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Research paper

Comparative Study of Ni Loading Methods Towards Superior CO_2 Conversion Over Ni/SBA-15

S.N. Bukhari[1], C.C. Chong[1], H.D. Setiabudi[1,2,*], N. Ainirazali[1], M.A.A. Aziz[3,4], L.P. Teh[5], N.H.R. Annuar[6]

[1]*Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia.*
[2]*Centre of Excellence for Advanced Research in Fluid Flow, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia.*
[3]*Sustainable Waste Management Research Group, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.*
[4]*School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.*
[5]*School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.*
[6]*Department of Chemistry, Faculty of Applied Science, Universiti Teknologi MARA (UiTM) Johor, Pasir Gudang Campus, 81750 Masai, Johor, Malaysia*
**Corresponding author E-mail: herma@ump.edu.my*

Abstract

A series of Ni/SBA-15 catalysts were successfully synthesized via conventional wet impregnation method (C-IM), P123-assisted impregnation method (P123-IM) and ultrasonic-assisted impregnation technique (US-IM) methods. The obtained results confirmed that the impregnation methods significantly influenced the physio-chemical properties of Ni/SBA-15 catalysts, which subsequently influenced the catalytic performances of catalysts. The catalytic performance of catalysts followed the order of Ni/SBA-15(P123-IM) > Ni/SBA-15(US-IM) > Ni/SBA-15(C-IM), indicating the superior performance of Ni/SBA-15(P123-IM) towards CO_2 methanation (CO_2 conv.: 91.1%, CH_4 selec.: 97.7%) and CO_2 dry reforming (CO_2 conv.: 82.6%, H_2/CO: 1.23). The excellent catalytic performances of CO_2 methanation and CO_2 dry reforming over Ni/SBA-15(P123-IM) were owing to its favorable textural properties; homogenous Ni dispersion, smaller NiO crystallite size (12.1 nm), and a higher concentration of metal-support interaction upon the introduction of P123 as the surfactant during the impregnation method. The P123-IM method successfully synthesized the favorable Ni/SBA-15 for superior CO_2 conversion and could be used in various applications

Keywords: *Ni/SBA-15; impregnation; CO_2 conversion; dry reforming; methanation.*

1. Introduction

Recycling of carbon dioxide (CO_2) into more valuable products via CO_2 methanation (CM) [1] and CO_2 dry reforming (CRM) [2-4] over metal-based catalysts have been studied extensively in recent years. Regarding the choice of metal, Nickel (Ni) has been recommended as the best candidate for CM and CRM reaction [4]. However, the Ni-based catalyst is always accompanied by agglomeration of Ni particles and coke formation, which causes a severe deactivation of the catalyst. Thus, the amelioration on the Ni particles distribution onto the support's surface has been the focus of the considerable research.

There are various catalyst preparation techniques have been reported in literature including conventional impregnation [3], co-precipitation [5], surfactant-assisted impregnation [6] and ultrasonic-assisted impregnation method [4]. Among all above-mentioned techniques, impregnation has been widely used owing to its advantages related to simplicity, cost, and time used. However, conventional impregnation method always accompanied with the agglomeration of metals, and thus reducing the catalytic performance of catalyst.

In recent years, surfactant-assisted impregnation method has attracted considerable attention due to its ability in producing better metal dispersion and smaller metal particles [6, 7]. The introduction of surfactant resulted in the formation of complexes between surfactant and metal precursor, which consequently improved the dispersion and stabilization of the metal [7]. In addition to this method, ultrasonic-assisted impregnation method is also preferred by researchers. The presence of ultrasound can eventually shorten the preparation time with faster mass transfer rate, and thus able to produce well-dispersed metal-based catalyst [8]. In addition, the synergetic effect of ultrasound provides a uniform environment for the nucleation and growth of metal particles, and thus inhibiting the agglomeration of metal particles [4].

Although several studies have reported the positive role of surfactant and ultrasound on the formation of well-dispersed metal-based catalyst, however as far as we are concerned, the comparative study between surfactant-assisted impregnation method and ultrasonic impregnation has not been reported in the literature. Thus, it is desirable to conduct the comparative study of the Ni loading methods (conventional wet impregnation method (C-IM), P123-assisted impregnation method (P123-IM) and ultrasonic-assisted impregnation technique (US-IM)) towards the properties and catalytic activity of the Ni-based catalyst. In the current study, SBA-15 has been chosen as support due to its high specific surface area (600-1000 m^2 g^{-1}), high thermal stability and 4.6-30 nm well-arranged hexagonal structure of mesopores [2].

2. Materials and methods

2.1 Catalysts Preparation

SBA-15 was prepared by mixing 4.9 g of triblock copolymer P123 (Aldrich, average molecular weight = 5800) with an aqueous 2M hydrochloric acid (HCl, 37 wt.%) and stirring them vigorously for 1 h at 313 K. Then, tetraethylorthosilicate (Merck, TEOS) (mass ratio of TEOS/P123 = 2.21) was dropped into the mixture solution and stirred for 1 day. The precipitate was filtered before being washed and air-dried in an oven at 383 K overnight. Lastly, calcination was done for 3 h at 823 K 3 h with a ramping rate of 2 K min^{-1}.

Impregnation of Ni metals was done using CIM, P123-IM, and US-IM, denoting as Ni/SBA-15(C-IM), Ni/SBA-15(P123-IM) and Ni/SBA-15(US-IM), respectively. For Ni/SBA-15(C-IM), SBA-15 support was mixed with aqueous solution of Ni salt precursor ($Ni(NO_3)_3 \bullet 6H_2O$) and stirred until most of the water was evaporated. Meanwhile, for Ni/SBA-15(P123-IM), it was synthesized by suspending SBA-15 support with the specific amount of P123 as surfactant before stirred with aqueous Ni salt precursor for 12 h at room temperature. For Ni/SBA-15(US-IM), a mixing between SBA-15 and aqueous Ni salt precursor was carried out by ultrasonic for 3 h. After impregnation process, the samples were air-dried at 823 K for 12 h. Calcination step took place at 550 °C for 3 h. The 5 wt.% of Ni and molar ratio of P123/Ni = 1/50 were controlled in this study.

2.2 Catalysts Characterization

The crystallinity structure of catalysts was examined by employing x-ray diffraction (XRD) (Philips X' Pert MPD, 3 kW) equipped with the CuKα source (λ = 1.5405Å). Bruneuer-Emmett-Teller (BET) (AUTOSORB-1 model AS1 MP-LP instrument) was used to investigate the properties (i.e., specific BET surface area and porosity) of the catalysts. Before measurement, degassing of samples were done at 473 K for 4 h. IR spectra was recorded using Agilent Cary 640 FTIR Spectrometer within the wavenumber of 500–4000 cm^{-1}.

2.3 Catalytic Testing

CM and CRM reactions were performed using fixed-bed quartz reactor (i.d. 11 mm, length 417 mm) under ambient pressure. The reduction was carried out using 0.2 g of catalyst treated in a flow of H_2 stream ($F_{Hydrogen}$ = 20 mL/min) for 1 h at 973 K. Then, the feeding gases were mixed continuously and passed through the catalyst in the reactor. The conditions for CM reaction were at T = 673 K, GHSV = 24,900 mL $g^{-1} h^{-1}$, H_2/CO_2 = 1/4. Meanwhile, the conditions for CRM reaction were at T = 1073 K, GHSV = 17,000 mL $g^{-1} h^{-1}$, CH_4/CO_2 = 1/1. A gas chromatograph equipped with a TCD (Agilent 6890 Chromatograph) was used to analyze the gas composition of reactants and products. The CO_2 conversion (X_{CO_2}) and CH_4 selectivity (S_{CH_4}) are computed using the following Eq. (1) and (2), respectively.

$$X_{CO_2}(\%) = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\% \tag{1}$$

$$S_{CH_4}(\%) = \frac{F_{CH_4,out}}{F_{CO_2,in} - F_{CO_2,out}} \times 100\% \tag{2}$$

Where F is the molar flow rate for a specific component. The calculation of H_2/CO ratio was according to Eq. (3).

$$\frac{H_2}{CO} = \frac{F_{H_2}}{F_{CO}} \tag{3}$$

3. Results and discussion

3.1 Characterization of the catalysts

Fig. 1 represents XRD patterns of Ni/SBA-15 catalysts using C-IM, P123-IM, and US-IM. From Fig. 1A, it could be observed that all catalysts exhibited (100), (110), and (200). This indicated the appearance of hexagonally ordered structures of Ni/SBA-15 (p6mm) with uniform and high quality of mesoporous packing [4]. It was observed that the introduction of P123-IM and/or US-IM significantly reduced the intensities of the (110) and (200) reflections, indicating structural deterioration of SBA-15.

For the wide-angle XRD pattern (Fig. 1B), it was observed that all catalysts exhibited five main peaks at 2θ = 37.3, 43.2, 62.9, 75.4, and 79.3°, attributing to face-centered cubic crystalline NiO structure on the catalyst [1]. The average NiO crystallite sizes were calculated and summarized in Table 1. It is clearly observed that Ni/SBA-15(P123-IM) possessed the smallest NiO crystallites size (12.1 nm), which might be due to the higher concentration in metal-support interaction upon the presence of P123 as the surfactant.

The presence of metal-support interaction was analyzed using FTIR analysis and the result was illustrated in Fig. 1C. All catalysts exhibited four peaks at 1060, 961, 801, and 510 cm^{-1}, assigning to asymmetric stretching vibrations of Si-O-Si, Si-O stretching vibration of Si-OH groups, symmetric stretching vibrations of Si-O-Si, and tetrahedral bending vibration of Si-O-Si bonds, respectively [3]. According to literature [9], the reduction in the peak intensity at 961 cm^{-1} could be evidenced the replacement of O-H with O-M to form the Si-O-M. Thus, it is rational to claim that the concentration of metal-support interaction followed the sequence of Ni/SBA-15(P123-IM) > Ni/SBA-15(US-IM) > Ni/SBA-15(C-IM), which in agreement with the reduction of the peak intensity at 961 cm^{-1}.

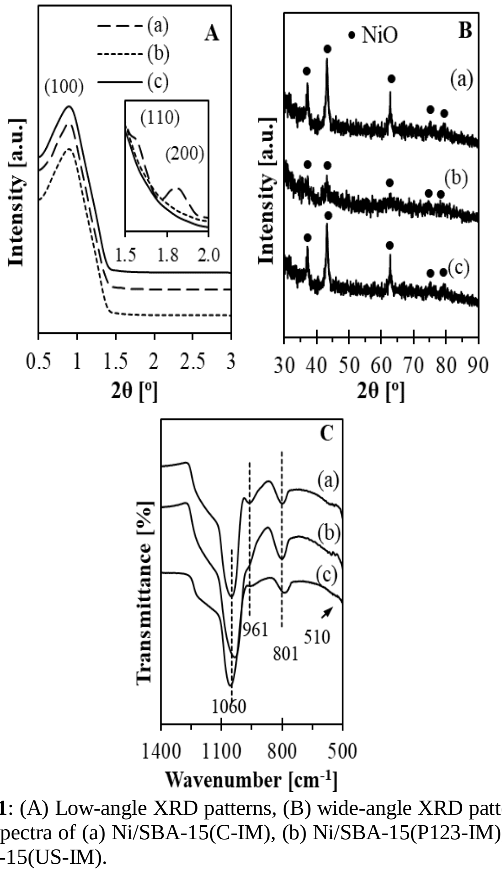

Figure 1: (A) Low-angle XRD patterns, (B) wide-angle XRD patterns and (C) IR spectra of (a) Ni/SBA-15(C-IM), (b) Ni/SBA-15(P123-IM), and (c) Ni/SBA-15(US-IM).

The specific surface area (S_{BET}), pore volume (V_P) and pore diameter (D_P) of all catalysts are tabulated in Table 1. An introduction of Ni onto the framework of SBA-15 support significantly decreased the S_{BET}, V_P, and D_P of the catalysts, implying that the Ni species blocked the mesoporous pores of SBA-15 [9]. However, a slight increase in D_P of Ni/SBA-15(US-IM) could be claimed to the plugging of NiO crystallites in pore mouth of SBA-15, and thus triggered the wall contraction and pores' expansion.

Table 1: Textural properties of SBA-15 and Ni/SBA-15 catalysts.

Catalysts	S_{BET} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)	D_P (nm)	D_{NiO} (nm)[a]
SBA-15	856	0.999	6.8	-
Ni/SBA-15(C-IM)	473	0.649	6.2	13.4
Ni/SBA-15(P123-IM)	335	0.322	4.5	12.1
Ni/SBA-15(US-IM)	423	0.940	7.2	12.9

[a] Calculated from XRD result using Scherrer equation.

3.2 Catalytic testing of the catalysts

Fig. 2A and Fig. 2B show the activity of catalysts towards CM and CRM, respectively. As noticed, the performances of the catalyst followed the order of Ni/SBA-15(P123-IM) > Ni/SBA-15(US-IM) > Ni/SBA-15(C-IM), indicating the most excellent catalytic activity of Ni/SBA-15(P123-IM) towards CM and CRM.

The catalytic performance of Ni/SBA-15(P123-IM) towards CM was about CO_2 conv. = 91.1% and CH_4 selec. = 97.7%. Meanwhile, for CRM reaction, the activity was about CO_2 conv. = 82.6% and H_2/CO ratio = 1.23. The superior catalytic activity and stability (Fig. 3C) of Ni/SBA-15(P123-IM) was owing to its favorable catalytic properties. The availability of better homogenous and well-dispersed NiO sites onto the SBA-15 support with the stronger metal-support interaction is the key success for an excellent catalytic activity of CO_2 conversion over Ni/SBA-15, which in agreement with Sidik et al. [10] for Ni/MSN.

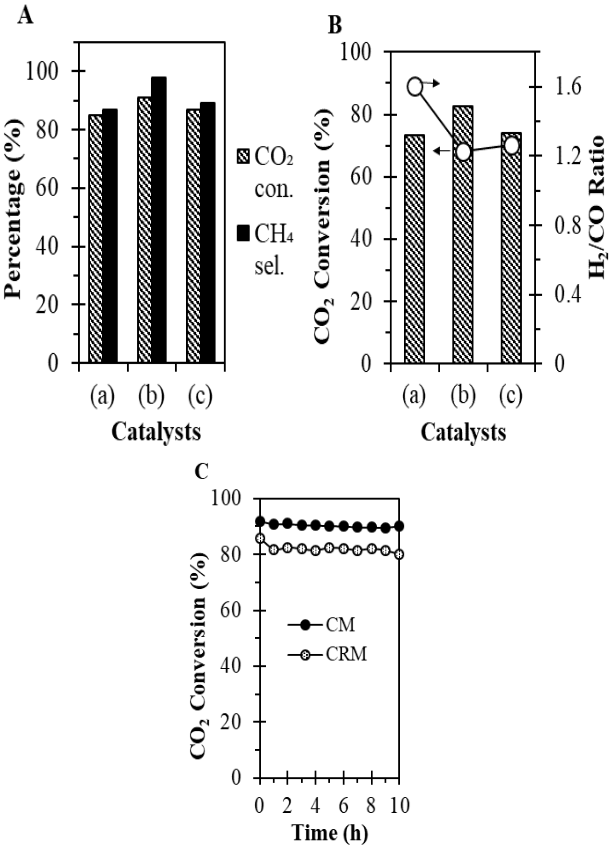

Figure 2: (A) CO_2 methanation (CM) and (B) CO_2 dry reforming (CRM) over (a) Ni/SBA-15(C-IM), (b) Ni/SBA-15(P123-IM) and (c) Ni/SBA-15(US-IM). (C) Stability test of Ni/SBA-15(P123-IM).

4. Conclusion

The comparison between C-IM, P123-IM and US-IM had been developed. Based on the results obtained, the catalytic performances followed the order of Ni/SBA-15(P123-IM) > Ni/SBA-15(US-IM) > Ni/SBA-15(C-IM), attributing the most excellent catalytic activities of Ni/SBA-15(P123-IM). This phenomenon was highly related with its favorable catalytic properties; better Ni dispersion, smaller NiO crystallites size, and a higher concentration of strong metal-support interaction. This P123-IM method can give many benefits in the synthesis of a promising metal-based catalyst which may be used in various applications.

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