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The Effects of Different Nickel–Ruthenium on SiO2 Catalyst Synthesis Methods toward Catalytic Activity of Methane Dry Reforming

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ABSTRACT. The presence of greenhouse gases in the atmosphere has triggered global warming and climate change. An effective approach to overcome these issues is to convert greenhouse gases into syngas. In this study, Ni-Ru/SiO_2 catalyst was used to catalyze the dry reforming process of methane (CH_4) and carbon dioxide (CO_2) into syngas. The catalyst was prepared using different synthesis protocols: sol gel-coprecipitation and impregnation methods. Characterization using Brunauer Emmett Teller analysis showed that the catalyst prepared using both methods exhibited comparable pore diameters and high surface areas. The X-ray diffractometer analysis also indicated the presence of different NiO, RuO_2, and SiO_2 phases. Furthermore, the activity of the catalyst was investigated using a fixed bed reactor. Based on the results, the optimum catalytic activity was obtained from the catalyst prepared via the sol gel-coprecipitation method, with an average CH_4 and CO_2 conversions of 37% and 50%, respectively. In addition, our catalyst also showed a 114% higher CH_4 conversion with an enhanced H_2/CO ratio compared to identical catalysts from other studies.

1. INTRODUCTION

According to the US Environmental Agency in 2018, the main components of greenhouse gases are carbon dioxide (CO_2) and methane (CH_4), with a percentage of 80% and 10%, respectively (Figure 1). The presence of greenhouse gases in the atmosphere can induce the rise of global surface temperature of up to 1.1°C [1]. This issue can trigger global climate change and reduce the stability of the climate system, as well as its tendency to cause global warming.

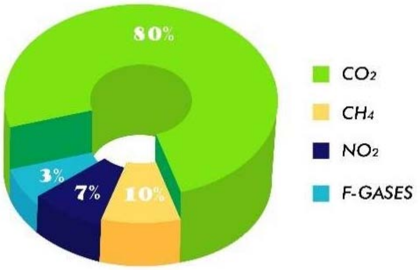

Figure 1. Percentage of Greenhouse Gas Components in the Atmosphere [2]

The National Oceanic and Atmospheric Administration Earth System Research Laboratory (2020) reported an increase in atmospheric CO_2 concentration, with an average of 1.84 ppm per year in the past 41 years (1979-2020). A similar phenomenon was also observed for CH_4 concentration in the atmosphere. In 2007-2013, an increase in CH_4 concentration with an average of 5.7 ± 1.1 ppb per year was reported. From 2014 to 2019, the rise of global CH_4 sharply increased to an average of 9.3 ± 2.2 ppb per year. In 2019, the CH_4 concentration reached 10.4 ± 0,6 ppb.

An effective approach to overcome these problems is to utilize the greenhouse gases via the decomposition of CH_4, involving CO_2 to produce synthetic gas (syngas). The syngas can be converted into alternative fuels, i.e., dimethyl ether (DME), methanol, and hydrogen [3]. The decomposition of CH_4 utilizing CO_2 is also called dry reforming (DMR). The DMR is a simple and environmentally friendly technique.

In order to optimize the dry reforming process of CH_4, an efficient catalyst is required. In this study, Ni-Ru/SiO_2 catalyst was employed as the catalyst for the dry reforming of CH_4. The use of nickel catalyst is due to its high catalytic activity. However, this metal is still vulnerable to coke poisoning and tends to deactivate quickly [4]. For these reasons, the addition of precious metals such as Ru to enhance the stability of the nickel catalyst in stimulating CO_2 activation and coke gasification is needed. Those statement is supported by previous research which CH_4 conversion at reforming reaction is increase to 64% from 30% by using Ru as a precious metals [5]. Another component that is crucial in catalyst design is catalyst support. SiO_2 is a promising candidate that can act as catalyst support owing to its mesoporous structure that is more favourable for the dry reforming of methane. Moreover, SiO_2 is selected because of its high thermal stability, well-ordered porous channels, and high surface area that can improve the dispersion and accessibility of the nickel catalyst active sites.

2. MATERIALS AND METHODS

2.1 Tools and Materials

The tools used in this project included an Erlenmeyer flask, a hot plate, a magnetic stirrer, a dropping pipette, an oven, a mortar with a pestle, a furnace, an 80-mesh sieve, a beaker glass, a glass stirrer, a measuring cylinder, a stand, clamps, a thermometer, a pH indicator, a glass funnel, a crucible dish, and a fixed bed reactor. The materials used in this study comprised $NiSO_4.6H_2O$, $Ru(NO)(NO_3)_x(OH)_y$, SiO_2, distilled water, NH_4OH, CH_4, CO_2, and N_2.

2.2 Block Diagram

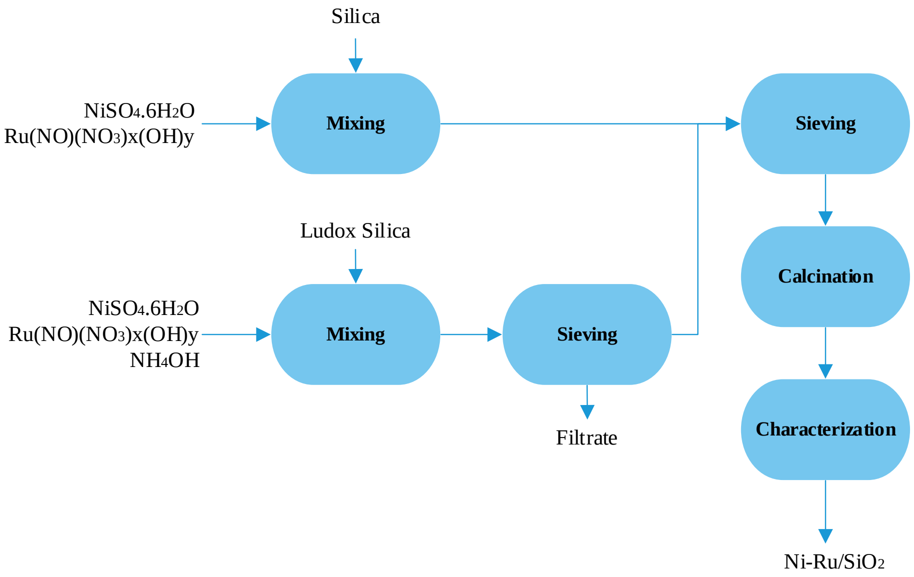

Figure 2. Block Diagram of Catalyst Synthesis

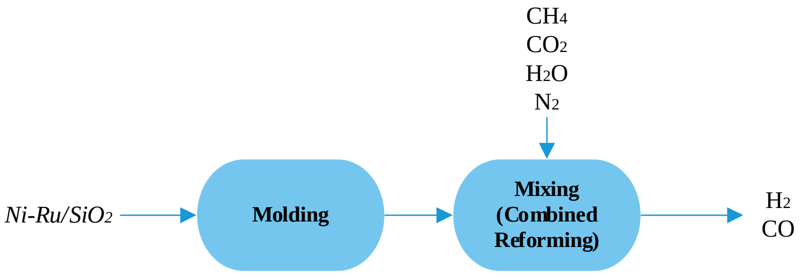

Figure 3. Block Diagram of Dry Reforming Process

2.3 Catalyst Synthesis

The catalyst preparation was conducted using two different synthesis protocols: via the sol gel-coprecipitation (NRS-SgCo) method and the impregnation (NRS-Im) method. The NRS-SgCo sample was prepared by dissolving 6.03 g and 7.42 g of $NiSO_4.6H_2O$ for the NRS-SgCo 1 and NRS-SgCo 2 samples respectively, in 100 mL of distilled water. As much as 1.5 g and 0.11 g of $Ru(NO)(NO_3)_x(OH)_y$ were added to the corresponding nickel precursor solution, followed by the addition of 30.14 g SiO_2 (Ludox). Afterward, the solution was mixed at a temperature of 70°C and a rotation speed of 180 rpm [6]. During the mixing process of sample NRS-SgCo, NH_4OH was gradually added into the solution until a pH of 9 was attained. The mixing process was carried out overnight and followed by filtration [7]. The preparation of the NRS-Im sample was initiated with the preparation of catalyst solution similar to the protocols used in the preparation of NRS-SgCo. However, the SiO_2 was used in the impregnation method. The solution was mixed at a temperature of 70°C and a rotation speed of 300 rpm until it transformed into a slurry.

The filtered NRS-SgCo sample and the NRS-Im sample that has become a slurry were dried in the oven at 110°C overnight [8]. Afterward, the NRS-SgCo and NRS-Im samples were ground using a mortar and pestle, followed by sieving with the 80-mesh sieve. The sieved NRS-SgCo and NRS-Im were then calcined in the furnace at 400°C with a temperature rise rate of 2°C per minute for 6 h.

2.4 Catalyst Characterization

The size and phase of the catalyst particles were characterized using an X-ray diffractometer (XRD) with Cu Ka radiation and the angle between transmitted beam and reflected beam (2 Theta) range is 3-90°. The surface area and porosity of the catalysts were measured using a Brunauer Emmett Teller (BET) surface analyzer via nitrogen adsorption at 77 K using the Nova Station A Quantachrom version 11.04 Instrument. The XRD patterns were analyzed using Xpert software to determine the peaks, full width at half maximum (FWHM), and phase of the catalyst material. The XRD patterns were normalized and plotted on OriginLab. The crystallite sizes were estimated using the Scherrer equation. The catalyst was then subject to catalytic performance investigation for the decomposition of CH_4 into syngas.

2.5 Decomposition of CH_4 into Syngas

The dry reforming technique was used to study the decomposition process of CH_4 into syngas. Initially, 15 catalyst pellets were prepared from 0.1 g of catalyst. The pellets were fabricated under a pressure of 20 bar. The pelletized catalyst was subsequently inserted into the reactor. The study was carried out with a $CO_2 : CH_4 : N_2$ volumetric flow rate ratio of 0 : 100 : 100 : 50. The production of syngas was conducted in a fixed bed reactor operated at atmospheric pressure and a temperature of 850°C. Afterwards, the syngas produced was analyzed using a gas chromatography using Parkin – Elmer gas chromaography instrument to determine the composition of the gas mixture.

3. RESULTS AND DISCUSSION

Syngas was produced using Ni-Ru/SiO_2 catalyst with an optimum CO_2, CH_4, and N_2 ratio as the reactants. The synthesis of the catalysts was carried out using different synthesis methods. The catalysts were characterized using XRD and BET. The catalytic performance of the catalyst to produce syngas was also investigated.

3.1 Catalyst Characterization Results

Prior to the catalytic performance investigation, the catalysts were characterized for their surface areas, pore diameters, pore volumes, phase compositions, and crystallite sizes. The characterization results are summarized in Table 1.

3.1.1 BET Analysis Results

The surface area, pore diameter, and pore volume of the catalysts were measured using a BET surface area analyzer. Using the surface areas of silica and final catalysts (Table 1), the decrease in the surface area of silica can be calculated. In the sample obtained from the sol gel-coprecipitation method, a surface area reduction of 54.7% and 51.13% was observed in samples 1 and 2, respectively. Meanwhile, the sample prepared using the impregnation method underwent a surface area decrease of 41.64% and 38.68% for samples 1 and 2, respectively. The surface area reduction is expected due to the presence of metal that covers the pores of the catalyst [9].

In this study, it was observed that the addition of nickel resulted in an increase in the surface area of the catalyst. This is in good agreement with a study conducted by Wang et al. (2018) that shows that the number of Ni active sites correspond to the ability of the Ni species to be reduced. The amount of Ni also affects the size and surface area of Ni particles [10].

From the pore diameter measurements presented in Table 1, it can be inferred that the catalyst prepared using both coprecipitation and impregnation methods exhibited comparable pore diameters.

Table 1. Characteristics of Ni-Ru/SiO_2 Catalysts

Catalyst	Method	Surface Area (m^2/g)	Pore Diameter (nm)	Pore Volume (cc/g)	Phase	Crystallite Size (nm)
**Ludox* Silica	Sol gel - Coprecipitation	135	22	-	-	-
**Solid Silica	Impregnation	250	20	-	-	-
NRS-SgCo 1	Sol gel - Coprecipitation	61.13	0.883	0.043	NiO RuO_2 SiO_2	90.6567 86.6738 103.3987
NRS-SgCo 2	Sol gel - Coprecipitation	65.98	0.883	0.047	NiO RuO_2 SiO_2	70.9792 76.9572 77.5182
NRS-Im 1	Impregnation	145.9	0.844	0.101	NiO RuO_2 SiO_2	114.41 41.4126 49.3669
NRS-Im 2	Impregnation	153.3	0.844	0.107	NiO RuO_2 SiO_2	71.5638 136.2165 17.1325

Remarks: * : www.sigmaaldrich.com
** : www.hwnanomaterial.com

3.1.2 XRD Analysis Results

A deep analysis of the XRD patterns using Xpert software was conducted to determine the type and crystalline phase composition of the Ni-Ru/SiO_2 samples. Based on the results depicted in Figures 4a,b,c, it can be seen that all samples contain silica in its amorphous form, which corresponds to the peak broadening at the 2θ of 20 to 21° (JCPDS No. 052-1279).

The XRD patterns of the catalysts prepared using the sol gel-coprecipitation method with different amounts of nickel showed an identical crystal structure, rhombohedral (Figure 4c). The rhombohedral NiO structure is indicated by the four peaks with the highest intensity at the 2θ of 18.6°; 48.67°; 64.28°; and 80.42° according to the JCPDS No. 085-1977. Meanwhile, the catalysts obtained from the impregnation process with different amounts of nickel resulted in different NiO crystal structures: the cubic structure at the 2θ of 6 2.8°; 75.45°; and 79.98° based on the JCPDS No. 002-1216 (Figure 4a) and monoclinic structure at the 2θ of 79.13° according to the JCPDS No. 072-1464 (Figure 4b).

In the samples synthesized using the sol gel-coprecipitation, the RuO_2 phase shows three peaks with the highest intensity at the 2θ of 28.32°; 35.06°; and 58.41°, ¬which corresponds to the orthorhombic structure according to the JCPDS No. 088-0323 (Figure 4c). The sample prepared using the impregnation method indicates RuO_2 phase with different crystal structures: tetragonal at the 2θ of 34.92°; 35.31°; 58.25° and 86.64° based on the JCPDS No. 088-0322 (Figure 4a) and cubic structure at the 2θ of 32.2° and 67.1° based on the JCPDS No. 050-1428 (Figure 4b).

The presence of NiO, RuO_2, and SiO_2 phases in all samples is in good agreement with some studies conducted by Wysocka et al. (2019), Liu et al. (2018), and Yuan et al. (2015). This implies that the catalysts were successfully synthesized.

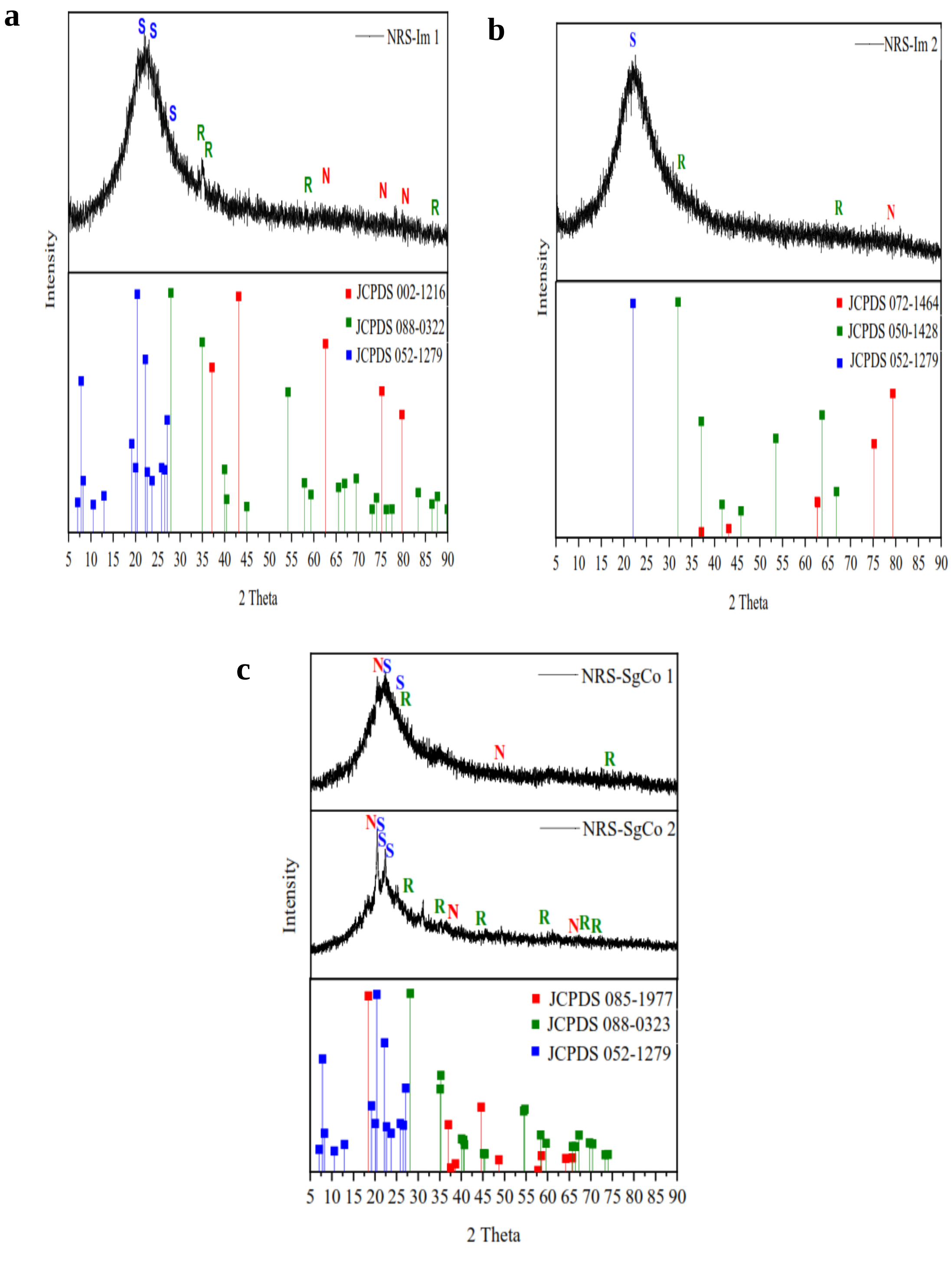

Figure 4. XRD patterns of (a) NRS-Im 1 sample, (b) NRS-Im 2 sample, and (c) NRS-SgCo 1 and NRS- SgCo 2 samples

3.2 Catalytic Activity Test Results

In this study, the dry reforming reaction was used in the production of syngas. The primary reaction of the dry reforming is stated in Equation (1).

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \qquad (1)$$

After catalyst characterization, the catalytic activity of the catalyst was investigated for the dry reforming reaction. The results of the catalytic activity tests are presented in Figure 5.

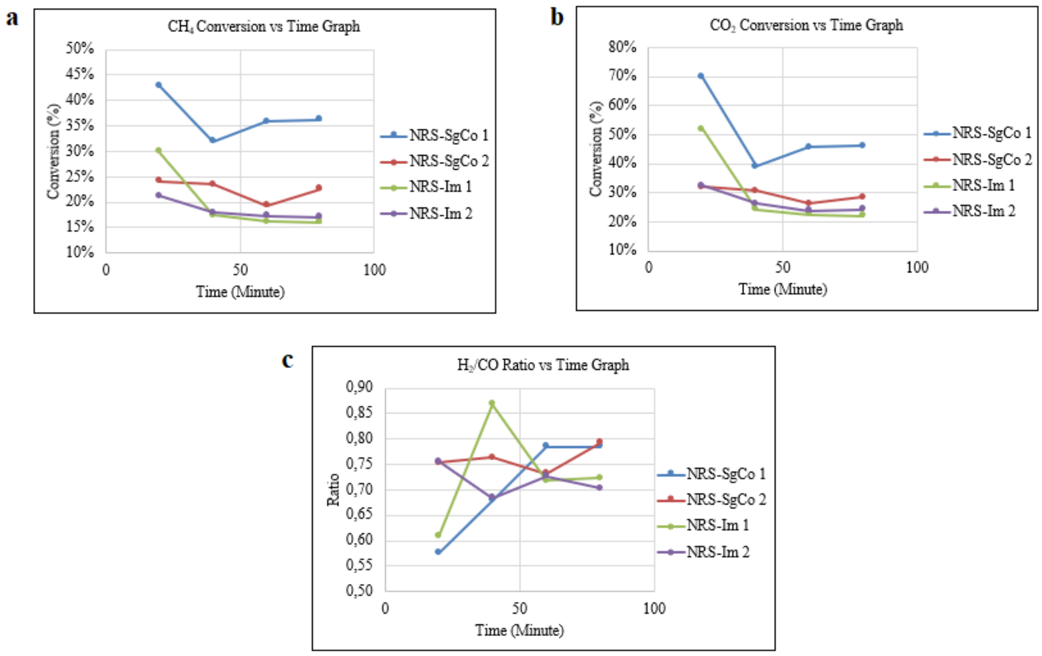

Figure 5. Results of the catalytic activity test: (a) Conversion of CH_4 vs. time, (b) Conversion of CO_2 vs. time, (c) H_2/CO Ratio vs. time

Based on Figure 6, the dry reforming process involving the catalyst prepared using the impregnation method shows lower CH_4 and CO_2 conversions than the reaction process with the catalyst prepared using the sol gel-coprecipitation method. This is likely due to the lower thermal stability of the catalyst prepared using the impregnation method. From the literature, the catalyst with lower thermal stability tends to induce a considerable surface area reduction [14]. The high surface area is important to enhance heat and mass transfers, resulting in the increased conversion efficiency of the reactants, CH_4 and CO_2, into products [15].

In this study, the ratio of H_2/CO obtained from the catalyst prepared using either impregnation or sol gel-coprecipitation techniques did not show any significant differences because of the identical pore diameters. Referring to the previous studies, the ratio of H_2/CO is influenced by the pore diameter of the catalyst [16]. The H_2/CO ratio in this study is in the range of 0.7-0.8. This ratio is the optimum ratio of syngas that can be utilized as an intermediate product for the production of gasoline or diesel [1].

The catalytic activity of the catalyst was compared with the activity of the materials prepared by Han et al. (2020), Miao et al. (2020), and Li et al. (2018). This was performed to understand the effectivity of the Ni-Ru/SiO_2 catalyst compared to other materials from the literature. The comparison of the catalytic activity with other materials is shown in Figure 6.

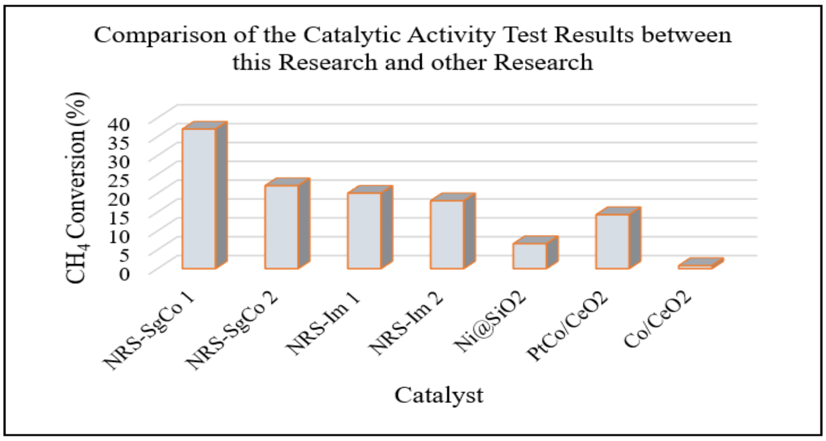

Figure 6. Comparison of the catalytic activity of the Ni-Ru/SiO_2 catalyst with other materials from the literature

According to Figure 6, the highest CH4 conversion was obtained using the catalyst prepared in this study (sample NRS-SgCo 1, NRS-SgCo 2, NRS-Im 1, and NRS-Im 2). As the CH4 conversion increases, the syngas production also increases. Compared to another study with a similar catalyst conducted by Wysocka et al. (2019), the H2/CO ratio obtained from this study is 114% higher. This implies that the selectivity of our Ni-Ru/SiO2 catalyst is significantly higher.

4. CONCLUSION

In summary, Ni-Ru/SiO_2 catalysts were successfully prepared using different synthesis protocols. The XRD analysis showed that the catalysts prepared using either sol gel-coprecipitation or impregnation methods indicated NiO, RuO_2, and SiO_2 phases. The results suggest that the sol-gel coprecipitation is a suitable method to optimize the performance of the catalyst due to higher thermal stability than the catalyst prepared using the impregnation method, which can be noticed from the higher CH_4 and CO_2 conversion. The Ni-Ru/SiO_2 catalysts prepared in this study also possess higher catalytic activity compared to other catalysts from the literature. Moreover, the Ni-Ru/SiO_2 catalyst also produced 114% higher amounts of syngas than another study from the literature with similar catalyst materials.

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