

# Ni/SBA-15 catalysts for methane dry reforming

R. Ahmed\*, S. Hodgson and M. Olea

Teesside University, School of Science & Engineering, Middlesbrough, Tees Valley, TS1 3BA, United Kingdom  
Kurdistan Institution for Strategic Studies and Scientific Research, Qirga, Slemani, As Sulaymaniyah, Iraq.

\*Corresponding author: R. Ahmed, Teesside University, School of Science & Engineering, Middlesbrough. E-mail: rawazahmed@outlook.com (or) rawazahmed@kissr.edu.krd

✉ rawazahmed@kissr.edu.krd

Citation: R. Ahmed (2020) Ni/SBA-15 catalysts for methane dry reforming Arch Chem Vol. S No. 1: 001

Copyright: © 2020 R. Ahmed, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Received: August 09, 2020; Accepted: August 14, 2020; Published: August 23, 2020.

## Abstract

**Purpose:** Ten catalyst samples, with increasing nickel loadings of 4 to 29 wt%, were prepared by impregnation of different nickel precursors on SBA-15 mesoporous silica support. A modified sol-gel method was used to prepare the support, which proved to have a high BET surface area of 834 m<sup>2</sup>/g, a very well-ordered mesoporous structure and narrow pore size distribution around 7.8 nm. Good dispersion and reasonably high loadings were obtained from less concentrated solutions of nickel acetate precursors, while the highest loading is obtained using nickel nitrate as precursor. The DRM reaction, using a model biogas, CH<sub>4</sub>/CO<sub>2</sub> ratio of 1.5:1, was operated isothermally at 550, 600, 650 and 700 °C, respectively. Although all catalysts showed high catalytic activity, the activity for those prepared using acetate precursor was higher at all four temperatures.

## Introduction

Biogas (60% of CH<sub>4</sub> and 40% of CO<sub>2</sub>) can be converted into syngas with suitable H<sub>2</sub>/CO ratio for methanol and Fischer-Tropsch syntheses, through the dry reforming reaction [1, 2]. Nickel catalysts are known to be very active for this conversion process, but they are easily deactivated, due to coke formation, particularly at temperatures higher than 700 °C, by CH<sub>4</sub> decomposition and Boudouard reaction. Therefore, many research studies were focused on the preparation of supported catalysts with improved activity and stability, by using different preparation methods and different supports [1, 2, 3, 4, 5, 6 and 7].

This work deals with the preparation of newly-developed nickel catalysts supported on mesoporous SBA-15 silica. A modified sol-gel method was chosen for the support preparation and impregnation method was used to incorporate the active phase, namely nickel, onto the support [4, 5]. The prepared Ni/SBA-15 catalysts with different Ni loading and different Ni precursor were tested in DRM reaction.

## Experimental

Ten Ni/SBA-15 catalysts were synthesized by impregnation method, with different Ni loading and Ni-precursor. Within this study, Ni acetate, nitrate and citrate, in different concentrations, were used as precursors. The impregnation was carried out at different temperatures, for different impregnation times, and different impregnation treatments. The following samples were prepared and labeled as shown in the Table 1.

The synthesized catalysts were tested in the CO<sub>2</sub> reforming of methane. The CO<sub>2</sub> reforming of methane reaction was conducted under atmospheric pressure and constant temperature, namely 550, 600, 650 and 700 °C respectively, in the CATLAB system. About 25 mg of each sample was firstly reduced under a 5 vol. % H<sub>2</sub> in Ar flow at 20 ml/min and then exposed to the reaction mixture 100 ml/min flow, with CH<sub>4</sub>/CO<sub>2</sub> = 1.5:1, for 3 hr. The analysis of the effluent was carried out using the quadruple mass spectrometer, QIC20. The following amu was measured: 2 (H<sub>2</sub>), 40 (Ar), 18 (H<sub>2</sub>O), 15 (CH<sub>4</sub>), 28 (CO), 32 (O<sub>2</sub>) (amu = 32), and 44 (CO<sub>2</sub>). The integrated software allowed the conversion of intensity of the amu into the pressure and as such, in this work, the conversions, X, of limiting reactant, CO<sub>2</sub>, was calculated according to the following equations:

$$X_{O_2} = \frac{P_{O_2}^o - P_{O_2}}{P_{O_2}^o} * 100$$

Table 1: Prepared Ni catalyst samples.

Precursor	SBA-15: Ni-salt :DI water (wt ratio)	IMP. Time, hr	Heat treatment		Label, XIMPNi
			IMP, Temp(°C)	Drying	
Ni-acetate (diluted)	3:1:30	20	90-95	vacuum oven, 100 °C, 1hr	4IMPNiA-Ad
	3:2:30				9IMPNiB-Bd
	3:3:30				11IMPNiC-Cd
Ni-acetate (concentrated)	3:1:10	10	90-95	dried at 120 °C, 10hr	4IMPNiA-Ac
	3:2:10				9IMPNiB-Bc
	3:3:10				12IMPNiA-Cc
Ni-nitrate	3:1:10	10	50-55	dried at 120 °C, 10 hr	6IMPNiN-A
	3:2:10				12IMPNiN-B
	3:3:10				29IMPNiN-C
Ni-citrate	3:2:10	1-2	RT	vacuum oven, 100 °C, 1hr	8IMPNiC-B
	3:3:10				15IMPNiC-C
	3:1:10				8IMPNiA-5

\*X is the wt.% of nickel loaded as NiO, determined from EDX, IMP refers to impregnation, NiA = Ni-acetate, NiN = Ni-nitrate and NiC = Ni-citrate, d = diluted, c = concentrated.

## Results/Discussion

Effect of Ni loading for ex-acetate samples: Three samples were prepared by using concentrated solutions of nickel nitrate as precursor. Catalytic activity results for these samples are shown in the Fig. 2 and Table 2. Similar CO<sub>2</sub> conversions were observed at all reaction temperatures for the samples with 12 wt% and 29 wt% Ni loading. On the other hand, the lowest Ni loading (6 wt %) gave lower conversions at 550 and 600°C, the same conversion at 650°C, and higher conversion (in fact was complete conversion) at 700°C, than the other two loadings. As seen from Table 2, all samples showed a very good catalytic activity, even at temperatures as low as 550°C. Extremely high CO<sub>2</sub> conversions were obtained above 600°C, with complete conversion for some of the samples at 650°C. To the best of our knowledge, no Ni/SBA-15 catalysts with such high activity were reported so far. Zhang reported the activity towards DRM reaction for a series of Ni/SBA-15 catalysts, with Ni loadings between 2.5 and 20 wt%, prepared by using the same preparation method but under slightly different preparation conditions [8]. The reaction temperature was between 700 and 850°C. As expected, the highest CO<sub>2</sub> conversion, around 90% for all their samples, was at 850°C. The same level of conversion was obtained on our catalyst samples but at 600°C. To conclude, the highest catalytic activity was shown by the catalysts obtained using Ni acetate as precursor. In particular, the best one seems to be the 9 wt% Ni for which a stability test was performed as well. The activity of this catalyst remained unchanged after 40 hrs time on stream measurements at 650°C.

The response somewhere in the range of CH<sub>4</sub> and CO<sub>2</sub> was concentrated as a component of temperature on every one of the four pre-diminished impetuses. As the CO<sub>2</sub> improving of CH<sub>4</sub> response is an endothermic response ( $\Delta H_{298} = 247 \text{ KJ.mol}^{-1}$ ), high activity temperatures are required to accomplish elevated levels of transformation. The essential goal of this examination is to create and incorporated reasonable impetus frameworks for the DRM response with the point of bringing down vitality utilization, with the most elevated transformation of both carbon dioxide and methane at least temperature. Clear test utilizing unadulterated SBA-15 silica demonstrated unimportant non-synergist gas stage changing preceding customary reactant tests. Fig. 1 shows the synergist movement profile of the three examples got from the weaken arrangements of nickel acetic acid derivation as forerunner, with NiO stacking from 4 wt% to 11 wt%, as decided from EDX estimations. The CO<sub>2</sub> change is reliant on the Ni content with enormous contrasts between 4 wt% and 9 and 11 wt%, particularly at low temperatures. Change progressively expanded with the response temperature for every impetus once the reactant movement is activated. A moderate increment in the reactant transformations with expanding temperature is watched for the high nickel content impetuses, while a quickly expanding of action was watched for the impetus with the most reduced Ni-content. Despite the fact that it isn't irregular that the movement is an element of the general metal stacking, the analyses demonstrated that, for our situation, there appeared to be an ideal degree of Ni stacking which gives the most elevated change. In this examination, the ideal degree of Ni stacking in the Ni impetus dependent on Ni-acetic acid derivation was seen as around 9 wt%. Over this level, the synergist movement

didn't increment observably and what is more, for the 9 wt% Ni impetus the total transformation was acquired at 650°C while for the other two, the temperature for the total change was 700°C. See Table 8 also for CO<sub>2</sub> transformations at various response temperatures for all the impetus tests examined.

Table 2: CO<sub>2</sub> conversion at different reaction temperatures.

Catalysts	550 °C	600 °C	650 °C	700 °C
	X <sub>CO2</sub> (%)	X <sub>CO2</sub> (%)	X <sub>CO2</sub> (%)	X <sub>CO2</sub> (%)
4IMPNiA-Ad	65	90	97	100
9IMPNiA-Bd	80	88	100	100
11IMPNiA-Cd	79	86	98	100
6IMPNN-A	69	87	96	100
12IMPNN-B	77	92	96	94
29IMPNN-C	76	94	98	97

<sup>a</sup> X<sub>i</sub> is the fractional conversion of CO<sub>2</sub>.

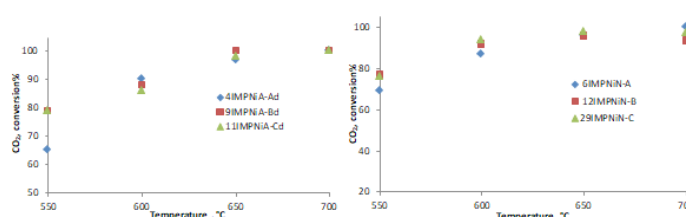


Fig. 1: Variation of CO<sub>2</sub> conversion with temperature for different Ni loadings, nickel acetate as precursor.

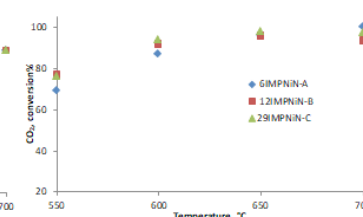


Fig. 2: Variation of CO<sub>2</sub> conversion with temperature for different Ni loadings, nickel nitrate as precursor.

## Conclusion

This research work proposed to synthesize and characterize supported nickel catalysts to be used for the DRM process. The main goals were reached. So far, the SBA-15 support and 10 nickel catalyst samples were prepared and extensively characterized by physical methods. The following were found out. The DRM reaction was applied, using a CH<sub>4</sub>/CO<sub>2</sub> ratio of 1.5:1, was operated isothermally at 550, 600, 650 and 700°C, respectively. Although all catalysts showed high catalytic activity, the activity for those prepared using acetate precursor was higher at all four temperatures, while the highest activity was seen for the 9IMPNiA-Bd sample. For this catalyst, the CO<sub>2</sub> complete conversion was obtained at 650°C, while for some of the other samples the temperature for complete conversion was 700°C. Finally, the Ni catalyst based on Ni-acetate exhibited also higher catalytic stability over a 40-hr test period. There was no carbon formed over these samples while for the ones obtained from Ni-nitrate, the amount of carbon increased with the Ni loading.

## References

- [1] Bradford, M. C. J., Vannice M. A., Catal. Rev. – Sci. Eng., 41 (1999) 1-42.
- [2] Hu, Y. H, Ruckenstein, E., Adv. Catal. , 48 (2004) 297-345.
- [3] Al-Fatish, A.S.A., Ibrahim, A.A., Fakeeha, A.H., Soliman, M.A., Siddiqui, M.R.H., Abasaed, A.E., Appl. Catal., A, 364 (2009), 150-155.
- [4] Steinhauer, B., Kasireddy, M.R., Radnik, J., Martin, A., Appl. Catal., A, 366 (2009), 333-341.
- [5] Hufschmidt, D., Bobadilla, L.F., Romero-Sarria, F., Centeno, M.A., Odriozola, J.A., Montes, M., Falabella, E., Catal. Today,

149 (2010) 394-400.

- [6] Supaporn Therdthianwong, Chairut Siangchin, Apichai Therdthianwong, *Fuel Processing Technology*, (2007).
- [7] Chen J., Wang R., Zhang T., Han S. *J. of Mol. Catal. A: Chem.*, 235(2005), 302-310.
- [8] Zhang, M., Ji, S., Hu, L., Yin, F., Li, C., and Liu, H., *Chinese Journal of Catalysis*, (2006), 27(9), 777-781.