

Coke Suppression by Holmium Promoter in Dry Reforming of Methane

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Summary: The present research mainly focused on the development of highly coke resistant catalysts. In this context, Ni/ZrO₂ novel catalysts with holmium (Ho) promoter were prepared using the polyol method and investigated, for CH₄-CO₂ reforming, at atmospheric pressure in the temperature range of 500–700 °C. For each catalyst, the Ni loading was fixed at 5 wt.%, while Ho loading was varied from 0.0–1.5 wt.%. Various techniques such as BET, H₂-TPR, CO₂-TPD, XRD, TGA and FESEM were used to characterize the prepared catalysts. The results demonstrated that the addition of Ho in Ni/ZrO₂ catalyst had a notable effect on carbon suppression. Moreover, CO₂-TPD results revealed that the incorporation of Ho in Ni/ZrO₂ catalyst fairly enhanced its Lewis basicity. These improvements in basicity favored the chemisorption and activation of CO₂ over the catalyst surface which in turn minimized coke deposition. Carbon deposition on the 1.5 wt.% Ho promoted catalyst (Ni-1.5Ho-Zr) was reduced about 92.7% compared to the un-promoted catalyst.

Keywords: Nickel catalyst; Polyol method; Holmium promoter; Basicity; Coke suppression.

Introduction

The huge consumption of fossil fuels and the adverse effects of climate variation triggered by the ever increasing worldwide energy demands have drawn massive attention. The emergence of new and alternate energy technologies is very crucial and indispensable to decrease these effects [1]. Many reforming technologies using heterogeneous catalysis approach have been introduced by many scientists in response to efficient utilization or the transformation of methane and/or carbon dioxide (greenhouse gases) to mitigate their harmful effects on the environment. Amongst all reforming technologies reported in the literature; steam methane reforming, partial oxidation and carbon dioxide reforming of methane are dominant [2].

Recently, significant attention has been paid to the catalytic carbon dioxide reforming of methane (also called dry reforming of methane) in consideration of the environmental security as well as potential industrial application features [3]. From environmental point of view, in comparison to steam reforming and partial oxidation of methane, carbon dioxide reforming of methane is more advantageous, since it has the tendency of, simultaneously, utilizing/mitigating two greenhouse gases (CH₄ & CO₂), while other processes handle only one greenhouse gas (CH₄) [4]. Also, dry reforming of methane has a potential advantage that would have an impact on the industrial sector. The process produces synthesis gas with low H₂/CO product ratio (1), which can be favorably used for production of oxygenated compounds and liquid hydrocarbons such as methanol and dimethyl ether in the Fischer-Tropsch synthesis network [5].

A combination of the dry reforming with steam reforming and/or partial oxidation reactions may also be used to tailor the desired hydrogen-to-carbon monoxide ratio in the syngas for gas to liquid (GTL) downstream requirements [6]. Furthermore, this process can be employed in remote gas field areas where water is scarce. However, dry reforming of methane (DRM) has two governing problems; firstly due to the endothermic nature of the process, high reaction temperature is required for the higher conversions of both

CH₄ and CO₂ and secondly catalyst deactivation due to rapid carbon deposition [7, 8]. Practically, carbon formation could originate from the following four side reactions: methane decomposition/cracking reaction (1), Boudouard reaction or CO disproportionation reaction (2), CO/H₂ reduction reaction (3) and CO₂hydrogenation reaction (4).



Thermodynamically, the Boudouard reaction (Eq. 2) is exothermic and favored at higher pressures and lower temperatures (< 973 K). On the other hand, methane decomposition reaction (Eq. 1) is an endothermic reaction and favored at higher temperatures and low pressures [9]. Nickel based catalysts are highly cost effective and very active for DRM reaction but also more susceptible to coking than noble metals. Coke formation in DRM has been interconnected, by numerous researchers with the size, morphology and distribution/dispersion of nickel species over the support; more specifically, it is originated by side reactions which are “structurally sensible” [4, 10]. It has been anticipated that if Ni species are highly as well as uniformly distributed on the oxide carrier serving as a support, carbon deposition could be suppressed and/or inhibited. However, the rapid deactivation of the Ni based catalysts is still a crucial challenge in the commercialization of this catalytic process [11]. Therefore, the search for or development of suitable Ni-based catalysts is still of paramount importance. Various approaches and techniques have been studied and introduced to suppress and/or minimize the growth of carbonaceous deposits, during DRM, over catalyst surface. In this context, one of the current approaches is related to the enhancement of the active metal dispersion by developing catalysts which have perovskites and hydrotalcites like structures [12]. Alternatively, other techniques include; use of different preparation methods to enhance the metal support interaction, use of bimetallic catalyst systems and addition/incorporation of metal and/or redox oxides as promoters to effect the acidity and/or basicity [13, 14]. Zirconium oxide (ZrO₂) supported Ni catalysts have been

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extensively investigated for DRM, due to their fairly high thermal stability and distinct chemical (acid-base and redox) characteristics [15]. In contrast, it has also been reported that Ni/ZrO₂ catalysts prepared by impregnation method have high initial activity, but deactivated with time on stream due to coke deposition and by active metal sintering. In order to enhance stability, ZrO₂ based catalysts were modified/doped with various basic promoters such as CaO, MgO and CeO₂ [9, 16]. It is well known that the incorporation of a basic support/promoter in DRM catalyst improves the CO₂ adsorption capacity and its dissociation rate, which afterwards boosts the gasification of carbonaceous deposits present on catalyst surface and consequently decreasing the extent of catalyst deactivation. Mekhemer [17] has studied the surface characterization of holmium oxide-zirconia catalyst and reported that the addition holmium oxide (Ho₂O₃) into zirconia produced or exposed highly reactive basic sites (O²⁻ and/or OH⁻) on the catalyst surface. Similar results were reported by Zhou and He in the case of Ho/TiO₂ photo-catalytic system [18].

In the present research, we have developed a series of Ho doped Ni/ZrO₂ catalysts, with different Ho loadings. The catalysts have been prepared by polyol process and tested in a tubular reactor for dry reforming of methane. The study focuses the suppression of carbon deposition on Ni/ZrO₂ catalyst, by the addition of Ho promoter. The use of the Ho as coke suppressing promoter, in Ni/ZrO₂ catalyst, for dry reforming of methane has rarely been studied before. Various characterization techniques have been employed in the present study to understand and contrast the prepared catalysts.

Experimental

Materials

All the chemicals were of analytical grade and used without further purification. Nano powders of zirconia (ZrO₂) supplied by MKnano® were used as a catalyst support throughout this study. Nickel acetate [Ni(OCOCH₃)₂·4H₂O; 99%] and holmium nitrate [Ho(NO₃)₃·5H₂O; 99%] (obtained from Sigma-Aldrich®) were used as Ni-metal and Ho-promoter precursors respectively. In addition, ethylene glycol, EG (C₂H₆O₂) and poly vinyl pyrrolidone (C₆H₉NO)_x (PVP) (MW = 58,000 kg.kmol⁻¹) (Alfa Aesar) were used as reducing/stabilizing and anti-nucleation (to avoid nanoparticle sintering and aggregation) agent respectively.

Catalyst Preparation

Nano ZrO₂ supported Ni-Ho novel catalysts, having (5 wt.%) Ni and (0.0–1.5 wt.%) Ho loading were prepared by polyol method as reported earlier [5]. In a typical polyol process, a particular amount of the nano support was added to (EG)-(PVP)-nickel-promoter precursor solution and agitated with a magnetic stirrer. Stoichiometric amounts of nickel acetate and holmium nitrate were used in order to obtain the desired loadings, whereas the ratio of PVP/Ni (w/w) was fixed at 2. To promote the formation of nano Ni colloid in the solution, the NaOH solution (1M) was added to control pH at 10. The suspension was then kept for 24 h at 30 °C under continuous stirring. The obtained suspension after

24 h was then heated up to 195 °C under reflux conditions for 3 h to reduce the Ni ions and to form nano Ni particles on the support. After completion of the reduction step, the homogeneous colloidal suspension was quickly cooled down to ambient temperature in an ice bath. Then, the catalyst was filtered and subsequently washed several times in excess of distilled water and acetone in order to remove the impurities and organic phase. Afterwards, the filtered catalyst was dried overnight at 120 °C and subsequently calcined at 500 °C for 4 h. For simplicity, the un-promoted and promoted catalysts are labeled as Ni- xHo- Zr (x = 0.0–1.5 wt.%) and Ni-Zr respectively. CH₄ and CO₂ conversions are calculated using the following equations 5 and 6:

$$\text{CH}_4 \text{ Conversion (\%)} = \frac{\text{CH}_4(\text{in}) - \text{CH}_4(\text{out})}{\text{CH}_4(\text{in})} \times 100 \quad (5)$$

$$\text{CO}_2 \text{ Conversion (\%)} = \frac{\text{CO}_2(\text{in}) - \text{CO}_2(\text{out})}{\text{CO}_2(\text{in})} \times 100 \quad (6)$$

Catalyst Testing

The dry reforming reaction was conducted at atmospheric pressure in a 9.4 mm I.D. and 48 cm long quartz tube fixed-bed continuous-flow microreactor (Thermcraft incorporated) using 0.6 g of the catalyst. The reactor assembly contains four independently heated zones; the reaction temperature was measured using a thermocouple (K-type) placed in an axial thermo-well centered in the catalyst bed. For each experimental run, the catalyst was first activated under H₂ flow (40 ml/min) at 600 °C for 2 h followed by N₂ flow (30 ml/min) for 20 min. The total flow rate and volume ratio of the feed gases (CH₄/CO₂/N₂) were 36 ml/min and 17/17/2 respectively. The reforming activity of catalyst was studied in temperature range of 500 °C to 700 °C. The effluent gases were analyzed by an online gas chromatograph (Alpha-MOS PR 2100) equipped with two thermal conductivity detectors; each for heavier and lighter components. After the reforming reaction, nitrogen gas was introduced to replace the reactant gases at the reaction temperature. Then the reactor was cooled to ambient temperature and subsequently the cooled catalyst was taken for various characterizations.

The reported results of catalytic activity tests present an average of triplicate runs. These runs were performed with good reproducibility and the conversions of methane and carbon dioxide were reproducible within ±3%. The schematic diagram of experimental setup used in this study (Fig. 1).

Catalyst Characterization

The specific surface areas of the fresh catalysts were determined by an automated gas sorption analyzer (Micromeritics Tristar II 3020). For each analysis, 0.3g of catalyst was used. Degassing of the samples, prior to the experiment, was conducted at 250°C for 3h to remove moisture content from the surface and pores of catalyst.

The temperature programmed reduction (TPR) and temperature programmed desorption (TPD) experiments had been completed in automatic chemisorption equipment (Micromeritics Auto Chem II 2920). For TPR, 70 mg of the

sample was subjected to a heat treatment (10 °C/min up to 1000 °C) at atmospheric pressure in a gas flow (40 ml/min) of 10% H₂/Ar mixture. Likewise, for (TPD) measurements, 70 mg of sample was first kept at 200 °C for 1 h under helium flow to remove physically adsorbed species from catalyst surface. Then, CO₂ adsorption was accomplished at 50 °C for 30 min by passing 10% CO₂/He mixture gas with a flow rate of 30 ml/min. Subsequently, the CO₂ desorption signal was recorded by TCD with a linear increase in temperature up to 800 °C with a temperature ramp rate of 10 °C/min.

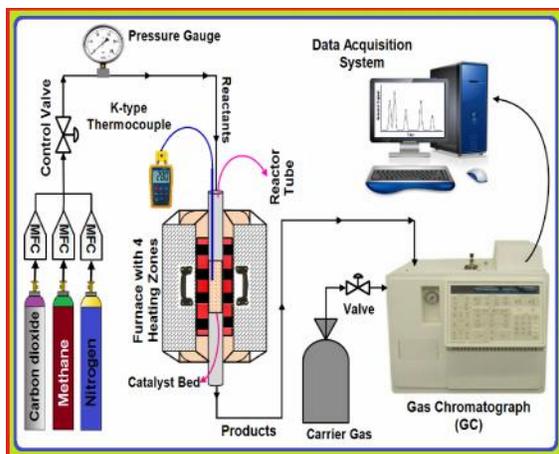


Fig. 1: Schematic diagram of experimental setup for dry reforming of methane.

The crystalline structure of prepared samples was characterized with powder X-ray diffraction (XRD) technique on a Bruker D8 Advance X-ray diffractometer equipped with Cu K α radiation source operated at 40 kV and 40 mA. The scanning step size and range of 2 θ for analysis were fixed at 0.01° and 10–80° respectively.

The thermo-gravimetric analyses (TGA) were conducted, to quantify the extent of carbon deposition over the spent catalyst, in air atmosphere using EXSTAR SII TG/DTA 7300 (Thermo-gravimetric/Differential) analyzer. For each analysis 10–20 mg of spent catalyst, was heated from ambient temperature to 800 °C at a heating rate of 20 °C/min and weight changes were measured.

Field emission scanning electron microscopy (FESEM) was used in order to study the morphology of the catalysts and to elucidate carbon formation over the spent catalysts. The SEM images for the spent catalyst samples were taken on JSM-7500F (Japan, JEOL Ltd.) scanning electron microscope.

Results and Discussions

Table-1: Textural properties, amount of coke deposition (estimated by TGA) and degree of reduction.

Catalyst	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)	Carbon Deposition (wt.%)	% drop in carbon Deposition	Total H ₂ consumption ¹ (mmol/g)	Degree of Reduction ² (%)
Zirconia	4.3	0.016	17.2	--	--	--	--
Ni-Zr	22.8	0.049	7.9	12.3	--	0.821	96.36
Ni-0.5Ho-Zr	29.6	0.055	6.7	7.4	39.8	0.825	92.28
Ni-1.0Ho-Zr	37.9	0.053	5.9	1.7	86.2	0.665	58.59
Ni-1.5Ho-Zr	47.1	0.062	5.5	0.9	92.7	0.658	51.69

1: From TPR experiments.

2: Ratio of amount H₂ consumed in H₂-TPR experiment to the theoretical quantity of H₂ needed for complete reduction.

Temperature Programmed Reduction (H₂-TPR)

Temperature programmed reduction (TPR) technique was employed to study the reduction behavior of the prepared catalysts. In general, peaks obtained at a specific temperature in TPR profile gave information about the combined status of interaction of the active metal and the support. (Fig. 2) presents the H₂-TPR profiles of Ni/ZrO₂ catalyst with and without addition of Ho promoter. For un-promoted catalyst only one broad reduction peak centered at around 450 °C was observed. This peak was ascribed to the reduction of NiO species having relatively weaker interaction with zirconia support. Likewise, for the Ho promoted catalysts, also one broad major reduction peak was observed; however, for these catalysts, the reduction peaks were shifted towards higher temperatures. For instance, the Ni-1.5Ho-Zr catalyst presented a major peak (centered at 550 °C) which could be ascribed to the reduction of Ni species strongly interacted with zirconia support. Actually, the transfer of reduction peaks towards higher temperature indicated that the incorporation of Ho had improved the metal support interaction in catalysts. In fact, for Ho promoted catalysts, the better metal-support interaction acted as a key factor which improved their coking resistance. It can be seen from TPR peaks and degree of reduction data reported in Table-1 that addition of Ho lowered the reduction degree which resulted in strong interaction between metal and support. The important impact of metal-support interaction on performance of catalyst, for DRM process, had also been reported by other researchers [19, 20]. In consideration of these TPR results, it was easy to claim that the addition of Ho in Ni/ZrO₂ catalyst had a strong influence on reduction behavior of prepared catalysts.

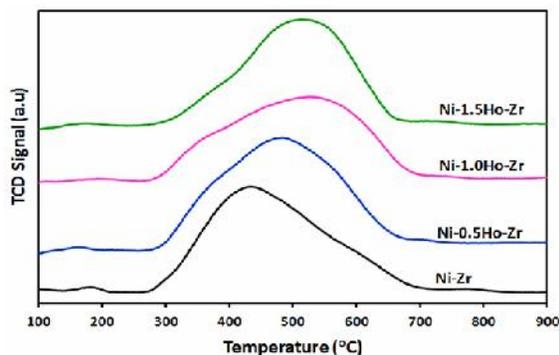


Fig. 2: H₂-TPR profiles of un-promoted and Ho promoted catalysts.

X-ray Diffraction and Energy Dispersive X-ray Spectroscopy (EDX)

The X-ray powder diffraction (XRD) patterns that show the crystalline phases of the promoted and un-promoted catalysts were presented in (Fig. 3a). It is obvious from XRD results that all catalysts exhibited well crystalline structure. In XRD patterns, the characteristic peaks observed at 2θ of 37.3° , 43.4° and 63° corresponded to (1 1 1), (2 0 0) and (2 2 0) planes of the cubic phase of NiO species respectively (JCPDS: 01-073-1519). Moreover, for both promoted and un-promoted catalysts, the 2θ values of reflections appeared 24° , 28.2° , 31.5° , 34.2° , 49.3° , 50.2° , 54.1° , 55.4° , 57.2° , 58.3° , 59.9° , 61.4° , 62.8° , 64.2° , 68.9° , 75.2° , 76.3° and 78.8° were attributed to the monoclinic phase of zirconia support (JCPDS: 00-007-0343). It is quite worthy to note that for all Ho promoted catalysts no bulk peak for Ho species was clearly observed in their XRD diffractograms. It is most likely owing to the low concentration and the highly uniform dispersion of Ho species throughout in these catalysts as very tiny particles that were beyond the detection limit of XRD (non-detectable clusters < 3 nm). The previously reported results of Mekhemer [17] fairly agreed our current results of holmium-zirconia supported catalyst system. Nevertheless, in order to confirm the presence of Ho species, energy dispersive X-ray (EDX) spectroscopy analysis was performed for Ho promoted catalyst. (Fig. 3b) presented the EDX spectrum of Ni-1.5Ho-Zr catalyst. The quantitative results revealed the presence of Ho, that confirmed the uniform dispersion of Ho in the catalyst.

Catalytic Performance

Blank tube test (i.e., without catalyst), that was performed prior to regular catalytic experiments under similar process conditions, exhibited negligible catalytic activity even at a temperature as high as 700°C . The results of catalytic activity in terms of CH_4 and CO_2 conversions at various reaction temperatures (500 , 600 & 700°C) revealed that for all Ho-promoted and un-promoted (i.e., Ni-Zr) catalysts, the activity increased with reaction temperature. Actually, the increase in catalytic activity with respect to reaction temperature reflected the strong endothermicity of the DRM reaction. These findings were in fair agreement with the literature and our previous work related to DRM [16, 21].

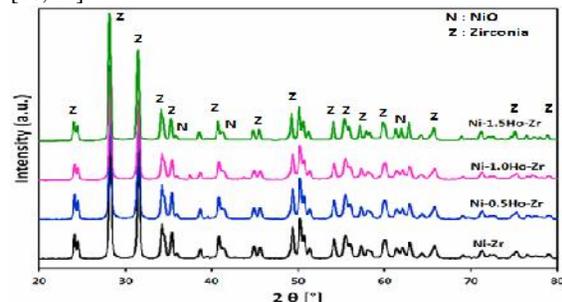


Fig. 3a: XRD patterns of un-promoted and Ho promoted catalysts.

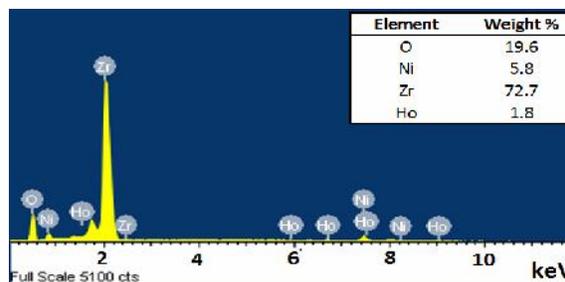


Fig. 3: (b) Energy dispersive X-ray spectroscopy (EDX) spectrum of fresh Ni-1.5Ho-Zr catalyst.

Moreover, from the obtained results, it was evident that the addition of Ho promoter in Ni/ZrO₂ catalyst had a notable effect on its catalytic performance. It is noteworthy that at all reaction temperatures, except at 500°C , un-promoted catalyst has exhibited relatively higher values of CH_4 conversions (Fig. 4a) than that of corresponding CO_2 conversions (Fig. 4b). On the other hand, all Ho promoted catalysts exhibited higher CO_2 conversions than the corresponding CH_4 conversions. In fact, in the case of un-promoted catalyst, the higher CH_4 conversion than CO_2 reflected the occurrence of methane decomposition/cracking reaction (Eq: 1). On the other hand, in the case of Ho promoted catalysts, the high activity of CO_2 reflected the existence of the reverse water gas shift (RWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$; $\text{H}_{298} = +41$ kJ/mol) [6, 11]. For methane reforming reactions, the literature stated that the surface adsorbed water species formed as a consequence of RWGS reaction could suppress/remove coke deposits from catalysts surface via steam gasification reaction ($\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$) [12]. Compared to un-promoted catalyst, the Ho promoted catalyst showed a great reduction in carbon deposition (about 92.7% for Ni-1.5Ho-Zr, 86.2% for Ni-1.0Ho-Zr and 39.8% for Ni-0.5Ho-Zr) as shown in Table-1. On the other hand, the average increase in CO_2 conversion was 17.6%, whereas the drop in methane conversion was 6.8% in the temperature range of 500 - 700°C .

In order to compare the long-term stabilities of un-promoted and Ho-promoted catalysts, their performance was compared at 700°C for 6 h time-on-stream (TOS). It is evident from results that for both un-promoted and Ho-promoted catalysts there were obvious changes in their catalytic performance. Overall, the un-promoted catalyst has exhibited high CH_4 conversion, while Ho promoted catalysts had shown high CO_2 conversion on TOS. For instance, after 6h TOS, Ni-1.5Ho-Zr at 700°C , exhibited a drop in methane conversion of 2.3%, whereas the increase in CO_2 conversion was 8.2% and carbon deposition was reduced by 93% compared to un-promoted catalyst. In our previous work we reported that the addition of Sr promoter in Ni/Al₂O₃ catalyst improved its coking resistance, but slightly decreased the catalytic activity [4]. Similar results related to decrease in catalytic activity had also been reported in the literature for alkaline earth metal promoted catalysts [22, 23].

The studies based on density functional theory (DFT) calculations revealed two types of active sites (defect/step sites and close-packed facets) for hydrocarbon

reforming reaction and for coke formation. Generally, a stepped Ni surface was considered to be much more active than a surface with close-packed terraces for coke formation. Therefore, it had been suggested that in order to avoid the coke formation, a small fraction of Ni active sites had to be blocked by a suitable promoter. This sort of blockage of Ni active sites by promoter did not stop the methane reforming reaction since it can still progress on the unblocked Ni active sites; however, it may affect the overall methane conversion [24]. Snoeck and Froment [25] studied the effect of potassium promotion on Ni based catalyst for steam reforming of methane. They proposed that the presence of potassium on the metal surface reduced the number of Ni active sites available for methane cracking; consequently it decreased the value of the lumped forward rate coefficient for methane cracking. By the same token, [26] reported that the partial coverage of the Co active sites by potassium decreased the net methane conversion in CO₂ reforming of methane. Thus, on the basis of these conclusions, it could be anticipated that the observed decrease in CH₄ conversion in the case of Ho promoted catalysts was probably due to the partial coverage of Ni active sites by Ho atoms which decreased the number of Ni active sites and exposed active metal surface available for methane reforming reaction. On the other hand, for Ho promoted catalysts, the increase in CO₂ conversion was credited to the relatively higher basicity of these catalysts than un-promoted catalyst (Fig. 4).

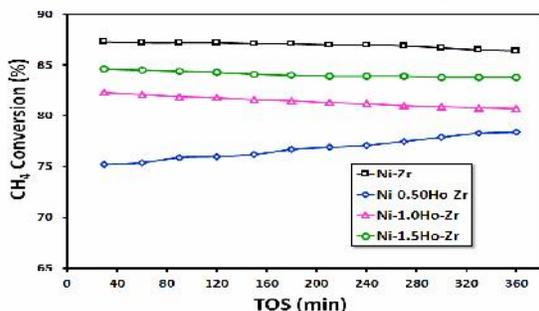


Fig. 4a: CH₄ Conversion of un-promoted and Ho promoted catalysts.

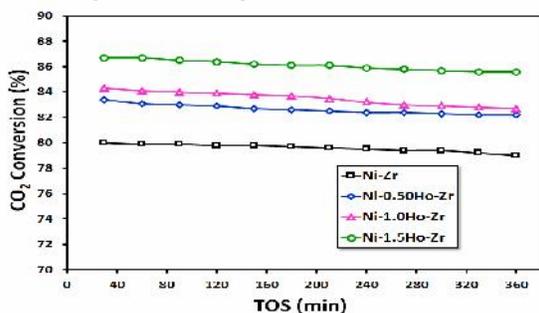


Fig. 4b: CO₂ Conversion of un-promoted and Ho promoted catalysts.

Luo *et al.* [27] investigated the role of surface oxygen in increasing the conversion of methane. They reported that during DMR process, complete dissociation of CO₂ (i.e., CO₂ → CO + O and then CO → C + O) generates surface oxygen species which enhance the CH₄ conversion

by the occurrence of this particular reaction [CH_x (s) + O (s) (x/2) H₂ + CO]. Our current findings are in agreement with these results. Since the CO₂ conversion was much higher for Ni-1.5Ho-Zr catalyst, so it is inferred that the surface oxygen species resulted from the CO₂ dissociation reaction over this catalyst increased the CH₄ conversion by above mentioned reaction. It is quite interesting to note that though the un-promoted catalyst had shown the highest methane conversion, it also had showed the highest carbon deposition (Table-1). Therefore, high CH₄ conversion coupled with high coking rate revealed that the methane decomposition side reaction (Eq: 1) was the major source of carbon deposition over un-promoted catalyst. It is believed that the carbon deposition over catalyst surface depended upon the oxidation rate of CH_x species and the available surface oxygen species got utilized to remove these carbon deposits [28]. It is also reported that the CO₂ chemisorption and dissociation over a transition metal surface was controlled by electronic transfer, which involved the formation of an anionic CO⁻² precursor. Additional studies pointed out that the stronger chemisorption of CO₂ and the weaker chemisorption of CH₄ were supportive for the suppression of coking [29]. Consequently, for DRM reaction, the good catalyst was that which not only had the better CH₄ conversion but it should also participated actively for CO₂ adsorption and dissociation/conversion to provide essential oxygen species required for carbon removal.

In comparison to all other Ho promoted catalysts, the highest CH₄ and CO₂ conversions were observed over a Ni-1.5Ho-Zr catalyst. Taking into account these catalytic activity results, we can argue that the addition of Ho promoter in Ni/ZrO₂ catalyst had a significant influence on the performance of catalysts.

Textural Properties

Table-1 summarized the results of textural properties (specific surface area, pore volume and pore diameter) for both un-promoted and Ho promoted fresh catalysts. The surface area was estimated by Brunauer, Emmett and Teller (BET) method while pore volume and pore size were calculated from the adsorption branch of the corresponding nitrogen isotherm, by Barrett, Joyner, and Halenda (BJH) method. It is apparent from the results that the addition of Ho promoter caused substantial changes in the textural properties of the parent catalyst.

High BET surface areas, bigger pore volumes and smaller pore diameters of Ho promoted catalysts revealed the enhancements in textural properties. For instance, the surface area of Ni-1.5Ho-Zr catalyst was 47.1 m²/g, almost two times higher (22.8 m²/g) compared to the un-promoted catalyst. Practically, the higher surface area might facilitate the adsorption of CO₂ at catalyst surface which, in turn, helped in removal of carbonaceous species from the catalyst surface by reverse Boudouard reaction (CO₂ + C → CO). It is obvious from Table 1 that the catalyst surface area had a significant impact on the amount of carbon deposition. In the case of Ho promoted catalysts larger surface area was one of the key features which made these catalysts better coke resistant than un-promoted catalyst.

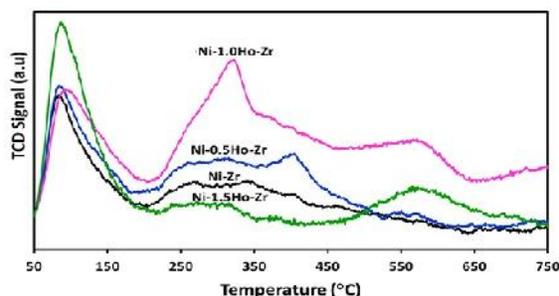


Fig. 5: CO₂-TPD profiles of un-promoted and Ho promoted catalysts.

Basicity Measurements (CO₂-TPD)

To estimate the Lewis basicity of the promoted and un-promoted catalysts, temperature programmed (TPD) experiments were conducted by using CO₂ as an adsorption gas. (Fig. 5) presents the CO₂-TPD profiles of the un-promoted and Ho promoted catalysts. It is apparent from results that the TPD patterns of un-promoted and Ho promoted catalysts were predominantly different from each other; Ho addition had a notable impact on adsorption behavior of these samples. Actually, the difference in TPD profiles, of the promoted and un-promoted catalysts, principally resulted from the difference of CO₂ (acidic gas) adsorption capacities of these catalysts. In the case of un-promoted catalyst only two major/distinct peaks were observed; one centered at around 90 °C and the other at around 320 °C. In this study, the existing basic sites, assignments were based on the fact that the CO₂ adsorbed on weaker basic sites desorbed at relatively low temperature, while that adsorbed on medium and stronger sites desorbed at relatively high temperatures [11]. On the basis of this judgment, for un-promoted catalyst the former peak was related to desorption of CO₂ species weakly bonded on the catalyst surface while the peak at a relatively higher temperature, was credited to the medium strength basic sites. On the other hand, for all Ho promoted catalysts more than two distinct CO₂ desorption peaks were observed. Moreover, in the case of promoted catalysts desorption peaks were not only more in numbers but also bigger in size (with respect to intensity). These results revealed that the Ho promoted catalysts had relatively better basicity than un-promoted catalyst. It has been reported in the literature that the catalysts having more basic sites/basicity or CO₂ adsorption capacity, they help in coke gasification during reforming reaction. Moreover the catalytic performance cannot be judged based only on the basicity as there are other factors involved in the activity performance such as active metal particle size, dispersion, metal support interaction etc. [30, 31]. The Ho belongs to the rare earth metals group; thereby addition of Ho in catalysts improved the surface basicity of the sample. The addition of Ho in catalysts exhibited several basic functionalities at the catalyst surface such as weak strength Ho-oxygen (Ho³⁺-O²⁻) pairs, medium strength basic OH⁻ groups/sites and strongly basic (isolated O²⁻) anions [17]. In comparison to un-promoted catalyst, the 1.5 wt.% Ho promoted catalyst (i.e., Ni-1.5Ho-Zr) showed three major CO₂ desorption peaks centered at 95 °C, 300 °C and 570 °C

that, respectively, indicated weak, moderate and stronger basic sites. On the basis of CO₂-TPD patterns shown in (Fig. 5), it can be concluded that the better basicity of Ho promoted catalysts made these catalysts less prone to coking while un-promoted catalyst (Ni-Zr) were largely affected by carbon deposition because of their relatively small CO₂ adsorption capacity.

Carbon Deposition Measurements

Spent catalysts were characterized by thermo-gravimetric analysis and by scanning electron microscopy technique to investigate the effect of the Ho promoter on carbon deposit and/or its elimination. Table 1 presented the quantitative results of carbon deposition for promoted and un-promoted spent catalysts. It is evident from the results that when the parent catalyst was doped with Ho promoter, it showed better coke resistance. Un-promoted (Ni-Zr) catalyst gave the highest weight loss of 12.3 wt.%, due to carbon gasification, while amongst all spent catalysts, Ni-1.5Ho-Zr catalyst (0.9 wt.%) provided the smallest weight loss. (Fig. 6) presents the differential thermo-gravimetric (DTG) profiles for both promoted and un-promoted spent catalysts. From the obtained results it was obvious that the Ho promoter had a significant effect on the amount of carbon deposition. In the case of un-promoted catalyst only one major positive peak centered at about 540 °C was observed, which was attributed to gasification of the filamentous type of carbonaceous species.

Similarly, for the Ho promoted catalysts, only one central positive peak was observed; however, for Ni-1.0Ho-Zr and Ni-1.5Ho-Zr samples, one very small negative peak at around 250–400 °C was also observed. In fact this negative peak is attributed to the oxidation of reduced Ni species presented in the catalysts. Moreover, in comparison to un-promoted catalyst the peaks were relatively smaller in the case of Ho promoted catalysts, which assured the better resistance of Ho promoted catalysts.

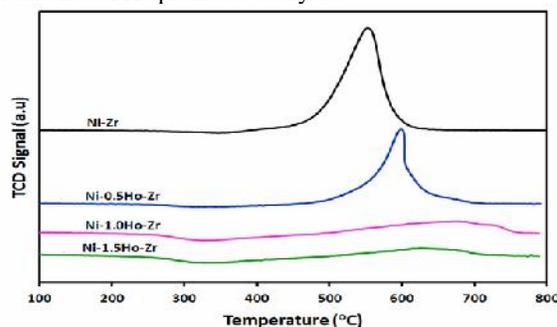


Fig. 6: DTG profiles of un-promoted and Ho promoted catalysts.

Formation of polydentate carbonaceous species/ions on holmium oxide surface, when CO₂ was adsorbed on it, was reported in the literature [32]. Indeed, such species were only obtained when CO₂ reacted with very strong surface basic sites (O²⁻ and/or OH⁻). Suttthumporn and Kawi [33] studied the role of surface oxygen species in enhancing CO₂ adsorption and they observed that similar oxycarbonate surface species intermediates (La₂O₂CO₃) were found at CO₂/La₂O₃ interfaces.

Additionally, Verykios [34] found that such surface oxycarbonates were very important for coke removal because, during DRM reaction, oxygen species were produced from these oxycarbonate intermediates which afterwards participated in reactions with surface carbon deposits to form CO. Scanning electron microscopy (SEM) images of spent catalysts exposed the nature and/or type of carbon deposition on these catalysts. (Fig. 6a) and (Fig. 6b) respectively presented the SEM micrographs of un-promoted (Ni-Zr) and the Ho promoted (Ni-1.5Ho-Zr) spent catalysts in. Un-promoted spent catalyst (Fig. 7a) showed a huge amount of carbon deposits of filamentous structure. On the other hand, Ni-1.5Ho-Zr spent catalyst (Fig. 7b) showed insignificant signs of carbon deposition.

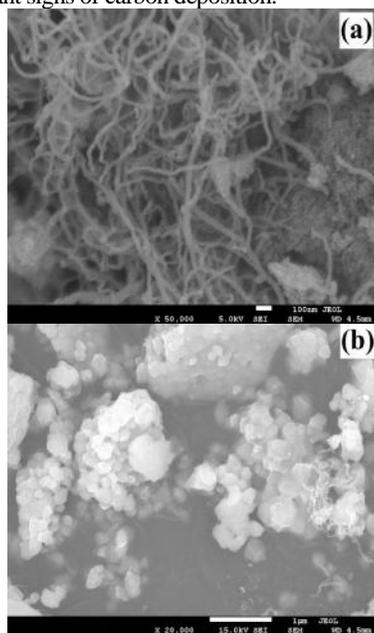


Fig. 7: SEM micrographs of (a) Ni-Zr; (b) Ni-1.5Ho-Zr spent catalysts.

Conclusions

The Ho promoted Ni/ZrO₂ catalysts were prepared by polyol process and tested for dry reforming of methane. The catalyst performance results revealed that the doping of Ni-Zr catalyst with Ho promoter significantly suppressed the accumulation of carbon deposits over the catalysts surface. This excellent tendency towards the coke resistance of Ho-promoted catalysts was credited to the improvements in basicity, increase in BET surface areas and enhancement of the metal support interaction in the catalysts. The Ho-promoted catalysts considerably accelerated the adsorption and dissociation of CO₂ over the catalyst surface which in turn generated mobile oxygen intermediates adjacent to the Ho-Ni boundary, where coke deposits were gasified consequently. Un-promoted catalyst exhibited the highest extent of carbon deposition (12.3 wt.%) which was confirmed by TGA, DTG and SEM analysis. On the other hand, Ni-1.5Ho-Zr catalyst showed excellent coke resistance with negligible amount of carbon deposition (0.9 wt.%) as compared to the un-promoted catalyst.

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