

SYNTHESIS AND CHARACTERIZATION OF NiAl_2O_4 SPINEL

INTRODUCTION

There is currently great interest in the synthesis of mixed oxide catalyst dispersed on inert supports, for use in catalytic oxidation process. In such process, the operation temperature can often exceed 1200°C , so supported noble metals, which sinter rapidly at temperature above 600°C are unsuitable. In principle, supported oxide catalysts should have much greater thermal stability, but problem arises because chemical reaction between the active phase and the support material might occur at high temperature.

Several studies on alumina-supported nickel catalysts have shown the formation of nickel aluminate spinel, NiAl_2O_4 , which has an important effect on the final catalyst. It seems that systems have well-dispersed nickel species on their surface (Cesteros *et al*, 2000).

Commercial catalysts that are more resistant to deactivation have been developed by stabilizing the nickel on the support. Spinel is increasingly being used since they are stable compounds with high resistance to acids and alkalis, high melting points and surface areas in the range $10\text{-}100\text{ m}^2/\text{g}$.

The most general method for preparing oxide spinels (the ceramic route) involves solid state reaction of the parent metal oxides which are mechanically mixed in the form of finely divided powders. However, for attaining complete reaction, a temperature of about 1027°C (or higher) has to be maintained for several days. Under these conditions, reaction sintering leads to materials having a very low surface area; typically of about $1\text{-}5\text{ m}^2/\text{g}$. Surface areas of about $10\text{-}15\text{ m}^2/\text{g}$ can be obtained by using, as spinel precursors, aqueous solutions of mixed metal tartrates or citrates which are subsequently vacuum dried and calcined at about 900°C . However, it should be evident

that a higher surface area is desirable for catalytic applications. So many researchers have attempted to improve their surface area coupled with the high activity.

The chemical routes to ceramics offer many advantages over traditional methods, including the potential to control product homogeneity and purity, to lower processing temperatures, and to control the size, shape and distribution of the resulting ceramic particles, increasingly necessary for producing advanced ceramics. Additionally, chemical techniques can often be used to process thin films and fibers. One of them called the "Oxide One Pot Synthesis (OOPS)" process, is very simple and straightforward. It provides several advantages, as compared to other chemical techniques, e.g. low processing temperature, high purity and homogeneity. Additionally, this process could provide new chemical, polymer and ceramics, in one or two steps directly from mineral source. Precursors containing any combination of Al, Si and group I or II are readily produced with triethanolamine, $N(CH_2CH_2OH)_3$, in ethylene glycol.

In 1996, Waldner *et al.* successfully synthesized $MgAl_2O_4$ via One Pot process directly from $Al(OH)_3$ and MgO or $Mg(OH)_2$ with triethanolamine, [TEA, $N(CH_2CH_2OH)_3$] in ethylene glycol (EG) provided, in one step, access to a polymer-like precursor to spinel. The $MgAl_2O_4$ spinel product has high surface area ($160\text{ m}^2/\text{g}$) readily produced by pyrolysis of these precursors when coupled with their low cost, ease of preparation and ready processability suggests that with proper development they may provide access to useful humidity sensors or filtration applications.

The most practical method for the preparation of oxide spinels is the sol-gel process. This process usually involves the hydrolysis and condensation of various metal alkoxide molecules under controlled conditions to form metal-oxygen-metal bridging units. Each substance would exert a defined effect on different reaction step, which in turn would produce materials with different textural structure, and surface properties.

Scope of work

In this work, the NiAl_2O_4 spinel precursor was prepared by Oxide One Pot Synthesis (OOPS). Various nickel salts [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{OH})_2$, or $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] were used as nickel source and the optimal condition for preparation was determined. The NiAl_2O_4 spinel precursor obtained were characterized by Mass Spectrometry (MS), Nuclear Magnetic Resonance Spectroscopy (NMR), Infrared Spectroscopy (IR) and Thermogravimetric Analysis (TGA). The effects of calcination temperatures, calcination times and steps of calcination temperature on spinel precursor products were studied. All calcined products were investigated by X-Ray Diffraction (XRD), Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET).

The appropriate conditions for sol-gel formation of NiAl_2O_4 precursor were also determined. The sol-gel process parameters such as spinel precursor sources, concentrations, solvents, pH values and gelation temperatures were studied. The chemical and physical properties of calcined sol-gel products were analyzed and compared to those obtained OOPS products.

LITERATURE REVIEWS

Spinels

The crystal chemistry of compounds that crystallize with the spinel structure has been reviewed by Gorter, Hafner, and Blasse. The general formula of spinel is AB_2O_4 , where A and B are metals with oxidation state of II and III, respectively. Many spinel compounds have been known, such as $MgAl_2O_4$, $ZnFe_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$, $MnAl_2O_4$ and $ZnAl_2O_4$. The spinel structure is cubic unit cell, containing 8 molecules of fcc oxygen sub-lattice, $(AB_2O_4)_8$. The unit cell of so called normal spinel has therefore 32 oxygen ions, 32 octahedral holes (half filled by B) and 64 tetrahedral holes (1/8 filled by A) (World and Dwight, 1993).

For certain spinel structures the cations may shift between the A and B sites. Inverse spinel results with general formula $B(AB)O_4$: A and half of B in octahedral sites, half of B in tetrahedral site. This is the structure of most of ferrites, the key materials for ceramic magnets and magnetic storage media (tapes, disks etc). Examples of inverse spinels include $FeMgFeO_4$, $FeNiFeO_4$, $FeCoFeO_4$, Fe_3O_4 , $NiAl_2O_4$ and $CuAl_2O_4$.

Additionally, mixed spinel structure is also possible, with wide variation in composition. The general formula of mixed spinel is therefore $(A_{1-x}B_x)(A_xB_{2-y})O_4$.

The spinels crystallize with the space group $Fd\bar{3}m$. The general features of the spinel structure are shown in Figure 1, where the unit cell of edge a is subdivided into eight octants with edge $a/2$. Ideally, the anions are positioned the same way in all octants. Each octant contains four anions (oxide ions) corners of a tetrahedron. The positions of the cations are indicated in Figure 1. For one octant, the occupied tetrahedral sites are the center and four corners. In the adjacent octant the central site is vacant and as a result of symmetry, half of the corner sites are occupied. The occupied

octahedral B sites are located only in the latter octant. The four metal ions and the oxygen, in this octant, constitute a cube with edge $a/4$. For many spinels, the anion sublattice is distorted because of the differences in sizes of the cations. The tetrahedral sites are relatively small and generally will not provide sufficient space for the A-site cations without expanding the site. This expansion is accomplished by a displacement of the four anions away from the tetrahedral cations along the body diagonals (111direction) of the octants containing central A-site metal ions. In the "octahedral octant," the anions are displaced in such a way that this oxygen tetrahedron shrinks by the same amount as the first expands. Thus, cubic symmetry is preserved. A quantitative measure of the anion displacement is the anion parameter u , which is shown in Figure 1 and is ideally equal to $3/8$. In addition to the unit cell edge, the u parameter is the only other variable distance in the spinel structure and from the u parameter, the position of every atom in the unit cell can be determined.

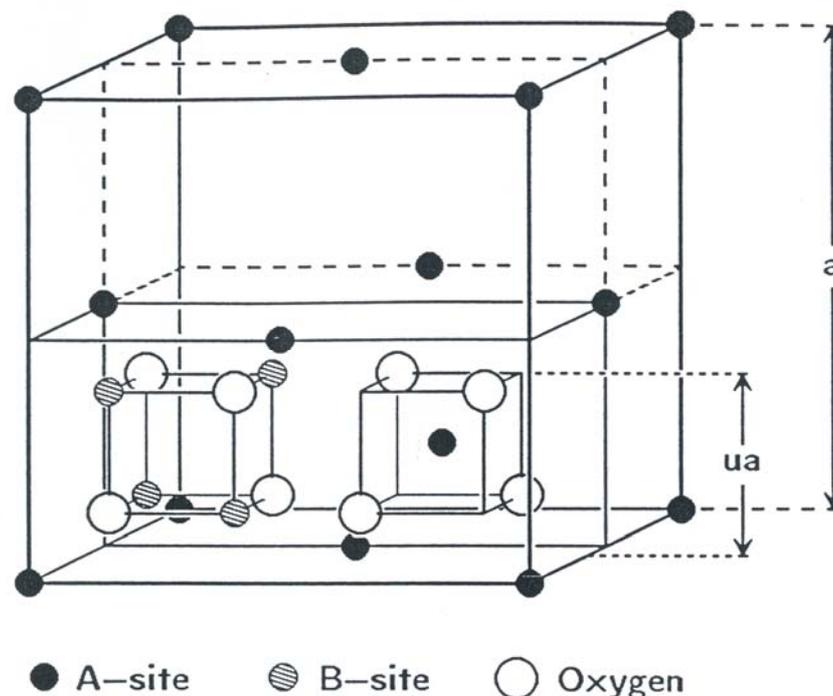


Figure 1 Two octants of the spinel unit cell.

Source: World and Dwight. (1993)

To consider the various interactions possible in the spinel structure, the symmetry of the cation outer-electron wave functions is important. In Figure 2, it can be seen that the A-site cations have the triply degenerate t_{2g} orbitals pointing away from all neighboring ions. B-site cations have the e_g orbitals pointing toward near-neighbor anions, while the t_{2g} orbitals point toward neighboring B-site cations.

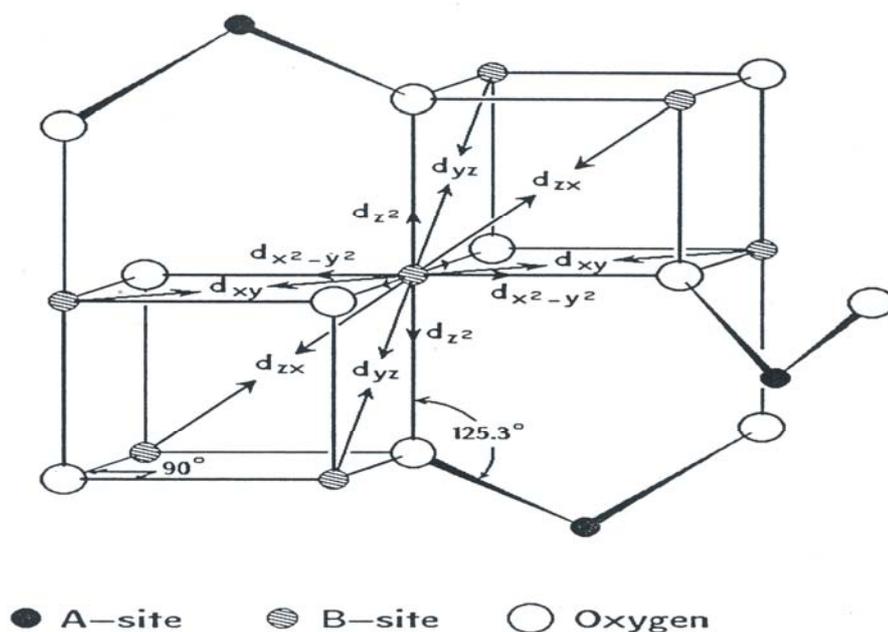


Figure 2 Orientations of the B-site cation d orbitals with respect to the spinel structure.

Source: World and Dwight. (1993)

Each oxide ion in the spinel structure is surrounded by one A- and three B-site cations arranged in a tetrahedron with the anion in the center. The angle AOB is about 125° , and the angle BOB is about 90° . The BB distance is $(1/4)a\sqrt{2}$, the AA distance is $(1/4)a\sqrt{3}$. The shorter BB distance is related to the fact that the oxide octahedra surrounding the B-site cations share edges, whereas the oxide tetrahedra surrounding the A-site cations do not have any contact.

Many compounds with the spinel structure have been reported in the literature. Most of them are oxides, although a number of spinels contain fluoride, chloride, cyanide, sulfide, selenide, and telluride ions.

It can be seen from Figure 2 that the B-site cations have t_{2g} orbitals directed in such a way that they can interact with other B-site cations by direct overlap of their wave functions. For this interaction to occur, the orbitals must extend far enough out in space to overlap. The degree of direct overlap increases from nickel to titanium as the nuclear charge is reduced. This type of behavior was studied by Rogers *et al.* for a series of normal vanadium oxide spinels. If the A-site cations are decreased in size, the unit cell volume decreases and the B-site V^{3+} ions are brought closer together. Rogers *et al.* observed that as the A-site ion decreased in size, the resistivity and activation energy decreased markedly, indicating an increase in the V^{3+} - V^{3+} overlap. It was possible by this technique to define a critical distance for overlap, R_c , below which the d-electrons of the transition metal ions are collective rather than localized. The concept of a critical distance was originally developed by Mott and Goodenough (1963) to explain the unusual magnetic and electrical properties of transition metal oxides where the metal ions had a $3d^n$ configuration with $n \leq 3$. For a number of oxide systems, critical distances for metal ions have been obtained that are useful in explaining changes in magnetic and electrical properties when localized electron states transform to delocalized states.

The magnetic properties of several of the spinels, in addition to their relatively low electrical conductivity compared to magnetic metals and alloys, have made them useful for a number of electronic device applications. Their intrinsic properties have led to the development of new ideas concerning the nature of magnetic exchange interactions. However, as with numerous other materials, more attention should be paid to development of synthetic methods that result in compounds of the highest purity and homogeneity.

1. Nickel aluminate spinel (NiAl₂O₄)

Nickel aluminate spinel (NiAl₂O₄) has been applied in numerous fields due to its high thermal stability and specific catalytic properties (Kou and Selman, 2000). It has also been proposed as a promising candidate anode for aluminium production because of its high resistance to alkalis and melting aluminium attack. The framework of the unit cell of a nickel aluminate spinel consists of 32 oxide ions in an almost perfect cubic close-packed arrangement. Thus, the unit cell composition is actually Ni₈Al₁₆O₃₂. Figure 3 shows part of the unit cell. The oxide ions form a face-centered cubic array, and there are octahedral sites at the center of the cube and in the middle of each cube edge, and tetrahedral sites in the middle of "cubelet." In the Ni₈Al₁₆O₃₂ spinel (inverse spinel structure), the 8 Ni²⁺ and 8 Al³⁺ ions are located in the octahedral sites, while the remained 8 Al³⁺ ions occupy tetrahedral sites (Rayner-Canham and Overton, 2003).

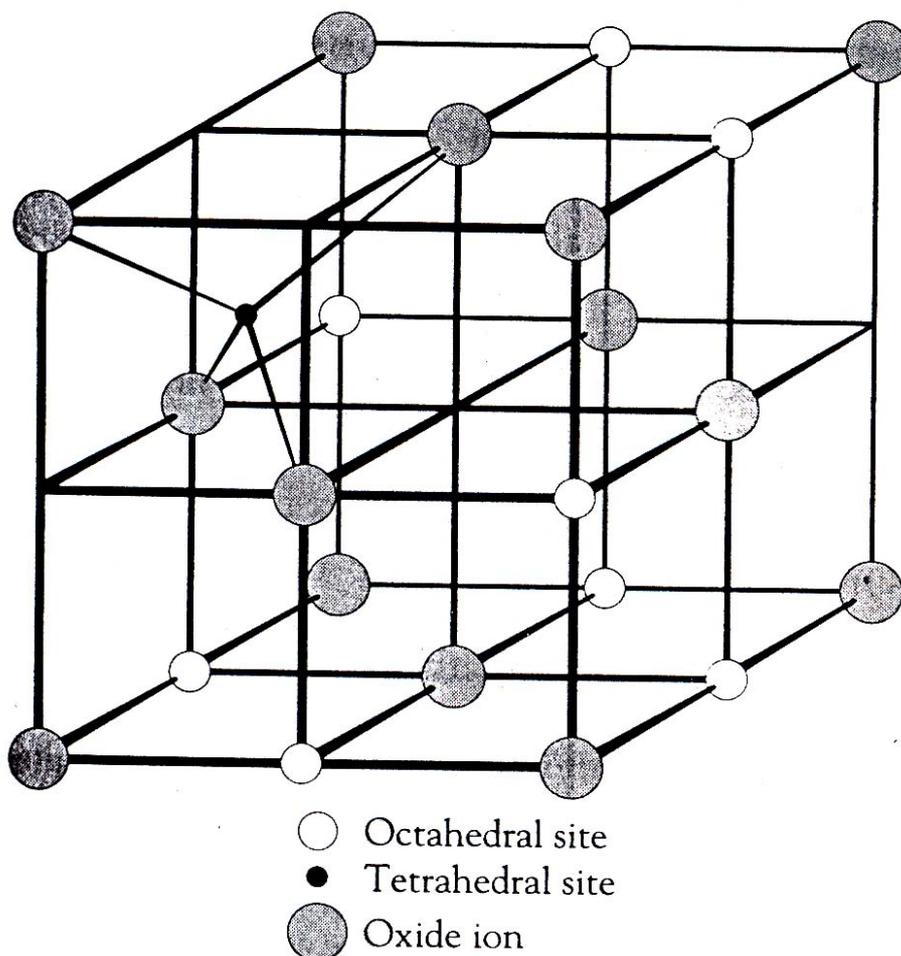


Figure 3 Part of the unit cell of the spinel structure showing the occupied lattice sites. Of the eight “cubelets” shown, the upper left front cubelet shows an occupied tetrahedral cation site, whereas the other seven cubelets have some occupied octrahedral cation site.

Source: Rayner-Canham and Overton (2003)

Nickel aluminate spinel can be prepared by many methods, such as solid-state reaction (Pettit, 1966), ion exchange zeolites method (Schmidt and Weidenthaler, 2001) and microwave-induced method (Peelamedu *et al*, 2002). The most general method is the solid-state reaction which involves the mixture of metal oxides followed by sintering in air. Although the mechanism of solid-state reaction has been intensely studied over

the past (Minford and Stubican, 1974), it is still difficult to prepare the stoichiometric NiAl_2O_4 and under reaction sintering leads to materials having a very low surface area. Thus many researchers have attempted to improve the textural, structural properties and surface area coupled with the high activity of the nickel aluminate spinel.

Rodeghiero *et al.* (1997) studied the transformation of Ni/Al layered double hydroxides to $\text{Ni/Al}_2\text{O}_3$ and $\text{Ni/NiAl}_2\text{O}_4$ composites via X-ray diffraction and electron microscopy. The Ni/Al layered double hydroxide powders, with $\text{Ni}^{2+}:\text{Al}^{3+}$ cation ratios varying from 0.5 to 3.3, were first synthesized by a coprecipitation route. The powders were then reduced in a tube furnace under hydrogen to yield $\text{Ni/Al}_2\text{O}_3$ or under a CO/CO_2 mixture to yield $\text{Ni/NiAl}_2\text{O}_4$. The reduced powders were uniaxially hot-pressed to form sintered pellets. In the case of the $\text{Ni/NiAl}_2\text{O}_4$ hot-pressed composites, the platelike morphology of the precursor was preserved in the final sintered microstructure. In contrast, due to the nucleation and growth mechanism that takes place in $\alpha\text{-Al}_2\text{O}_3$, the $\text{Ni/Al}_2\text{O}_3$ hot-pressed composites exhibited no microstructural memory.

Wang and Shen (1998) studied the rotation-coalescence of confined particles in $\text{Ni}_{1-x}\text{O/NiAl}_2\text{O}_4$ composites, indicated that the $\text{Ni}_{1-x}\text{O/NiAl}_2\text{O}_4$ powders of specified molar ratios (1:9, 32:1, 69:1, designated as N_1S_9 , N_{32}S_1 , N_{69}S_1) were sintered and annealed at 1873 K for 1–80 h and studied by transmission electron microscopy with regard to the orientation change of the intragranular particles. It was found that the N_1S_9 and N_{32}S_1 specimens contain only intergranular particles; whereas the N_{69}S_1 specimen contains both inter- and intragranular particles in the late stage of sintering. In N_{69}S_1 specimen, the intergranular spinel particles, either isolated or slightly coalesced as sausage-like chains, were able to detach from the Ni_{1-x}O grain boundaries and became parallel-epitaxial with respect to the host Ni_{1-x}O grains upon annealing. The orientation change can be ascribed to Brownian rotation and coalescence of the particles, and the rotation of the particles mostly proceeds over non-specific contact planes due to the dragging effect in the coalescence process. The epitaxial spinel particles could possibly be

preserved in the Ni_{1-x}O grains when the intergranular particles were coalesced to a larger size to suppress grain boundary separation.

Jin *et al.* (1999) synthesized a new kind of solid looping material, $\text{NiO}/\text{NiAl}_2\text{O}_4$, based on integration of NiO , as solid reactant, with a composite metal oxide of NiAl_2O_4 , as a binder, for applying it to chemical-looping combustion. The chemical looping combustion including reduction (fuel with metal) and oxidation (air with the reduced metal oxide) could make a breakthrough in simultaneous contribution to both energy and environmental issues. The reactivity of the reduction and oxidation was investigated by TGA (thermogravimetric analysis). The results obtained here indicated that the new looping material, $\text{NiO}/\text{NiAl}_2\text{O}_4$, might significantly improve reaction rate, conversion, and regenerability in cyclic reaction, compared with the other materials. In addition, the carbon deposition can be completely avoided by addition of water vapor at a ratio of $\text{H}_2\text{O}/\text{CH}_4 = 2.0$. These results suggest that this new looping material of $\text{NiO}/\text{NiAl}_2\text{O}_4$ may play a vital role in developing chemical-looping combustion.

Cesteros *et al.* (2000) studied and correlated some of the key factors in the preparation of NiAl_2O_4 , such as precipitation and calcinations temperatures, to the reducibility of the final spinel. All the samples were characterized by X-ray diffraction, nitrogen physisorption, scanning electron microscopy, temperature-programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS) techniques. Spinel was obtained with high area ($110\text{--}220 \text{ m}^2/\text{g}$) compared with those usually reported. XPS showed that these spinels can be surface reduced. The largest amount of metallic nickel phase was found in the spinel prepared by precipitation at 348 K and calcinations at 773 K. This spinel also had the lowest initial temperature of reduction (TPR).

Cesteros *et al.* (2000) synthesized nickel spinels in order to be used as supports of nickel catalysts for the hydrodechlorination of 1,2,4-trichlorobenzene in the gas phase. All the samples were structurally characterized using X-ray diffraction (XRD),

BET, temperature-programmed reduction (TPR), scanning electron microscopy (SEM) and temperature-programmed desorption (TPD) techniques. The Ni/NiAl₂O₄ catalysts tested had high conversions and selectivities towards benzene. This is due to their reduction degree (XRD) and structural surface properties (BET area, SEM, TPD). The most active and selective catalyst yields 87% benzene at 523 K for a conversion of 82%. These Ni/spinel catalysts desorb large amounts of hydrogen at lower temperatures (<625 K) which can compete with the aromatic compounds to be adsorbed on the surface of the catalyst. The amount of low-temperature hydrogen and the fact that it competes with the aromatic molecules favour a more exhaustive hydrodechlorination.

Lieberthal and Kaplan (2001) developed a new process to produce sintered α -Al₂O₃ reinforced with sub-micron Ni particles. The process is based on the infiltration of ceramic performs with liquid salts, which are reduced during pressureless sintering to form metal particles. The reduction occurs within the open pores of the ceramic perform, after evaporation of the metal salts in to the gas phase. By controlling the partial pressure of oxygen during the sintering process, a reaction between the Ni particles and the alumina matrix can be invoked to form Ni-spinel (NiAl₂O₄) particles. Three point bending experiments show an increase in strength for the nickel-reinforced alumina and a significant increase for the spinel- reinforced alumina.

Ishida *et al.* (2002) made fine spherical particles of NiO/NiAl₂O₄, and investigated the oxidation of fuel by the solid oxide particles and the oxidation of the reduced particles by air stream. The reactions with circulation of reacting solid particles were performed at elevated temperatures, the results at 1200°C by use of hydrogen as fuel are presented. The features of the reactions are discussed based on the analyses of the composition of the exhaust gas. Examination of the surface of the solid particles by a scanning microscope revealed that the condition of the solid particle in both reduction and oxidation columns was much milder than that in the TGA experiment, and significant change of the particle was not observed.

Joo and Jung (2002) carried out CH_4/CO_2 dry reforming out to make syn gas on the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts calcined at different temperatures. The $\text{Ni}/\text{Al}_2\text{O}_3$ (850°C) catalyst gave good activity and stability whereas the $\text{Ni}/\text{Al}_2\text{O}_3$ (450°C) catalyst showed lower activity and stability. The $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst calcined at 850°C for 16 h ($\text{Ni}/\text{Al}_2\text{O}_3$ (850°C)) formed the spinel structure of nickel aluminate, which was confirmed by TPR. The carbon formation rate on the $\text{Ni}/\text{Al}_2\text{O}_3$ (850°C) catalyst was very low till 20 h, and then steeply increased with reaction time without decreasing the activity for CH_4 reforming. The $\text{Ni}/\text{Al}_2\text{O}_3$ (450°C) catalyst showed high carbon formation rate at the initial reaction time and then, the rate nearly stopped with continuous decreasing the activity for CH_4 reforming. Even though the amount of carbon deposition on the $\text{Ni}/\text{Al}_2\text{O}_3$ (850°C) catalyst was higher than that on the $\text{Ni}/\text{Al}_2\text{O}_3$ (450°C) catalyst, the activity for CH_4 reforming was also high, which could be attributed to the different type of the carbon formed on the catalyst surface.

Han *et al.* (2004) prepared nickel aluminate by solid-state reaction, an excess of NiO in products was observed, which was explained as the result of Al_2O_3 dissolving into spinel at high temperature. To reduce NiO and improve the formation of NiAl_2O_4 , four factors were investigated in this study. The results showed that the milling time and starting materials had an important effect on the excess of NiO while the sintering temperature and sintering time had little effect on it.