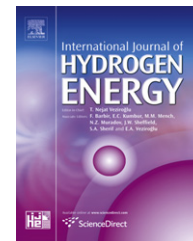


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# Autothermal reforming of methane over nickel catalysts supported on nanocrystalline MgAl<sub>2</sub>O<sub>4</sub> with high surface area

Zeinab Mosayebi<sup>a,b</sup>, Mehran Rezaei<sup>a,b,\*</sup>, Abolfazl Biabani Ravandi<sup>a</sup>, Narges Hadian<sup>a,b</sup>

<sup>a</sup> Catalyst and Advanced Materials Research Laboratory, Chemical Engineering Department, Faculty of Engineering, University of Kashan, Kashan, Iran

<sup>b</sup> Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan, Iran

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## ABSTRACT

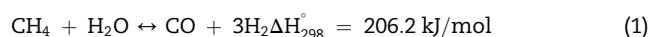
In this paper autothermal reforming of methane (ATR) was carried out over MgAl<sub>2</sub>O<sub>4</sub> supported Ni catalysts with various Ni loadings. MgAl<sub>2</sub>O<sub>4</sub> spinel with high specific surface area, as nanocrystalline carrier for nickel catalysts was synthesized by co-precipitation method with the addition of pluronic P123 triblock copolymer as surfactant. The prepared samples were characterized by XRD, BET, TEM, SEM, TPR and TPH techniques. The results demonstrated that methane conversion is significantly increased with increasing the Ni content and methane conversion of 15% Ni/MgAl<sub>2</sub>O<sub>4</sub> was higher than that of other catalysts in all operation temperatures. Furthermore the influences of H<sub>2</sub>O/CH<sub>4</sub>, and O<sub>2</sub>/CH<sub>4</sub> molar ratio in feed and GHSV on activity of 5% Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst were investigated.

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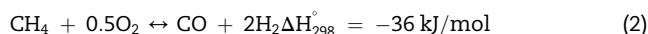
## 1. Introduction

There has been substantial interest in recent years in alternative routes for conversion of natural gas (methane) to syngas, a mixture of CO and H<sub>2</sub>, which can be used to produce chemical products with high added values, such as hydrocarbons and oxygenated compounds [1]. There are three major thermochemical techniques used to produce syngas from hydrocarbon fuels, i.e. steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR) [2–4].

The SR gives a high yield of H<sub>2</sub>, but reaction is endothermic and requires external heat input (Eq. (1)).



The POX is an exothermic process and may require external cooling. A lower H<sub>2</sub>/CO ratio is also obtained in POX (Eq. (2)). In addition, the partial oxidation reaction is very fast, which can be started quickly.



ATR is a chemical combination of steam reforming and partial oxidation and it is an economical process for the production of hydrogen. Therefore, both the steam reforming and partial oxidation reactions take place. The hydrocarbon feed (methane or a liquid fuel) is reacted with both steam and oxygen to produce a hydrogen-rich gas. In the autothermal reforming, the partial oxidation reaction supplies all the heat needed to drive the catalytic steam reforming reaction [5,6].

\* Corresponding author. Catalyst and Advanced Materials Research Laboratory, Chemical Engineering Department, Faculty of Engineering, University of Kashan, Kashan, Iran. Tel.: +98 361 5912469; fax: +98 361 5559930.

E-mail address: [rezaei@kashanu.ac.ir](mailto:rezaei@kashanu.ac.ir) (M. Rezaei).

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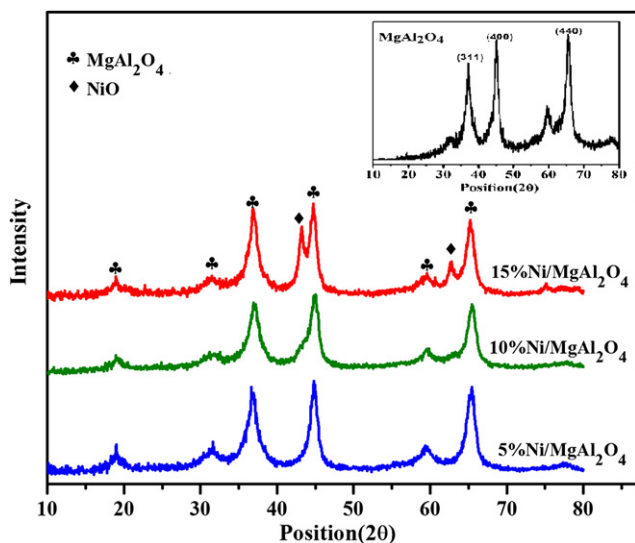
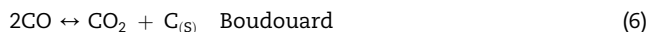
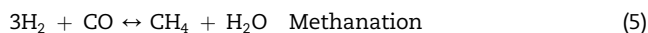
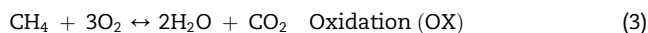


Fig. 1 – XRD patterns of calcined catalysts and  $\text{MgAl}_2\text{O}_4$  carrier (upper inset).

The side reactions occur in the autothermal reformer are listed below:



The main features of ATR are: (1) Low energy requirement, due to the opposite contribution of the exothermic methane oxidation and endothermic steam reforming [7,8]; (2) Low specific consumption; (3) High gas space velocity (at least one order of magnitude higher than the traditional steam reforming); and (4) Preset  $\text{H}_2/\text{CO}$  ratio easily regulated by inlet  $\text{CH}_4/\text{H}_2\text{O}/\text{O}_2$  ratios and  $\text{CO}_2$  recycling [9,10]. Operation at low

steam to carbon (S/C) ratio improves the syngas composition and reduces the  $\text{CO}_2$  recycle, which decreases the investment and energy consumption. However, the reduction of S/C ratio favors soot formation in the ATR reactor and carbon formation in the pre-reformer [11]. Commercial ATR catalyst is a nickel catalyst adapted to the ATR conditions [12]. Nickel catalysts supported on alumina ( $\text{Ni}/\text{Al}_2\text{O}_3$ ) are commercially used in steam reforming of methane mainly due to their low cost [11]. However, these catalysts suffer deactivation, generally because of coke formation [13–15]. One of the main challenges of methane reforming process is to decrease the deleterious effect of coke formation. An effective way in preventing coke formation is addition of alkali or alkaline earth oxides such as  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$  and so on to support [16].

Among the catalyst supports, magnesium aluminate spinel,  $\text{MgAl}_2\text{O}_4$ , has been widely used in industrial applications [17]. This material has unique properties, such as high melting temperature (2135 °C), high mechanical strength at elevated temperature, high chemical inertness, good thermal shock resistance and catalyst properties [18]. For many of its applications especially as catalyst support, a high surface area, small crystalline size, high porosity and more active sites, is more desired. In this paper, nanocrystalline magnesium aluminate with high surface area was synthesized by a simple co-precipitation method by addition of pluronic P123 triblock copolymer as surfactant and employed as a support for nickel catalyst in autothermal reforming of methane.

## 2. Experimental

### 2.1. Preparation of support

$\text{MgAl}_2\text{O}_4$  nanopowder was prepared by co-precipitation method with surfactant-assisted. In a typical preparation, desired amount of pluronic P123 block copolymer surfactant (Poly(ethylene glycol)-block, Poly(propylene glycol)-block, Poly(ethylene glycol), MW: 5800, Aldrich) was dissolved in distilled water under vigorous stirring to form a transparent solution. The P123/ $\text{MgAl}_2\text{O}_4$  molar ratio was chosen 0.01. After that, stoichiometric amounts of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck) were added to water containing P123. Then an ammonia solution was added dropwise to the well

Table 1 – The structural properties of catalyst support and calcined catalysts.

Sample	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Pore size (nm)	Crystallite size (nm)		
			(311)	(400)	(440)
$\text{MgAl}_2\text{O}_4$	0.64	11.16	5.53	5.68	4.47
Sample	$\text{MgAl}_2\text{O}_4$	5% Ni/ $\text{MgAl}_2\text{O}_4$	10% Ni/ $\text{MgAl}_2\text{O}_4$	15% Ni/ $\text{MgAl}_2\text{O}_4$	
$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	184	139	121	104	
Ni area ( $\text{m}^2 \text{g}^{-1}_{\text{Ni}}$ )	–	2.41	2.65	1.86	
Ni size (nm)	–	11.15	25.35	54.21	
Dispersion (%)	–	8.96	3.94	1.84	

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