Synthesis of NiAl₂O₄ with high surface area as precursor of Ni nanoparticles for hydrogen production

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SYNOPSIS

NiAl₂O₄ with high surface area was synthesized by the combustion method, evaluating the effect of urea/nitrate (U/N) ratio. The use of a stoichiometric U/N ratio resulted in a material with high surface area and homogeneous nanocrystallites, while the excess of fuel resulted in a non-porous material with low surface area. The formation of superficial Ni nanoparticles resulted in excellent stability on CO₂ methane reforming. This can be attributed to the rearrangement of nickel in the aluminate matrix and the migration of nickel particles through carbon filaments at the surface during the activation process.

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1. Introduction

Spinel oxides have been applied in several fields, such as refractory materials, pigments, sensors and catalysts, due to their thermal stability, catalytic and magnetic properties [1–4]. Nickel aluminate (NiAl₂O₄) is a mixed cation oxide with normal spinel structure, where Al occupies the octahedral sites and Ni occupies the tetrahedral sites [5]. It can be used as support for catalysts due to its resistance to high temperatures and acidic or basic environments, providing chemical and physical stability for the catalyst.

Different methods have been suggested for the preparation of spinels with high surface areas. The most conventional is based on a solid–state reaction, where the metal oxides are mechanically mixed, resulting in finely divided powders. However, these materials present low surface areas and need high temperature of calcination and long reaction times [6]. On the other hand, the co-precipitation method can easily produce spinels with high surface area, around 100 m² g⁻¹, but an enormous effort is necessary to ensure a homogeneous material with uniform particle sizes and composition [1]. Sol–gel routes have been used to synthesize nickel alumina with large surface area, but this method requires expensive metal alkoxide precursors [2,7].

The combustion method has been proposed to synthesize nanosized materials and is particularly useful in the production of ultrafine ceramic powders with small average particle size. This is an easy and fast method, with the advantage of using inexpensive precursors, producing homogeneous nanosized crystallites, and highly reactive materials [8].

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The combustion synthesis technique consists of the contact of a saturated aqueous solution of a desired metal salt and a suitable organic fuel boiling until the mixture ignites and a self-sustaining and fast combustion reaction takes off, resulting in dry crystalline oxide powder [9–11]. The large amount of gases released during the reaction produces a flame that can reach temperatures above 1000 °C.

Kingsley et al. [12] described the preparation of aluminates with various metal nitrates (Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu and Zn) using urea or carboxyhydrate as fuel. The surface area depends on both the metal nitrates and fuel. The surface areas of the prepared materials using carboxyhydrate are higher, varying from 45 to 85 m² g⁻¹, compared with the materials prepared with urea (1–20 m² g⁻¹). Mimani [13] evaluated different fuels (hexamethylenetetramine, urea, carboxydradize and glycine) for production of MAI₂O₄ (M = Mn, Cu and Zn). In the case of manganese aluminate, urea was the best fuel, producing porous materials with high surface area. The copper and zinc aluminates prepared with carboxydradize and glycine presented the best results for mesoporous materials. The fuel/oxidizer ratio was evaluated by Alinejad et al. [14] in the combustion synthesis of MgAl₂O₄ by using sucrose and PVA solution as fuels. The increase of fuel/oxidizer ratio caused agglomeration of materials with average crystallite sizes in the range of 12.7–17.5 nm. Nickel aluminate materials prepared by combustion are less explored in the literature. Chen et al. [15] studied the use of glycine as fuel at stoichiometric ratio, obtaining non-porous NiAl₂O₄ materials with low surface area.

The aim of this paper is to investigate the effect of fuel/oxidizer ratio in the preparation of NiAl₂O₄ materials by the combustion synthesis using urea. Morphological and structural properties will be evaluated, as well as the catalytic activity in CO₂ reforming of methane after activation by methane oxidation.

2. Experimental

2.1. Catalyst preparation

NiAl₂O₄ was prepared by the combustion method using urea as fuel. A mixture of Ni(NO₃)₂·6H₂O (Vetec) and Al(NO₃)₃·6H₂O (Vetec) with desired molar ratio was melted on a hot plate (150 °C), and urea was added to the molten nitrates. The basin was then introduced in a furnace pre-heated at 600 °C where the combustion reaction took place.

The stoichiometric composition of the redox mixture was calculated based on the total oxidizing and reducing valences [16]. The stoichiometric ratio of urea to nitrate (U/N) needed to obtain NiAl₂O₄ powders is 2.2, assuming complete combustion, according to reaction (1).

\[3\text{Ni(NO₃)₂} + 6\text{Al(NO₃)₃} + 20\text{CO} \rightarrow 3\text{NiAl₂O₄} + 32\text{N₂} + 20\text{CO₂} + 40\text{H₂O} \] (1)

The U/N ratios used in this work were 1.0, 1.5 and 2 times the stoichiometric value of 2.2. The samples were calcined in flowing air at 700 °C for 3 h to clean the surface from the carbon residues. The prepared samples will be referred as NiAlₓ, where x = 1:1, 1.5:1 or 2:1, depending on the U/N ratio.

2.2. Catalyst characterization

Specific surface areas were measured by N₂ adsorption measurements at liquid nitrogen temperature (BET), using a Micromeritics ASAP 2000 apparatus. Before analysis the samples were degassed for 24 h at 200 °C in vacuum.

The crystalline phases were determined by X-ray diffraction (XRD) using the powder method. The diffraction patterns were recorded on a Rigaku DMax 2200 diffractometer with an Anton Paar XRK 900 chamber. The diffractograms were recorded in the range of 10° ≤ 2θ ≤ 90° with a step size of 0.05° and speed of 0.15° min⁻¹. The crystallite sizes were calculated using the Debye-Scherrer equation.

Temperature-programmed reduction (TPR) was performed in a conventional equipment, using a thermal conductive detector (TCD). A mass of 35 mg of catalyst was inserted into a quartz reactor and dehydrated at 200 °C for 2 h, flowing pure argon and then reduced with a mixture of 1.74% H₂/Ar (30 mL min⁻¹), rising the temperature up to 1000 °C at 10 °C min⁻¹.

Scanning electron microscopy (SEM-FEG) was performed in a FEI Quanta equipment, operating with acceleration voltage of 20 kV. EDS was carried out on a Oxford Mod. INCA, Penta FET ×3 equipment. The samples were suspended in isopropl alcohol and dropped in a holey carbon coated copper grid before analysis.

2.3. Catalytic tests

Temperature-programmed surface reaction (TPSR) was carried out using a U-shaped flow reactor, coupled to a mass spectrometer QMS-200 (BALZER). Initially, the sample was dried in He flow at 200 °C (10 °C min⁻¹) for 30 min, then activated switching to a mixture CH₄/O₂ = 2, at a heating rate of 10 °C/min up to 800 °C, for 30 min [17]. Subsequently, the sample was purged with He, cooled to room temperature and fed with a flow mixture of CH₄/CO₂/He (1:1:18) (100 mL min⁻¹), rising the temperature up to 900 °C.

The dry reforming of methane was also measured in continuous flow fixed-bed U-shaped reactor, at atmospheric pressure. The effluent gases were analyzed by gas chromatography (Shimadzu GC-A17) equipped with molecular sieve and Poraplot Q columns. The reaction was studied in the temperature range of 500–800 °C. Before each test, the catalysts were activated as described above. The total flow rate was 200 mL min⁻¹ and the feed composition was CO₂/CH₄/He = 1/1/18, using 50 mg of catalyst.

3. Results and discussion

3.1. Catalyst characterization

The combustion method involves self-ignition of an aqueous solution containing an oxidizer (the corresponding metal nitrates) and an organic fuel, such as urea. The rapid evolution and large volume of gases released during the process cool
immediately the products, thus limiting the occurrence of agglomeration and leading to the formation of nano crystalline powder. The properties of these materials, such as surface area and crystallite sizes, are strongly dependent on the fuel/oxidant ratio [18].

The nitrogen adsorption–desorption isotherms of these samples are shown in Fig. 1. The NiAl1:1 sample showed a profile close to type IV, indicating a mesoporous material. The hysteresis loop at high relative pressures indicates the presence of agglomerates or compacted spherical particles of fairly uniform size and arrays. The other two samples showed isotherms of type II, characteristic of non-porous or macro-porous materials. The hysteresis is associated to slit-shaped pores or plate-like particles. The porosity was analyzed following the BJH method of the adsorption branch isotherm, since it is known that this branch represents the best approximation for equilibrium conditions [19].

The specific surface areas (SBET) together with pore radius (Rp) and pore volume (Vp) are presented in Table 1. The NiAl1:1 catalyst showed a high surface area (186 m²/g), similar to that reported in the literature, when using an expensive alkoxide precursor and very long preparation time by the sol–gel method [2,7,19,20]. The NiAl1:1 presented also unimodal pore size distribution in the range of 3–6 nm and pore volume of 0.18 mL/g, indicating mesoporous materials. On the contrary, the samples with excess of urea, NiAl1.5:1 and NiAl2:1, presented lower surface area (10 m²/g) and a non-porous material.

These results can be explained mainly through the flame temperature that was reached during the preparation. The temperatures measured during the combustion are displayed in Fig. 2. The combustion process with excess of urea caused a slower ignition of the reactant mixture and the maximum temperature was much higher. The NiAl1:1 sample showed maximum peak at 918 °C with an ignition time of 86 s, while the NiAl1.5:1 and NiAl2:1 samples shifted the peaks to 1177 and 1237 °C and ignitions after 132 and 164 s, respectively. These results show that the excess of urea favors complete combustion during the synthesis, accompanied by the evolution of a large amount of gases, which contributes to the

<p>| Table 1 – Textural data of all catalysts. |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} (m²/g)</th>
<th>R_p (nm)</th>
<th>V_p (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl₁:₁</td>
<td>186</td>
<td>3.8</td>
<td>0.18</td>
</tr>
<tr>
<td>NiAl₁.₅:₁</td>
<td>&lt; 10</td>
<td>122.2</td>
<td>0.008</td>
</tr>
<tr>
<td>NiAl₂:₁</td>
<td>&lt; 10</td>
<td>131.1</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Fig. 1 – Isotherms obtained for all catalysts by N₂ physisorption.

Fig. 2 – Evolution of temperature as a function of time for combustion synthesis of (a) NiAl₁:₁, (b) NiAl₁.₅:₁ and (c) NiAl₂:₁.
formation of materials with good crystallinity. However, agglomeration occurred at higher temperature, lowering the surface area, increasing average crystallite sizes and forming non-porous materials.

X-ray diffractograms of the samples (Fig. 3) presented only a NiAl$_2$O$_4$ cubic spinel-type structure (JCPDS 10-0339). All samples showed mean crystallite nanosizes, as presented in Table 2. The crystallite size is strongly dependent on the fuel/oxidant ratio, which increases with increasing urea loading. The high heat released during combustion with excess of urea favors sintering of NiAl$_2$O$_4$ particles. Moreover, the excess of urea changed the distribution of crystallite sizes. The NiAl$_{1:1}$ sample showed uniform particle sizes for most crystallographic planes (as shown in Table 2), suggesting a homogeneous material with uniform particle sizes [7]. On the other hand, the NiAl$_{1.5:1}$ and NiAl$_{2:1}$ samples presented variable crystallite sizes. Nanosized crystallites of NiAl$_2$O$_4$ were obtained by Han et al. [21] applying the sonochemical method, but with very poor crystallinity.

The lattice parameters (Table 2) increased in the following order NiAl$_{1:1}$ < NiAl$_{1.5:1}$ < NiAl$_{2:1}$ and are very close to those reported in the literature [7,20]. The lattice parameters in a spinel structure are affected by lattice disorder and distribution of cations. The cation distribution in this structure generally has the nickel ions in the tetrahedral coordination and the aluminum in the octahedral coordination. However, at high temperatures a random ordering occurs and some nickel ions changed to octahedral coordination, while the Al$^{3+}$ ions changed from octahedral to tetrahedral coordination [22]. As the ionic radius of Ni$^{2+}$ ion is larger than the Al$^{3+}$ (69 pm vs. 54 pm), the substitution of Al$^{3+}$ by Ni$^{2+}$ results in lattice expansion [2]. Han et al. [21] proposed that the effect of distribution of Ni$^{2+}$ and Al$^{3+}$ cations can be evaluated by the $I_{(220)}/I_{(440)}$ intensity ratio. Table 2 shows clearly that there is a migration of nickel to octahedral coordination with increasing amount of urea, since the $I_{(220)}/I_{(440)}$ ratio increases, resulting in the expansion of the lattice.

The reducibility of the nickel based-catalysts has been extensively studied by TPR. Based on the reduction temperature, different nickel species can be found. Up to 327 °C it is attributed the reduction of bulk nickel oxide to metallic Ni$^0$. In the range of 327–727 °C it is due to the reduction of dispersed nickel oxide interacting with the support, while between 727 and 1000 °C it is assigned to the reduction of nickel aluminate to metallic Ni$^0$ [21].

TPR results for different samples are shown in Fig. 4. The TPR profile of the NiAl$_{1:1}$ catalyst showed a reduction peak at 788 °C, which can be related to the reduction of nickel aluminate [19,20,23,24]. The NiAl$_{1:5:1}$ sample presented small peaks at low temperatures (465 and 506 °C), indicating the presence of segregated nickel oxide at the surface [25]. Both NiAl$_{1:5:1}$ and NiAl$_{2:1}$ samples showed a broad peak at high

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### Table 2 – Crystallography parameters of all catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a_0) (nm)</th>
<th>(I_{(220)}/I_{(440)})</th>
<th>(I_{(220)}/I_{(440)})</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Family crystallographic planes [hkl]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[111]</td>
</tr>
<tr>
<td>NiAl$_{1:1}$</td>
<td>0.8032</td>
<td>0.25</td>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td>NiAl$_{1.5:1}$</td>
<td>0.8047</td>
<td>0.33</td>
<td></td>
<td>15.8</td>
</tr>
<tr>
<td>NiAl$_{2:1}$</td>
<td>0.8092</td>
<td>0.35</td>
<td></td>
<td>18.4</td>
</tr>
</tbody>
</table>

\(a_0\) – lattice parameter of NiAl$_2$O$_4$ structure, \(Δ\) – average crystallite size in all planes.
temperature indicating the presence of NiAl2O4. The shift of the main peak to higher temperature can be associated with the maximum temperature achieved during the combustion with excess of urea. Molina and Poncelet [24] verified on the Ni/Al2O3 catalyst that with increasing temperature of calcination the reduction peak is shifted to higher temperature.

3.2. Catalytic activity

Prior activity tests the catalysts were activated using the methane oxidation methodology, with a mixture of O2/CH4, molar ratio 1:2, as described by Souza et al. [17]. This activation method enhanced and stabilized markedly the activity of the Ni/Al2O3 catalysts for CO2 reforming of methane [17]. Temperature programmed surface reaction (TPSR) results for NiAl1:1 and NiAl2:1 are shown in Fig. 5. The NiAl2:1 sample presented a large induction period and the activation was more difficult than for the NiAl1:1. Methane consumption for the NiAl1:1 catalyst started at temperatures as low as 470 °C, while for the NiAl2:1 catalyst it occurred later and suddenly at 725 °C.

After activation of the catalysts the XRD results (Fig. 6) showed that the NiAl2:1 catalyst presented only partial reduction of NiAl2O4 to Ni0. On the other hand, the NiAl1:1 catalyst showed almost complete transformation of NiAl2O4 to Ni0. Therefore, the reduction ability can be related to the average crystallite sizes of Ni0 (Table 2). Thus, the easier activation of NiAl1:1 during TPSR is closely related to its higher reducibility.

According to Souza et al. [17] the nickel particles are rearranged in the matrix of the aluminate during the activation. The nickel ions migrate to the surface and Ni0 particles coexist with NiAl2O4 phase at the surface. The micrograph of the NiAl1:1 catalyst after activation is shown in Fig. 7 and exhibits dispersed metallic particles over the NiAl2O4 matrix. This is clearly shown by EDS analysis: the NiAl2O4 matrix is seen in spectrum 3 and Ni0 particles in spectrum 1. Small dispersed Ni0 particles over the matrix are seen in spectrum 2, showing both nickel particles and NiAl2O4 phase, due to the small depth of the metallic nickel layer.

Indeed, the metallic Ni0 particles are the active sites for the dry reforming of methane reaction. The hard reduction behavior of NiAl2:1 is because of its more stable phase (due to its higher crystallinity). The big particle sizes on the NiAl2:1 sample require greater amount of energy to detach the nickel from the aluminate phase and its reduction at the surface. Thus, its activation occurs at higher temperature.

The conversion of CO2 as function of the temperature is displayed in Fig. 8A. The CO2 conversion was always higher than CH4 conversion, which is ascribed to the occurrence of the reverse water-gas shift reaction, simultaneously with the reforming. Consequently the H2/CO ratio was lower than 1, mainly at low temperatures, as can be observed in Fig. 8B. The influence of the temperature on the CO2 conversion shows that the catalytic activity at low temperatures decreases in the following order: NiAl1:1 > NiAl1.5:1 > NiAl2:1. The conversion for NiAl2:1 catalyst started only at 550 °C. For a conversion of 50% the reaction temperature for the NiAl2:1 was 100 °C higher than for NiAl1:1 catalyst. The bigger crystallites of nickel aluminate (about 5 times) of the NiAl2:1 catalyst difficult the reduction to metallic Ni0.

The stability tests at 900 °C are displayed in Fig. 9. The literature showed that the NiAl2O4 spinel or NiAl2O4–Al2O3 solid solution for the methane reforming deactivates very fast. However, they were reduced with H2, and the deactivation

![Fig. 5 – TPSR profiles of samples (A) NiAl1:1 and (B) NiAl2:1.](image1)

![Fig. 6 – XRD patterns of the samples NiAl2:1 and NiAl1:1 after methane oxidation activation. O → NiAl2O4 and X → Ni0.](image2)
was basically related to the deposition of inactive carbon. This problem was solved by introducing a promoter to enhance the activity and stability [26–29]. Here, the catalysts were activated unlikely, using the methane oxidation and results showed excellent stability for more than 40 h, presenting H2/CO ratio and CO2 conversion close to the thermodynamic equilibrium. It seems that this activation process with CH4/O2 induces the formation of carbon filaments at the surface, modifying surface properties. Certainly, these nano carbon filaments carried out the nano metallic Ni0 particles at the surface, increasing the active surface sites for the reaction, according to the literature [17].

The presence of carbon after the reaction was investigated by SEM. Indeed, Fig. 10 shows carbon filaments deposited over the catalyst surface, confirming the presence of structured carbon with a typical morphology of sinuous and defective structure and with 150 nm diameter. These filaments stretch away from the catalyst particle, thus encapsulating much lighter particles and no layered coke formation. Metallic Ni0 particles over and at the end of these filaments were observed, which confirm the migration of Ni0 particles from the structure through the carbon filaments. These carbon filaments may not deactivate the catalyst, but on the contrary, carried nickel particles migrating easily through the filaments with the formation of small clusters which are very active species.

The literature reported that the origin of inactive carbon during CO2 reforming of CH4 may occur via CH4 decomposi- tion and CO disproportionation. The CH4 decomposition on Ni supported catalyst occurs via CHx fragmentation that depends strongly on the Ni particle sizes. The deep CH4 dehydrogena- tion needs large ensemble of metal clusters because the CHx species require the concomitant occupation of higher coor- dination sites [6,28]. Concerning the CO disproportionation it is accepted that the CO chemisorption on metallic sites involves charge transfer and formation of CO3 anionic precursor with acid support, favoring the CO disproportionation. Since deactivation was negligble in our study, the carbon filaments over the surface may facilitate the migration of nickel particles impeding the deactivation. Regarding that strong deactivation of Ni/Al2O3 catalysts occurred when the
catalyst was reduced with hydrogen \[6,17,28,30\] where the Ni particles were originated from the NiO forming Ni aggregates that after the reduction are susceptible for the CO disproportionation during the dry reforming. On the contrary, here the NiAl\(_{1:1}\) catalyst presented only very small metallic Ni\(_0\) particles, while the NiAl\(_{1.5:1}\) exhibited Ni\(_0\) and NiAl\(_{2O4}\) particles. The dispersed Ni\(_0\) over nickel aluminate is less susceptible for sintering.

4. Conclusions

Nickel aluminates with high surface area were obtained by the combustion method using urea as fuel. The oxidant/fuel ratio modifies the surface area, affected the crystallite sizes and nickel atomic position in the matrix of the aluminate. The material prepared with a stoichiometric oxidant/fuel ratio presented average crystallite sizes of 4 nm and high surface area. On the other hand, the excess of fuel produced materials with lower surface area, and higher crystallites sizes of 16 nm, causing the migration of nickel atoms to the octahedral position.

The NiAl\(_{1:1}\) exhibited higher activity than the NiAl\(_{1.5:1}\) and NiAl\(_{2:1}\) catalysts at lower temperature. The migration of metallic Ni\(_0\) after reduction through the carbon filaments detached from the aluminate surface as active cores to the surface, allowed higher dispersion nickel particles.

XRD results showed that the crystallinity depends on the maximum flame temperature reached during the combustion. The higher the U/N ratio the higher is the maximum flame temperature of combustion affecting the crystalline particle sizes. These catalysts presented excellent stability for more than 40 h for the CO\(_2\) reforming of methane, which is attributed to the activation procedure with CH\(_4\)/O\(_2\) and the presence

![Graph A](image1.png)

**Fig. 8** – Catalytic activities as a function of temperature for dry reforming of methane: (A) H\(_2\)/CO ratio and (B) conversion of CO\(_2\). Reaction conditions: 50 mg of catalyst and 200 mL/min of 1:1:18 (CH\(_4\):CO\(_2\):He), with each point taken after 30 min of reaction.

![Graph B](image2.png)

**Fig. 9** – Deactivation test at 800 °C as a function of time on stream for dry reforming of methane. (A) ratio H\(_2\)/CO and Conversion of methane (B). Reaction conditions: 50 mg of catalyst and 200 mL/min of 1:1:18 (CH\(_4\):CO\(_2\):He).

![Graph C](image3.png)

**Fig. 10** – SEM analysis of NiAl\(_{2:1}\) sample after time on stream using methane activation.
of very small crystallites migrating through the filaments to the Ni aluminate surface.

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