Energy Source from Hydrogen Production by Methane Dry Reforming

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Abstract

The energy crisis and global warming challenges have forced scientific community for searching new alternate energy resources for future demands. Hydrogen is a clean fuel option and it is expected to be the future fuel. A great attention and interest, in the last years, have been given to reforming process which consumes CH_4 to produce hydrogen. The objective of the present study is to evaluate the selectivity and yield of hydrogen over γ-Al_2O_3 supported and Sr promoted Ni based catalysts from CH_4-CO_2 reforming. It is obtained that selectivity and yield of H_2 increase with the increase of reaction temperature. The lowest carbon formation (3.8 wt%) and hence the optimum stability was obtained using 0.75wt% Sr promoter.

Keywords

CH_4, CO_2, Hydrogen production, Ni, Selectivity, Sr, Yield

1. Introduction

With the depletion of world's oil productivity, we're facing a global energy crisis. We are reaching the end of our dependence on non-renewable sources of energy like oil, coal and natural gas. Hydrogen energy will inevitably replace fossil fuel energy in the near future due to the fact that the burning of hydrogen is pollution free. The cleanest way to produce H_2 is certainly from H_2O by using sunlight in combination with a photovoltaic cell via water electrolysis (Appleby et al. 1990, Andrews and Shabani 2012). However, the practical way to produce H_2 comes from fossil fuel sources for the time being. One of the best ways to connect the fossil energy and hydrogen energy will be the production of H_2 from CH_4, due to its high H/C atomic ratio and great abundance in reserves. Direct conversion of CH_4 with the assistance of oxidants has received much more attention and is thermodynamically more favorable (Lunsford 1993, Li et al. 2010). Development of Ni-based catalysts, having better activity and long term stability, for methane reforming using carbon dioxide (MRC) has attracted the attention of researchers in the recent years. For this reason, research focus has been on carbon suppression over catalyst surface (Hu and Ruckenstein 2002, Bradford et al. 1999, Hu et al. 2004). Although a lot of efforts have been made to counter this problem, carbon deposition prevention has not only been still a great challenge for Ni based catalyst but also a hurdle for MRC commercial use. MRC is an environmentally friendly process as it utilizes greenhouse gases. Moreover the process yields synthesis gas with lower H_2/CO ratio as desired feedstock for Fischer-Tropsch synthesis (Jing et al. 2004). The main reaction of the methane reforming process to generate hydrogen is:

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ (1)
While the side reactions include:
$CO_2 + H_2O \rightarrow CO + H_2$ (2)
$CH_4 \rightarrow C + 2H_2$ (3)
$2CO \rightarrow C + CO_2$ (4)
$C + H_2O \rightarrow CO + H_2$ (5)

Since Ni-based catalysts deactivate rapidly, therefore these catalysts are doped with selective promoters to decrease carbon deposition and prolong catalyst life (Claridge et al. 1994, Claridge et al. 1998, Frusteri et al. 2001, Al-Fatish et al. 2009).

SanJose´-Alonso et al. (2011) studied effect of Sr addition to Co/Al_2O_3 catalyst and found that the addition Sr as promoter could prevent the catalyst from carbon deposition. Addition of 10wt% Sr to 5wt%Ni/SrO-SiO_2 catalyst resulted in enhanced dispersion of Ni particles, metal-support interaction and CO_2 adsorption. Thus Sr played a key role in improving catalytic activity and long term stability (Jing et al. 2004).

Sutthiumporn and Kawi (2011) studied the promotional effect of alkaline earth elements on Ni-La_2O_3 catalysts and concluded that Sr addition enhanced CH_4 and CO_2 conversions and reduced coke formation over catalyst surface.
In this paper, the study of selectivity and yield performances of hydrogen production, over Ni/γ-Al_2O_3 catalyst, from methane reforming of carbon dioxide will be performed. Additionally effect of Sr addition on carbon deposition for Ni/γ-Al_2O_3 catalyst will be studied.

2. Experimental

2.1 Catalysts Development & Activity

Nickel nitrate salt ($Ni(NO_3)_2.6H_2O$) precursor and γ-Al_2O_3 support were used to prepare Ni/γ-Al_2O_3 catalysts by the wet impregnation method. The catalysts were dried at 110 °C, calcined at 600°C and then activated with H_2. Catalytic activity was monitored in a fixed-bed continuous-flow reactor. The experimental setup is as shown in (Figure 1). The reforming of CH_4 was carried out at atmospheric pressure in a 9.4 mm i.d. and 48 cm long stainless steel-tube using 0.6 g of catalyst. The volume ratio of the feed gases, $CH_4/CO_2/N_2$ was 5/5/1 with total flow of 36 ml/min. The reaction temperatures used were 500, 600 and 700°C. The effluents were analyzed with GC (Varian Star 3400) and selectivity and yield were calculated.

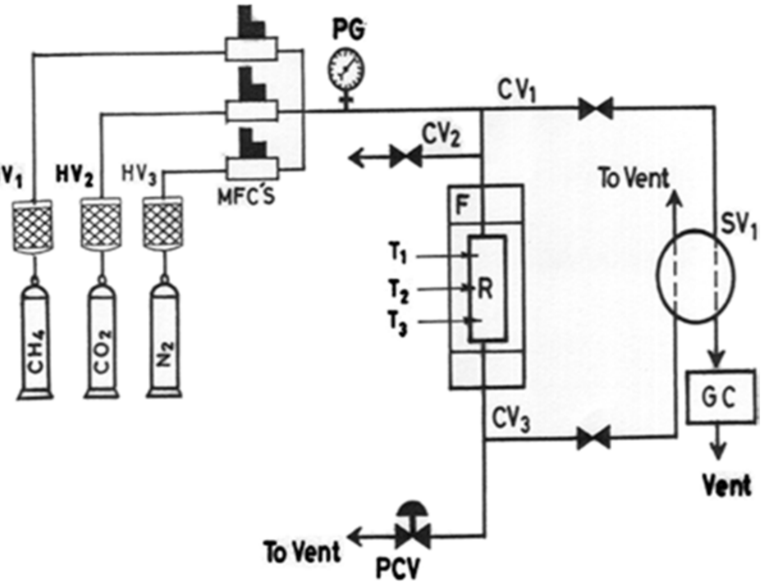

Figure 1: Schematic diagram of experimental setup for CO_2 reforming of CH_4

3. Results and Discussion

The effects of Sr promoter, catalyst activity and stability test of various catalysts, as well as results of catalyst characterization are presented. Usually, during the methane reforming process the active metal clusters are successively oxidized and reduced due to the simultaneous existence of oxidative (due to the presence of CO_2 and H_2O) and reductive (due to the presence of CH_4 and H_2) atmospheres (Ruckenstein and Wang 2002). Several mechanistic studies have proposed that during the methane dry reforming reaction, CH_4 is decomposed first on the active metal sites to yield reactive surface carbonaceous species, which are then oxidized to CO by the oxygen that originate from CO_2. In view of that, the rate of carbon deposition on the catalyst surface is dependent on the relative rates of the formation of carbon deposits and its oxidative removal. The large amount of carbon deposition will take place when the rate of the oxidative removal is slower than the former (Juan-Juan et al. 2009).

3.1 Effect of Sr loading on Ni/γ-Al_2O_3 catalyst

The results of Sr loading to Ni/γ-Al_2O_3 catalysts using different reaction temperatures (500, 600 and 700°C) are shown in Figure 2. The result shows that hydrogen selectivity increased with reaction temperature. Albarazi, et al. (2013) and Chen et al. (2010) reported similar findings, where H_2 selectivity increased, due to increase in methane conversion, as the reaction temperature was increased. In fact the addition of Sr promoter slightly enhances the selectivity. This is probably due to the easy oxidation of carbon attached with the hydrogen of the methane molecules in the presence of Sr. The maximum enhancement of 4.5% in selectivity was obtained for 0.75wt% Sr promoted catalyst at 600°C reaction temperature. At 600°C, the further addition of the Sr promoter beyond 0.5wt% did not provide further increase in selectivity. Similar results were obtained at 700°C reaction temperature. Moreover, at 600°C and 500°C, the selectivity of H_2 somewhat declined with the promoter addition that exceeds 0.75wt%. The highest selectivity values for all promoted and non-promoted catalysts were obtained at 700°C reaction temperature. The hydrogen yield for various Sr loadings at different reaction temperatures is shown in Figure 3. The result shows that the yield of hydrogen increased about 80% as the reaction temperatures increased from 500°C to 700°C. A maximum enhancement of about 9% is obtained at 600°C for 0.5wt% Sr promoted catalyst. Moreover, at600–700°C reaction temperatures the addition of Sr promoter up to 0.75wt% increased the hydrogen yield to some extent, however; beyond 0.75wt%a slight decrease in hydrogen yield was observed. The yield values were almost constant for catalysts having loading > 1.0wt% Sr at all reaction temperatures.

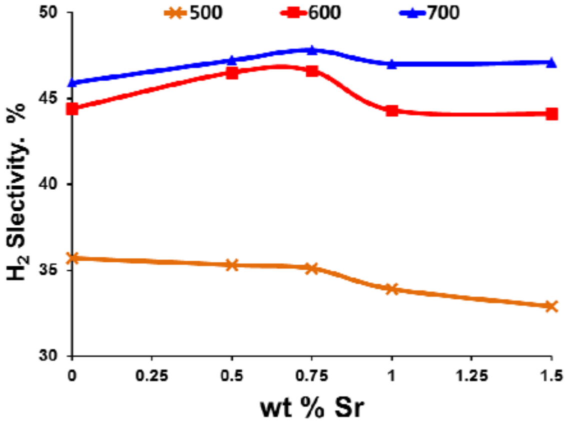

Figure 2: Effect of reaction temperature on H_2 selectivity using Ni-Sr/γ-Al_2O_3

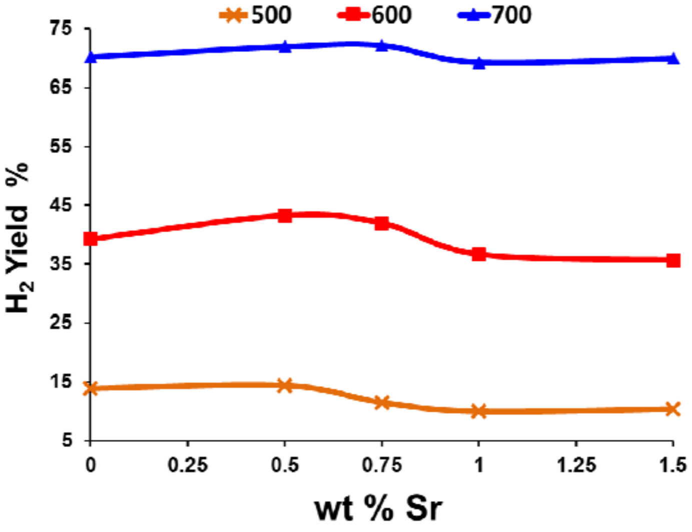

Figure 3: Effect of reaction temperature on H_2 yield using Ni-Sr/γ-Al_2O_3

4. Catalyst Characterization

4.1X-ray Diffraction (XRD)

The XRD diffraction patterns for fresh and spent catalysts are shown in Figure 4. Peaks corresponding to the alumina support and Ni species were detected in all the samples, while no bulk diffraction peak of Sr specie was detected in any Sr promoted sample. In fact the absence of Sr peaks is probably due to presence of Sr in low concentration in catalysts which is difficult to detect by means of XRD. The diffraction peaks detected at $2\theta = 45.6^\circ$; $2\theta = 60.5^\circ$ and $2\theta = 66.7^\circ$ are ascribed to γ-Al_2O_3 (JCPDS: 00-029-0063). For NiO (JCPDS: 01-073-1519) the diffraction peak observed at $2\theta = 37.2^\circ$, 43.2° and 63° correspond to the reflections (111), (2 0 0) and (2 2 0), respectively.In case of non-promoted spent catalyst the diffraction peak detected at $2\theta = 26^\circ$ is assigned to graphitic carbon. However no carbon peak was observed in case of 0.75wt% Sr promoted catalyst which assures the better resistance, towards coke formation, of this catalyst than non-promoted sample.

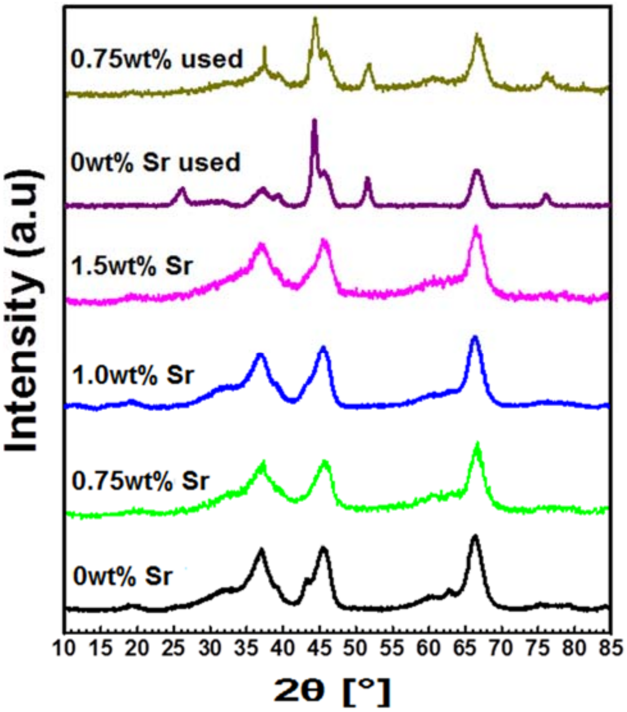

Figure 4: X-ray diffraction patterns of Srpromoted and non-promoted fresh and used catalysts.

4.2Textural Properties and Thermo Gravimetric Analysis

Results from surface area measurements and carbon formation on spent catalysts are summarized in Table 1. From the obtained results it is observed that addition of Sr in the Ni-alumina catalyst modifies the textural properties of the catalyst, which is evidenced from the higher specific surface areas of Sr promoted fresh catalysts than non-promoted catalyst. Moreover, it is worth noting that surface areas of all spent catalysts are decreased after 6 h of reaction. The evidence of the lower BET of the spent catalyst could be partly ascribed to the sintering of active metal component and to the coke formation over catalyst surface during reaction. The formation of coke deposits is verified by TGA results. It is quite worthy to note that the Sr promoted spent catalysts showed small decrease in surface area as compared to non-promoted catalyst, which indicates that Sr promoter has significant effect on catalytic behavior of catalyst. The lowest coke formation (3.8 wt%) was obtained when Ni/γ-Al_2O_3 catalyst promoted with 0.75wt% Sr loading. Therefore, the optimum carbon reduction about (50%) is obtained using 0.75wt% Sr loading on Ni-based catalyst. Thus on the basis of these findings it inferred that Sr promoter improved catalyst stability as it reduces the amount of the coke formation.

Table 1: Ni/γ-Al_2O_3 catalysts' textural properties and coke formation

Sr(wt%)	**S_{BET} [a] (m^2/g)**	**S_{BET} [b] (m^2/g)**	**Carbon deposition [b,c]**
0	189.53	154.54	8.2
0.5	193.35	163.42	4.7
0.75	193.88	167.93	3.8
1	193.13	164.39	4.9
1.5	192.49	165.84	4.4

a: fresh catalyst before reaction; b: spent catalyst; c:Determined from TGA

Figure 5a and 5b depicts the SEM micrographs of non-promoted and promoted spent catalysts respectively. It is apparent from the micrographs that the non-promoted (0wt% Sr) catalyst (Figure 5a) is covered by considerable amount of carbon deposition with filamentous structure. Conversely, the spent catalyst with 0.75wt% Sr (Figure 5b) demonstrated negligible signs of carbon deposition. Since no significant carbon deposits were detected in SEM micrograph of 0.75wt% Sr promoted catalyst, so it is easy to say that this catalyst is better than non-promoted (i.e., 0wt% Sr) catalyst.

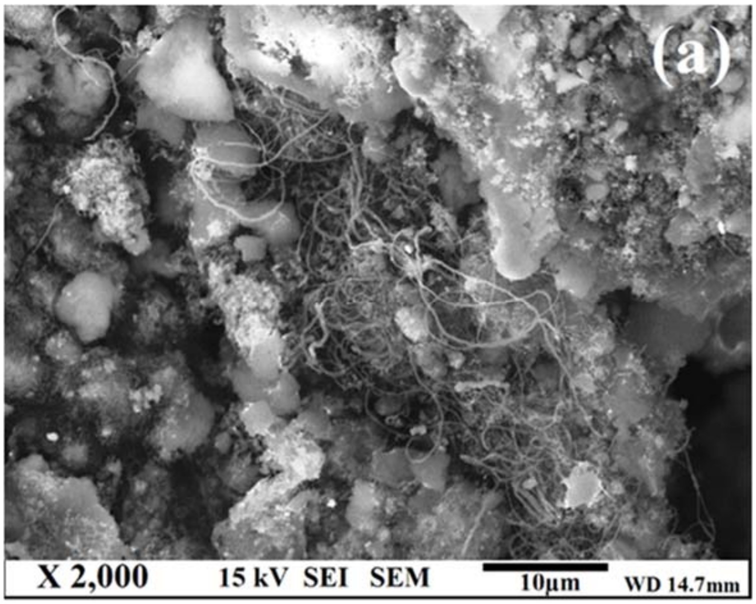

Figure 5a: SEM micrograph of non-promoted (0wt% Sr) used catalyst.

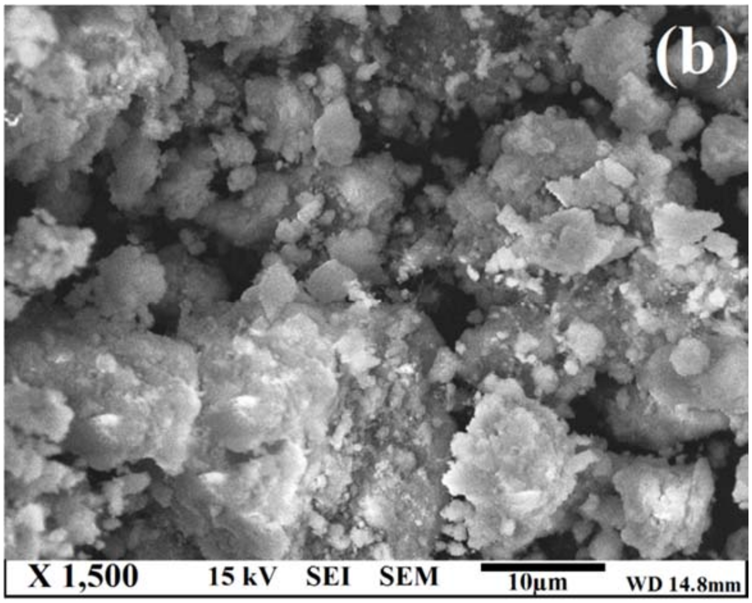

Figure 5b: SEM micrographs 0.75wt%Sr promoted catalyst

4.3 Stability Studies

Generally, the catalyst stability is associated with the phenomenon of deactivation due to carbon deposition, sintering and/or loss of active surface due to its oxidation under reaction conditions. Most of the times all these phenomena take part side by side but in some case one of these dominates and causes severe deactivation. Having seen the extent of carbon formation, low or high,over all prepared catalysts; it is worthy to perform the stability test to compare these catalysts. The time on stream (TOS) analysis was carried out at 700°C reaction temperature**.** Figure 6 shows the selectivity measurement over period of 360 min for non-promoted(0wt% Sr) and 0.75wt % catalysts. It is evident that the catalyst promoted with 0.75wt% Sr gives thebest performance since it provides comparatively high and stable trends of selectivity. This finding is consistent with the lowest carbon formation obtained on loading 0.75wt% Sr. Moreover, it is apparent from results that for non-promoted catalyst the selectivity increased after 190 min on TOS. The increase in H_2 selectivity in case of non-promoted catalyst is probably occurrence of methane cracking side reaction (Eq. 3).

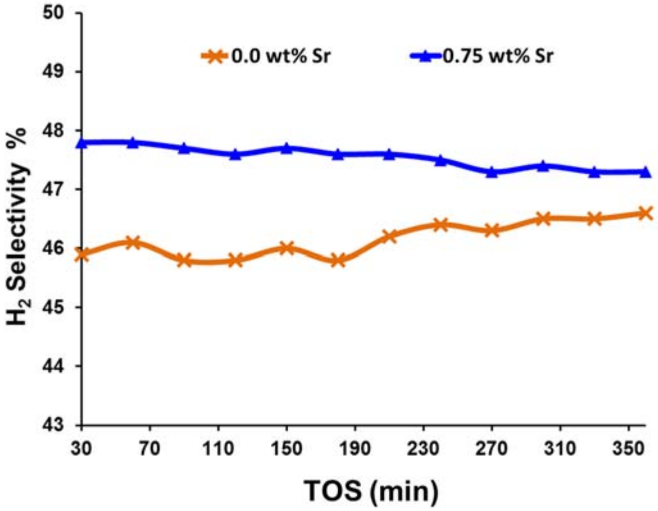

Figure 6: H_2 Selectivity versus time on stream for Sr promoted and non-promoted catalysts at reaction 700^{o}C with F/W= 60 (ml/min.g_{cat})

5. Conclusions

This paper investigates the application of the CH_4 reforming of CO_2 for producing H_2 where Sr-Ni/γ-Al_2O_3 catalyst is used. The optimum reaction temperature was found to be at 700°C. The promoted catalysts at 700°C exhibited excellent activities without significant deactivation. The Ni-Sr/γ-Al_2O_3 gave the lowest carbon deposition with 0.75wt% Sr loading. The findings were verified by XRD, TGA and SEM. The present study showed that dry reforming of CH_4 could be utilized in the steady continuous production of H_2 using Ni-Sr/γ-Al_2O_3 catalyst.

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Biography

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