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# Impregnation vs. sol-gel and sol-gel-plasma dispersion of nickel nanoparticles over Al<sub>2</sub>O<sub>3</sub> employed in combined dry reforming and partial oxidation of greenhouse gases to syngas

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## ABSTRACT

This paper is focused on the fabrication of Ni/Al<sub>2</sub>O<sub>3</sub> nanocatalyst via impregnation, sol-gel and hybrid sol-gel plasma techniques. Physicochemical properties of the samples were characterized by XRD, FESEM, TEM, EDX, BET and FTIR analyses. Also, used nanocatalysts were characterized via TG-DTG, FESEM, EDX and XRD analyses. The catalytic performance of the nanocatalysts was investigated. XRD patterns proved that for sol-gel based samples, amorphous behaviour was intensified and concentration of prone planes to coke deposition was decreased especially in plasma treated one. FESEM images were exhibited that homogenous particle size distribution was obtained for the sample which prepared by sol-gel-plasma method. TEM and EDX analyses reported the promoted nickel dispersion for sol-gel based samples especially in plasma treated sample. Owing to the BET results utmost surface area 297 m<sup>2</sup>/g was declared for sol-gel-plasma catalyst. Sol-gel-plasma catalyst indicated the higher catalytic activity compared to the others. In addition, conducted stability test during 2880 min asserted that, deactivation was occurred in all samples but sol-gel-plasma catalyst is more stable. After stability test, sol-gel-plasma catalyst roughly preserved its structure while active phase migration was took place for the others. Also, based on EDX and TG-DTG results, more uniform dispersion and lowest amount of coke deposit was found for sol-gel-plasma catalyst.

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## Introduction

Today's, concentration of greenhouse gases (GHG) such as CO<sub>2</sub> and CH<sub>4</sub> is rapidly growing. Higher amounts of GHG leads

environmental problems like global warming, rise in sea level and thus omitting many cities from the universal map [1,2]. Therefore, the major concerns of the humanity and investigations in the field of GHG reduction have gained plenty of attentions in recent decades [3–5]. One of these fields is

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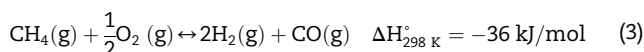
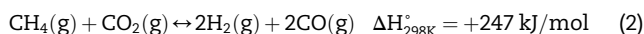
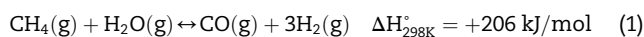
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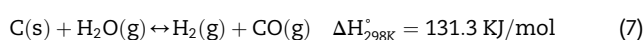
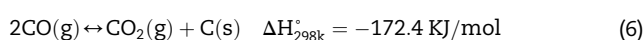
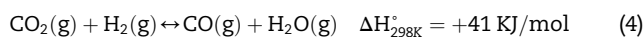
methane reforming process that has three main branches which are as follows: (i) Steam reforming of methane (SRM) reaction No 1, (ii) Partial oxidation of methane (POX) reaction No 2 and (iii) Dry reforming of methane (DRM) reaction No 3 [6–8].



As shown above, methane in the presence of steam, oxygen or  $\text{CO}_2$  turns into synthesis gas with various  $\text{H}_2/\text{CO}$  ratios [9–11]. Methane reforming processes are catalytic reactions and conventional catalyst of them is  $\text{Ni}/\text{Al}_2\text{O}_3$  which was synthesized via impregnation method [12,13]. Large potential of carbon deposition is the main problem of methane reforming processes which in turn leads to the catalyst deactivation and reaction cease [14–16].

Among the above noted reactions, DRM might be an appropriate choice for GHG reduction amounts, but the major drawback means coke deposition remains unsolved [17–19]. Investigations present that better results might be found in combined reactions [20–22]. Syngas production via utilization of combined partial oxidation and steam reforming of  $\text{CH}_4$  was evaluated by Chan and et al. [23]. It was reported for a constant  $\text{CH}_4/\text{O}_2$  ratio, adding of steam leads to the lower coke formation and higher  $\text{H}_2/\text{CO}$ . Moreover, for  $\text{CH}_4/\text{O}_2 \geq 5$ , steam introduction causes to higher  $\text{H}_2$  yield and less amount of the energy consumption [23,24]. Itkulova and et al. reported addition of 20 vol% steam to DRM, reduces the amount of required energy, promotes hydrogen yield and improves catalyst dispersion [25].

Combined  $\text{CO}_2$ - reforming/partial oxidation of methane (CRPOM) is another form with some benefits which are as follows: (i) part of required energy supplies by exothermic POX so, fewer amounts of energy and lower cost is needed [26–28]. (ii) Oxygen addition, causes less carbon formation compared individual reactions such as DRM. However, oxygen addition from less coke deposition point of view is useful, but it must be added in controlled amounts. Lower amount won't have the desired effects and high amount results in less selectivity, hot spot formation and sintering [29–31]. Moreover, some side reactions take place during CRPOM. These reactions which affect the catalytic performance are as follows: (i) Reverse water gas shift reaction (RWGS) reaction No 4, (ii) Methane decomposition (MD) reaction No 5, (iii) Boudouard reaction (BD) No 6 and (iv) carbon-water reaction (CW) reaction No 7.



Better characterization such as smaller particle size, uniform dispersion and strong interaction between metallic active phase and support are very effective in the rate of coke deposition. Moreover, superior physiochemical properties are

obtainable by utilization of an appropriate synthesis method. Therefore, choose another method except conventional impregnation such as sol-gel, combustion and precipitation might be led to the better coke resistance.  $\text{Li-Ni}/\text{Al}_2\text{O}_3$  catalysts were synthesized via impregnation and precipitation methods by Ito and et al. They reported that the precipitated one has high nickel dispersion, better catalytic activity and well stability during DRM [32]. Sol-gel, impregnation and combination of them were applied for synthesis of  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  by Ji et al. Results proved the excellent coke resistance of sol-gel synthesized catalyst [33]. Enhanced performances of sol-gel prepared catalysts were reported by some other researches [34–36]. Superior results of them is belongs to the nature of sol-gel technique that is a suitable method for homogeneous materials synthesis especially nanocatalysts with high surface area and uniform particle size distribution [15,37,38].

Moreover, in some studies to better catalytic performance achievement, a conventional or new synthesis method was combined by some treatments such as plasma or ultrasonic irradiation [39,40]. Plasma treatment was employed by Rahemi and et al. for promotion of impregnated  $\text{Ni}/\text{Al}_2\text{O}_3$  and  $\text{Ni}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ . More uniform dispersion, high surface area and strong metal-support interaction (SMSI) were attained for plasma treated samples [41]. Furthermore, outstanding impact of plasma treatment is in agreement with Yu et al. [42] and other studies [41,43]. To the best of our knowledge, utilization of sol-gel-plasma method in synthesis of  $\text{Ni}/\text{Al}_2\text{O}_3$  has not been previously done. Therefore, in this work,  $\text{Ni}/\text{Al}_2\text{O}_3$  nanocatalysts with various methods: impregnation, sol-gel and sol-gel-plasma were synthesized and their performance was evaluated for CRPOM. The attributes of generated nanocatalysts were investigated by BET, FESEM, TEM, XRD, FTIR and EDX analyses. Also, used catalysts (after the 2880 min stability test) were evaluated by TG-DTG, EDX, FESEM and XRD analyses. Moreover, effect of the  $\text{CH}_4/\text{CO}_2$  molar ratio and various GHSV over the catalytic performance were explored.

## Materials and methods

### Materials

$\text{Al}$ -tri-sec-butoxide and  $\gamma\text{-Al}_2\text{O}_3$  were applied as support precursors. Ethanol and Deionized water were used as solvent.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was employed as precursor of active phase. Moreover, acetyl acetone utilized as chelating agents. Whole of the precursors were provided by Merck Company.

### Nanocatalyst preparation and procedures

Nanocatalysts were generated via hybrid sol-gel-plasma, sol-gel and impregnation techniques. As exhibited in Fig. 1 for impregnation method, at first required amount of nickel nitrate was deliquesced in deionized water. This solution was denoted as active phase solution. Then, commercial  $\gamma\text{-Al}_2\text{O}_3$  support impregnated with the active phase solution and mixed at  $80^\circ\text{C}$  for 1 h. After, drying of samples carried out during 8 h under air flow and at  $120^\circ\text{C}$ . Subsequently, calcination was performed under air flow, at  $850^\circ\text{C}$  and for 5 h. Finally,  $\text{Ni}/\text{Al}_2\text{O}_3$  was shaped and formed by adding bentonite.

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