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Syngas Production from Dry Reforming of Methane over Nano Ni Polyol Catalysts

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***Abstract*—Dry reforming of methane (DRM) is an environment friendly process since it utilizes two major greenhouse gases (CH_4 and CO_2) to produce valuable syngas. Polyol process was adopted to prepare nano supported (Al_2O_3, ZrO_2 and CeO_2) Ni based nano catalysts for DRM reaction. All catalysts were prepared in ethylene glycol medium with polyvinylpyrrolidone as a nucleation-protective agent. The main objective of this study was to develop a suitable catalyst, for syngas production, which possessed high activity, stability and minimum coking rate during DRM. The catalytic activities of the prepared catalysts were evaluated in the temperature range 500-800 ℃. The obtained results revealed that catalytic performance depends on the nature of support. Amongst all tested catalysts, Ni-Zr Pol showed highest activity (87.2%) and stability (%D.F= -0.46). On the other hand Ni-Al Pol catalyst exhibited acceptable activity (84.8%) with minimum coking rate (0.015 g/g_{cat}.h) while Ni-Ce Pol showed smallest activity (83.2%) with large amount of coke deposition (0.025 g/g_{cat}.h).**

***Index Terms*—CO_2/CH_4 reforming, nano-Ni, nano support, polyol method, activity.**

I. INTRODUCTION

High chemical stability and huge transportation cost of methane, major component of natural gas, from remote regions to industrial complexes have restricted its wider industrial applications. To overcome this difficulty, numerous research activities and technologies are in progress to transform methane into various valuable commercial products via direct and/or indirect methane chemical conversion routes [1]. The indirect transformation of methane, via synthesis gas (mixture of H_2 and CO) route, in to other liquid hydrocarbons has gained world-wide attention from the last decade. There are several methods for the conversion of methane into syngas for example partial oxidation using oxygen, carbon dioxide reforming (also named dry methane reforming) and steam reforming [2]. However as compared to other syngas production processes, dry methane reforming (DRM) reaction is industrially advantageous since it yields syngas with H_2/CO product ratio close to unity which is more suitable for liquid hydrocarbon production via Fischer–Tropsch synthesis and in the production of oxygenated compounds [3]. The main drawback of DRM is its endothermic nature which requires fairly high temperatures to achieve high conversion values. This severe operating condition could cause catalyst deactivation due to accumulation of coke over catalyst surface and/or sintering of the active metal particles [4]. Generally, the catalysts used for the DRM are categorized into two groups: (i) supported noble metals (Pt, Pd, Rh, Ru) and (ii) non-noble transition metals (Ni, Co, Fe) [5]. In comparison to noble and other transition metals, Ni seems to be the most promising choice because it is cheaper, and comparatively more active and selective. However Ni based catalysts have a tendency to deactivate due to sintering, coking, phase transformation and loss of active component [6], [7]. In the literature, numerous metallic oxides such as Al_2O_3, SiO_2, MgO, TiO_2, ZrO_2 and CeO_2 have been investigated as supports for DRM [8]. Amongst these supports, CeO_2 and ZrO_2 possess some distinct properties such as high oxygen storage capacity and high thermal stability [8], [9]. These unique properties favor them as DRM catalyst supports. Zheng et al. [10] have studied the cyclic stepwise methane reforming reactions, with steam and CO_2, over nanocomposite Ni/ZrO_2 and conventional Ni/ZrO_2 catalysts. They found that nanocomposite Ni/ZrO_2 exhibited excellent activity and recycling stability than conventional ZrO_2-supported Ni catalyst. Gonzalez-Delacruz *et al.* [11] have carried out the steam and dry reforming reactions of methane over Ni/CeO_2 powder samples prepared by combustion synthesis. The prepared catalyst showed better stability in case of dry reforming than in steam reforming of methane. Traditional catalyst preparation methods involve the precipitation and/or impregnation techniques; the latter has broadly been used for the preparation of Ni-supported catalysts for different areas of study such as DRM [12]. However, the conventional impregnation method does not provide adequate control over the final size, morphology and dispersion of active metal particles. In the literature several other preparation methods such as surfactant assisted route, sol-gel, polyol and combustion synthesis were investigated as alternatives to traditional methods [12]-[15]. The polyol process, as an alternate to conventional preparation methods, has attracted much recent attention due to having a potential to overcome the above mentioned problems. Most recently, Bayrakdar *et al.* [16] have applied Al_2O_3 supported nano Ni catalysts prepared by polyol method for partial oxidation of methane and obtained very promising results in terms of activity and stability.

This study mainly focuses on the preparation of nano Al_2O_3, ZrO_2, and CeO_2 supported Ni based nano catalysts by polyol method and their application in CO_2-CH_4 reforming

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reaction for syngas production. To the best of our knowledge, Ni based catalysts prepared by polyol method, especially nano Al_2O_3, ZrO_2 and CeO_2 supported, have rarely been studied and applied in this reforming reaction. Various characterization techniques have been employed to compare these polyol catalysts.

II. EXPERIMENTAL

A. *Materials*

All the chemicals were of analytical grade and used without further purification. Nano powders of alumina (γ-Al_2O_3; S_{BET} = 180 m^2/g), ceria (CeO_2; S_{BET} = 40 m^2/g), zirconia (ZrO_2; S_{BET} = 35 m^2/g) supplied by MKnano® were used as the catalyst supports throughout this investigation. Nickel acetate [$Ni(OCOCH_3)_2{\bullet}4H_2O$; 99%] (obtained from Sigma-Aldrich®) was used as Ni metal precursor. Moreover, ethylene glycol, ($C_2H_6O_2$) (EG) and polyvinylpyrrolidone $(C_6H_9NO)_x$ (PVP) (Mol.wt = 58,000 $gmol^{-1}$) (Alfa Aesar) were used as reducing/stabilizing and anti-nucleation agent (avoid nanoparticle sintering and aggregation) respectively.

B. *Catalyst Preparation*

Nano supported (CeO_2, ZrO_2 and Al_2O_3) Ni catalysts (5 wt% Ni loading) were prepared by polyol method. In the polyol process, a given amount of the nano support (5g) was added to (EG)-(PVP)-nickel precursor solution and agitated with magnetic stirrer. Then 0.4 g (1M) NaOH was added to promote the formation of nano Ni colloid in the solution under controlled pH 10. The suspension was then kept for 24 h at 30 ℃ under constant stirring. The nickel acetate concentration was 0.05M in order to obtain of 5 wt% Ni loading, whereas the ratio of PVP/Ni (w/w) was kept at 2. The obtained suspension after 24 h was then heated up to boiling point of EG (195 ℃) under reflux conditions for 3 h to reduce the Ni ions and formation of nano Ni particles on support. Then the homogeneous colloidal suspension was rapidly cooled down to room temperature in an ice bath. The catalyst thus obtained was separated by filtration, and subsequently washed several times with excess of acetone and distilled water in order to remove organic phase. Afterwards, the filtered catalyst was dried overnight at 120 ℃ and subsequently calcined at 500 ℃ for 4 h in furnace. The catalysts prepared by polyol process from the respective nano supports, i.e., CeO_2, ZrO_2 and Al_2O_3 will be denoted as Ni-Ce Pol, Ni-Zr Pol and Ni-Al Pol respectively. The flow chart of the polyol process is shown in Fig. 1.

C. *Catalyst Testing*

The CO_2-CH_4 reforming reaction was conducted at atmospheric pressure in a 9.4 mm I.D. and 48 cm long, quartz tube, fixed-bed continuous-flow microreactor (Thermcraft incorporated) using 0.6 g of the catalyst. The reactor assembly has four independently heated zones; the reaction temperature was measured using a K-type thermocouple placed in an axial thermowell centered in the catalyst bed. For each experiment the catalyst was first activated under H_2 flow (40 mL/min) at 500 ℃ for 2 h. The total flow rate and volume ratio of the feed gases ($CH_4/CO_2/N_2$) were 36 mL/min and 17/17/2 respectively throughout in this study. The reforming activity was studied at temperature range 500 ℃ to 800 ℃ while the effluent gases were analyzed by an online gas chromatograph (Varian Star CX3400) equipped with a thermal conductivity detector. A schematic diagram of experimental setup used for DRM reaction is shown in Fig. 2.

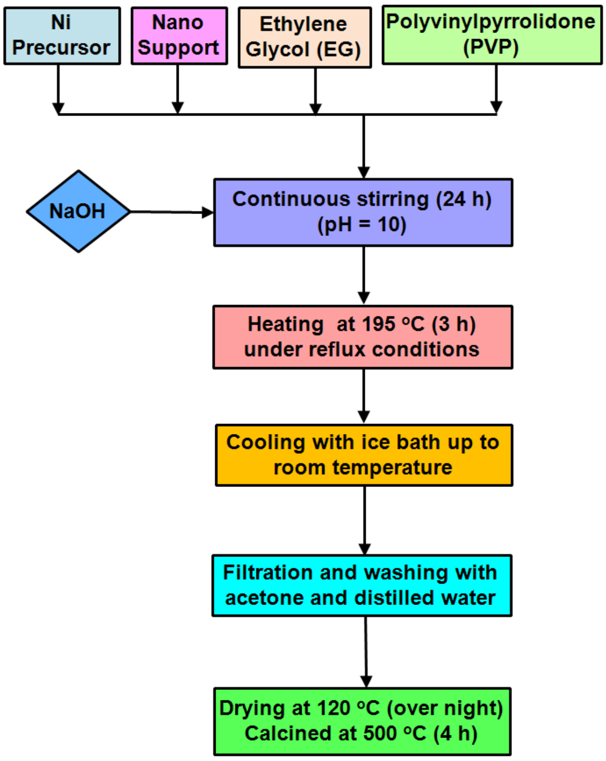

Fig. 1. Flow chart of the polyol process for catalyst preparation.

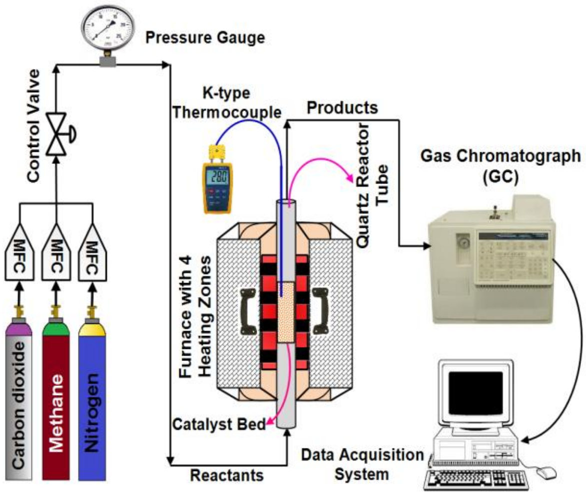

Fig. 2. Schematic diagram of experimental setup used for DRM reaction.

D. *Catalyst Characterization*

The specific surface area of the fresh and used catalyst was measured, at a temperature of liquid nitrogen (-196 ℃), with the help of Micromeritics Tristar II 3020 surface area and porosity analyzer. For each analysis, 0.3 g of catalyst was used. The degassing of the samples, before experiment, was completed at 250 ℃ for 3 h to take out the moisture and other adsorbed gases from surface and pores of sample. The temperature programmed desorption (CO_2-TPD) and CO pulse chemisorption measurements were performed in an automatic chemisorption equipment (Micromeritics Auto Chem II 2920) with a thermal conductivity detector. For CO_2 temperature programmed desorption (CO_2-TPD) measurements, the 70 mg of sample was first held at 200 ℃ for 1 h under He flow to remove physically adsorbed and/or weakly bound species. Then, CO_2 adsorption was carried out at 50 ℃ for 30 min by passing CO_2/He mixed gas (V/V, 10/90) with a flow rate of 30 mL/min. Afterwards the CO_2 desorption signal was recorded by TCD with linear temperature increase up to 800 ℃ at a rate of 10 ℃/min.

The metal dispersion of the catalysts was measured by CO chemisorption at 50 ℃. Prior to the pulse chemisorption experiments, all samples were reduced under H_2 flow (25 mL/min) at 1000 ℃ and subsequently flushed under He flow.

The quantity of coke deposition on spent catalysts was estimated by thermo-gravimetric analysis (TGA) in air atmosphere using EXSTAR SII TG/DTA 7300 (Thermo-gravimetric/Differential) analyzer. For this analysis 10-20 mg of spent catalyst, was heated from room temperature to 800 ℃ at a heating rate of 20 ℃/min.

III. RESULTS AND DISCUSSIONS

A. *Textural Properties*

The specific surface area, pore volume (P.V) and average pore size (P.D) of fresh and spent catalysts are summarized in Table I and Table II respectively. The pore volume and pore size were calculated from adsorption branch of the corresponding nitrogen isotherm by applying Barrett, Joyner, and Halenda (BJH) method. It is apparent from Table II that surface area of spent catalyst is decreased after 6 h of reaction. In fact thermal sintering of active metal and/or carbon deposition over catalyst surface, as evidenced by TGA results (Table III), are responsible of this change. It is quite obvious that Ni-Al Pol and Ni-Zr Pol spent catalysts showed small percentage change in surface area and pore volume as compared to Ni-Ce Pol catalyst, which indicates that alumina and zirconia supported polyol catalysts are thermally stable and less prone to coking.

TABLE I: TEXTURAL PROPERTIES OF FRESH POLYOL CATALYSTS

Catalysts	**S_{BET} [m^2/g]**	**P.V [cm^3/g]**	**P.D [nm]**
Ni-Al Pol	143.987	0.706	16.008
Ni-Zr Pol	22.822	0.049	7.921
Ni-Ce Pol	30.197	0.053	7.388

TABLE II: TEXTURAL PROPERTIES OF SPENT POLYOL CATALYSTS

Catalysts	**S_{BET} [m^2/g]**	**P.V [cm^3/g]**	**P.D [nm]**
Ni-Al Pol	137.162	0.699	19.021
Ni-Zr Pol	19.924	0.050	17.260
Ni-Ce Pol	24.312	0.078	9.125

B. *Temperature Programmed Desorption (CO_2-TPD)*

In order to get information about the strength and number of basic sites present in the catalysts, temperature-programmed desorption (TPD) experiments were carried out by using CO_2 as a probe gas. The strength of basic sites, i.e., weak, intermediate, strong and very strong were estimated from the area under the corresponding CO_2 desorption pattern, for the temperature ranges of 50–200, 200–400, 400–650 and >650 ℃, respectively. The CO_2-TPD curves of polyol catalysts are presented in Fig. 3. It is apparent from TPD profiles that all polyol catalysts showed at least two CO_2 desorption peaks: first peak centered at lower temperature (around 50–200 ℃) and second peak centered at relatively higher temperature (around 200–400 ℃). These desorption peaks are assigned to the low and medium strength basic sites respectively. On the basis of TPD profiles the basicity of the catalysts can be arranged in the following order: Ni-Al Pol > Ni-Ce Pol > Ni-Zr Pol. It has been reported in literature that the catalytic performance is correlated with the basicity and strength of basic sites of the catalyst in DRM. The logic behind this fact is that basic catalysts could improve the adsorption of CO_2 (acidic gas) in DRM reaction that supplies more surface oxygen species on the catalyst surface, for gasification of intermediate carbonaceous species resulted from CH_4 decomposition. However, it is quite difficult to judge the performance of a catalyst, i.e., its activity, stability and coke resistance only on the basis of the basicity because the catalytic performance also depends on several other important factors including the active metal particle size, dispersion, degree of reduction and metal support interaction [17].

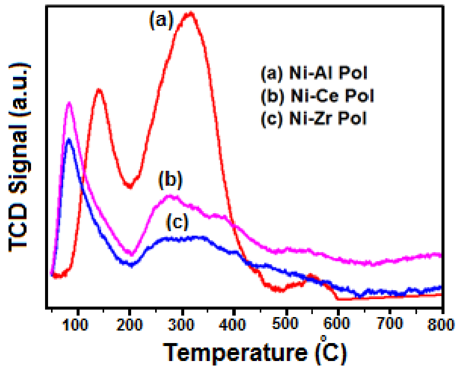

Fig. 3. CO_2-TPD patterns of Ni-based polyol catalysts

C. *Catalytic Performance*

The catalytic performance of polyol catalysts, in terms of CH_4 and CO_2 conversions, at various temperatures is illustrated in Fig. 4. It is quite surprising that at 500 ℃ reaction temperature, all catalysts showed CO_2 conversion (Fig. 4a) greater than corresponding CH_4 (Fig. 4b) conversion, while at higher temperatures opposite results are obtained. In fact the higher conversion of CO_2 than CH_4, at 500 ℃, indicates the occurrence of the reverse water gas shift (RWGS) reaction ($CO_2 + H_2 \leftrightarrow H_2O + CO$; $\Delta H_{298} = +41$ kJ/mol) [8]. On the other hand, the higher CH_4 conversion than CO_2 at reaction temperature > 500 ℃ is probably due to the occurrence of methane cracking reaction. Another important observation is that, for all catalysts, the catalytic activity increased as the reaction temperature increased. For instance, at 500 ℃ reaction temperature, Ni-Al Pol and Ni-Zr Pol catalysts showed 27.7% & 23.9% CH_4 conversion, while at 600 and 800 ℃ the same catalysts showed 69.8% & 65.6% and 95.9% & 96.7% CH_4 conversions respectively. In fact the increase in activity with temperature is in agreement with the thermodynamicity of the process (endothermic reaction). All samples showed their highest catalytic activity at 800 ℃. In order to compare the long-term stability of polyol catalysts, 700 ℃ was fixed as reaction temperature in this study. The catalytic performance of Ni-based polyol catalysts, at 700 ℃ for 6 h time-on-stream (TOS), in terms of CH_4 conversion and H_2/CO is presented in Table III. It is apparent that, in comparison to all polyol catalysts, Ni-Zr Pol catalyst has shown high as well as stable catalytic activity on TOS. For instance the CH_4 conversion over Ni-Zr Pol catalyst was 87.2% at the start of the reaction which remained nearly constant (86.8%), with negligibly small drop after 6 h of reaction. This small decline in conversion assures its higher stability over other polyol catalysts. The higher activity and stability for Ni-Zr Pol catalyst is credited to its unique properties including its high thermal stability, redox behavior, reducibility and surface acidity [9].

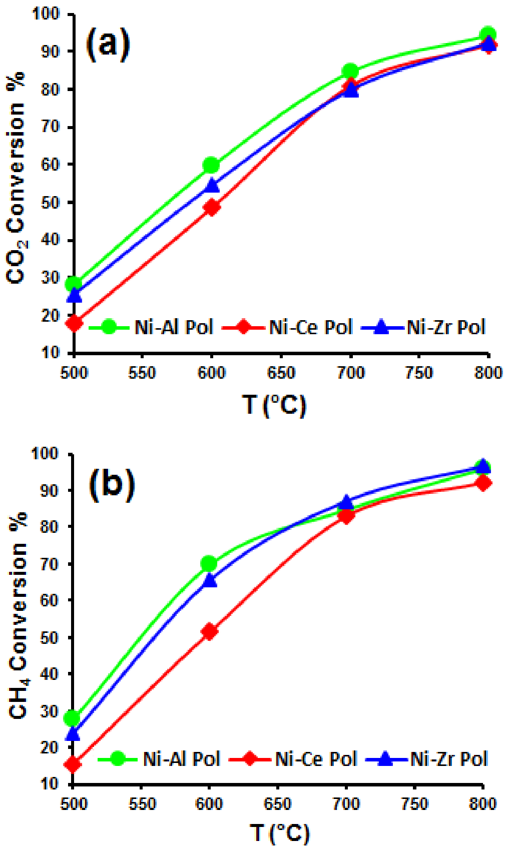

Fig. 4. Variations of (a) CO_2 and (b) CH_4 conversions for Ni-based impregnated and polyol catalysts at different temperatures; F/W= 60 mL/min.g_{cat}).

Moreover, it can be seen (Table III) that for Ni-Al Pol and Ni-Zr Pol catalysts the CH_4 conversion, more or less, decreased except for Ni-Ce Pol catalyst over which the CH_4 increased with TOS. In fact the increasing CH_4 conversion for Ni-Ce Pol catalyst is probably due to rapid thermal decomposition of methane which resulted in H_2/CO ratio (>1) and higher amount of coke deposition. Thermodynamic investigations, under typical reaction conditions, revealed that generally, there are four possible reactions which favor coke formation during DRM process [18], including methane decomposition/cracking reaction (1), CO disproportionation, i.e., Boudouard reaction (2), CO/H_2 reduction reaction (3) and CO_2 hydrogenation reaction (4):

$$CH_4 \leftrightarrow C + 2H_2 \tag{1}$$

$$2CO \leftrightarrow C + CO_2 \tag{2}$$

$$CO + H_2 \leftrightarrow C + H_2O \tag{3}$$

$$CO_2 + 2H_2 \leftrightarrow C + 2H_2O \tag{4}$$

TABLE III: CATALYTIC PERFORMANCE OF NICKEL-BASED POLYOL CATALYSTS

Catalysts	**% Conversion**		**H_2/CO**	**%D.F**	**Coke [g/g_{cat}.h]**
	CH_4 (Ini)	**CH_4** (Fin)			
Ni-Al Pol	84.8	84.3	0.99	-0.59	0.015
Ni-Zr Pol	87.2	86.8	1.07	-0.46	0.02
Ni-Ce Pol	83.2	85.3	1.08	+2.46	0.025

The variation of the product H_2/CO ratio over different catalysts is presented in (Table III). It is evident from the results that for all catalysts the H_2/CO remains between 0.99 and 1.08 i.e., close to the stoichiometric value for DRM reaction. The H_2/CO ratio closer to the stoichiometric value, in case of all polyol catalysts, is indicating that these catalysts are not influenced by RWGS reaction. Since, the existence of RWGS reaction results in H_2/CO ratio (<1) because it consumes some amount of H_2 produced in reaction. The results of carbon deposition and percentage of catalyst deactivation calculated after 6 h of reaction in terms of methane conversion (DF = [(Final CH_4 conversion – Initial CH_4 conversion)/Final CH_4 conversion] x100) is presented in Table III. It is obvious that in comparison to Ni-Al Pol catalyst the Ni-Zr Pol catalyst has exhibited smaller deactivation factor however, the amount of coke deposition over Ni-Zr Pol catalyst is slightly higher than Ni-Al Pol. The relatively higher amount of carbon deposition over Ni-Zr Pol catalyst might be due to its less basicity than Ni-Al Pol catalyst. Moreover, from the obtained results it could be inferred that even though carbon deposition is slightly higher over Ni-Zr Pol catalyst but it is not taking part in catalyst deactivation, as confirmed from its high stability and very low deactivation factor (%DF = -0.59).

D. Catalyst Deactivation and CO Pulse Chemisorption

Carbon deposition has long been recognized as the main reason for metal supported catalyst's deactivation in methane reforming reactions. Numerous theoretical and experimental studies on DRM mechanism have revealed that during DRM process, CH_4 is decomposed first on active metal sites to form reactive surface carbonaceous species near gas-metal interface, which are then oxidized to CO by interacting with oxygen that originated from CO_2 [19]. In view of that, the rate of coke deposition on catalyst surface is dependent on the relative rates of the carbon formation and its oxidative removal. Hence, if the rate of the carbon gasification by CO_2 is less than the rate of carbon formation, the large volume of carbon deposit will accumulate over gas-metal interface, which can afterward polymerize. These polymerized carbon atoms can contribute to catalysts deactivation via two ways: (i) encapsulating the active metal particles or diffusing through the active metal after dissolving, and (ii) detaching active metal particles from the support [20]. It is believed that the carbon formation is more easily favored by acidic supports than basic supports and additionally, coke deposition occurs more easily on bigger particles than smaller ones [21]. Since Ni particle size and its dispersion over support has a strong influence on catalyst deactivation and carbon deposition. CO pulse chemisorption experiments were carried out to observe the changes in Ni particle size and their distribution. The results of active metal dispersion and the average metal particle size for all fresh polyol catalysts are presented in Fig. 5. The highest active metal dispersion and smallest metallic crystallite size were attained for Ni-Al Pol catalyst, which were responsible for its better stability and resistance towards coking. Whereas among all the tested catalysts lowest Ni dispersion and biggest Ni crystal size were observed in case of Ni-Ce Pol catalyst. In fact the highest coke deposition in case of Ni-Ce Pol catalyst is due to the presence of bigger Ni particle in this catalyst.

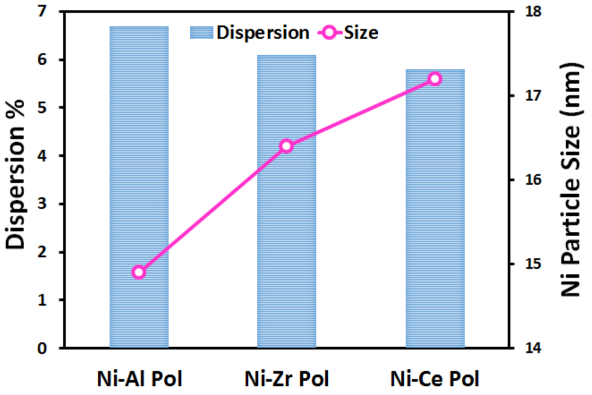

Fig. 5. Ni dispersion and Ni particle size for polyol catalysts obtained from CO chemisorption.

IV. CONCLUSION

Nano Al_2O_3, ZrO_2 and CeO_2 supported Ni based catalysts were prepared by polyol method and tested in dry reforming of methane. The results revealed that polyol process has a great potential to be used as catalyst preparation method for DRM reaction. Amongst all tested catalyst, highest activity and stability for syngas production was obtained by Ni-Zr Pol catalyst. Although, in Comparison to Ni-Zr Pol catalyst the Ni-Al Pol catalyst has exhibited relatively small activity; however, this catalyst showed minimum carbon deposition. The higher tendency towards coke resistance of Ni-Al Pol catalyst is credited to its higher basicity and smaller Ni crystallites.

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