

Nickel catalyst supported on magnesium and zinc aluminates (MgAl_2O_4 and ZnAl_2O_4) spinels for dry reforming of methane

(Catalisador de níquel suportado em espinélios de aluminatos de magnésio e de zinco (MgAl_2O_4 e ZnAl_2O_4) para reforma a seco de metano)

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Abstract

Materials such as MgAl_2O_4 and ZnAl_2O_4 assessed in the reaction of dry reforming of methane to produce syngas were synthesized by microwave-assisted combustion method using urea as fuel. Samples of synthesized oxides were calcined at 800 °C for 2 h and impregnated with 5% nickel. The impregnated samples were calcined at 850 °C for 4 h to obtain the desired phases. The results of the catalytic tests showed that the catalysts are active for the reaction of dry reforming of methane, and the catalyst that showed the best performance for methane conversion was 5% Ni/ MgAl_2O_4 calcined at 850 °C/4 h.

Keywords: chemical synthesis, powder diffraction, oxides, dry reform, nickel catalysts.

Resumo

Materiais, tais como MgAl_2O_4 e ZnAl_2O_4 , avaliados em reações de reforma a seco de metano para produzir gás de síntese foram sintetizados pelo método de combustão assistida por micro-ondas usando ureia como combustível. As amostras dos óxidos sintetizados foram calcinadas a 800 °C durante 2 h e impregnadas com 5% de níquel. As amostras impregnadas foram calcinadas a 850 °C durante 4 h para se obter as fases desejadas. Os resultados dos testes catalíticos mostraram que os catalisadores são ativos para as reações de reforma a seco de metano, e o catalisador que mostrou o melhor desempenho para a capacidade de conversão de metano foi 5% de Ni/ MgAl_2O_4 calcinado a 850 °C/4 h.

Palavras-chave: síntese química, difração de raios X, óxidos, reforma a seco, catalisadores de níquel.

INTRODUCTION

Currently, with the discovery of pre-salt wells, new challenges have emerged from the environmental and technological standpoint. One of these challenges is to reuse the high CO_2 content present in the natural gas associated with oil that can cause problems related to corrosion, causing damage to pipelines and processing plants. From the environmental standpoint, burning the gas would contribute to increased emissions of greenhouse gases. Another possible solution would be the reinjection of part of this gas into the well, which has some limitations. Reforming methane with CO_2 is an interesting alternative to use the associated natural gas through its conversion into syngas and subsequent production of liquid fuels. Dry reforming of methane is highly endothermic. It is favored by high temperatures and low pressures ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$; $\Delta H = +247$ kJ/mol). As in steam reforming, the catalyst used in the dry reform is very susceptible to coke formation on

its surface, which can promote its deactivation. In addition, extra care should be taken with respect to sintering both of the support as of the active phase. However, dry reforming of methane could bring two important advantages. Firstly, the consumption of CO_2 together with CH_4 allows the simultaneous valorization of these two greenhouse gases into molecules with higher added value. Secondly, the syngas obtained has an equimolar composition (H_2 : CO ratio of 1) that is the best suited for direct use in Fischer-Tropsch synthesis to produce hydrocarbons with high yield [1-4].

Among the catalysts used in the dry reforming of methane, noble metals of VIII-A group, except for osmium, and not noble metals, such as Cu, Ni and Co, deposited on suitable supports such as structured oxides have been studied for this type of reaction [5-11]. Industrially, the metal chosen as catalyst is Ni, since it has activity comparable to noble metals. However, it quickly deactivates due to the formation of carbonaceous deposits [12-14]. Considering the high cost and limited availability of noble metals, it is more attractive

to develop a nickel catalyst of high catalytic performance and resistant to deactivation due to coke formation using a defined structure or solid solution with La, Al or Mg (spinel, fluorite, and perovskite) [15-18]. Catalysts based on Ni are used on the production of synthesis gas because has a high activity and selectivity and are less expensive than noble metal as platinum, but the major disadvantage of this reaction is the quick deactivation catalysts, as a result of carbon deposition. The carbon source during inactive dry reform can occur through the decomposition of methane (CH_4), yielding a carbon atom and two molecules of water ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{C} + 2\text{H}_2\text{O}$) and/or through the Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) [19, 20]. In last years, much effort has been devoted to the development of Ni base catalysts with improved performance, i.e. less deposition of coke and increased metal stability against sintering [21-23]. To inhibit deactivation of nickel catalysts many researchers have investigated the support effect in the carbon deposition [23-27]. The magnesium aluminate support in the spinel form was studied due to its high mechanical resistance at high temperatures and high chemical inertness, good thermal shock resistance, and good catalytic properties [28]. Based on the literature, it was observed the importance of support function, principally, because it promotes the burning of carbon deposited on the metal during the reaction of dry reforming of CO_2 .

Among the various synthesis methods used for the preparation of catalyst supports, the microwave-assisted combustion method has proved to be effective and rapid, both with respect to the desired microstructure and for obtaining nanosized particles, generally produced from this synthesis methodology. This paper aims to synthesize oxide-type supports structured by the microwave-assisted combustion method for application as catalytic support for nickel in order to produce synthesis gas through dry reforming of CO_2 . Therefore, magnesium and zinc aluminates (MgAl_2O_4 and ZnAl_2O_4) were studied, which were impregnated with 5% nickel to check the influence of the support on the selectivity and conversion of methane into synthesis gas.

EXPERIMENTAL

Synthesis of catalytic supports: the catalytic supports spinel-type structured oxides MgAl_2O_4 and ZnAl_2O_4 were synthesized through microwave-assisted combustion method [10-30]. The reagents used in the synthesis process were metal nitrates from Sigma Aldrich and Alfa Aesa, used as oxidants, and urea used as reducing fuel. The urea was dissolved in distilled water under constant agitation at 40-60 °C; after, the hydrated metal nitrates were added to the urea solution at 70-80 °C for 20 min under agitation to ensure good homogenization. Then, the mixture was placed in a microwave oven under high power (650 W) for approximately 5 min. The resulting materials were calcinated at 800 °C, at heating rate of 10 °C.min⁻¹, for 2 h in a muffle-type furnace. The nickel impregnation was carried out by wet impregnation method using as precursor

a 5 wt% nickel nitrate solution [31]. The suspension formed by nickel solution and the impregnated material remained under stirring at 70-80 °C for 4 h. After solvent evaporation, the collected solid was dried for 12 h in an oven at 100 °C and then calcined at 850 °C, 10 °C.min⁻¹, for 4 h.

Characterization: the X-ray diffraction (XRD) patterns were recorded on a Shimadzu diffractometer, XRD 7000, with $\text{CuK}\alpha$ radiation (1.542 Å), current of 30 mA, step of 0.02° and scan speed of 0.01 °/s. All XRD patterns were registered in the range of 5° <2θ< 90°. The Rietveld refinement was performed using the MAUD program 2.26 in order to identify the crystalline phases. The N_2 adsorption/desorption isotherms at 77 K were obtained from ASAP 2020 equipment (Micromeritics) and analyzed using the BET and BJH models to calculate specific surface and pore distribution, respectively. The morphology of the samples was observed by a high-resolution scanning electron microscope (Zeiss).

Catalytic test: approximately 30 mg of catalyst, placed in a U-type borosilicate micro-reactor, were previously activated at 400 °C, 10 °C.min⁻¹, using 15 mL.min⁻¹ of N_2 (99.999%) at 1 atm and kept at 400 °C for 40 min. Then the dry reforming reaction of CH_4 was carried out in a continuous flow; the temperature was increased from 400 up to 750 °C (heating rate of 10 °C.min⁻¹) and kept at 750 °C for 5 h, with a constant stoichiometric feed mixture of CH_4 and CO_2 (1:1). The reactor output was connected to a stainless steel line heated at 120 °C with a gas chromatograph Varian CP 3800, equipped with an automatic valve for the injection of gaseous samples and TCD detector. The products were separated by a VF5-ms column (0.25 mm x 30 m x 0.25 μm) using 2 mL.min⁻¹ of N_2 (99.999%) as carrier gas. The column oven temperature program was as follows: from initial temperature of 35 to 100 °C at heating rate of 20 °C.min⁻¹. The data were collected every 15 min on stream for 5 h.

RESULTS AND DISCUSSION

The results of X-ray diffraction of MgAl_2O_4 and ZnAl_2O_4 , Figs. 1 and 2, show that both samples are crystalline. The MgAl_2O_4 and 5% Ni/ MgAl_2O_4 were identified as spinel, according to JCPDS No. 01-075-1797 and JCPDS No. 01-082-2424 (Fig. 1); similar phases were reported in [32]. Magnesium aluminate spinel can in general be obtained either by sol-gel or by microwave-assisted combustion method, since the pure structure of this material is generally obtained when its precursors are calcined above 700 °C; calcination below this temperature leaves aluminum and magnesium hydroxide residues [33]. The advantages of using magnesium aluminate spinel as a catalyst or catalytic support is because it has interesting properties for catalysis such as thermal shock resistance, good mechanical strength at room and high temperatures, low thermal expansion and good catalytic properties [34].

Figs. 2a and 2b show the zinc aluminate spinel whose structure was identified as ZnAl_2O_4 based on JCPDS

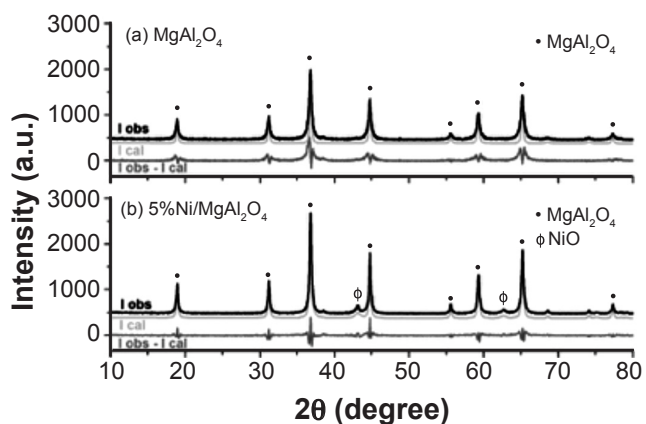


Figure 1: X-ray diffraction patterns of MgAl₂O₄ (a) and 5% Ni/MgAl₂O₄ (b).

[Figura 1: Difratoformas de raios X do MgAl₂O₄ (a) e 5% Ni/MgAl₂O₄ (b).]

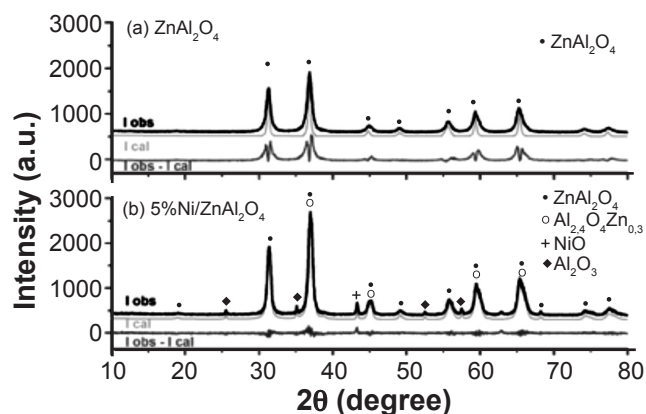


Figure 2: X-ray diffraction patterns of ZnAl₂O₄ (a) and 5% Ni/ZnAl₂O₄ (b).

[Figura 2: Difratoformas de raios X de ZnAl₂O₄ (a) e 5% Ni/ZnAl₂O₄ (b).]

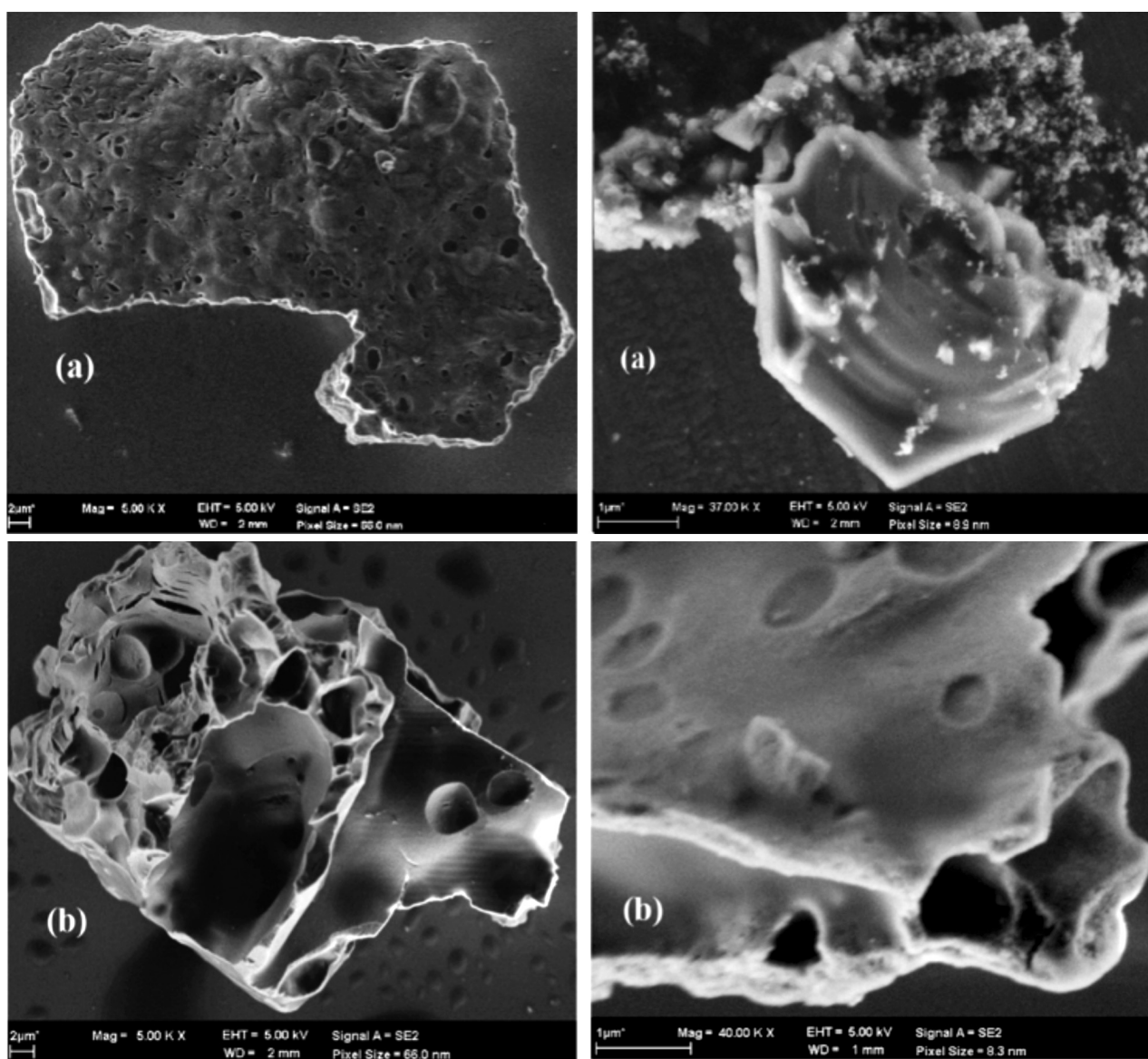


Figure 3: SEM micrographs of (a) 5% Ni/MgAl₂O₄ and (b) 5% Ni/ZnAl₂O₄.

[Figura 3: Micrografias obtidas por microscopia eletrônica de varredura de (a) 5% Ni/MgAl₂O₄ e (b) 5% Ni/ZnAl₂O₄.]

Table I - Results of BET and BJH analyses of MgAl_2O_4 and ZnAl_2O_4 .

[Tabela I - Resultados de análises de BET e BJH do MgAl_2O_4 e ZnAl_2O_4 .]

Sample	S_{BET}^a ($\text{m}^2 \cdot \text{g}^{-1}$)	D_p^b (nm)	V_p^c ($\text{cm}^3 \cdot \text{g}^{-1}$)
MgAl_2O_4	5.3	2.5	0.003
ZnAl_2O_4	4.1	2.9	0.003

^aBET surface area; ^bpore diameter calculated by BJH model; ^cpore volume.

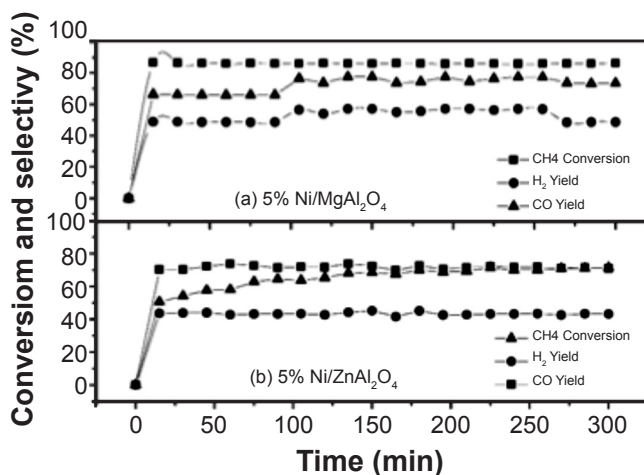


Figure 4: Conversion of CH_4 and H_2 and CO yields for (a) 5% Ni/ MgAl_2O_4 and (b) 5% Ni/ ZnAl_2O_4 .

[Figura 4: Conversão de CH_4 e rendimentos de H_2 e CO para (a) 5% Ni/ MgAl_2O_4 e (b) 5% Ni/ ZnAl_2O_4 .]

No. 01-071-0968. In Fig. 2b besides the spinel phase the $\text{Zn}_{0.3}\text{Al}_{2.4}\text{O}_4$ and the Al_2O_3 phases were also observed; the NiO is also present, but in small percentage. Secondary phases, $\text{Zn}_{0.3}\text{Al}_{2.4}\text{O}_4$ and Al_2O_3 , appeared after impregnation with nickel during synthesis. This can be demonstrated by the increased intensities of these phases in the sample with Ni, Figs. 2a and 2b. The increased intensity of NiO in the sample impregnated with nickel was also observed for the Mg aluminate spinel. It is possible that NiO can be found on the surface of nanoparticles due to the high porosity of the zinc aluminate spinel (Table I). Table I shows the adsorption parameters of MgAl_2O_4 and ZnAl_2O_4 . The specific surface area and pore distribution were determined by BET [35] and BJH [36] models, respectively. It was observed that MgAl_2O_4 sample showed largest surface area in comparison to ZnAl_2O_4 sample. Pore volume and pore diameter were similar for both samples.

Fig. 3 shows micrographs of Ni/ MgAl_2O_4 and Ni/ ZnAl_2O_4 , in which fine particles, small and hard agglomerates with spongy aspect and cylindrical shape are observed. Some depressions and pores observed could be formed by synthesis process, since the combustion favors the formation of CO_2 and release water molecules or gases during the explosive reaction that occurs during ignition.

The results of dry reforming of methane (Fig. 4a) showed that Ni/ MgAl_2O_4 converted 83% of CH_4 into CO and H_2 for 300 min at reaction temperature of 750°C without previous

reduction; no other conversion products were observed. Studies have shown that NiO and MgO are miscible due to the similarities of their crystalline structure as well as because the cations radii are very close, therefore, they can form solid solution at high temperatures, which leads to a system almost homogeneously mixed. Due to this fact, there is a strong interaction between NiO and MgO, and nickel can be uniformly dispersed on the support and the nickel segregation on the support surface is suppressed during its pre-reduction at 500°C for 3 h [37]. The Ni/ ZnAl_2O_4 showed lower CH_4 conversion rate of 70%, Fig. 4b. In general, the structural behavior of the catalyst leads to conversion and selectivity results in reform processes, and this becomes clear with Ni/ ZnAl_2O_4 , where the CH_4 conversion rate was lower than Ni/ MgAl_2O_4 . Nickel impregnation causes the appearance of new phases aggregated to the spinel as its percentage decreases, and the Al_2O_3 phase is formed as a function of temperature. According to [38], this phase interferes with the methane conversion, favoring gas-shift reactions.

CONCLUSIONS

The materials synthesized by the microwave-assisted combustion showed spinel phases desired for use as catalytic support. The results of reactions showed that the MgAl_2O_4 and ZnAl_2O_4 spinels impregnated with 5% NiO were effective as catalysts for the dry reforming of methane. However, catalyst Ni/ MgAl_2O_4 showed the best conversion rate justified by its microstructure, since NiO and MgO are miscible due to the presence of similarities in their crystalline structure, and also because their cation radii are very close, therefore, they can form solid solution at high temperatures, which leads to a system almost homogeneously mixed.

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