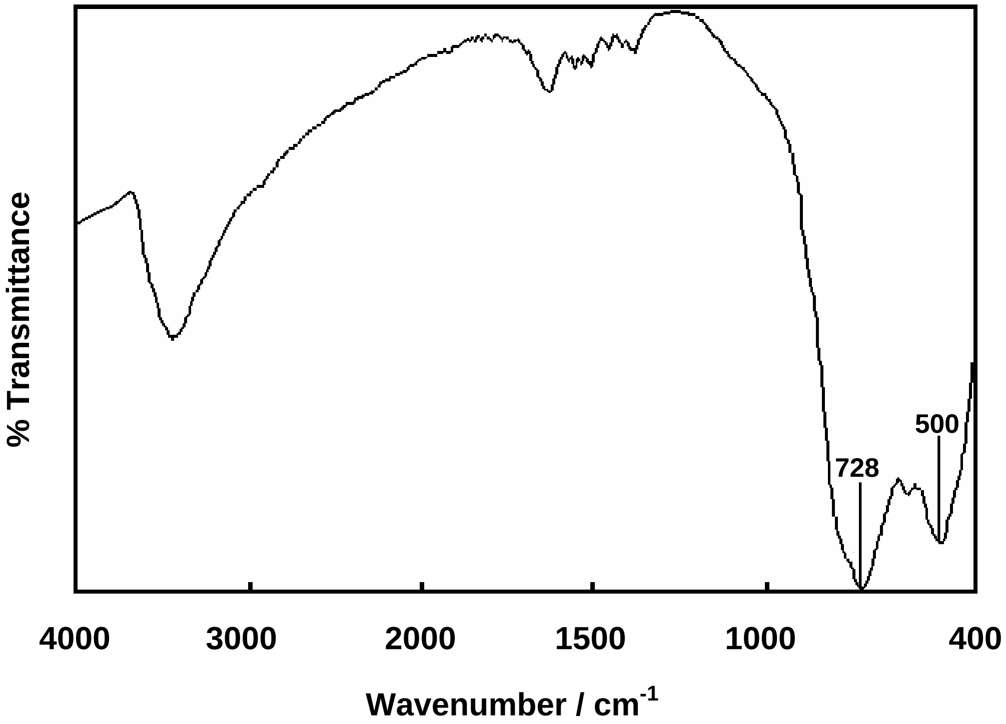

Figure 5. FTIR spectrum of the spinel precursor pyrolysed at 500°C for 5 h and then at 1000°C for 5 h

FTIR spectrum (Figure 5) shows two characteristic peaks of the spinel phase at approximately 728 and 500 cm^{-1}. The peak at 728 cm^{-1} is associated with the lattice vibrations of tetrahedrally coordinated Al-O. The peak at 500 cm^{-1} is associated with stretching vibration mode of Al-O for the octahedrally coordinated aluminium ion [17-18]. The broad peak at 3447 cm^{-1} represents the hydroxyl peak from either physisorbed water or hydrogen-bonded hydroxyl groups on the spinel surface.

The surface area of $NiAl_2O_4$ measured by BET analysis was 31 m^2/g while the pore volume examined by single point adsorption analysis was 0.10 cm^3/g and the pore size determined by adsorption average pore width analysis was 13 nm.

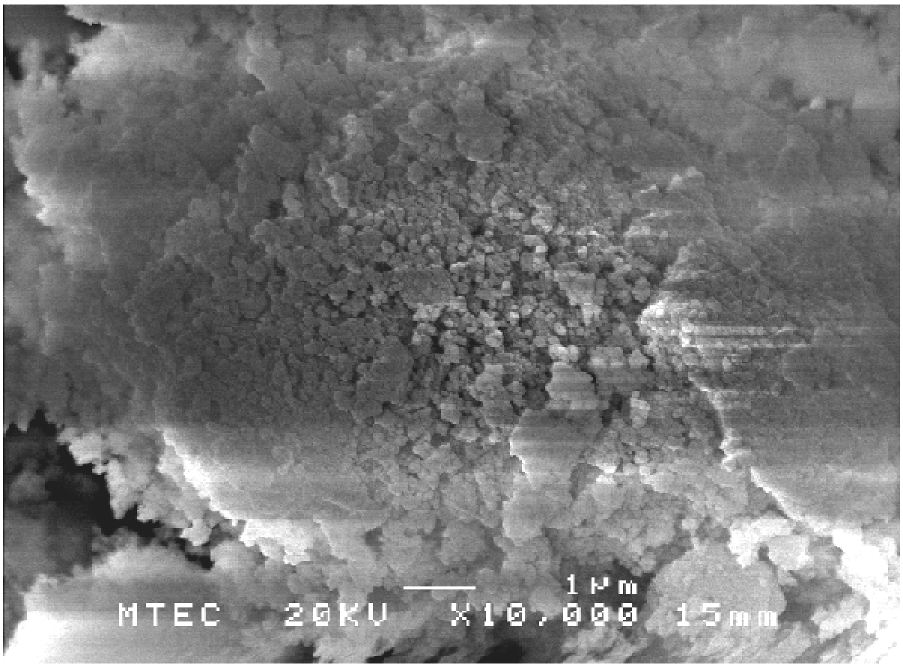

Figure 6. Scanning electron micrograph of $NiAl_2O_4$ (magnification x10,000)

The SEM micrograph of the $NiAl_2O_4$ powder is shown in Figure 6. The powder was irregularly shaped with blocky particles possibly due to the agglomeration generated during the precursor pyrolysis. The results from BET and SEM indicated that the powder obtained did not have a large surface area. However, the $NiAl_2O_4$ from the one-pot process was a highly pure compound compared with those from other previous methods [1-6].

Conclusion

The product obtained from the one-pot process was found to be a simple nickel-aluminium complex which was effective for use as a precursor for preparing pure $NiAl_2O_4$. Thus the "One Pot" process offers an inexpensive, straightforward alternative to solid-solid reaction, co-precipitation and other chemical techniques of ceramic processing, and retains the advantages of purity, homogeneity, low processing temperatures. In addition, owing to the ease of preparation and the process capability, the one- pot process may be used to prepare $NiAl_2O_4$ for catalyst applications.

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