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Study of Mass Transfer Resistant Effect during Syn Gas and Hydrogen Production through CO2/CH4 Dry Reforming on La/Mg Supported Co-Ni/MSU-S Zeolite

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ABSTRACT

In this study five different catalysts xLa/MgyCo-7Ni /MSU-S are synthesized through sol-gel procedure and further tested for XRD, HRTEM, FT-IR, H_2*-TPR,* CO_2*-TPD, and* O_2*-TPO skills. The mass transfer resistant effect, stability and activity of the catalytic samples were observed for syn gas and* H_2*gas synthesis at different reaction temperatures and various space velocities (GHSV) at atmospheric pressure. Space velocities of* $2.4\text{-}\ 3.2 \times 10^4$ $mL/g^{-1}h^{-1}$ *were used for the determination of mass transfer resistant effect, catalytic performance and composition of the catalyst at different reaction temperatures (700-800 °C) retaining constant atmospheric pressure during* CO_2/CH_4 *dry reforming reaction. The reaction outcomes showed that nanoparticles of nickel are highly discreted upon the promotion of Mg, La & Co oxides over MSU-S (mesoporous zeolite) through firmly contact of metal ions with HO-Si-groups of zeolite. Oxides of La (*La_2O_3*) in 1-3LayCozNi/MSU-S, which showed greater catalytic activity than 1-3Mg supported such catalysts. Among all five catalysts the N-/MSU-S doped with 3%La and 2%Co confirmed the best active catalyst in all respects with stability up to 75 h at of 750 °C. The catalyst also showed less mass transfer resistant effect at (GHSV) of 24000* $mL/g^{-1}h^{-1}$ *than 32000* $mL/g^{-1}h^{-1}$

Keywords: *mass transfer resistant effect,xLa/mgyCozNi/MSU-S; H2 and syn gas synthesis; methane dry reforming; greater stability and activist*

INTRODUCTION

Hydrogen is clean energy source of energy due to its recent utilization in modern industries and other fuel cells. The synthesis of Hydrogen, ammonia synthesis, from

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MDR (methane dry reforming) with carbon dioxide is valuable & hot topic toward hydrogen economy research [1].

The preparation of syngas ($CO+ H_2$) and hydrogen through MDR with CO_2 ($CO_2 + CH_4 \rightleftharpoons 2\ CO + 2\ H_2$, ΔH°at 25 °C (298K) had gotten significant consideration for usage in environmental optimization and industry [2-4].

The methane reforming reactions are considered as clean and energy efficient technologies either carried out in the presence of CO_2 (dry reforming) [5] or reaction with H_2O (steam reforming) reaction [6].

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^o = 247\ kJ/\ mol \qquad (1)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2, \qquad \Delta H^o = 206\ kJ\ mol \qquad (2)$$

The production of syn-gas from methane (Eq.1) has been studied extensively as synthetic gas can be used for the preparation of some liquid hydrocarbons of low molecular weights (MW) and other such organic products used in the industry. MDR (methane dry reforming) is superior method than SR (steam reforming) technique (Eq. 2) to accomplish the compulsory syn-gas contents for Fischer-Tropsch reaction to synthesize useful products [7].

It has been pointed out that rare earth metals are best catalysts for MDR reaction [8] but due to the heavy costs of noble metal catalysts researchers prefer to use Ni-based catalysts for this reaction [9-13].

Whereas, the main drawback of MDR reaction is because of decrease in catalytic activity by Coking (carbon deposition) [14] at the surface of catalytic material during decomposition of methane ($CH_4 \rightleftharpoons 2H_2 + C$) and CO bifurcation ($2\ CO \rightleftharpoons CO_2 + C$) Boudouard reaction [15, 16]. The deactivation problem was controlled by different researchers due to incorporation of metals and their oxides like Al_2O_3, CaO, MgO, CeO_2 and La_2O_3, for the betterment of catalytic activity of such catalysts of nickel (Ni) origin [17-21].

The supports such as La_2O_3, ZrO_2 and MgO act along Ni hinder the addition of carbon in nickel based catalysts. Particularly, oxide La_2O_3 reacts with CO_2 and gives $La_2O_2CO_3$, which easily speeds up elimination on the surface carbon containing materials [17].

Additionally, the research on $La_2NiO_4/\ \gamma\text{-}Al_2O_3$ [22], and the comparative studies among $LaNiO_3$ Vrs MCM-41, $LaNiO_3$ Vrs SiO_2 and $LaNiO_3$ Vrs SBA-15 [23], showed insight about increase of surface area activity on basis of thermal stability and the effect of supporting oxide towards the change of CO_2 in syngas.

Further, presence of metallic particles on the surface of MSU-S decrease deposition of carbon. The perovskite [24] and other [25, 26] catalyst utilized for MDR of methane where the mass transfer resistance produce during MDR reaction over La/Mg promoted Co-Ni based on the surface of MSU-S catalysts is not present in scientific reports so far.

Five different catalysts $_x$La/Mg $_y$Co-Ni based MSU-S were assembled by known method (sol-gel), and evaluated by different experimental techniques like H_2 temperature-programmed reduction (H_2-TPR), X-ray diffraction (XRD), The high resolution transmission microscopy (HRTEM), gravimetric/differential scanning calorimetric analysis based on temperature (TG/ DSC), Fourier transform Infra-red (FTIR) and method based on temperature-programming for carbon dioxide and oxygen (CO_2-TPD), (O_2-TPO), respectively. The performance based on these catalysts for MDR reaction of CO_2 were done and evaluated at variation of temperatures and mass transfer resistance effect.

RESEARCH METHODOLOGY

Preparation of supporting material MSU-S and Catalysts

The supporting material MSU-S zeolite was arranged as reported by Pinnavaia *et al.* [27] taking different components are mixed in the following amounts. NaOH (0.507 g), $NaAlO_2$ (0.352 g), deionized water (DW) 10 mL, sodium silicate (25.578 g) at 35 °C and stirred for 4h. This gel type of solution was taken in autoclave at 110 °C for 12 h. At the end of mixing cetyltrimethylammonium bromide (CTAB) was added at 25 °C room temperature (RT) while pH is maintained around 9-10. The gel obtained was heated at 140 °C for 48 h in autoclave and dried, followed by calcinations at 550 °C in the presence of common air for 6 hrs.

Preparation of catalysts

Five catalytic samples of xLa/Mg-Co zNi supported MSU-S catalysts were made ready by using reported method [28]. Later on these catalysts have given some ordinary names for identification such as, 1%La 2 %Co7 % Ni/MSU-S, 1%Mg2 %Co7 %Ni/MSU-S, 3%La2%Co7Ni/ MSU-S and 3%Mg2%Co7%Ni/MSU-S. All prepared catalysts were sieved via 40-60 meshes before their application for catalytic process.

Characterization of catalysts

XRD was taken at rate of 1 °C/min scanning at PAN analytical automatic diffractometer taking Ni-filtered Cu K_α radiation ($\lambda = 0.154\ 06$ nm) at setting of 40 kV and 50 mA.

The FTIR spectra were taken on BIO-RAD FTS 3000 spectrophotometer, whereas TG/DSC was taken in air on a STA 409 PC/PG at 30-850 ºC at a heating rate of 10ºC/min. The Tecnai G2 F20 microscope present in Hong Kong used for High Resolution TEM images of unused and spent 3%La 2%Co 7%Ni/MSU-S catalyst.

The techniques like CO_2 & O_2TPD, Hydrogen TPR and oxygen TPO along TCD detector were taken by gas chromatograph (GC) system present in university laboratory at building 7 [28].

The catalytic activity and stability

The MDR was done by a quartz reactor at 1 atm with monitoring temperature of by K-type thermocouple during reaction. Quantities of methane and Carbon dioxide were monitored by controller for mass flow (D07-7B/ZM, made in Beijing Chinese Company. The ratio of carbon dioxide and methane at 1:1 with speed of 60 mL/min having speed of gas hour space velocity (GHSV) of 24000 - 32000 mL $g^{-1}h^{-1}$ at 700–750 ºC during reaction. The changing of methane, carbon dioxide and selectivities for syngas and hydrogen and further yield of carbon (Coking) are calculated by using formulas as reported in literature (28.

RESULTS AND DISCUSSION

XRD Pattern study

The XRD (small-angle) for MSU-S supporting material (Fig. 1A) and wide angle XRD were done. They showed an ordered hexagonal structural shape [29, 30] and curves at $2\theta = 1.98°$, 3.4° and 3.9° having similarity with cards (100), (110) and (200) pattern of P6mm [31] The XRD patterns of fresh and spent catalysts are recorded as shown in the figure. These peaks at $2\theta = 43.3^o$ and 37.3º and 62.7º were accredited to NiO (24). XRD study showed that after reactivity, there were distinctive diffraction curves of Ni^o at $2\theta = 51.8^o$ and 43.9º (26) due to changing of NiO species into Ni^o at spent 3La2Co7Ni/MSU-S catalyst Fig 1B(c).

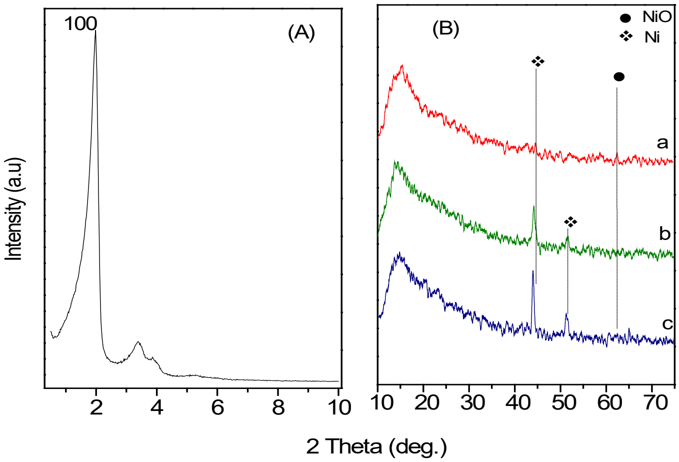

Fig. 1 (A) XRD (small-angle) of MSU-S fresh (B) Large XRD for unused and spent (a, b) 3%La 2%Co 9%Ni based MSU-S, (c) spent 3%La 2%Co 9%Ni based MSU-S during 75 h reaction.

H_2-TPR

Fig. 2 exhibited the H_2-TPR profiles, which can be seen that 3La2Co 7Ni/MSUS-S (Fig. 2a) having peak at 359 °C which due to Co^{3+} to Co^{2+} [31]. The H_2-TPR peak at 449 was showed NiO reduction to metallic Ni^o [20, 32]. The graphs at 618 & 597°C showed La_2CoO_4 reduction [33] while graph over 679 °C & 719 °C confirmed reduction of La_2NiO_4 [33]. While the reduction curve at 343°C is noted in the case of 3%Mg 2%Co and 7 % Ni based MSUS-S (Fig. 2b), showing reduction of Co^{+2} [31] as well as the curve of 453°C exhibited NiO reduction. However there was no spinel structure, such as La_2CoO_4 or La_2NiO_4 was found in the H_2-TPR pattern of 3%Mg 2%Co and 7 % Ni based MSUS-S, probable due to metallic Mg. Meanwhile the study of Xu *et al* [34] and Djaidja *et al* [35], confirmed the reduction at 859 °C was accredited Al_2O_3 and NiO reduction as shown in Fig. 2b.

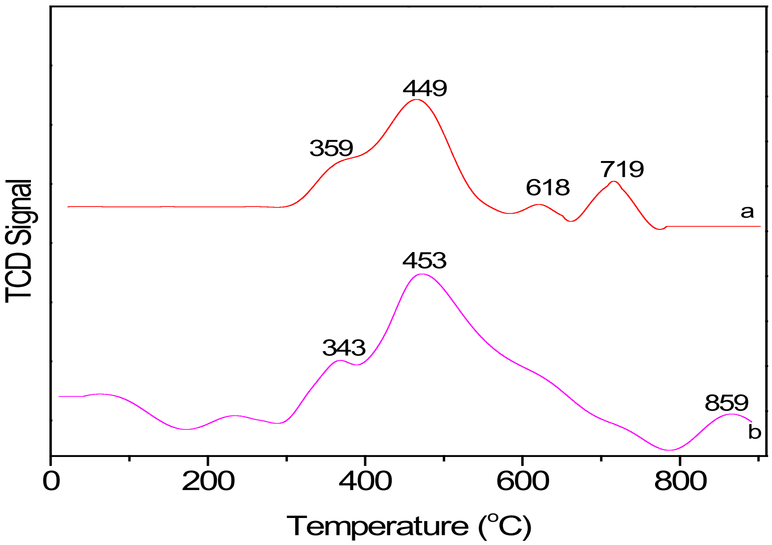

Fig. 2 H_2-TPR pattern of fresh (a) 3%La (b) 3 %Mg 2%Co and 7 % Ni based MSUS-S catalyst.

CO_2 –TPD

The CO_2-TPD (Fig. 3b) which realized CO_2 desorption peaks for different catalysts showing 3 types of positions on catalysts. The weak curves at 164 and 173 °C for CO_2 desorption may accredited for carbon dioxide adsorption.

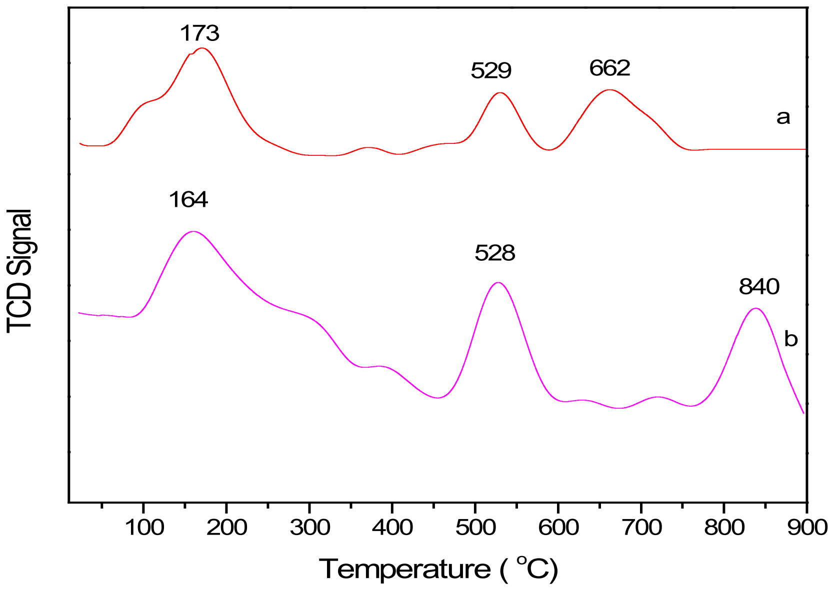

Fig. 3 The CO_2-TPD unused catalysts (a) 3%La (b) 3%Mg 2%Co and 7 % Ni based MSUS-S

FT-IR spectra

Figure 4 showed the FT-IR spectrum with peaks for absorption at range of 3438 & 1630 cm^{-1} [38] were stretching and bending vibrations respectively for OH groups [39]. Curves for symmetric and asymmetric stretching for Si-O-Si showed at 1390, 1076, 810 and 460 cm^{-1} for mesophorous material [40].

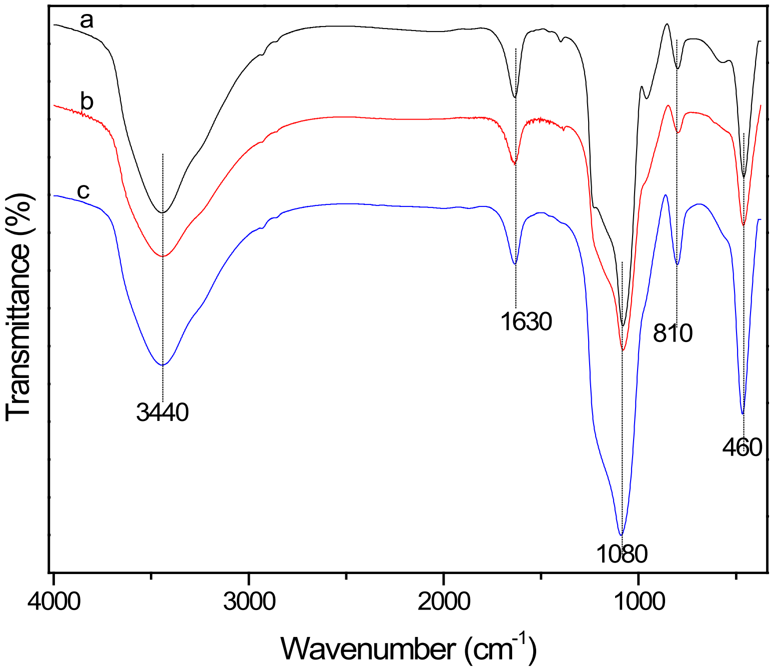

Fig. 4 FT-IR spectrum of zeolite (a) MSU-S; fresh (b) spent at 10 ºC (c) spent at 75 ºC 3% La 2%Co and 7 % Ni based MSUS-S catalyst

According to the report of Camblor *et al* [41] the peaks at 956 cm^{-1} weak curves at and pointed for the defect sites of (Si-OH).

HRTEM

The high resolution images of TEM for unused and spent 3%La 2%Co and 7 % Ni based MSUS-S is shown in Fig. 5. It is confirmed that support and all other catalysts are stable as fresh and after reaction. Fig 5B showed ordered hexagonal mesoporous arrays pattern [30], the both black strips with 2.6 nm distance (Fig. 5B) confirmed with results of reported literature [43]. The nanoparticles of Co, Ni and La are highly distributed on MSU-S zeolite and showed amorphous shape of zeolite. The TEM studies exhibited that supporting zeolite remained intact after reforming reaction (Fig. 5C and 5D) and particles retained with constant size in Fig 5 C & D. It is confirmed from HRTEM images that the said catalyst was stable at high temperature.

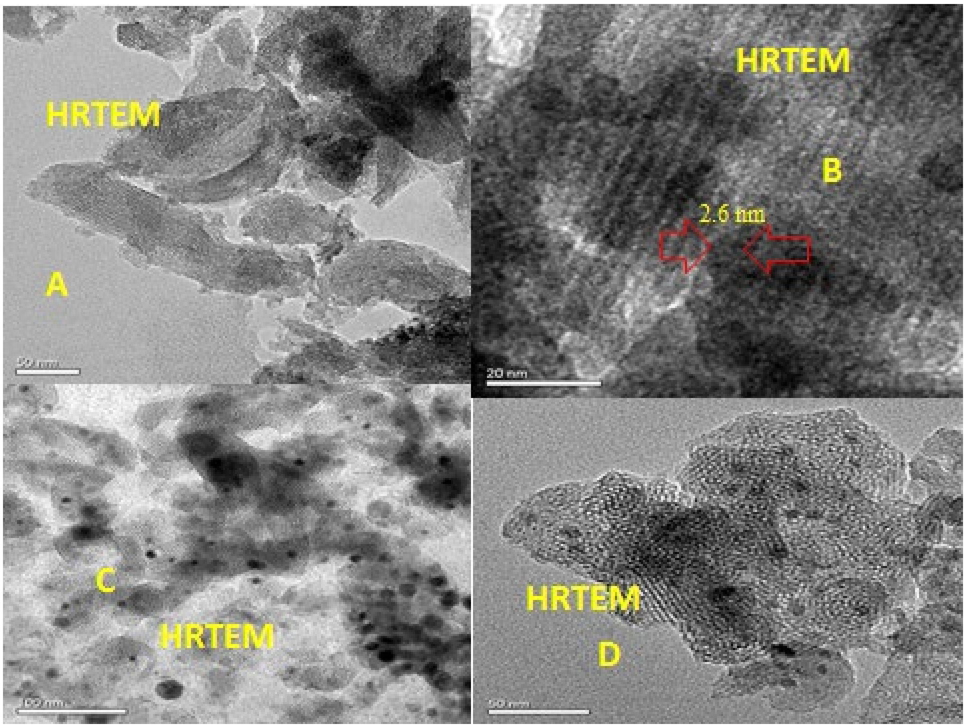

Fig. 5 HRTEM unused (A, B) & spent (C, D) 3%La 2%Co & 7 % Ni based MSUS-S at 750 ºC.

Studies of catalytic performance

Catalytic performance of xMg/La-yCo-Ni based MSU-S

The catalytic activity was done for selectivities for Carbon monoxide and hydrogen, conversion of methane and carbon dioxide, as well as coking was given in (Fig. 6A-C). It is confirmed that the change of methane on 3%La 2%Co and 7 % Ni based MSUS-S is higher than all other catalytic materials with speed rate of 24-32 L g^{-1} h^{-1} at time on stream of 10h.

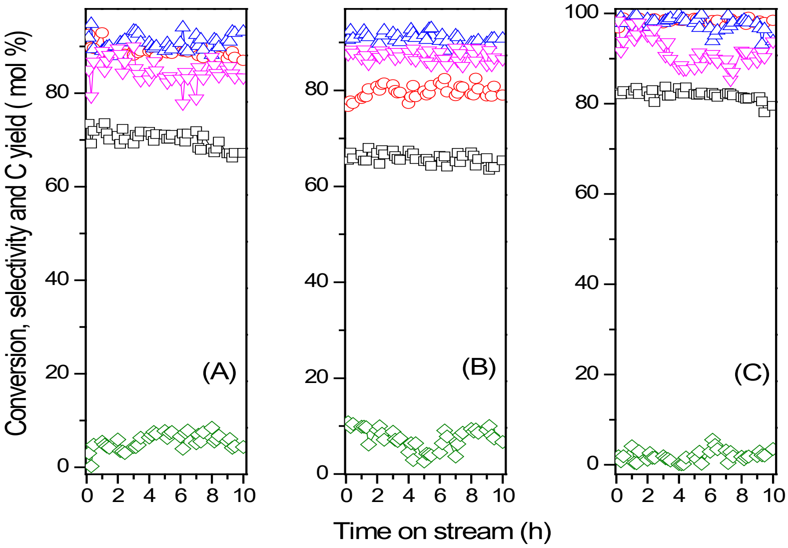

Fig. 6 Selectivity CO (△) H_2 (▽) Conversions CH_4 (□) CO_2(○), carbon (◇) at (a) 1 %La (b) 3 % Mg (c) 3% La 2%Co and 7 % Ni based MSUS-S at 700 °C, with 24 L $g^{-1}h^{-1}$ GHSV, CH_4/CO_2 =1:1. Study showed that best catalyst (3La 2Co7Ni/MSUS-S) performed an efficient work than all other four catalysts. The reason for best performance is the presence of basic oxide La_2O_3 which react with CO_2 and form $La_2O_2CO_3$ species [37]. The H_2-TPR result showed the reduction of La_2NiO_4 [33] to form basic oxide La_2O_3. This basic oxide (La_2O_3) interacted with CO_2 to reduce the carbon deposition. The reason for low performance is the carbon deposition (coking), for other catalysts.

$H_2 + CO_2 \rightleftharpoons H_2O + CO$; $\square H_{298} = 41.2$ kJ/mol (1)

$2CO \rightleftharpoons CO_2 + C$; $\square H_{298} = -171$ kJ/mol (2)

$CH_4 \rightleftharpoons 2H_2 + C$; $\square H_{298} = 75$ kJ/mol (3)

This deposition of carbon (coking) is from (Eq. (2 & 3) side reactions.

Studies of mass transfer resistant effects

Experiments proved that high temperature is encouraging for the occurrences of MDR reaction which is actually endothermic in nature. So, therefore, the reaction at high temperature such as 750 °C showed better performance than lower temperature 700 °C. The conversions of methane and carbon dioxide on best catalyst (3%La 2%Co and 7 % Ni based MSUS-S) remained more than 90% & more than 97%, respectively (Fig. 7A-C) at 750°C. Further results showed change of methane and carbon dioxide remain constant with rise in (GHSV), confirmed increase in mass velocities of the reactants as Zhang reported [44], that rise of mass flow at rate of 10×10^{-5} g h/mL, the mass transfer resistance becomes ignorable. This is suggested that catalytic activity remained high and stable at 24 L g^{-1} h^{-1} as compared with 32 L g^{-1} h^{-1}.

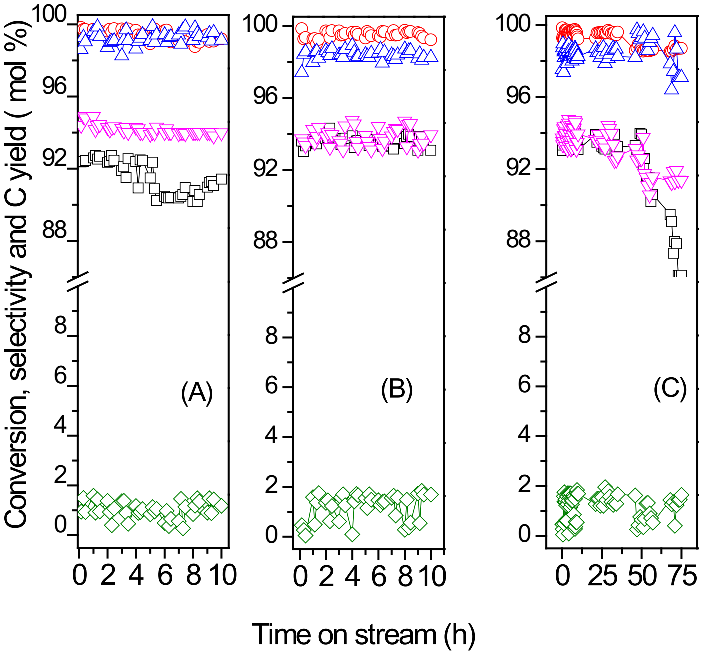

Fig. 7 Selectivity CO (△) and H_2 (▽) Conversions CH_4 (□) and CO_2(○) as well as carbon (◇) over 3% La 2%Co and 7 % Ni based MSUS-S (A) 10 h at 750 °C with GHSV=32 L $g^{-1}h^{-1}$ (B) 10 h and (C) 75 h at 750 °C with GHSV=24 L $g^{-1}h^{-1}$, CH_4/CO_2 =1:1.

The thermal stability and catalytic activity of La_2O_3 supported with (1: 3) for the said catalyst interrelated with variation of La/Ni in weight ratios. These catalysts played very vital role in DRM reaction, where the changing rate of CH_4 into product in descending order of 82% to 71% with change mass ration of La (1:3) at reaction temperature of 700 °C (Fig. 6C, A). Furthermore the amount of water collected in ice trap during catalyst evaluation studies at 1% La based catalyst was more than that collected over 3% based catalyst. The reason for such type of reaction is named reverse water gas shift (RWGS) for H_2 and carbon dioxide. The greater amount of La and La_2O_3 is promising material for the removal of deposited carbon during reaction.

The coking determined over spent 3%La doped catalyst was observed in least amount than over other catalysts.

CONCLUSION

These five xLa/Mg yCo zNi supported MSUS-S were synthesized by known method (sol–gel). In MDR reaction, catalyst 3%La 2%Co and 7 % Ni based MSUS-S remained the best at 700-750 ºC. At this temperature the change (conversion ratio) of CH_4 and CO_2 remained highest. The unused and spent catalysts characterized via FT-IR, XRD, Carbon dioxide-TPD, OxygenTPO, Hydrogen TPR, and HRTEM. The results of evaluation and characterization for all catalysts indicated MSU-S as a good hydrothermal support. MSU-S has noted stable during MDR at 750 ºC for long time duration of 75 h time on stream. The best catalyst (3La2Co7Ni/MSUS-S) with mesoporous structure was found intact at 750 ºC. It was confirmed that 3% La 2%Co and 7 % Ni based MSUS-S catalyst showed outstanding performance and remained thermally stable for synthesis gas and H_2 yield at 750 ºC for 75 h time on stream. Studies of mass transfer resistant showed that catalyst 3La2Co7Ni/MSUS-S exhibited better performance with flow of lower GHSV.

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REFERENCES

1. E. Ruckenstein, Y. H. Hu, (1995). Carbon dioxide reforming of methane over nickel alkaline earth metal oxide catalysts, Appl. *Catal.,* **133**, 149.

2. P. Ferreira-Aparicio, R. A. Guerrero, A. Rodro, I. guez-Ramos, (1998). Comparative study at low and medium reaction temperatures of syngas production by methane reforming with carbon dioxide over silica and alumina supported catalysts. *Appl. Catal. A*., **170**, 177.

3. J. H. Bitter, K. Seshan, J. A. Lercher, (1997). The State of Zirconia Supported Platinum Catalysts for CO_2 / CH_4 Reforming, J. *Catal*., **171**, 279.

4. G. S. Gallego, C. B. Dupeyrat, J. Barrault, E. Florez, F. Mondrago, (2008). Dry reforming of methane over $LaNiByO_3$ (B = Mg, Co) perovskites used as catalyst precursor. *Appl. Catal A Gen.*, **334**, 251.

5. Z. W. Liu, H. S. Roh, K.W.Jun, (2003). Carbon dioxide reforming of methane over $Ni/La_2O_3/Al_2O_3$, *J. Ind. Eng. Chem*., **3**, 267.

6. W. J. Seung, J. Y. Won, B, Changhyun, K. Yongchan, (2013). Minimization of hot spot in a microchannel reactor for steam reforming of methane with the stripe combustion catalyst layer, *Int. J. Hydrogen Energy*, **38**, 13982.

7. A. Djaidja , H. Messaoudi , D. Kaddeche , A. Barama, (2015). Study of Ni-M/MgO and Ni-M-Mg/Al (M=Fe or Cu) catalysts in the CH_4/CO_2 and CH_4/H_2O reforming, *Int J Hydrogen Energy*, **40**, 4989.

8. D. Pakhare, J. Spivey, (2014). A review of dry (CO_2) reforming of methane over noble metal Catalysts, *Chem. Soc. Rev.,* **43**, 7813.

9. A. K. Albarazi, P.Beaunier, P.D. Costa, (2013). Hydrogen and syngas production by methane dry reforming on SBA-15 supported nickel catalysts: On the effect of promotion by $Ce_{0.75}Zr_{0.25}$ O_2 mixed oxide, *Int. J. Hydrogen Energy*, **3 8**, 127.

10. J.Ni, L.Chen, J. Lin, M. K.Schreyer, Z. Wang, S. Kawi, (2013). High performance of Mg-La mixed Oxides supported Ni catalysts for dry reforming of methane: The effect of crystal structure, *Int J Hydrogen Energy*, **38**, 13631.

11. H. HamidehEltejaei, B. Reza, T. Jafar, M. R. Omidkhah, M. Rezaei, R. Zanganeh, A. Zamaniyan, A. Z. Ghalam, (2012). Methane dry reforming on Ni/ $Ce_{0.75}Zr_{0.25}$ O_2 - $MgAl_2O_4$ and Ni/ $Ce_{0.75}Zr_{0.25}$ O_2 g-alumina: Effects of support composition and water addition, *Int. J. Hydrogen Energy*, **37**, 4107.

12. D. S. Jose´-Alonso, M. J. Illan-Gomez, M. C. Roman-Martı´nez, (2013). Low metal content Co and Ni alumina supported catalysts for the CO_2 reforming of methane, *Int. J. Hydrogen Energy,* **38**, 223.

13. N. Rahemi, M. Haghighi, A. A. Babaluo, M. F. Jafari, S. Khorram, (2013). Non-thermal plasma assisted synthesis and physicochemical characterizations of Co and Cu doped Ni/ Al_2O_3nanocatalysts used for dry reforming of methane, *Int. J. Hydrogen Energy*, **38**, 16048.

14. J. M. Ginsburg, J. Piña, T. E. Solh, H. I. De-Lasa, (2005). Coke formation over a nickel catalyst under methane dry reforming conditions: Thermodynamic and kinetic models. *Ind. Eng. Chem. Res*., **44**, 4846.

15. Q. Wang, J. Luo, Z. Zhong, A. Borgna, (2011). CO_2 capture by solid adsorbents and their applications: current status and new trends. *Energy Environ. Sci.,* **4**, 42.

16. M. C. J. Bradford, M. A. Vannice, (1999). CO_2 reforming of CH_4. *Catal- Rev, Sci. Eng*., **41**, 1.

17. Z.Y. Hou, O. Yokota, T. Tanakai, T. Yashima, (2003). Characterization of Ca-promotedNi/α-Al_2O_3 catalyst for CH_4 reforming with CO_2, Appl. Catal. A. Gen. 253, 381.

18. V. R. Choudhary, B.S. Uphades A. S. Mamman, (1995). Large enhancement in methane to syngas conversion activity of supported Ni catalysts due to pre-coating of catalyst supports with MgO, CaO or rare-earth oxide, Catal. Lett. 32, 387.

19. L. L. Xu, H. L. Song, L. J. Chou, (2012). Mesoporous nano-crystalline ceria zirconia solid solutions supported nickel based catalysts for CO_2 reforming of CH_4. Int. J. Hydrogen Energy, 37, 18001.

20. X. E. Verykios, (2002). Catalytic dry reforming of natural gas for the production of chemicals and Hydrogen, Chem. Ind. 56, 238.

21. M. Rezaei, S. M. Alavi, S. Sahebdelfar, P. Bai, X. M. Liu, Z. F. Yan. (2008). CO_2 reforming of CH_4 over nano crystalline zirconia-supported nickel catalysts. Appl Catal B Environ, 77 346.

22. B. S. Liu, C. T. Au, (2003). Carbon deposition and catalyst stability over La_2NiO_4/γ-Al_2O_3 during CO_2 reforming of methane to syngas, Appl. Catal. A. Gen. 244, 181.

23. N. Wang, X. P. Yu, Y. Wang, W. Chu, M. A. Liu (2013). comparison study on methane dry reforming with carbon dioxide over $LaNiO_3$ perovskite catalysts supported on mesoporous SBA-15, MCM-41 and silica carrier. Catal. Today, 212, 98.

24. Y. Nai-Tao, K. Yasotha, K. Sibudjing, (2013). $La_{0.6}$ Sr $_{0.4}$ Co $_{0.8}$ Ni $_{-0.2}$ O $_{-3-\delta}$ hollow fiber membrane reactor: Integrated oxygen separation CO2 reforming of methane reaction for hydrogen production. Int. j. Hydrogen energy, 38, 4483.

25. J. J. Guo, H. Lou, Y. H. Zhou, X. M. Zheng. (2003). CO_2 reforming of CH_4 over nickel and cobalt catalysts prepared from La-based perovskite precursors, J. Nat. Gas Chem. 12, 17.

26. N. A. Pechimuthu, K. K. Pant, S. C. Dhingra, (2007). Deactivation studies over Ni-K/CeO_2-Al_2O_3, catalyst for dry reforming of methane, Ind. Eng. Chem. Res., 46, 1731.
27. Y. Liu, W. Z. Zhang, T. J. (2001) Pinnavaia, Steam-stable MSU-S aluminosilicate mesostructures assembled from zeolite ZSM-5 and zeolite beta seeds, Angew Chem. Int. Ed. 40, 1255.

28. R. Amin, B. S. Liu, Y. C. Zhao, Z. B. Huang, (2016) Hydrogen production by corncob/CO_2 dry reforming over CeO_2 modified Ni-based MCM-22 catalysts, Int. j. Hydrogen energy, 41,12869.

29. Y.B, Zhang, X. F. Qian , Z. K. Li, J.Yin, Z. K. Zhu. (2004) Synthesis of novel mesoporous silica spheres with starburst pore canal structure, J Solid State Chem., 177, 844.

30. R. Z. Shang, L. Z. Jun, W. Dong, H. S. Yu, D. Feng et al. (2005) CTAB-assisted fabrication of mesoporous composite consisting of wormlike aluminosilicate shell and ordered MSU-S core, J. Solid State Chem. 178, 85.

31. Z. Hu, K. Q. Sun, W. Z. Li, B. Q. Xu. (2010) NOx storage and reduction performance of Pt–CoOx–BaO/Al_2O_3 catalysts: Effects of cobalt loading and calcination temperature, Catal. Today, 1 58, 432.

32. T. Kimura, T. Miyazawa, J. Nishikawa, S. Kado, K. Okumura, T. Miyao, S. Naito, K Kunimori, K Tomishige, (2006) Development of Ni catalysts for tar removal by steam gasification of biomass, Appl. Catal. B. Environ., 68, 160.

33. C.B. Dupeyrat, G. Valderrama, A. Meneses, F. Martinez, J. Barrault, J. Tatibouët, (2003) Pulse study of CO_2 reforming of methane over $LaNiO_3$. Appl. Catal. A. Gen., 248, 143.

34. L. Xu, H. Song, L. Chou, (2013) Ordered mesoporous MgO-Al_2O_3 composite oxides supported Ni based catalysts for CO_2 reforming of CH_4: Effects of basic modifier and mesopore Structure, Int J hydrogen energy, 38, 7307.

35. A. Djaidja, S. Libs, A. Kiennemann, A. Barama, (2006) Characterization and activity in dry reforming of methane on NiMg/Al and Ni/ MgO catalysts. Catal. Today, 113, 194.

36. H.S. Roh, K.W. Jun, W. S. Dong, J. S. Chang, S. E. Park, Y.I. Joe, (2002) Highly active and stable Ni/Ce–ZrO2 catalyst or H_2 production from methane, J. Mol. Catal. A. Chem. 181, 137.

37. B. S. Liu, G. Rui, R. Z. Chang, C. T. Au. (2008) Dehydrogenation of ethyl benzene to styrene over LaVOx/SBA-15 catalysts in the presence of carbon dioxide. Appl. Catal. A. Gen., 335, 88.

38. S. Zhai, J. Zheng, J. Li, D. Wu, Y. Sun, F. Deng, (2005) Treatment of calcined MSU-S with $NaAlO_2$ solution in the presence of CTAB: Change of acidic and catalytic properties Micropor. Mesopor. Mater. 83, 10.

39. M. S. Ghattas, (2006) Cobalt-modified mesoporous FSM-16 silica: Characterization and catalytic study, Micropor. Mesopor. Mater. 97, 107.

40. Y. H. Zhang, Y.C. Liu, Y. X. Li, (2008) Synthesis and characteristics of Y-zeolite /MCM-48 bioporous molecular sieve. Appl. Catal. A. Gen., 345, 73.

41. M. A. Camblor, A. Corma, (1993). Infrared spectroscopic investigation of titanium in zeolites. A new assignment of the 960 cm-1 band, J. Chem. Soc. Chem. Commun., 6, 557.

42. C. E. A. Kirschhock, R. Ravishankar, F. Verspeurt, P.J. Grobet, P. A. Jacobs, J. A. Martens (1999). Identification of Precursor Species in the Formation of MFI Zeolite in the TPAOH-TEOS-H2O System. J. Phys. Chem. B. 103, 4965.

43. R. Mokaya. (2000) Template directed stepwise post synthesis alumination of MCM-41 mesoporous silica. Chem. Commun. 1541).

44. W. D. Zhang. (2007) Studies on CO_2 reforming of methane to syngas over Ni-based catalysts modified by rare earth oxide, *Ph. D dissertation, Tianjin University*, P R China, 90.

45. R. Bouarab, O.Cherifi, A. (2005). Auroux, Effect of the basicity created by La_2O_3 addition on the catalytic properties of Co (O)/SiO_2 in CH_4+CO_2 reaction. *Thermochem Acta.,* 434, 69.