Short communication

Preparation of Ni/Pt catalysts supported on spinel (MgAl$_2$O$_4$) for methane reforming

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Abstract

MgAl$_2$O$_4$ was synthesized through hydrolysis of metallic alkoxides of Mg^{2+} and Al^{3+}. The formed spinel precursor phase was calcined at temperatures between 600 and 1100 °C, for 4 h. The spinel was utilized as a Ni/Pt catalyst support. The Ni/MgAl$_2$O$_4$ catalysts (15% Ni, w/w) containing small amounts of Pt were tested for methane steam reforming. The solids were analyzed by X-ray diffraction (XRD), temperature programmed reduction (TPR) with H$_2$ and catalytic tests. The spinel phase was formed at temperatures above 700 °C. The addition of small amounts of Pt to Ni/MgAl$_2$O$_4$ promoted an increase in surface area. This probably caused the considerable increase in methane conversion.
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Keywords: MgAl$_2$O$_4$; Synthesis; Catalysts; Methane; Reforming

1. Introduction

Spinel is a ternary oxide with a chemical formula of AB$_2$O$_4$, where A is a divalent metallic cation in a tetrahedral site and B is a trivalent metallic cation in an octahedral site of the cubic structure. Magnesium aluminate spinel (MgAl$_2$O$_4$) has a specific combination of desirable properties such as: high melting point (2135 °C), high resistance to chemical attack, good mechanical strength from room temperature to high temperatures, low dielectric constant, excellent optical properties, low thermal expansion and good catalytic properties [1–5]. Conventionally, the spinel (MgAl$_2$O$_4$) is prepared through a reaction in the solid state using MgO and Al$_2$O$_3$ [6,7]. In this process, the mixture is calcined at high temperatures such as 1400–1600 °C. An effort to synthesize MgAl$_2$O$_4$ at lower temperatures has been reached by using chemical synthesis processes, especially chemical co-precipitation [8] and sol–gel processes [9,10], where the spinel phase is formed at temperatures around 700 °C. According to Montouillont et al. [11], the MgAl$_2$O$_4$ can be formed at temperatures lower than 675 °C by the co-precipitation method involving the dehydration of a solution of metallic ion complexes with triethanolamine. However, these chemical processes have

disadvantages over the conventional solid-state reaction. The co-precipitation method has difficulties in pH control because there is solid precipitation and the removal of anions that are in the solids as impurities, changing the final composition. The sol–gel method, which uses a mixture of aluminium and magnesium salts that are submitted to pyrolysis, also has impurities in the solids. Catalysts obtained through nickel impregnation in inorganic supports have been employed in industry to catalyze the steam reforming of hydrocarbons [12–14]. Due to its resistance to sintering, the magnesium aluminate spinel has been used as a catalyst support for methane reforming [15,16]. Guo et al. [17] observed a high activity and stability of a Ni/MgAl$_2$O$_4$ catalyst for dry reforming of methane, which was attributed to the interaction between the active phase Ni and the support, resulting in highly dispersed active Ni species. They also observed that this catalyst exhibited higher activity and better stability when compared to Ni/γ-Al$_2$O$_3$ and Ni/MgO-γ-Al$_2$O$_3$ catalysts. Tomishige et al. [18] observed that the addition of small amounts of Pt (0.09%) to Ni/Al$_2$O$_3$ catalyst resulted in a significant increase of its activity in methane reforming with CO$_2$ and O$_2$. It was found that the addition of Pt, Pd and Ir (<0.3%, by weight) in Ni/γ-Al$_2$O$_3$ catalysts (15% Ni, w/w) strongly promoted conversion of methane in an autothermal reforming reaction [19]. Another study showed that there was a significant promotion in both activity and stability due to the addition of noble metals (Pt, Pd and Rh) in

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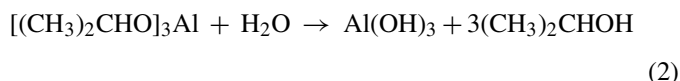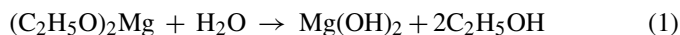*E-mail address:* foletto@smail.ufsm.br (E.L. Foletto).

$Ni_{0.03}Mg_{0.97}O$ for reforming of CH_4 with CO_2 to produce synthesis gas [20].

In the present work, results are presented for the $MgAl_2O_4$ spinel synthesis via an alkoxides hydrolysis with further calcination at temperatures between 600 and 1100 °C. The performance of the Ni catalysts supported on $MgAl_2O_4$ and impregnated with different platinum amounts was investigated in the reforming of methane.

2. Experimental

Non-stoichiometric amounts of Al and Mg were used in this work to form a solid compound of spinel, with excess Al with the following formula: $MgO·1.4Al_2O_3$. In the preparation of the precursor, the following reactants were utilized: aluminium isopropoxide $[(CH_3)_2CHO]_3Al$ and magnesium ethoxide $(C_2H_5O)_2Mg$, both from Aldrich (purity > 98%). This material was utilized as a support in the preparation of platinum and nickel catalysts.

For the precursor synthesis, two solutions 0.2 M of metallic alkoxides were prepared using alcohols as the solvent. The first solution was prepared by dissolving 62.8 g of aluminium isopropoxide (0.308 mol) in 1540 mL of isopropanol and the second one was prepared by dissolving 12.56 g of magnesium ethoxide (0.110 mol) in 550 mL of methanol. Both solutions were mixed in a 5 L beaker then heated to the methanol boiling point and under vigorous stirring 330 mL of water was added. The amount of water added to the system was five times higher than stoichiometric to perform the alkoxides hydrolysis, as shown in the reactions (1) and (2).

$$(C_2H_5O)_2Mg \ + \ H_2O \ \rightarrow \ Mg(OH)_2 + 2C_2H_5OH \quad (1)$$

$$[(CH_3)_2CHO]_3Al \ + \ H_2O \ \rightarrow \ Al(OH)_3 + 3(CH_3)_2CHOH \quad (2)$$

After adding water, the system was kept under heating and stirring for 3 h to complete the hydrolysis reaction. The formed material was separated from the alcohols by filtration and further dried in an oven at 120 °C for 24 h, resulting in a fine powder. This fine powder (a mixture of Mg and Al hydroxides) was put in a 100 mesh sieve and calcined in an oxidizing atmosphere (air) at temperatures of: 600, 700, 800, 900, 1000 and 1100 °C, for 4 h, to form the spinel phase.

To obtain the Ni/Pt catalysts, spinel calcined at 1100 °C was used as a support because this sample had a superior sintering-resistance. First of all, nickel was impregnated through successive wet impregnations with aqueous solutions of nickel nitrate hexahydrate, where the nominal content of nickel in the catalyst was kept at 15% (by weight). The impregnation was carried out at 80 °C. Then, samples were dried in an oven for 4 h, followed by calcination at 500 °C for 5 h in air. From the nickel-impregnated material ($Ni/MgAl_2O_4$), a deposition with platinum was performed using hexachloroplatinic acid, via a wet-impregnation method. The nominal contents of platinum were: 0.05, 0.1, 0.2 and 0.3% (by weight). Samples were named S15-0, S15-0.05, S15-0.1, S15-0.2 and S15-0.3, where 15 is the Ni content in the samples, and 0, 0.05, 0.1, 0.2 and 0.3, is the Pt content in the samples, respectively.

Samples were characterized by X-ray diffractometry (XRD) (equipment Shimadzu model XD-7, with Cu Kα radiation). The average size of the spinel crystallites was determined through the Scherrer equation (using silicon as standard):

$$D = \frac{K\lambda}{h_{1/2}} \cdot \cos\theta$$

where D is the average crystallite size, K the Scherrer constant (0.9×57.3), λ the wavelength of incident X-rays (0.15405 nm), $h_{1/2}$ the peak width at half height and θ corresponds to the peak position (in this work, $2\theta = 37$).

Analyses by temperature programmed reduction (TPR) were performed to determine the metallic area of the catalysts. TPR was carried out with Micromerits Chemisorb 2705 equipment, using 50 mg of catalyst and a temperature ramp from 25 to 1000 °C at 10 °C min^{-1}. A flow rate of the 30 mL min^{-1} of 5% H_2/N_2 was used. The measurement of metallic dispersion was determined from the hydrogen adsorption and desorption peaks in the reduced sample. The metallic surface was calculated for a stoichiometry of 1:1 (H:Ni) at room temperature.

The catalytic activity was measured over a temperature range of 400–600 °C at atmospheric pressure, using 250 mg catalyst in a fixed-bed quartz reactor (9 mm i.d.). Before reaction, catalysts were reduced at 600 °C for 2 h in 5% H_2/N_2. The reactant feed was $H_2O:CH_4 = 4:1$ at a flow rate 40 mL min^{-1}. The exit gases were analyzed by gas chromatography (GC-17A, Shimadzu) equipped with two detectors, using a Carboxen column. In this study, the catalytic activity was expressed in terms of CH_4 conversion.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms of the precursor and the precursor calcined at temperatures between 600 and 1100 °C. It can be seen that the precursor which is a mixture of aluminium and magnesium hydroxides, is an amorphous material. After calcinations at 600 °C the formation of the spinel phase occurs. However, the formed solid also has impurities, probably the presence of aluminium and magnesium hydrox-
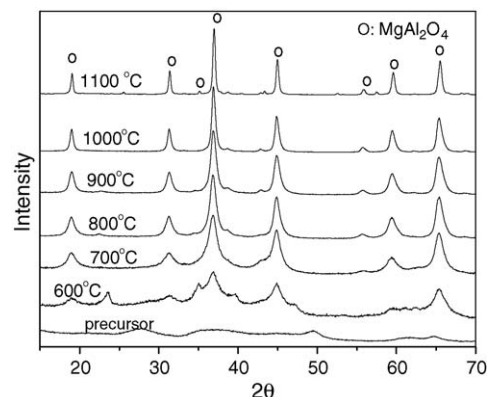

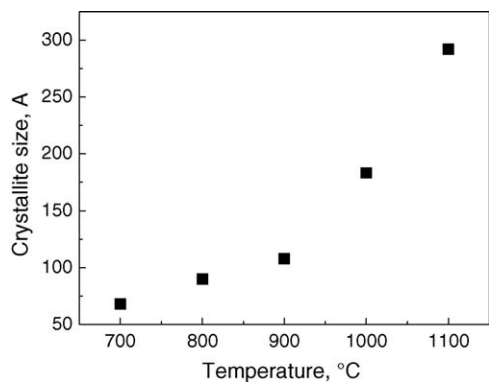Fig. 1. Diffractograms of precursor and calcinated samples.

Fig. 2. Crystallite size of the spinel powder, as a function of the calcination temperature.

Fig. 4. Diffractograms of the support and sample containing 15% of Ni.

ides which were not converted [3]. Nevertheless, calcination at temperatures of 700 °C or higher promoted the formation of the pure spinel phase. Comparing these data with the literature, this method of preparation allows the formation of a pure spinel phase at temperatures of the order of 700 °C. Similar results were obtained by other authors using the sol–gel method [9,10].

It can also be seen that by increasing the temperature there is an increase in the intensity and reduction in the width, at half high, of the X-ray diffraction peaks. To verify the influence of the calcination temperatures on the size of crystallites, the equation of Scherrer was utilized. The results are shown in Fig. 2, where it can be seen that by increasing the temperature there is an exponential increase in the size of the crystallites. For example, the sample calcined at 1100 °C has a size of crystallite of the order of 342 Å, five-fold higher than the one calcined at 700 °C (68 Å).

Fig. 3 shows the TPR profiles for the Ni and Pt catalysts. It can be seen that as the platinum content is increased, there is a decrease in the reduction temperature of the nickel oxide. This decrease of reduction temperature can be explained by the spillover phenomenon of hydrogen; i.e., platinum is reduced at lower temperatures than nickel, and begins to adsorb hydrogen dissociatively. Then, during the reduction process, the presence of the noble metal in the catalyst creates hydrogen adsorption and dissociation sites. The generated atomic hydrogen migrates to
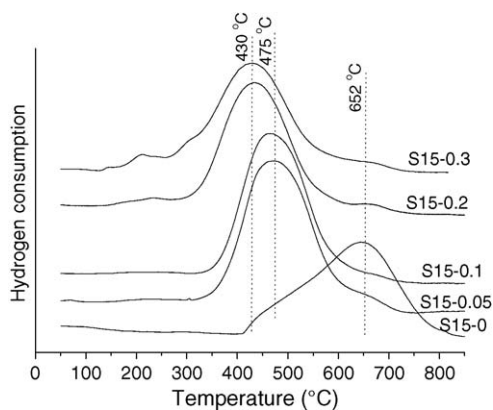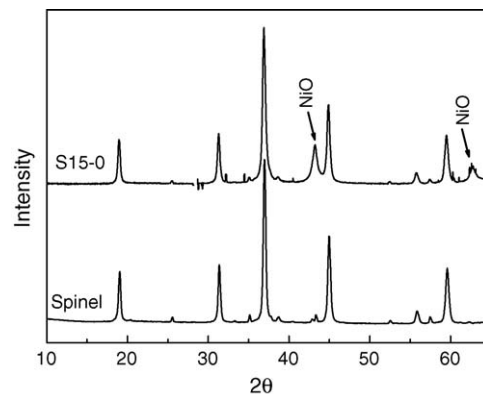
the region containing nickel and reduces this metal more easily than if it was in the molecular form [20,21]. It was observed that by adding a small amount of Pt (0.05%), the reduction temperature decreases by 177 °C (652–475 °C), however when higher amounts of Pt are added, for example, 0.3%, there is a reduction of just 45 °C in relation to the sample with 0.05% of Pt (475–430 °C). Comparatively, the sample prepared with 0.3% of platinum (S15-0.3) shows a nickel reduction temperature slightly lower than the one prepared with 0.2% of platinum (S15-0.2), showing that the addition of large amounts of platinum is not necessary.

Fig. 4 shows the X-ray diffractograms of the support (obtained at 1100 °C) as well as the sample containing 15% of nickel before thermal activation. Diffraction peaks characteristic of the NiO crystalline phase are observed.

Fig. 5 shows CH_4 conversion with temperature over the Ni/MgAl$_2$O$_4$ catalysts with various Pt loadings. As expected, the conversion is strongly dependent on the temperature. The CH_4 conversion increased with increasing temperature for all the catalysts investigated. The sample without platinum (S15-0) showed a lower conversion comparing to the Pt containing samples. Similar results were obtained by Dias and Assaf [19]. The sample containing 0.1% Pt showed the highest CH_4 conversion for the temperature range examined. This sample also showed the highest metallic surface area (Fig. 6). The samples containing Pt amounts above 0.1% demonstrated a lower
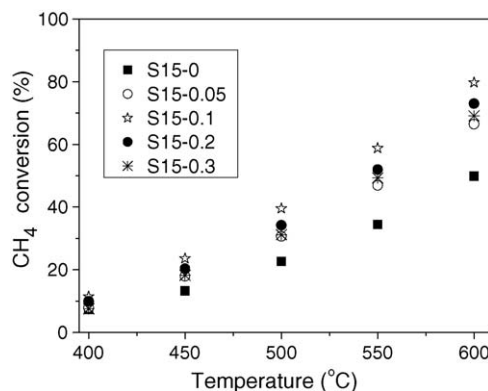

Fig. 3. TPR analysis of catalysts.

Fig. 5. Influence of temperature on equilibrium values of CH_4 conversion, for catalysts with different platinum contents.
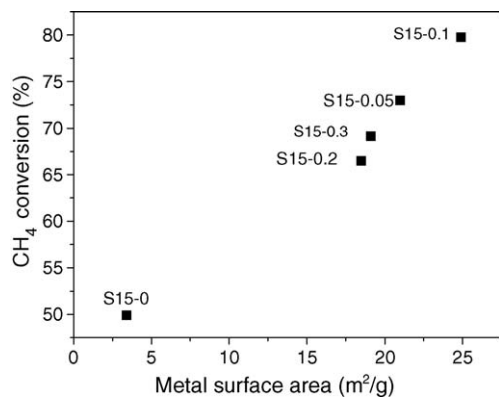
Fig. 6. Conversion of methane at 600 °C vs. metal surface area.

activity. This result suggests that the sample S15-0.1 showed a better distribution of the active phases and that may be related to the interaction between the active phases (Ni and Pt) and the support.

Fig. 6 shows that there is a proportional relation between CH_4 conversion and the metal surface area, corroborating the results by Dias and Assaf [19]. The sample without platinum (S15-0) showed a lower metallic area compared to Pt containing samples. This result demonstrates that the metal Pt causes an increase in area of the catalyst. It is known that the addition of noble metals to nickel catalysts favors the reduction of nickel [18,20,22].

4. Conclusions

Pure spinels $MgAl_2O_4$ using the sol–gel method via an alkoxides hydrolysis were prepared at calcination temperatures of 700 °C or higher. The catalysts obtained with this method were active for methane steam reforming. The catalytic activity of $Ni/MgAl_2O_4$ improved significantly by the addition of Pt. This noble metal promoted an increase in the surface area. Preparation of Pt/Ni catalysts supported on $MgAl_2O_4$, obtained at other temperatures (700–1000 °C), will be developed for further studies of methane reforming.

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