

Metgas Production from Bi-reforming of Methane over La-modified Santa Barbara Amorphous-15 Supported Nickel Catalyst

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An integrated process of steam reforming coupled with CO₂ reforming of methane (bi-reforming) has emerged as a promising reforming technique among pre-existing technologies. Syngas with a H₂/CO ratio of about 2 (called Metgas) is desirable for the production of methanol and liquid hydrocarbons. La-modified and unmodified Santa Barbara Amorphous-15 (SBA-15) supports were synthesised by one-pot and hydrothermal techniques. These supports were further impregnated with Ni(NO₃)₂ metal precursor solution using an incipient wetness impregnation method. The methane bi-reforming reaction was carried out in a tubular fixed-bed quartz reactor under atmospheric pressure at varying temperature of 1,023 - 1,073 K with CH₄/H₂O/CO₂ = 3/2/1 and gas hourly space velocity (GHSV) of 36 L g_{cat}⁻¹ h⁻¹. The physicochemical properties of both catalysts were scrutinised by BET, X-ray diffraction (XRD) and H₂ temperature-programmed reduction (H₂-TPR). The BET results showed that La-modified SBA-15 support possessed higher surface area of 737 m² g⁻¹ in comparison with the unmodified SBA-15 support counterpart (669 m² g⁻¹). An inevitable decline in surface area was observed after NiO addition for both supports due to the successful diffusion of NiO particles into the mesoporous channels of supports. XRD measurements confirmed the presence of NiO and amorphous SiO₂ phases for both 10 % Ni/La-SBA-15 and 10 % Ni/SBA-15 catalysts. No characteristic peaks were detected for La₂O₃ phase reasonably owing to the incorporation of La₂O₃ into the framework of SBA-15 support. Both reactant conversions and gaseous product yields improved considerably with an increase in reaction temperature for both catalysts. A desirable H₂/CO ratio of about 2 was achieved at reaction temperature of 1,048 - 1,073 K. La-modified SBA-15 supported Ni catalyst exhibited greater activity and selectivity than those of unmodified counterpart.

1. Introduction

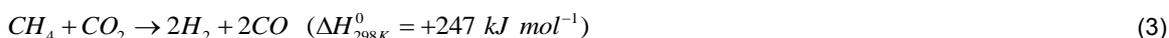
One of the major challenges in chemical industry is to discover energy-efficient and inexpensive processes for converting abundantly available natural gas, especially methane into value-added chemicals and green fuels to reduce the significant dependence on fossil fuels due to the depletion of petroleum-based resources. Synthetic gas (a mixture of H₂ and CO) conventionally produced via steam reforming (SR), partial oxidation (PO) and dry reforming (DR) of methane has been widely regarded as a promising energy source since it can be used as a feedstock for Fischer-Tropsch synthesis (FTS) to generate environment-friendly synthetic diesel (Basini, 2005). There are certain shortcomings associated with these reforming technologies. The SR of methane yields a high H₂/CO ratio of 3 unsuitable for methanol and FTS (Olah et al., 2013). Although PO of

methane can produce a H₂/CO ratio of close to 2, the formation of local hot spots during reaction and temperature instability due to its highly exothermic nature are unavoidable (Wilhelm, 2001). The main problem related with DR of methane is the low syngas ratio (H₂/CO < 1) (Selvarajah et al., 2016). Carbonaceous deposition from methane decomposition and Boudouard reactions (Eqs(1) and (2)) is other limitation associated with these conventional reforming processes (Pakhare and Spivey, 2014).

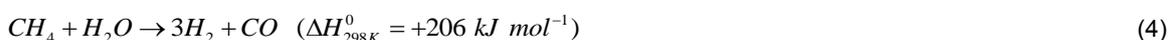


The intuitive approach to achieve syngas with a desired H₂/CO ratio of 2 (referred as metgas) is by combining dry reforming and steam reforming of methane processes as shown in Eqs(3) - (5) (Olah et al., 2013). The combination of dry and steam reforming (bi-reforming) of methane is an eco-friendly and efficient method because it utilises two major greenhouse gases (CH₄ and CO₂) and greatly reduces coke formation (Ryi et al., 2014).

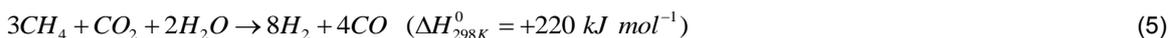
Dry reforming of methane:



Steam reforming of methane:



Bi-reforming of methane:



In reforming reactions, Ni-based catalysts exhibited comparable activity to noble metals and are relatively cost-effective (Danilova et al., 2015). These catalysts suffered from fairly rapid deactivation due to severe carbon formation and the coalescence of active sites (Albarazi et al., 2015). The utilisation of suitable support and promoter could hinder coke deposition and improve catalytic stability (Huirache-Acuna et al., 2013). SBA-15 support has recently received considerable attention due to its large surface area, uniform pore size, high thermal stability and great surface-to-volume ratio (Arcotumapathy et al., 2015). Ni/La₂O₃ reportedly exhibited high catalytic activity and stability for DR of methane due to the strong chemisorption of CO₂ and the formation of La₂O₂CO₃ intermediate phase (Zhang and Verykios, 1996) gasifying surface carbon species (CH_x) (Omogbe et al., 2016). The best of our knowledge, there was no previous work about the synergic effect of both SBA-15 and La₂O₃ supports on Ni-based catalyst for methane bi-reforming reaction. The objective of this paper was to investigate the physicochemical properties and catalytic performance of La-modified SBA-15 supported Ni catalyst for bi-reforming of methane reaction at stoichiometric condition.

2. Experimental

2.1 Catalyst preparation

10 % Ni/SBA-15 and 10 % Ni/La-SBA-15 catalysts were prepared by one-pot hydrothermal technique followed by incipient wetness impregnation method. The La-SBA-15 support was synthesised using tetraethyl orthosilicate (TEOS supplied by Merck Millipore), lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O from Sigma Aldrich) as precursors. Non-ionic triblock co-polymer, EO₂₀PO₇₀EO₂₀ (P123 obtained from Sigma Aldrich) was used as the structure directing agent. Approximately 3.13 g of P123 was added to 110 mL of 1.6 M HCl solution and subsequently stirred for 2 h at 313 K followed by adding 0.31 g of La(NO₃)₃·6H₂O. 7.06 mL of TEOS solution was introduced drop wise to avoid gel formation and the resulting mixture was agitated continuously for 24 h at 313 K. The white solution was then transferred to a Teflon-lined stainless steel autoclave and treated hydrothermally for 24 h at 373 K. The resulting precipitates were filtered out and washed with distilled water to obtain neutral solid, which was further dried overnight in an oven at 333 K and calcined at 823 K in air for 5 h at a heating rate of 2 K min⁻¹. The similar procedure without La(NO₃)₃·6H₂O addition was also implemented for the preparation of SBA-15 support. The as-prepared SBA-15 and La-SBA-15 supports were further impregnated with an accurately calculated amount of Ni(NO₃)₂·6H₂O aqueous solution in a rotary evaporator (BÜCHI Rotavapor R-200) for 2 h followed by drying overnight at 333 K and air-calcination for 5 h at 973 K with a ramping rate of 2 K min⁻¹ to produce 10 % Ni/SBA-15 and 10 % Ni/La-SBA-15 catalysts.

2.2 Catalyst characterisation

N₂ physisorption measurements of support and catalyst were performed at 77 K using a Micromeritics ASAP-2010 instrument. Samples were previously outgassed in flowing N₂ at 573 K for 1 h. X-ray diffraction (XRD) measurements were also conducted on a Rigaku Miniflex system, which used Cu monochromatic X-ray radiation with wavelength, $\lambda = 1.5418 \text{ \AA}$ in the angular range of $3^\circ - 80^\circ$ and was operated at 30 kV and 15 mA. In order to achieve high-resolution patterns, small scan speed of 1° min^{-1} and step size of 0.02° were implemented during XRD runs. The average crystallite size of detected phase was estimated using Scherrer equation (Patterson et al., 1939). H₂ temperature-programmed reduction (H₂-TPR) of uncalcined catalysts was analysed in an AutoChem II-2920 system. Prior to each measurement, the specimen was pre-heated in He inert gas (50 mL min^{-1}) for 30 min at 373 K. The catalyst was reduced in 10 % H₂/Ar mixture under a flow rate of 50 mL min^{-1} from 373 K – 1,173 K with a heating rate of 10 K min^{-1} .

2.3 Bi-reforming of methane reaction

The bi-reforming of methane runs were carried out in a quartz tube fixed-bed continuous flow reactor at stoichiometric feed composition (detailed reactant partial pressure given as; $P_{\text{CH}_4} = 45 \text{ kPa}$, $P_{\text{CO}_2} = 30 \text{ kPa}$ and $P_{\text{H}_2\text{O}} = 20 \text{ kPa}$) and reaction temperature range of 1,023 – 1,073 K under atmospheric pressure. 0.1 g of catalyst was held by quartz wool in the middle of reactor, which was placed upright in a split temperature-controlled furnace. Prior to methane bi-reforming reaction, catalyst was activated in-situ for 2 h under 60 mL min^{-1} of 50 % H₂/N₂ mixture at 923 K with a ramping rate of 10 K min^{-1} . The Alicat mass flow controllers were used for accurately controlling the flow rate of CH₄ and CO₂ reactants as well as N₂ diluent gas whilst KellyMed KL-602 syringe pump was employed for precisely feeding purified water. These reactants were subsequently vaporised and rigorously mixed before reaching catalyst bed. High gas hourly space velocity, GHSV of $36 \text{ L g}_{\text{cat}}^{-1} \text{ h}^{-1}$ was used for all reactions to ensure the negligible internal and external transport resistances. The composition of gaseous product stream from the outlet of fixed-bed reactor was analysed in a gas chromatograph (Agilent 6890 Series GC system) equipped with a thermal conductivity (TCD) detector.

3. Results and discussion

3.1 Characterisation results

3.1.1 Textural Properties

Table 1 summarises the textural properties of siliceous supports and Ni-based catalysts including Brunauer-Emmett-Teller (BET) surface area (S_{BET}), total pore volume (V_{P}) and average pore diameter (D_{P}) obtained from N₂ adsorption/desorption isotherms. Calcined SBA-15 and La-SBA-15 supports possessed high BET surface area of $669.5 \text{ m}^2 \text{ g}^{-1}$ and $737.3 \text{ m}^2 \text{ g}^{-1}$. The doping of nickel oxide has a significant impact on the physical attributes of supports as seen in Table 1. An unavoidable drop in BET surface area of about 27.38 % and 19.55 % for 10 % Ni/La-SBA-15 and 10 % Ni/SBA-15 catalysts was observed in comparison with the corresponding employed supports. This observation would indicate that NiO particles successfully penetrated into the mesopores of supports (Li et al., 2015). The average pore diameter of Ni-based catalysts was inferior to that of respective supports further confirming the presence of NiO nanoparticles inside the mesoporous structure of siliceous supports.

Table 1: Physical properties of supports and Ni-based catalysts

Material	$S_{\text{BET}} (\text{m}^2 \text{ g}^{-1})^{\text{a}}$	$V_{\text{P}} (\text{cm}^3 \text{ g}^{-1})^{\text{b}}$	$D_{\text{P}} (\text{nm})^{\text{c}}$	$d_{\text{NiO}} (\text{nm})^{\text{d}}$
SBA-15	669.5	1.18	7.06	-
La-SBA-15	737.3	1.22	6.64	-
10 % Ni/SBA-15	538.6	0.89	6.64	14.50
10 % Ni/La-SBA-15	535.4	0.87	6.51	17.40

^a Brunauer-Emmett-Teller (BET) surface area.

^b Total pore volume obtained at $p/p^0 = 0.99$.

^c Average pore diameter calculated by Barrett-Joyner-Halenda (BJH) desorption method.

^d Average crystallite size of NiO phase, computed from Scherrer equation.

3.1.2 X-ray diffraction measurement

The crystalline structure of catalysts and supports was analysed by XRD measurements as shown in Figure 1. The Joint Committee on Powder Diffraction Standards (JCPDS) database was used as references for interpreting XRD patterns (JCPDS powder diffraction file, 2000). As seen in Figure 1 (a) and (b), the broad diffraction peak at 2θ of about 22.3° for both supports belonged to the amorphous SiO₂ phase of SBA-15

framework in agreement with Landau et al. (2005). The characteristic peaks for La_2O_3 phase were not detected (see Figure 1 (b)), suggesting the fine metal dispersion on support surface or the incorporation of La_2O_3 phase into SBA-15 framework. The NiO phase was also observed for both catalysts (see Figure 1 (c) and (d)) with typical high diffraction peaks at $2\theta = 37.2^\circ$, 43.3° , 62.9° and 75.6° (JCPDS card No. 47-1049). The average crystallite size of NiO phase was estimated from Scherrer equation as 14.5 and 17.4 nm for the corresponding 10 % Ni/SBA-15 and 10 % Ni/La-SBA-15 catalysts.

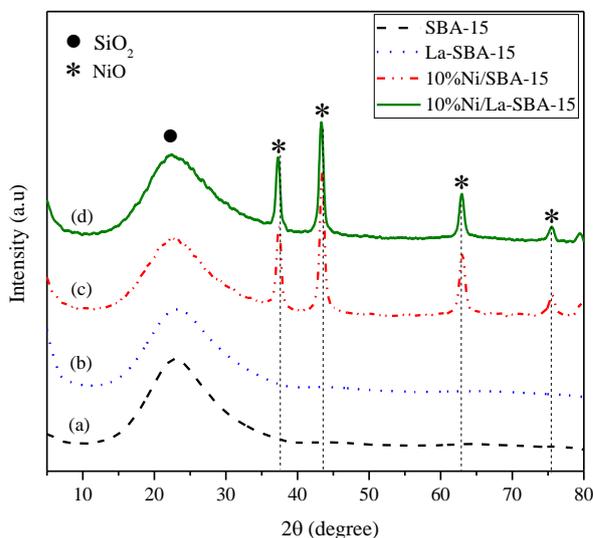


Figure 1: X-ray diffraction patterns of (a) SBA-15 support, (b) La-SBA-15 support, (c) 10 % Ni/SBA-15 catalyst and (d) 10 % Ni/La-SBA-15 catalyst

3.1.3 H₂ temperature-programmed reduction analysis

The H₂-TPR profiles for La-modified and unmodified SBA-15 supported Ni catalysts are illustrated in Figure 2. Two main peaks (α and β) located at ~ 540 K and ~ 660 K, were observed for both catalysts. The low intensity peak α was assigned to the reduction of large NiO particles weakly attached on support surface, whereas peak β was ascribed to the reduction of smaller NiO particles resided inside the mesoporous channels of siliceous supports. The intensity of peak α was significantly lower than that of peak β for both catalysts suggesting that the amount of NiO nanoparticles located in mesopores with strong metal-support interaction was superior to larger NiO particles on surface of support.

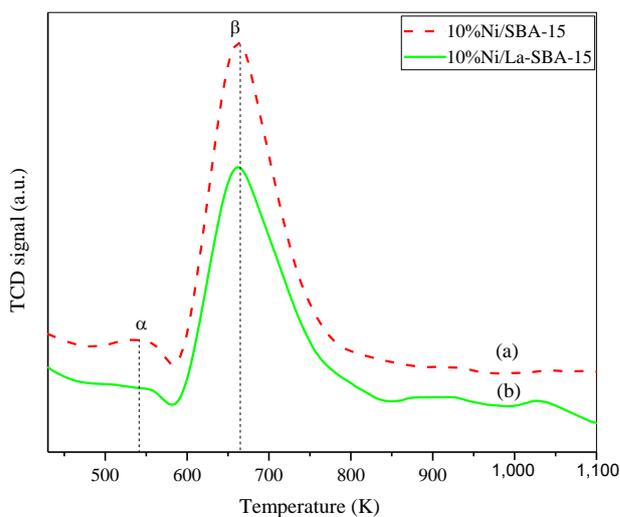


Figure 2: Hydrogen temperature-programmed reduction behavior of fresh (a) 10 % Ni/SBA-15 and (b) 10 % Ni/La-SBA-15 catalysts

3.2 Catalytic evaluation for methane bi-reforming reaction

As seen in Figure 3 (a), CH₄ and CO₂ conversions increased with rising reaction temperature from 1,023 K to 1,073 K for both catalysts reasonably due to the endothermic nature of methane bi-reforming reaction (see Eq(5)). Regardless of reaction temperature, 10 % Ni/La-SBA-15 catalyst exhibited greater CH₄ and CO₂ conversions than those of 10 % Ni/SBA-15 catalyst. The same behaviour was also observed for H₂ and CO₂ yields (Figure 3 (b)). These observations were attributed to the presence of La₂O₃ phase possessing basic property and excellent oxygen storage capacity hindering carbonaceous deposition on catalyst surface (Zhang and Verykios, 1996).

Figure 4 shows that H₂/CO ratio improved slightly with growing reaction temperature and reached to above 2 at 1,048 K - 1,073 K for both catalysts. The greater ratio of H₂ to CO than the stoichiometric H₂/CO ratio of 2 for methane bi-reforming reaction was most likely owing to the predominance of side reaction i.e. methane steam reforming given in Eq(4).

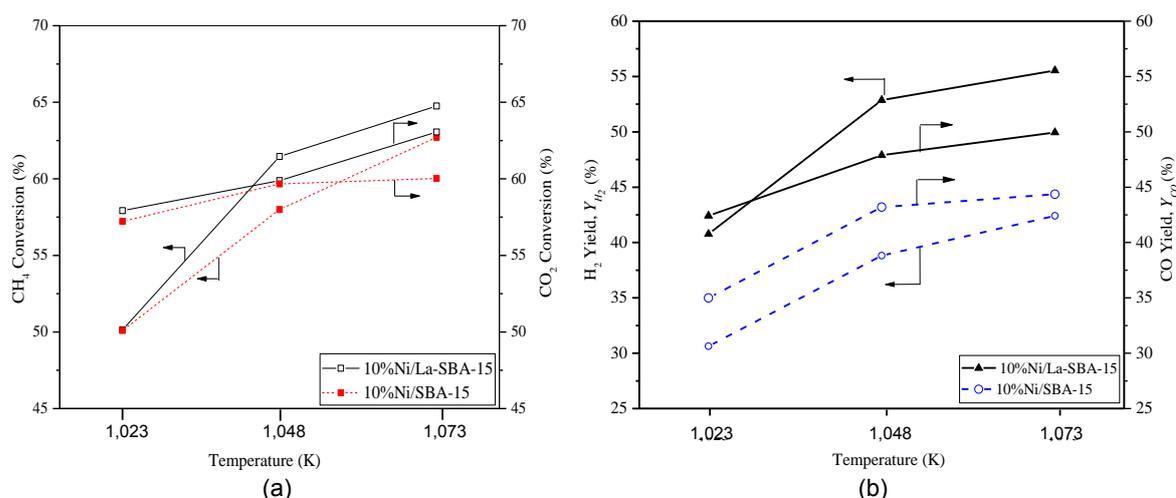


Figure 3: Effect of reaction temperature on (a) CH₄ and CO₂ conversions, and (b) gaseous product yield over 10 % Ni/La-SBA-15 and 10 % Ni/SBA-15 catalysts at $P_{CH_4} = 45$ kPa, $P_{CO_2} = 30$ kPa and $P_{H_2O} = 20$ kPa

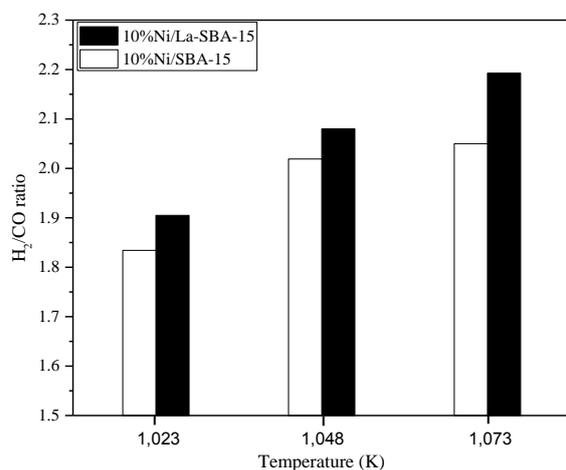


Figure 4: Effect of reaction temperature on H₂/CO ratio over 10 % Ni/La-SBA-15 and 10 % Ni/SBA-15 catalysts at $P_{CH_4} = 45$ kPa, $P_{CO_2} = 30$ kPa and $P_{H_2O} = 20$ kPa

4. Conclusions

La-modified SBA-15 supported Ni catalyst successfully prepared by the one-pot hydrothermal technique possessed high BET surface area of 535.4 m² g⁻¹. Both NiO and SiO₂ phases were detected for both La-modified and unmodified Ni-based catalysts whilst La₂O₃ particles were well dispersed on catalyst support. Catalytic activity and yield for both catalysts improved significantly with increasing reaction temperature

rationally due to the endothermic character of methane bi-reforming reaction. The enhancement of H₂/CO ratio with reaction temperature was also observed for both catalysts and the desirable H₂/CO ratio of about 2 was achieved at temperature of 1,048 K - 1,073 K. The 10 % Ni/La-SBA-15 catalyst exhibited greater activity and product yield than those of 10 % Ni/SBA-15 catalyst reasonably due to the basic property and excellent oxygen storage capacity of La₂O₃ phase.

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