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Pseudomorphic Reaction: A New Approach to Produce Bulk Mesoporous Silica as Catalyst Support in Methane Reforming

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ABSTRACT

Pseudomorphism is known as a suitable technique for producing mesoscale pore in silica powders along with preservation of particle morphology. Herein, silica discs with several millimeter dimensions have been prepared using the mentioned method. This method has been utilized through application of pseudomorphism reaction of preshaped bodies by immersion in a solution containing surfactant and swelling reagents. The pseudomorphism reactions were performed in time and temperature controlled conditions. Mesoporous silica disc, because of its large surface area, has been considered here as catalyst support in methane steam reforming. The silica support has been utilized in production of Ni-silica catalyst through impregnation method. The physical properties of the synthesized mesoporous support and nanocatalysts have been characterized by nitrogen adsorption-desorption surface measurement (BET- BJH method) and Archemideous immersion analysis as well as field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), inductively coupled plasma (ICP) analyses techniques. Investigation on catalytic behavior of prepared samples in steam reforming of methane showed that Ni/S1 sample has superior catalytic activity in comparison with Ni/S0 sample (Methane conversion of 85% and hydrogen yields more than 60% at 620 °C).

1. INTRODUCTION

Mesoporous materials have characteristics such as ordered mesoporous structure, homogeneous pore size distribution, large specific surface area and pore volume, controllable size, morphology and in some cases chemical structure and surface functionality [1- 6]. Since the first report on synthesis of mesoporous silica, by Mobil and Waseda University in 1990, preparation of this material has been developed using supramolecular self-assembly reaction of surfactants and silica precursors due to availability, chemical and thermal stability of silica as well as its functionalizing by organic molecules for catalytic site addition onto the surface [6-10]. Mesoporous silica has larger surface area and less bulk density (D= 2.65 cm^3/gr) than other metal oxides. In addition, its definite microstructure such as the pore shape and morphology makes it suitable for catalytic reactions involving mass transfer and surface reactions. Then it can be a good candidate for applications such as catalyst support or liquid chromatography column packing [11, 12].

In order to use mesoporous silica as catalyst support, its conventionally produced powders, however, have limited applications and mesoporous shaped silica bodies are rarely available. The most important problem encountered while using conventional shaping methods such as extrude or pressing, is surface area decreasing originated from pore wall destruction or pore filling with silica during shaping and heat treatment procedures for bulk material sintering [13].

According to Galarneau et al., one of the best methods for producing meso sized pores in silica powders along with preservation of particle morpholohy is pseudomorphic reaction. In this procedure, silica based materials are dissolved in alkaline solution and subsequently reprecipitated in presence of surfactants, that results in porous structure without changing the original morphology. The key parameter for preserving the morphology in pseudomorphism reaction is then associated with balance of dissolution and precipitation rate of silica. This can be fulfilled by controlling alkalinity, dilution, the type and amount of surfactant in

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addition to temperature and time of reaction as well as presence of the swelling agent [10- 12, 14- 15].

Because of the low humidity needed for pressing the shaped bodies in comparison with extrusion, the former shaping method is selected which can lead more precise controlled size bodies due to less contraction during drying of the discs.

Previous researches focused on investigation of different parameters of pseudomorphic transformation on silica powders to use it as high performance liquid chromatography (HPLC) filter, however, the aim of this work is developing the mentioned idea for preparation of mesoporous silica with millimeter sized disc shape as catalyst carrier support in methane steam reforming (MSR) in a fixed bed reactor system.

According to literature review, mesoporous silica (especially MCM-41) as catalyst support in powder form was used in carbon dioxide or steam reforming of methane. Silica supported noble metals are more active and stable with reduced carbon formation, but their costs limit the commercial applications. Although nickel based catalysts are considered as good replacements for noble metals in industrial uses due to their low cost and catalytic performance, the conventional supported nickel catalysts used for methane reforming are very active for carbon formation that leads to rapid deactivation of the catalyst. It is known that large nickel particles increase the formation of coke, which blocks the active nickel sites [16- 22]. Several attempts like use of different preparation methods, adding promoters such as alkali metals have been made so far to inhibit the nickel growth on catalyst surface and subsequently to reduce the coke deposition [23- 26].

Y. Zhang et al. [27] prepared Ni/SiO_2 powder catalyst using dielectric barrier discharge (DBD) plasma decomposition of nickel nitrate, followed by hydrogen reduction to reduce the particle size for MSR with very low steam to methane molar ratio (S/C=0.5). Methane conversion enhanced to 40% via this modification in comparison with conversion value of about 20% reported for conventionally prepared catalyst at 700°C.

Y. Matsumura et al. [28] investigated the catalytic properties of 20 wt.% Ni impregnated on SiO_2 powder catalyst with mean crystallite size of 15 nm. They reported that the methane conversion of MSR in presence this catalyst is about %14.8 at 500°C with S/C=2 and the catalyst was completely deactivated at 4 h-on-stream.

Due to industrial uses of the shaped catalysts, some efforts have been made for finding optimum geometric shape of the bulk catalysts [29], but most of them have utilized different conventional forming methods which lead to reduction of its surface area and subsequently catalytic behavior, therefore here, we have tried to increase the surface area of pre-shaped silica by using pseudomorphic reaction. Here in, it is tried to minimize the nickel particle size, by using mesoporous catalyst support to enhance its catalytic performance. Since nickel particles are located inside the pores of catalyst support, the pore walls inhibit the nickel particles migration and growth at high temperature.

2. MATERIALS METHOD

2.1. Chemicals

The diatomaceous earth as silica source has been obtained from Amertat Shimi pharmaceutical Co. in Iran. All other chemicals including silicic acid (purity: >99%), poly vinyl alcohol (PVA) (purity: 97-96%), sodium bicarbonate(purity: extra pure), graphite (purity: extra pure), calcium carbonate (purity: >99%), cethyltrimethylammonium bromide (CTAB) (purity: 98%), tri methyl benzene (TMB) (purity: >97%), sodium hydroxide (NaOH) (purity: 99.98%) and nickel nitrate ($Ni(NO_3)_2.6H_2O$) (purity: 99.999%) were purchased from Merck.

2.2. Synthesis of silica

Diatomaceous earth (0.06gr) has been mixed with silicic acid (0.0012gr) as binder and desired amounts of pore forming agents such as poly vinyl alcohol (PVA), sodium bicarbonate, graphite and calcium carbonate. After humidifying by deionized water, it was pressed in 5mm diameter mold under different pressures followed by sintering to prepare disc shaped silica denoted as S0.

Since the sintering conditions are dependent on pressed powder characteristics and considering the fact that the sintering temperature is about 0.6-0.8 of its melting point (Tm=1983K), here in, we have investigated the effect of time (0.5 and 1h) and temperature (800, 1000 and 1200°C) on strength of sintered samples only by observing. Therefore, the optimum time and temperature of sintering is 1h at 1000°C. In this condition the samples are sound without any cracks.

2.3. Synthesis of mesoporous silica discs

The prepared silica discs (S0) were introduced in basic solution containing CTAB as surfactant. An aqueous solution was prepared under stirring conditions. The molar ratios of mixed reactants are SiO_2: CTAB: NaOH: H_2O=1:0.3:1:400. Since each S0 spice was about 0.055gr, the required amount of CTAB, NaOH and H_2O were 0.1, 0.036 and 6.6gr, respectively. The whole solution was transferred to a Teflon lined stainless steel autoclave and silica disc was put inside a solution, temperature of which was kept at 373K for different reaction times. Then as synthesized discs were washed for several times to remove the alkaline species, controlled by pH of the filtrate solution, before they have been dried over night at 100°C. Finally, the discs were calcined at 550°C for 7h by heating rate of 1°C/min to remove the surfactant. The effect of trimethylbenzene (TMB) as swelling agent was also investigated in this paper. Table 1 lists the syntheses condition utilized for preparation of disc samples.

TABLE 1. Sample prepared with different synthetic conditions

Sample Name	Time of reaction (day)	Molar ratio of TMB
S1_2	2	-
S1_4	4	-
S1_6	6	-
S1_10	10	-
S1_10_T Or S1	10	1.3

2.4. Synthesis of Ni supported on silica discs

Each silica disc (S0 and S1) was impregnated in about 0.036cc of 1M nickel nitrate solution and after keeping for 20h at 40°C, it was filtered and dried. Finally the samples were calcined in air with heating rate of 4°C/min at 700°C for 4h. The samples were denoted as Ni/S0 and Ni/S1, respectively.

3. MATERIAL CHARACTERIZATION

3.1. Porosity determination by archemides method

Archimedes method was used to determine the effect of pore-forming agents on prepared silica discs porosity. In this method, discs must be completely dipped in a beaker filled with boiling water for 5h, following by keeping it in cooled water for 24h.

Then the mass of immersed sample (m_1) is determined by weighing in water. After that, liquid that remains on the surface of the sample must be removed with a damp sponge and the mass of saturated sample (m_2) is determined by weighing in air. The mass of dried sample (m_3) is then determined in air after drying in oven. The open porosity in volume percent (P) is calculated as follows:

$$P = \frac{m_2 - m_3}{m_2 - m_1} \times 100 \qquad (1)$$

3.2. Nitrogen adsorption/desorption isotherms

Nitrogen sorption experiments were used to determine the textural properties of mesoporous materials in terms of surface area, pore size and pore size distribution. The N_2 adsorption/desorption isotherms were obtained at 77K on a surface analyzer (Bel Japan Inc.). For experiments, 50mg of samples were analyzed, after pre-treatment of samples under vacuum at 150°C for 2h to have a clean surface.

The specific surface area was determined by the Brunauer, Emmet & Teller (BET) method and total pore volume and pore diameter were obtained through Barrett, Jovner & Halenda (BJH) method.

3.3. FESEM

The morphology and composition of samples were investigated by field emission scanning electron microscopy (FESEM) (TE-Scan Co, Mira3 Model) after coating the samples with gold.

3.4. ICP

Solid composition was determined by inductively coupled plasma spectrometer (ICP) (model: Vista pro). The presence and amount of impregnated nickel in silica discs have been characterized by ICP.

3.5. XRD

X-ray diffraction (XRD) patterns were obtained using Philips PW 3710 instrument diffractometer, with Cu-Kα radiation operated at 40kV and 30mA, in order to identify the crystalline phases in the samples. A 2θ range of 5-70° and step size of 0.02° by scanning rate of 0.5 ° s^{-1} were applied to collect data of XRD patterns. The crystallite sizes of the crystalline metal oxides were determined using the Scherrer equation.

$$d = 0.9\lambda/\beta\cos\theta \qquad (2)$$

Where, d is the crystal size, λ is the wavelength of Cu-Kα radiation, β is the full width half maximum and θ is the Bragg diffraction angle [30].

3.6. Catalytic test

Catalytic tests were performed in a fixed bed continuous flow reactor (diameter: 16mm, height: 1000mm) operated at atmospheric pressure.

The reactor was placed in a vertical furnace. In each experiment, 0.8 gr of freshly synthesized catalyst was loaded in the reactor on a thin porous layer in the middle of the reactor. The reduction of NiO to metallic nickel was performed at reforming reaction temperature (550, 620, 690 and 760°C) for 1 h in presence of pure H_2 with the flow rate of 70 ml min^{-1}. The reforming reaction was performed in the range of 550-760°C for 1.5h with gas hourly space velocity (GHSV) 10^4 ml/ (g_{cat}.h).

The gaseous stream containing a mixture of CH_4 (99.995%) and Ar (99.995%) with the flow rate of 75 ml min^{-1} and 156 ml min^{-1}, respectively, and steam to methane molar ratio(S/C) of 2 were used [31].

The reactor effluent of reforming cycles was passed through a condenser to remove any liquid or solid fine particles.

Then, the dried gas was analyzed using an online gas chromatography (GC) with a thermal conductivity detector (TCD). GC-TCD is a technique used to analyze inorganic gases (Argon, hydrogen, carbon dioxide, etc.) and small hydrocarbon molecules such as methane. This technique is based on separation of phases or compounds through an adsorption column.

The TCD compare the thermal conductivity of two gas flows: the pure carrier gas and the sample. The different constituents exhibit characteristic retention times, and under the chromatogram the defined retention time is proportional to the concentration of the compound expected at this retention time. The calibration measurements are made with a characteristic gas composition, which provides a standard and the possibility to calculate precisely the composition of the desired specimen [32]. Here in, the obtained dry gas was analyzed for 9 min using an online GC Bruker 450 equipped with TDX-01 column and argon was applied as carrier gas. The methane conversion ($\%X_{CH_4}$) and hydrogen production yield are determined as follows:

$$\%X_{\mathrm{CH_4}} = \left(1 - \frac{(moles\ of\ \mathrm{CH_4})_{out}}{(moles\ of\ \mathrm{CH_4})_{in}}\right) \times 100 \tag{3}$$

$$\%\mathrm{H_2}\ Yield = \frac{(mols\ of\ \mathrm{H_2})_{out}}{2(moles\ of\ \mathrm{CH_4})_{in}} \times 100 \tag{4}$$

4. RESULTS AND DISCUSSION

4.1. Porosity determination by archemides method

The porosity of silica discs were affected by applied pressure and pore-forming agents. Since the higher applied pressure causes porosity decreasing of the shaped body, then lowest pressure was preferred for preparation of a disc having high porosity but keeping adequate green strength of the sample to be handled. Actually, the compacted powder should withstand mechanical operations during the translocation before sintering.

Experiments done here showed that the powders mixture didn't consolidate under pressures lower than the 340MPa and they were laminated at pressures higher than 680MPa. So, pressure of around 340MPa has been selected as the optimum condition.

To investigate the effect of additives on porosity of the original silica discs (S0 series), 5 wt. % pore-forming agents such as poly vinyl alcohol (PVA), sodium bicarbonate, graphite and calcium carbonate were added to the precursors. Silica discs porosity estimated by Archimedes method is presented in Table 2.

TABLE 2. Sample porosity in presence of different Pore-forming agents

Sample	Pore-forming agent	Porosity (vol. %)
S0	-	**46**
S0-1	PVA	**50**
S0-2	sodium bi carbonate	**28**
S0-3	graphite	**40**
S0-4	calcium carbonate	**53**

The open porosity of S0-2 sample was decreased due to glass phase formation inside the pores in presence of sodium silicate. Black powder of graphite was visually observed in sample S0-3 even after sintering at 1200°C. Although a slightly increase of porosity observed in S0-4, titration of this sample indicated the presence of calcium ions.

The mentioned impurities may be harmful in pseudomorphic reaction step or finally in catalytic behavior. Comparing the Archimedes porosity of S0-1 with the blank sample (S0), did not show any meaningful differences. In conclusion, addition of the mentioned physical pore forming reagents has been omitted in the next part of this research.

4.2. Nitrogen adsorption/desorption isotherms

The surface properties of samples are summarized in Table 3 By comparing BET and BJH results of S0 with S1_2, S1_4 and S1_6, S1_10, it was deduced that increasing the reaction time results in surface area enhancement and pore size decrease of discs. Due to limited solubility of alkyl ammonium cations with alkyl chains longer than 22 carbon atoms, the maximum achievable pore size under typical alkaline conditions in the presence of these surfactants as template should be around 4 nm [14, 17].

It was suggested that the main process is dissolution of silica up to 6 days and after that the precipitation in presence of template affects the kinetics of reaction. As the pore size of S1_10 was about 9.5nm (>4nm), the longer reaction time more than 10 days seems to be needed for completing the pseudomorphic transformation.

TABLE 3. Surface properties of various samples

sample	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3g^{-1})
S0	6.6	57.94	0.095
S1_2	10.4	43.3	0.1
S1_4	11.4	25.5	0.07
S1_6	39	11.22	0.093
S1_10	56	9.5	0.15
S1_10_T or S1	86	5.56	0.12

Regarding obtained results, the pseudomorphic transformation can be described as a progressive process occurring inside a bead, in which at first poorly ordered mesostructure is formed and then it gradually rearranges into well-defined ordered domains via short distance mass transfer phenomena. [9, 17]

As F. Fajula and other researchers reported, the kinetics of mesoporous silica synthesis in the presence of TMB was faster due to formation of low polar siloxane sites in vicinity of TMB molecules that promotes the silanol condensation. Also TMB acts as a swelling agent so the pore size was increased up to 9 nm. [14, 19- 20]. Therefore, effect of TMB addition has been investigated in sample S1_10_T. Comparing S1_10 and S1_10_T indicates that the surface area was increased in presence of TMB which is originated from faster kinetics of the reaction.

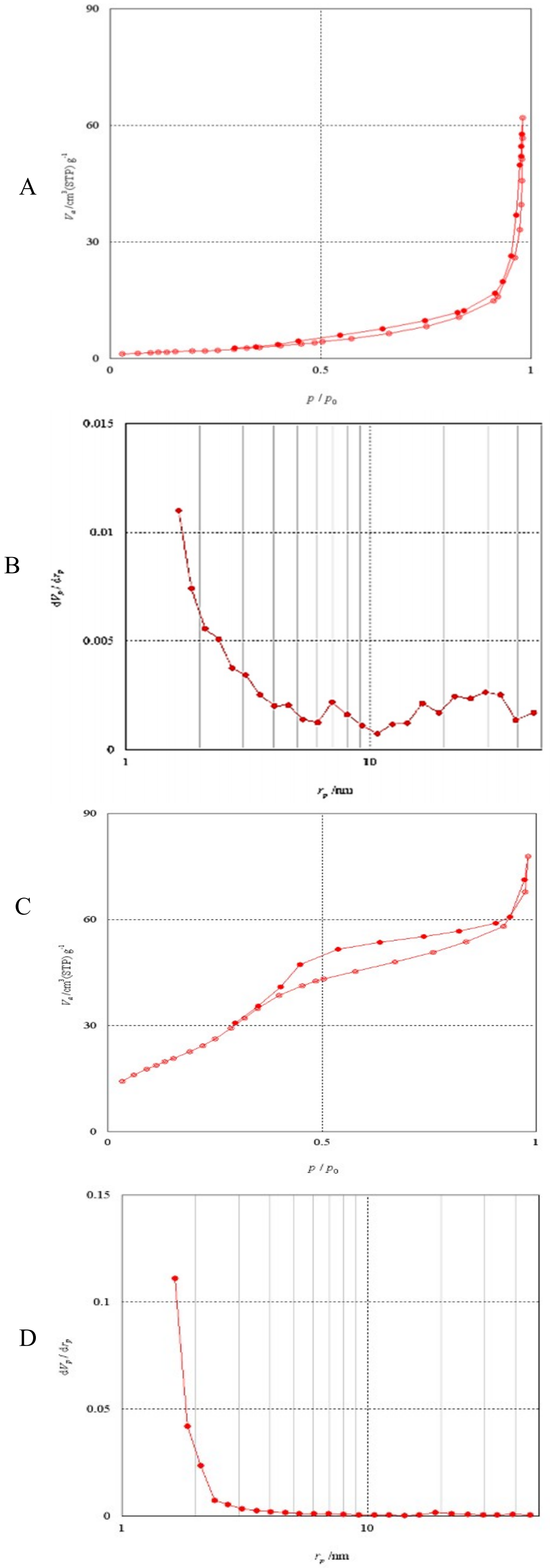

Figure 1. BET & BJH graphs of Adsorption/desorption isotherm of samples A, B: S0, C, D: S1

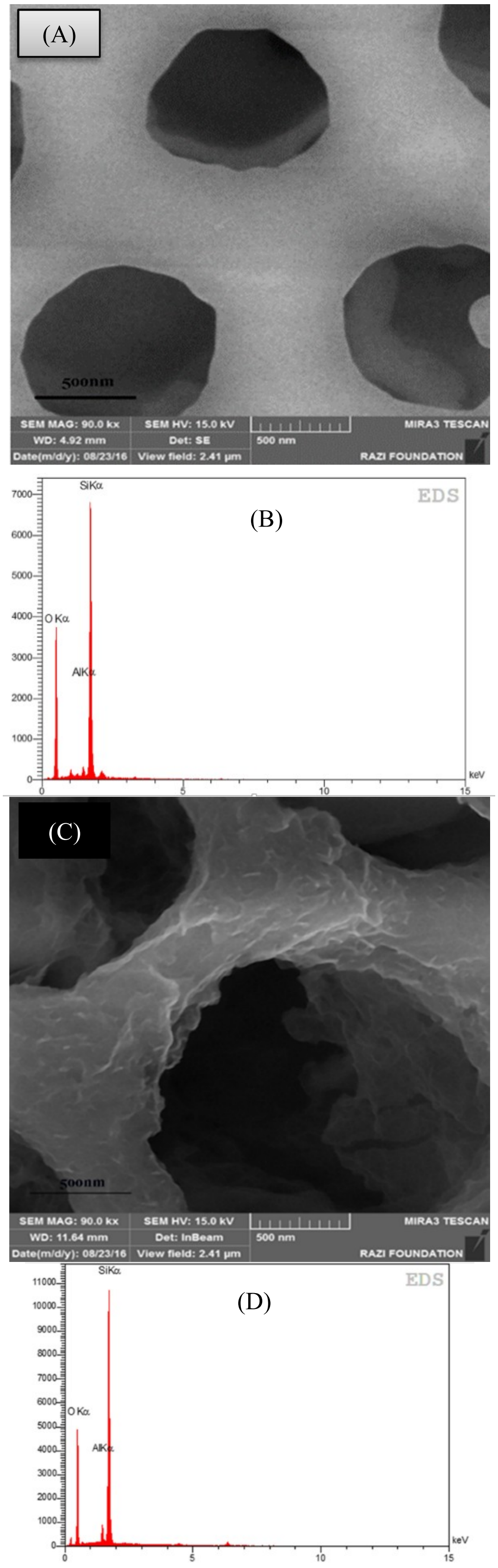

Figure 2. FESEM and EDS results of the prepared discs A, B: S0, C, D: S1

4.3. FESEM

FESEM images of silica discs S0 and S1 are shown in Fig. 2**.** Pore wall transformation during pseudomorphic reaction and retaining of the silica disc morphology are clearly observed in Fig. 2 (C). These phenomena are completely in agreement with Inayat et al. which have emphasized on unchanged original silica pore system during pseudomorphism phenomena. According to these authors, if the dissolved siliceous building blocks are too mobile and enter the primary pores before they form a new solid structure, then the primary pore system will be destructed and remaining pores will be filled with the new material [21].

EDS elemental analysis of S0 and S1 samples is represented in Fig. 2 which confirm that there is no differences between their chemical compositions and that of the diatomaceous earth. This is important in terms of their application as catalyst support due to poisoning effect of both sodium and carbon in catalytic reactions. Then, removal of sodium by washing as well as burning out of carbon in silica samples after pseudomorphism reaction are achieved which can be deduced from EDS analysis results.

4.4. ICP

The actual nickel content impregnated in both silica supports, measured by ICP are about 3.8%wt. The results confirm that the loading closely reflect their intended weight-loadings. Both samples show equivalent Ni loadings, thus the differences in catalyst activity didn't arise from variations in Ni loading.

4.5. XRD

XRD patterns were used to identify the crystalline phases in the samples. Fig. 3 shows the XRD profiles of samples Ni/S0 and Ni/S1. All XRD patterns in Fig. 3 show peaks at around 22, 29, 32 and 37° which are characteristic of cristobalite form of silica. The XRD analysis confirmed that silica in diatomaceous earth was transformed to cristobalite at 1000°C as sintering temperature and its phase was not changed during the pseudomorphism reaction.

The XRD pattern of Ni/S0 shows peaks at 2θ value of around 38, 44 and 63° corresponding to NiO (111), (200) and (220) planes, respectively, indicating the presence of nickel oxide peaks after calcination. The crystallite size of NiO in Ni/S0 which was calculated using Scherrer's formula considering the (200) diffraction line, is about 27 nm.

As indicated in Ni/S1 profiles, the intensity of the peaks were decreased and broadened in comparison with Ni/S0 and no crystalline phase regarding the NiO were detected, suggesting that the crystallite size of NiO in Ni/S1 is smaller than that in Ni/S0. It seems that NiO species are dispersed in pores of the S1 support, that limits NiO particle growth, so Ni particle size on S1 support is so small that is undetectable by XRD, therefore crystallite size of this sample couldn't be calculated by Scherrer equation.

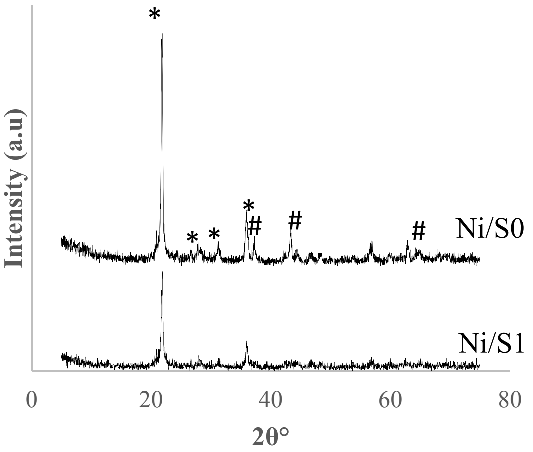

Figure 3. XRD graph of the Ni/S0 and Ni/S1 samples; *:SiO_2, #: NiO

4.6. Catalytic test

In order to investigate the effect of pseudomorphic transformation on silica supports, a number of catalytic tests were carried out in MSR process.

Conversion of methane and hydrogen production yield of MSR in presence of both catalyst samples at different reaction temperature are shown in Fig. 4 and 5, respectively. Both of them were enhanced by increasing the reaction temperature, due to the fact the MSR reaction is endothermic.

Results of this research showed that the methane conversion at higher temperatures (about 750°C), is independent of the type of catalyst supports. So, it seems that by increasing the temperature the side reactions such as methane cracking and Boudouard reaction occur in addition to MSR as the original reaction. The effect of pseudomorphic transformation on silica support at about 620°C is more obvious.

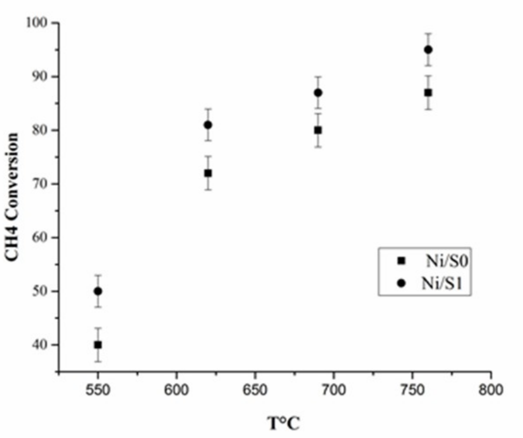

Figure 4. %Methane conversion in presence of catalysts at different temperatures

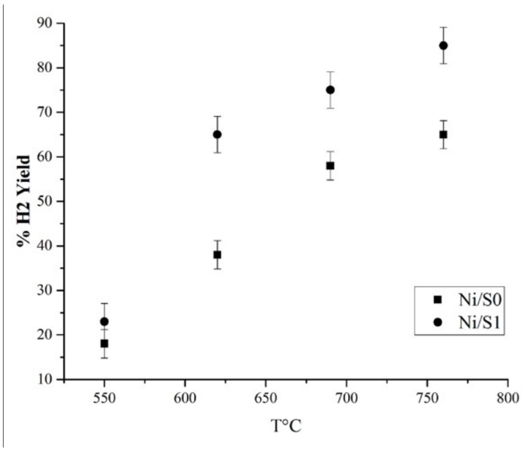

Figure 5. %Hydrogen yield in presence of catalysts at different temperatures

Due to smaller size and better distribution of nickel particles on S1 silica support than in S0 originated from its larger surface area, conversion of methane and also hydrogen yield of MSR in presence of Ni/S1 catalysts were increased by about 20% compared with those of the Ni/S0.

5. CONCLUSION

Mesoporous silica discs, as catalyst support, were prepared by using pseudomorphic reaction. In comparison with conventional preparation methods like pressing or extruding of mesoporous powders, shaped bodies with higher specific surface area were obtained by pseudomorphic reaction. In preshaped silica, since the transformation is controlled by diffusion of reactants into silica disc, more time is needed to form mesoporous silica. TMB as swelling reagent, promote the rate of pseudomorphic reaction and consequently reduce the time of reaction. By incorporation of Ni particles in pores of S1 support, their mobilities were restricted by pore walls and therefore, aggregation of Ni nanoparticles were limited during sintering at high temperature, so the smaller Ni particles leaded to more methane conversion and hydrogen yield in methane steam reforming in presence of Ni/S1 catalyst.

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