Preparation of Mesoporous Nanocrystalline Ni-MgAl₂O₄ Catalysts by Sol-Gel Combustion Method and Its Applications in Dry Reforming Reaction

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Abstract

A surfactant assisted sol-gel combustion method was employed for the synthesis of mesoporous nanocrystalline magnesium aluminate spinel with **the** high specific surface area as support for nickel catalysts in the dry reforming reaction. The prepared samples were characterized by X-ray diffraction (XRD), N₂ adsorption (BET), Fourier transform infrared spectroscopy (FTIR), temperature programmed reduction and oxidation (TPR, TPO) techniques. The effects of several process parameters such as metal nitrate to citric acid (**MN/CA**) and citric acid to PEG (polyethylene glycol), (**CA/PEG**) ratios, pH and calcination temperature were investigated. The obtained results showed that the addition of surfactant has a significant effect on the surface area. The XRD analysis showed that the single-phase MgAl₂O₄ was formed at 700 °C. The results revealed that the catalyst with 10 wt. % Ni content **and 97.1 (m² g⁻¹) surface area and particle size of 14.6 (nm)** exhibited high CH₄ and CO₂ conversions. In addition, CO₂ conversion was higher than the CH₄ conversion in all temperatures because of the occurrence of reverse water gas shift reaction.

Keywords: Nanostructure; MgAl₂O₄; sol-gel combustion; dry reforming; nickel catalyst

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1. Introduction

Syngas is a mixture of H_2 and CO and used as a feedstock in metallurgical and chemical processes. CO_2 reforming of methane is a convenient process due to produce synthesis gas and at the same time to remove two major greenhouse gases (CO_2 and CH_4) from the environment [1, 2]. Dry reforming of methane is an endothermic reaction and requires high temperature and low pressure to achieve high conversion levels. The most important obstacle in using this reaction is the deactivation rate of catalysts due to coke aggregation and sintering of metals and nickel is active catalysts for dry reforming process [3-9]. Although noble metal catalysts are more active than nickel catalyst and have less sensitivity to coke formation [10,11], high cost and limited access prohibited the industrial use of these catalysts. There are many ways to improve the activity and stability of Ni based catalysts by following aspects, catalyst preparation method, selecting the support type and adding the promoters [2, 9, 12, and 13]. $\gamma-Al_2O_3$ [2], MgO [14], SiO_2 [15] supported Ni catalysts have been extensively employed for dry reforming process. Also, some promoters such as alkali and alkaline earth [16, 1], transition metals [18], rare earth metal oxides [19, 20] are added to support to prevent coke formation. Among employed supports in dry reforming, magnesium aluminate spinel has received more attention because of industrial applications and unique characteristics like high melting point temperature, good thermal shock resistance and high mechanical strength and catalytic properties [20-23]. In recent years, numerous different and inexpensive processing techniques have been developed to synthesize single-phase $MgAl_2O_4$ such as hydrothermal synthesis [24], co-precipitation [25], microwave [26], etc. In many of its applications especially as a catalyst support, a high surface area, small crystalline size, high porosity and more active sites, are more desired. Due to the good thermal stability, low density and sintering-resistance ability, there

has been growing interest in the utilization as catalyst support for catalytic reforming. Additionally, due to its basic nature, this support will enhance the chemisorption of the CO₂ which is beneficial for the catalytic activity providing the oxygen to form CO and also causing the elimination of the coke [27].

Among the different preparation methods for preparation of magnesium aluminate, the sol-gel combustion method has received considerable attention due to its relatively simple synthesis scheme such as high product homogeneity, lower processing temperatures, inexpensive precursors and high purity of synthesized powder [28]. This method is a combination of the chemical sol-gel process and the combustion process. In this route a redox reaction occurs between salts of the desired metals and some organic fuel, which the fuel is citric acid and metal nitrates are used as metal and oxidant source, giving a voluminous and fluffy product with large surface area [29,30] and the liberated energy leads to the synthesis of oxide powder at lower temperatures [31,32].

In this work, Ni-MgAl₂O₄ catalysts with high surface area and mesoporous structure were prepared by combustion sol-gel method using Polyethylene glycol and citric acid as surfactant and fuel, respectively and the effects of several process parameters were investigated on the structural properties of the samples. In addition, the samples were employed in the dry reforming reaction for the production of synthesis gas.

2. Experimental

2.1. Catalyst Preparation

The Ni-MgAl₂O₄ was synthesized by a sol-gel combustion method with Polyethylene glycol (MW: 8000) as a surfactant. Appropriate amounts of (Al(NO₃)).9H₂O, Merck) and (Mg(NO₃)).6H₂O, Merck) were dissolved in distilled water. Then (Ni(NO₃)).6H₂O, Merck) was added to the prepared solution. After that, citric acid was added to the solution by a metal nitrate

to the citric acid molar ratio of 2. The PEGS powder (citric acid to PEGS molar ratio of 3) was added to form a clear solution. After that the ammonia solution (25 wt. %) was added drop wise to adjust the pH value at 9. Then the green solution was heated under continuous stirring at 90°C to evaporate water until the gel was formed. The dried gel was heated at 250 °C for 1 h and burnt under combustion process. The burnt gels were calcined at 700°C for 4 h. Increasing in calcination temperature can increase the agglomeration degree and decrease the specific surface area. It was inferred that 700 °C is sufficient for calcination and formation of out-layer MgAl_2O_4 spinels. The high activity of Ni/MgO- Al_2O_3 may be due to the presence of out-layer MgAl_2O_4 spinels since the out-layer MgAl_2O_4 spinels inhibit the reaction between NiO and Al_2O_3 or MgO, which is forming a stable and inactive NiAl_2O_4 or NiO-MgO compound [33]. Fig. 1 shows a diagram of the sample preparation.

2.2. Catalyst Characterization

X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu-K_α monochromatized radiation source and a Ni filter in the range $2\theta=10\text{-}80^\circ$ to examine the crystallinity of the prepared samples. The N_2 adsorption/desorption analysis was carried out at boiling temperature of nitrogen (-196°C) using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The samples were purged with nitrogen gas for 2h at 200°C using VacPrep 061 degas system (Micromeritics). Temperature programmed reduction (TPR) analysis was used for evaluating the reduction properties of prepared catalysts with Micromeritics chemisorb 2750 gas-adsorption equipment. In the TPR measurement, 50 mg catalyst was subjected to a heat treatment ($10^\circ\text{C}/\text{min}$) in a gas flow (30 ml/min) containing a mixture of H_2 : Ar (10:90). Prior to TPR experiment, the samples were heat treated under an inert atmosphere (Ar) at 200°C for 1h. The H_2 uptake amount during the reduction was measured using a thermal conductivity detector (TCD). Temperature-programmed oxidation

(TPO) of the spent catalysts was carried out using a similar apparatus by introducing a gas flow (30 mL/min) containing a mixture of O₂: He (5:95) and the temperature was increased up to 800°C at a heating rate of 10°C/min.

2.3. Catalytic Reaction

The catalytic evaluation was performed in a vertical quartz fixed-bed reactor (inner diameter = 7 mm) under atmospheric pressure. For each reaction test, 200 mg of the prepared sample was crushed and sieved to 0.25-0.5 mm and charged into the reactor. Prior to the reaction, the catalysts were reduced in situ at 600°C for 4h in flowing H₂ (20ml/min). After that the reactant gas feed containing a mixture of CH₄ and CO₂ (CH₄/CO₂ = 50/50 vol.%), was introduced into the reactor at a total flow rate of 50 ml min⁻¹ and the activity tests were carried out at different temperatures, ranging from 550 to 700°C in steps of 50°C that were kept for 30 min at each temperature. The gas composition of reactants and products were analyzed using a gas chromatograph equipped with a TCD and a Carboxen 1000 column.

3. Result and discussion

3.1. Structural Properties

Fig.2. shows the IR spectra of the as-prepared and calcined samples. The bands around 3400 cm⁻¹ and 1650 cm⁻¹ are related to the hydroxyl group of adsorbed water (OH band) and carbonyl of the carboxyl group of citric acid (CO band), respectively. As can be seen the bands centered in the region of 1380-1420 cm⁻¹ related to the vibration modes of NO₃ groups removed by calcination. A strong absorption in the range of 800-400 cm⁻¹ could be attributed to the characteristic metal-oxygen (M-O) vibrations [13].

The XRD patterns of the samples synthesized without and with surfactant under different CA/PEG molar ratios are shown in Fig.3. The diffraction patterns of the samples display the

existence of the peaks corresponding to (311), (400), (440) and (511), which confirm the presence of MgAl_2O_4 spinel phase. In addition, the XRD patterns confirmed the formation of $\text{Mg}_{1-x}\text{Ni}_x\text{Al}_2\text{O}_4$ phase in the prepared samples [34]. As can be seen in Fig. 4, the peak at $2\theta=44^\circ$ is related to NiO phase, which is disappeared with the increase of the CA/PEG molar ratio. The crystallite sizes were calculated by Scherrer formula and the obtained results are presented in Table 1. As can be seen, with the increase in CA/PEG molar ratio, the intensity of the peaks corresponding to spinel phase increased, corresponding to the bigger crystallite size of the samples. The obtained results showed that the citric acid in the surfactant molar ratio has a significant influence on the specific surface area. The sample prepared without surfactant exhibited the lowest surface area and the sample with citric acid to surfactant ratio of 3 possessed the highest surface area. The sample prepared without surfactant exhibited the lowest surface area and the sample with citric acid to surfactant ratio of 3 possessed the highest surface area.

The specific surface areas for the samples were converted to equivalent particle size was calculated using the BET (Brunauer–Emmet–Teller) and the following equation [35]:

$$D_{\text{BET}} = \frac{6000}{\rho \times S_{\text{BET}}} \quad (1)$$

Where D_{BET} (nm) is the average particle size, S_{BET} is the specific surface area expressed in m^2/g and ρ is the theoretical density of sample in g/cm^3 . As can be seen, increasing in CA/PEG molar ratio decreased the equivalent particle size. These results were in agreement with XRD results.

The pore size distribution, as calculated by the BJH method from the desorption branch of the nitrogen isotherm, displays that the prepared samples contain mesopores with pore size between 2 and 40 nm (Fig. 4a).

The N₂ adsorption/desorption profiles for the prepared samples are shown in Fig. 4b. It is seen that the sample showed a mesoporous structure. According to the IUPAC classification the N₂ isotherms are type IV isotherms with H2 type hysteresis loop for all samples. This type of hysteresis is characteristic of solids consisting of particles crossed by nearly cylindrical channels or made by aggregates (consolidated) or agglomerates (unconsolidated) of spherical particles. In this case pores can have non-uniform size or shape.

Fig. 5 shows the XRD patterns of the samples synthesized with different metal nitrate to citric acid ratios. It is seen that increasing in metal nitrate to citric acid ratio decreased the intensity of the peaks corresponding to spinel phase, due to decreasing the crystallite size of the samples.

The structural properties of the samples are shown in Table 2. As can be seen, the highest specific surface area was obtained for the sample prepared with a MN/CA molar ratio of 2. The results showed that there is a limit for MN/CA molar ratio above that the specific surface area decreased due to excessive heat released during the calcination. In the combustion reaction if the mixture became fuel richer the combustion temperature was lowered. Generally, the lower combustion temperature is beneficial to increase specific surface area and decrease crystallite size. On the other hand, the specific surface area of the powders synthesized by the solution combustion method is largely dependent on the amount of gases released during combustion [23, 36]. It is seen that increasing in MN/CA molar ratio up to 2 increased the specific surface area and decreased the crystalline size and particle size. But a further increase in MN/CA ratio has a negative effect on the specific surface area and also increased the particle size due to excessive heat released during the calcination.

Fig. 6a and 6b displays the effects of MN/CA molar ratio on the pore size distribution and N₂ adsorption/desorption isotherm, respectively. The results showed that the prepared samples contain mesopores with a pore size between 2 and 20 nm (Fig. 6a). The N₂

adsorption/desorption profiles of the samples are shown in Fig. 6b. As can be seen the prepared samples exhibited type IV isotherm with H2 hysteresis loop.

Fig. 7 displays the XRD patterns of the samples calcined at different temperatures. As can be seen, the intensity of peaks corresponding to spinel phase increased with increasing in calcination temperature, which means the bigger crystallite size of the samples calcined at higher temperatures.

The structural properties of the samples are presented in Table 3. It is seen that the calcination temperature has a significant effect on the specific surface area. The results indicated that increasing in calcination temperature from 700 to 800°C decreased the specific surface area and increased the crystallite size and theoretical particle size. **With the increase of the calcination temperature, citric acid as fuel was burned and a large volume of heat and gas was liberated. This can remarkably destroy the pore walls and increase the pore size, which leads to a decrease in the specific surface area [12].**

Fig. 8a and b shows the pore size distributions and N₂adsorption/desorption isotherms of the sample calcined at different temperatures. It is seen that the samples exhibited mesoporous structure with pore size distribution between 2 and 60 nm at all calcination temperatures. By increasing the calcination temperature, the pore size distribution shifted to larger values. The nitrogen adsorption/desorption isotherms can be classified as type IV isotherm with H3 hysteresis loop. This type of hysteresis is usually found in solids consisting of aggregates or agglomerates of particles forming a slit shaped pores (plates or edged particles like cubes), with a non-uniform size and/or shape.

The XRD patterns of the samples prepared under different pH values are shown in Fig. 9. As can be seen, all major diffraction peaks belonged to MgAl₂O₄.

The structural properties of the samples prepared under different pH values are shown in Table 4. As can be seen, increasing in pH value up to 9 increased the specific surface area and

decreased the theoretical particle size. Further increase in pH value does not have a significant effect on the specific surface area. By increasing the pH value, the OH groups on the surface increase, as a result, the negative charge on the surface increases, and then an electrostatic repulsion force is established between nanoparticles and inhibits particles from aggregation.

The pore size distribution displays that the prepared samples contain mesopores with a pore size between 2 and 40 NM (Fig. 10a). The increase in pH value does not have a significant effect on the pore size distribution. The N₂ adsorption/desorption profiles for the prepared samples are shown in Fig. 10b. According to the IUPAC classification the N₂ isotherm is a type IV isotherm with type H3 hysteresis loop for all samples except for the sample prepared under the pH value of 3, which showed a type H2 hysteresis loop.

3.2. Catalytic Performance

Temperature programmed reduction (TPR) profile of the calcined 10%Ni-MgAl₂O₄ catalyst with the highest surface area (prepared under the pH value of 9) is shown in Fig. 11. Only one wide reduction peak appears at 800°C. This high reduction temperature could be ascribed to the reduction of NiO strongly interacted with alumina in the form of nickel aluminate.

The CH₄ and CO₂ conversions at different temperatures are shown in Fig 12. The CH₄ and CO₂ conversions increased with increasing the reaction temperature due to the endothermic nature of the reaction. It is seen that the CO₂ conversion is higher than CH₄ conversion at all temperatures because of the occurrence of reverse water shift gas reaction (CO₂ + H₂ ↔ CO + H₂O). According to equation 2, dry reforming is an endothermic reaction and requires high temperatures to attain good conversion levels.

The conversions of methane and carbon dioxide were calculated by means of equations (3) and (4), respectively:

$$\text{Methane conversion: } X_{CH_4} = \frac{CH_{4(in)} - CH_{4(out)}}{CH_{4(in)}} \times 100\% \quad (3)$$

$$\text{Carbon dioxide conversion: } X_{CO_2} = \frac{CO_{2(in)} - CO_{2(out)}}{CO_{2(in)}} \times 100\% \quad (4)$$

The H₂/CO molar ratios at different temperatures over 10%NiMgAl₂O₄ catalyst is shown in Fig. 13. It is seen that the H₂/CO ratios are less than one in CO₂ reforming because of the occurrence of reverse water gas shift reaction. In dry reforming process, by increasing the temperature the endothermic dry reforming reaction proceeds better and hence the H₂/CO ratio increases.

The short time stability of catalyst was investigated for 300 min under dry reforming condition at 700°C, Fig. 14. The results showed a good stability for 10%NiMgAl₂O₄ catalyst without any decrease in CH₄ conversion during the reaction.

Temperature programmed oxidation (TPO) profile of spent 10%NiMgAl₂O₄catalyst was shown in Fig. 15. Only one peak is observed at 600-800 °C in Fig. 15. The observed peak was assigned to a filamentous form of carbon.

4. Conclusion

NiMgAl₂O₄ catalyst with high surface area was synthesized by surfactant-assisted sol-gel combustion method and employed in dry reforming of methane. The obtained results showed that the citric acid to surfactant molar ratio and calcination temperature has a significant influence on the specific surface area. The results revealed that increasing in calcination temperature decreased the specific surface area and increased both the crystallite and particle sizes due to the thermal sintering of magnesium aluminate. The results showed that increasing in CA/PEG molar ratio increased the specific surface area and decreased the equivalent particle size. The results showed that there is a limit for MN/CA molar ratio above that the specific

surface area decreased due to excessive heat released during the calculation . The furthermore an increase in pH value does not have a significant effect on the specific surface area and increasing in pH value up to 9 increased the specific surface area and decreased the theoretical particle size. The 10%NiMgAl₂O₄ catalyst revealed high CH₄ and CO₂ conversions in dry reforming reaction.

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References

- [1] A. Ranjbar, M. Rezaei, Preparation of nickel catalysts supported on CaO_2Al₂O₃ for methane reforming with carbon dioxide, International Journal of Hydrogen Energy, 37 (2012) 1-7.
- [2] J. Newnham, K. Mantri, M. H. Amin, J. Tardio, S. K. Bhargava, Highly stable and active Ni-mesoporous alumina catalysts for dry reforming of methane, International Journal of Hydrogen Energy, 37 (2012) 1454-1464.
- [3] H. Li, H. Xu, J. Wang, Methane reforming with CO₂ to syngas over CeO₂-promoted Ni/Al₂O₃-ZrO₂ catalysts prepared via a direct sol-gel process, Journal of Natural Gas Chemistry, 20 (2011) 1-8.
- [4] N. Hadian, M. Rezaei, Z. Mosayebi, F. Meshkani, CO₂ reforming of methane over nickel catalysts supported on nanocrystalline MgAl₂O₄ with high surface area, Journal of Natural Gas Chemistry, 21 (2012) 200-206.

- [5] K. Sutthiumporn, S. Kawi, Promotional effect of alkaline earth over Ni–La₂O₃ catalyst for CO₂ reforming of CH₄: Role of surface oxygen species on H₂ production and carbon suppression, *International Journal of Hydrogen Energy*, 36 (2011) 14435-14446.
- [6] P. Djinović, J. Batista, A. Pintar, Efficient catalytic abatement of greenhouse gases: Methane reforming with CO₂ using a novel and thermally stable Rh–CeO₂ catalyst, *International Journal of Hydrogen Energy*, 37(2012):2699-2707.
- [7] B. Nematollahi, M. Rezaei, M. Khajenoori, Combined dry reforming and partial oxidation of methane to synthesis gas on noble metal catalysts, *International Journal of Hydrogen Energy*, 36 (2011) 2969-2978.
- [8] W. Shen, H. Momoi, K. Komatsubara, T. Saito, A. Yoshida, S. Naito, Marked role of mesopores for the prevention of sintering and carbon deposition in dry reforming of methane over ordered mesoporous Ni–Mg–Al oxides, *Catalysis Today*, 171 (2011) 150-155.
- [9] M. García-Diéguez, I.S. Pieta, M.C. Herrera, M.A. Larrubia, L.J. Alemany, Nanostructured Pt- and Ni-based catalysts for CO₂-reforming of methane, *Journal of Catalysis*, 270 (2010) 136-145.
- [10] N. Wang, W. Chu, T. Zhang, X-S. Zhao, Synthesis, characterization and catalytic performances of Ce-SBA-15 supported nickel catalysts for methane dry reforming to hydrogen and syngas, *International Journal of Hydrogen Energy*, 37 (2012) 19-30.
- [11] H. Eltejaei, H. R. Bozorgzadeh, J. Towfighi, M. R. Omidkhah, M. Rezaei, R. Zanganeh, A. Zamaniyan, A. ZarrinGhalam, Methane dry reforming on Ni/Ce_{0.75}Zr_{0.25}O₂–MgAl₂O₄ and Ni/Ce_{0.75}Zr_{0.25}O₂– γ -alumina: Effects of support composition and water addition, *International Journal of Hydrogen Energy*, 37 (2012) 4107-4118.
- [12] E. Navaei Alvar, M. Rezaei, H. Navaei Alvar, Synthesis of mesoporous nanocrystalline MgAl₂O₄ spinel via surfactant assisted precipitation route, *Powder Technology*, 198 (2010) 275-278.

- [13] H. Arandiyan, J. Li, L. Ma, S.M. Hashem nejad, M.Z. Mirzaei, J. Chen, H. Chang, C.Liu, C. Wang, L. Chen, Methane reforming to syngas over $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_3$ ($0 \leq x \leq 1$) mixed-oxide perovskites in the presence of CO_2 and O_2 , *Journal of Industrial and Engineering Chemistry*, 18 (2012) 2103-2114.
- [14] X. Yan, C-j Liu, Effect of the catalyst structure on the formation of carbon nanotubes over Ni/MgO catalyst, *Diamond and Related Materials*, 31 (2013) 50-57.
- [15] X. Yan, Y. Liu, B. Zhao, Z. Wang, Y. Wang, C-j Liu, Methanation over Ni/SiO₂: Effect of the catalyst preparation methodologies, *International Journal of Hydrogen Energy*, 38 (2013) 2283-2291.
- [16] X. Yu, N. Wang, W. Chu, M. Liu, Carbon dioxide reforming of methane for syngas production over La-promoted NiMgAl catalysts derived from hydrotalcites, *Chemical Engineering Journal*, 209 (2012) 623-632
- [17] N. Wang, W. Chu, T. Zhang, X-S. Zhao, Manganese promoting effects on the Co–Ce–Zr–O_x nano catalysts for methane dry reforming with carbon dioxide to hydrogen and carbon monoxide, *Chemical Engineering Journal*, 170 (2011) 457-463
- [18] M. García-Diéguez, E. Finocchio, M.Á. Larrubia, L.J. Alemany, G. Busca, Characterization of alumina-supported Pt, Ni and PtNi alloy catalysts for the dry reforming of methane, *Journal of Catalysis*, 274 (2010) 11-20
- [19] T. Y. Kim, S. M. Kim, W. S. Lee, S. I. Wo, Effect and behavior of cerium oxide in Ni/ γ -Al₂O₃ catalysts on autothermal reforming of methane: CeAlO₃ formation and its role on activity, *International Journal of Hydrogen Energy*, 38 (2013) 6027-6032.
- [20] A. Jahangiri, H. Pahlavan zadeh, H. Aghabozorg, Synthesis, characterization and catalytic study of Sm doped LaNiO₃ nanoparticles in reforming of methane with CO_2 and O_2 , *International Journal of Hydrogen Energy*, 37 (2012) 9977-9984.

- [21] G. D.B. Nuernberg, E. L. Foletto, C. E.M. Campos, Humberto V. Fajardo, Neftalí L.V. Carreño, Luiz F.D. Probst, Direct decomposition of methane over Ni catalyst supported in magnesium aluminate, *Journal of Power Sources*, Volume 208 (2012) 409-414.
- [22] Q.Y. Chen, C.M. Meng, T.C. Lu, X.H. Chang, G.F. Ji, L. Zhang, F. Zhao, Enhancement of sintering ability of magnesium aluminate spinel (MgAl_2O_4) ceramic nanopowders by shock compression, *Powder Technology*, 200 (2010) 91-95.
- [23] J. Bai, J. Liu, Ch. Li, G.g Li, Q. Du, Mixture of fuels approach for solution combustion synthesis of nanoscale MgAl_2O_4 powders, *Advanced Powder Technology*, 22 (2011) 72-76.
- [24] X. Zhang, Hydrothermal synthesis and catalytic performance of high-surface-area mesoporous nanocrystallite MgAl_2O_4 as catalyst support, *Materials Chemistry and Physics*, 116, (2009) 415-420.
- [25] Z. Mosayebi, M. Rezaei, N. Hadian, F. Zareie Kordshuli, F. Meshkani, Low temperature synthesis of nanocrystalline magnesium aluminate with high surface area by surfactant assisted precipitation method: Effect of preparation conditions, *Materials Research Bulletin*, 47 (2012) 2154-2160.
- [26] I. Ganesh, R. Johnson, G.V.N. Rao, Y.R. Mahajan, S.S. Madavendra, B.M. Reddy, Microwave-assisted combustion synthesis of nanocrystalline MgAl_2O_4 spinel powder, *Ceramics International*, 31 (2005) 67-74.
- [27] A. Horvatha, L. Guazia, A. Kocsonyaa, G. Safranb, V. La Parolac, L.F. Liottac, G. Pantaleoc, A.M. Veneziac, Sol-derived $\text{AuNi/MgAl}_2\text{O}_4$ catalysts: Formation, structure and activity in dry reforming of methane, *Applied Catalysis A: General* 468 (2013) 250– 259.
- [28] S. Alamolhoda, S.A. Seyyed Ebrahimi, A. Badiei, Optimization of the Fe/Sr ratio in processing of ultra-fine strontium hexaferrite powders by a sol–gel auto-combustion method in the presence of trimethylamine, *Iranian International Journal Science*, 5 (2004) 173–179.

- [29] J. Huang, H. Zhuang, W.L. Li, Synthesis and characterization of nano crystalline $\text{BaFe}_{12}\text{O}_{19}$ powders by low temperature combustion, *Materials Research Bulletin*, 38 (2003) 149-159.
- [30] M. Ramzi Ben Romdhane, S. Baklouti, J. Bouaziz, T. Chartier, J-F.Baumard, Dispersion of Al_2O_3 concentrated suspensions with new molecules able to act as binder, •*Journal of the European Ceramic Society*, 24 (2004) 2723-2731
- [31] Z. Haijun, J. Xiaolin, L. Zhanjie, Li. Zhenzhen, The low temperature preparation of nanocrystalline MgAl_2O_4 spinel by citrate sol–gel process, *Materials Letters*, 58 (2004) 1625-1628.
- [32] S. Biamino, C. Badini, Combustion synthesis of lanthanum chromite starting from water solutions: Investigation of process mechanism by DTA–TGA–MS, *Journal of the European Ceramic Society*, 24 (2004) 3021-3034.
- [33] J. Guo, H. Lou, H. Zhao, D. Chai, X. Zheng, Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels, *Applied Catalysis A: General* 273 (2004) 75–82.
- [34] I. Robert, P. Barvinschi. Characterization of $\text{Mg}_{1-x}\text{Ni}_x\text{Al}_2\text{O}_4$ solid solutions prepared by combustion synthesis. *Journal of the European Ceramic Society* 31.5 (2011): 739-743.
- [35] M. Rezaei, M. Khajenoori, B. Nematollahi, Synthesis of high surface area nanocrystalline MgO by pluronic P123 triblock copolymer surfactant, *Powder Technology* 205 (2011) 112–116.
- [36] I. Ganesh, B. Srinivas, R. Johnson, B.P. Saha, Y.R. Mahajan, Effect of fuel type on morphology and reactivity of combustion synthesised MgAl_2O_4 powders, *Br. Ceram. Trans.* 101 (2002) 247–254.

Fig. 1. The preparation diagram of Ni-MgAl₂O₄

Fig. 2. FTIR spectra of 10% Ni-MgAl₂O₄ prepared with CA/PEG = 3, CA/MN = 2 and pH = 7, (a) before and (b) after calcination at 700 °C.

Fig. 3. X-ray diffraction patterns of the samples prepared under different CA/PEG molar ratios: MN/CA=2, pH= 7, calcination temperature = 700°C.

Fig. 4.(a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different CA/PEG ratios: MN/CA = 1, pH= 7, calcination temperature = 700°C.

Fig. 5. X-ray diffraction patterns of the samples prepared under different MN/CA ratios, CA/PEG=3, pH= 7, calcination temperature = 700°C.

Fig. 6. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different MN/CA ratios, CA/PEG=3, pH= 7, calcination temperature = 700°C.

Fig. 7. X-ray diffraction patterns of the samples prepared under different calcination temperatures, CA/PEG = 3, MN/CA.= 2, pH= 7.

Fig. 8. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different calcination temperatures, CA/PEG = 3, MN/CA.= 2, pH= 7.

Fig. 9. X-ray diffraction patterns of the samples prepared under different pH values, CA/PEG = 3, MN/CA.= 2, calcination temperature 700°C.

Fig. 10. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different pH values, CA/PEG = 3, MN/CA.= 2, calcination temperature 700°C.

Fig. 11. Temperature-programmed reduction profile of 10% Ni/MgAl₂O₄ catalyst.

Fig. 12. (a) CH₄ conversion and (b) CO₂ conversion in dry reforming (reaction conditions CH₄/CO₂=1:1, GHSV=12000 (ml/h gcat).

Fig. 13.H₂/CO ratio over 10%Ni-MgAl₂O₄at different temperatures

Fig. 14. The stability over 10%Ni/MgAl₂O₄ catalyst (reaction conditions: CH₄/CO₂=1:1, GHSV=12000 (ml/h g_{cat})).

Fig. 15. Temperature-programmed oxidation curve of the spent 10%Ni/MgAl₂O₄ catalyst

Table. 1. Effect of citric acid to polyethylene glycol (CA/PEG) molar ratio on the structural properties of the samples, metal nitrate to citric acid (MN/CA) ratio of 1, pH= 7, calcination temperature = 700 °C.

CA/PEG	S_{BET}	Pore volume	Pore size	Crystallite size (nm)			Particle size
molar ratio	($\text{m}^2 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	(nm)	(311)	(400)	(440)	(nm)
0	87.07	0.107	4.1	14.82	12.67	9.78	15.27
1	92.94	0.145	4.32	10.60	12.7	9.81	14.31
2	103.58	0.130	3.08	10.58	12.67	9.78	12.84
3	108.43	0.142	3.93	8.23	12.67	12.45	12.26
4	106.79	0.152	3.95	7.41	25.34	9.78	12.45

Table. 2. Effect of MN/CA molar ratio on the structural properties of the samples, CA/PEG = 3, pH= 7, calcination temperature = 700°C.

MN/CA	S _{BET}	Pore volume	Pore size	Crystallite size (nm)			Particle size
molar ratio	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(nm)	(311)	(400)	(440)	(nm)
1	91.22	0.134	4.02	12.36	38.03	17.12	14.58
2	95.81	0.239	6.31	8.24	10.87	11.42	13.88
3	85.71	0.295	5.02	10.59	12.68	19.57	15.22
4	67.19	0.120	4.39	12.35	12.67	8.56	19.8

Table. 3. Effect of calcination temperature on the structural properties of the samples,

CA/PEG = 3, MN/CA.= 2, pH= 7.

Calcination temperature (°C)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore size (nm)	Crystallite size (nm)			Particle size (nm)
				(311)	(400)	(440)	
700	95.81	0.239	6.31	8.24	10.87	11.42	13.88
800	65.33	0.184	7.63	8.23	30.43	13.7	20.36

Table. 4. Effect of pH on the structural properties of the samples, CA/PEG = 3, MN/CA.= 2, calcination temperature 700 °C.

pH	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Particle size (nm)
3	66.79	0.164	5.36	19.91
5	79.16	0.177	7.15	16.8
7	95.81	0.239	6.31	13.89
9	97.11	0.158	4.81	13.69
10	92.13	0.201	5.01	14.44

Fig. 1. The preparation diagram of Ni-MgAl₂O₄

Fig. 2. FTIR spectra of 10% Ni-MgAl₂O₄ prepared with CA/PEG = 3, CA/MN = 2 and pH = 7, (a) before and (b) after calcination at 700 °C.

Fig. 3. X-ray diffraction patterns of the samples prepared under different CA/PEG molar ratios:
MN/CA=2, pH= 7, calcination temperature = 700°C.

Fig. 4. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different CA/PEG ratios: MN/CA = 1, pH= 7, calcination temperature = 700°C.

Fig. 5. X-ray diffraction patterns of the samples prepared under different MN/CA ratios, CA/PEG=3, pH= 7, calcination temperature = 700°C.

Fig. 6. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different MN/CA ratios, CA/PEG=3, pH= 7, calcination temperature = 700°C.

Fig. 7. X-ray diffraction patterns of the samples prepared under different calcination temperatures, CA/PEG = 3, MN/CA.= 2, pH= 7.

Fig. 8. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different calcination temperatures, CA/PEG = 3, MN/CA.= 2, pH= 7.

Fig. 9. X-ray diffraction patterns of the samples prepared under different pH values, CA/PEG = 3, MN/CA.= 2, calcination temperature 700°C.

Fig. 10. (a) Pore size distributions and (b) N₂ adsorption/desorption isotherms of the samples prepared under different pH values, CA/PEG = 3, MN/CA.= 2, calcination temperature 700°C.

Fig. 11. Temperature-programmed reduction profile of 10% Ni/MgAl₂O₄ catalyst.

Fig. 12. (a) CH₄ conversion and (b) CO₂ conversion in dry reforming (reaction conditions CH₄/CO₂=1:1, GHSV=12000 (ml/h gcat)).

Fig. 13. H_2/CO ratio over 10%Ni-MgAl₂O₄at different temperatures.

Fig. 14. The stability over 10%Ni/MgAl₂O₄ catalyst(reaction conditions: CH₄/CO₂=1:1, GHSV=12000 (ml/h g_{cat}).

Fig. 15. Temperature-programmed oxidation curve of the spent 10%Ni/MgAl₂O₄ catalyst

NiMgAl₂O₄ catalysts were synthesized by surfactant assisted sol gel combustion method and the catalysts were studied in CO₂ reforming of methane.