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Effects of calcination and activation temperature on dry reforming catalysts

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Abstract The effect of calcination temperatures on dry reforming catalysts supported on high surface area alumina Ni/γ-Al₂O₃ (SA-6175) was studied experimentally. In this study, the prepared catalyst was tested in a micro tubular reactor using temperature ranges of 500, 600, 700 and 800 °C at atmospheric pressure, using a total flow rate of 33 ml/min consisting of 3 ml/min of N₂, 15 ml/min of CO₂ and 15 ml/min of CH₄. The calcination was carried out in the range of 500–900 °C. The catalyst is activated inside the reactor at 500–800 °C using hydrogen gas. It was observed that calcination enhances catalyst activity which increases as calcination and reaction temperatures were increased. The highest conversion was obtained at 800 °C reaction temperature by using catalyst calcined at 900 °C and activation at 700 °C. The catalyst characterization conducted supported the observed experimental results.

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1. Introduction

The process of dry reforming shows considerable interest from both industrial and environmental viewpoints and receives attention of the scientific world in general and catalysis special-

ists in particular (Al-Fatesh, 2010; Bradford and Vannice, 1999; Wang and Lu, 1996; Song and Guo, 2006). Methane and carbon dioxide are two of the cheapest and most abundant carbon-containing materials that can be transformed into useful products. On the other hand the two gases are undesirable greenhouse gases and are both consumed by this reaction. Since greenhouse gases cause warming of earth and climate change, there are incentives for reducing their concentration in the atmosphere (Hu and Ruckenstein, 2004; Dyrsen and Turner, 1994). The network reactions in dry reforming may be summarized as the follows:

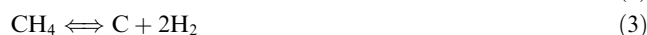
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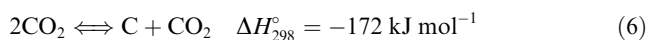
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The principal aspect of dry reforming catalyst depends on supported Ni (Nagaoka et al., 2003; Gadalla and Bower, 1988). However, the major difficulty of these reactions is the rapid coke deposition, which causes catalyst deactivation, catalyst destruction and reactor blockage. It is generally acknowledged that catalyst deactivation is due to coke formation within the pores of the catalyst, which leads to breakup of the catalyst particles (Xu et al., 2001; Kim et al., 2000). The coke that forms on surface originates mainly either from CO disproportionation or methane decomposition reactions. The former is exothermic and is favored at temperatures below 973 K and higher pressures:



Considerable rates of carbon deposition take place in the presence of cobalt, iron, and nickel catalysts at temperature above 623 K. The form of carbon deposited on metal surface generated during this reaction depends on reaction conditions; amorphous and filamentous carbons predominate in the lower temperature range of 623–873 K, and a graphitic structure predominate at 973 K or higher temperatures. The latter (methane decomposition) as shown in reaction (3) is endothermic and is favored by high temperatures and low pressures. Carbon formation by CH_4 decomposition is a structure sensitive reaction (Al-Fatesh, 2003, 2010; Alonso et al., 2009; Aydinoglu et al., 2009).

The effect of calcination temperatures on the activity of alumina supported nickel catalyst in dry reforming process was studied by Joo and Jung (2002). They used two calcination temperatures 450, 850 K, and found that even though the amount of carbon deposited for catalyst calcinated at 850 K was higher than that formed for catalyst calcinated at 450 K, the activity of catalyst calcined at 850 K was higher than that for catalyst calcinated at 450 K. The difference in activity was due to different types of carbon formed on catalyst surface. The resistivity decreased with increasing calcination time. The chemical reaction was controlled initially by the reaction itself and later by diffusion. The simple increase of calcination time had no appreciable effect on the reaction velocity.

Chen et al. (2005) found that the calcination temperature could greatly affect the catalyst activity. A higher reduction temperature was necessary to ensure the complete reduction of NiO on the catalysts calcined at higher temperatures, such as 773 and 873 K. With the increase of the calcination temperature from 673 to 723 K, the activity/selectivity was almost the same. However, with further increase in the calcination temperature to 773 K and up to 873 K, CH_4 conversion and syngas selectivity decreased. Their results revealed that calcination at relatively low temperatures is an important factor in lowering the Ni loading of the catalysts.

Rezgui and Guemini (2008) investigated the effect of the pretreatment conditions on the catalytic performance of the Pt–Ni–WO_x/ASA catalysts prepared by a sol–gel method. The collected data showed that the catalytic activity of these solids was strongly dependent on their calcination and reduction temperatures. Their observations may be summarized as follows:

- The catalysts activities depended strongly on their calcination temperatures; the incorporation of Pt shifted the optimum calcination temperature to lower values.
- The density of acid sites is strongly influenced by the catalyst calcination temperature; it increased to reach a maxi-

imum and then decreased. Besides, the solids catalytic performance was totally related to their acidities, the higher the sample acidity the higher its activity. Sun et al. (2007) studied the effects of calcination temperature on BET surface area and average pore diameter. In catalyst or catalytic material preparation, the thermal treatment process, especially the calcination temperature, highly affects the development of surface properties and the phase structure of the material prepared. The TG pattern showed an obvious weight drop when temperature increased from 273 to 723 K. This weight loss may be due to the evaporation of moisture, methanol solvent, and butanol generated during hydrolysis and the decomposition of nitrate, respectively. A steady horizontal TG line after 723 K indicates no further weight loss. In the DTA pattern, the negative peak at 373 K indicated the occurrence of an endothermic process, which was reasonably attributed to the evaporation of moisture since no reaction would occur below 473 K.

This paper deals with the effect of calcination temperatures and activation treatments on the catalysts of 3 wt% Ni/ γ -Al₂O₃ catalyst used in the dry reforming of CH_4 .

2. Experimental

2.1. Catalyst preparation

The wet impregnation method was used to prepare the catalyst. Supported Ni/ γ -Al₂O₃ (SA-6175) catalysts were prepared using nickel nitrate salt ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as precursor and alumina (SA-6175) with BET 230 m²/g as a support. The catalysts were dried for 10 h at 120 °C and calcined from 500 to 900 °C for 2 h. The catalysts were activated inside the reactor from 500 to 800 °C by passing hydrogen at a rate of 40 ml/min for 2 h followed by 20 min of N₂ at a rate of 30 ml/min.

2.2. Catalytic reaction

The reaction of CO_2 reforming of methane was carried out at atmospheric pressure in a 9.4 mm i.d. and 48 cm long stainless steel-tube fixed-bed microreactor (Zeton altimira 2000) using 0.75 g of catalyst. The reaction temperature was measured by a thermocouple placed in the centre of the catalyst bed. The volume ratio of the feed gases (methane/carbon dioxide/nitrogen) was 5/5/1. The total flow rate was 33 ml/min with a space velocity of 44 ml/min g_{cat}⁻¹. The investigation covered the reaction temperatures of 500, 600, 700 and 800 °C. The effluents were analyzed using an online gas chromatography (Varian Star cx 3400) equipped with a thermal conductivity detector. The conversions of CH_4 and CO_2 ; H₂/CO ratio; carbon yield and drop in conversion due to coking were all determined.

2.3. Catalyst characterization

The catalysts were characterized by different techniques. The structure of the synthesized catalysts was examined by X-ray diffraction (XRD), unisantis XMD-300 diffractometer using Cu K α radiation. Diffraction peaks recorded in a 2 θ range between 10° and 80° were used to identify the structure of the samples. The amount of surface carbon was evaluated by thermogravimetric analysis (TGA) and differential thermal

analysis (DTA) in an air atmosphere up to 800 °C on a Perkin-Elmer, Pyris Diamond thermogravimetric/differential analyzer TG/DTA 6300 at a heating rate 20 °C/min. Spent and fresh catalysts were characterized by BET surface area by ASAP 2020. The catalyst surface concentrations of acidic and basic centres were determined by temperature-programmed desorption of ammonia (NH₃-TPD) and carbon dioxide (CO₂-TPD), respectively, using a TPD/R/O 1100 Thermo Electron instrument.

3. Results and discussion

In this section, the results of activity tests and stability of the prepared catalysts, as well as the catalyst characterization are presented. The reaction temperatures used were 500, 600, 700 and 800 °C. The outlet gas analysis presents the steady state values obtained after repeating the analysis for five to seven times. These runs were performed with good reproducibility. In the present work, conversions of CH₄, CO₂, H₂/CO ratio, coke and deactivation factor were determined. In this work, conversions of methane and carbon dioxide were calculated according to the following formulae:

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

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

In addition, the molar H₂/CO ratio was obtained from the product gas composition:

$$\text{H}_2/\text{CO} = \frac{\text{mole of H}_2 \text{ produced}}{\text{mole of CO produced}}$$

The coke yield and the deactivation factor are defined as:

$$\text{Coke yield } (\%) = \frac{\text{moles of C formed}}{\text{moles of (CH}_4 + \text{CO}_2) \text{ in feed}} \times 100$$

Deactivation Factor (DF)

$$= \frac{\text{final CH}_4 \text{ conversion} - \text{initial CH}_4 \text{ conversion}}{\text{initial CH}_4 \text{ conversion}} \times 100$$

Initial conversion was calculated after 30 min on stream, while final conversion was calculated at the end of time on stream.

3.1. Effect of calcination

Pretreatment of catalysts is established to be among the effective means of enhancing the catalytic performances. Therefore, calcinations and activation are indispensable processes for dry reforming reaction of methane with carbon dioxide. The catalysts were dried for 12 h at 120 °C. During the drying period the solution retained by the porous support may migrate by capillary flow and diffusion and the solute redistributed by desorption and re-adsorption. On the other hand, as the solvent evaporates, precipitation of solute happens as the solution becomes supersaturated and brings crystallization of the precursors in the pores and outer surface of the carrier. The drying process contributed to the distribution of the catalyst within the support (Zechayer, 1989; Regalbuto, 2007). The calcination of deposited precursors brings about several transformations and solid state reactions which included: decomposition of the dried precursor, solid state reactions of the

supported oxide, solid state reactions of the support, reaction between deposited oxides and the support and sintering of various phases. A high temperature must be employed to ensure decomposition of salt used in the preparation (Gates and Knozinger, 2006; Hagen, 2006; Satterfield, 1980; Caberry, 1976; Yan et al., 2003).

The catalysts were calcined at various temperatures (500, 600, 700, 800 and 900 °C) for 2 h. The formation of the final prepared catalyst depended on the calcination temperature. To obtain information about the effect of calcination temperature, experiments had been carried out in which the calcination temperature was varied between 500 and 900 °C. The catalysts were activated inside the reactor by passing hydrogen gas. The conversions CH₄ and CO₂ in CO₂ reforming of CH₄ over Ni/Al₂O₃ were investigated and the results are summarized in Fig. 1. X-ray diffraction (XRD) was also performed to characterize the structural properties of the calcined catalysts. In the CO₂ reforming reaction of methane, several reaction temperatures were used in the range between 500 and 800 °C. The results obtained showed that in general, increasing the reaction temperatures and calcination temperature increased the conversion of methane and CO₂ for all supported catalysts used.

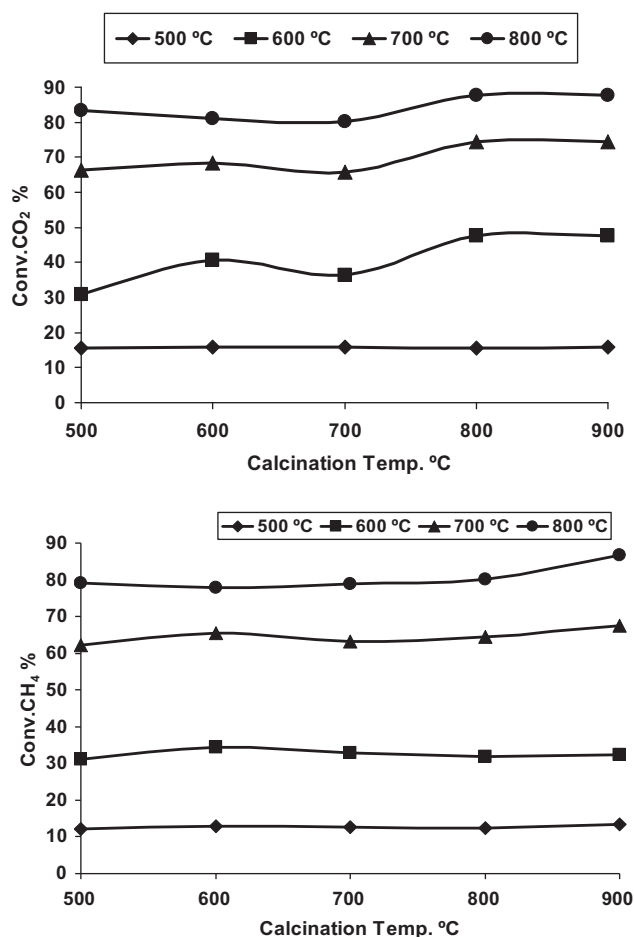


Figure 1 CH₄ and CO₂ catalytic conversions over 3 wt% Ni/γ-Al₂O₃ for various calcination temperatures at 500–800 °C, reaction conditions: CH₄:CO₂ = 1:1, P = 1 atm, F/W = 660 ml/h_{g_{cat}}.

Table 1 Time on stream stability test for 3 wt% Ni/ γ -Al₂O₃.

Reaction temp. (°C)	Initial conversion ^a (%)		Final conversion ^b (%)		H ₂ /CO ^c	DF ^d (%)
	CH ₄	CO ₂	CH ₄	CO ₂		
700 ^e	73.7	79.0	73.0	80.1	0.91	-0.95
700 ^f	70.3	75.7	68.0	66.4	0.93	-3.30
500 ^e	13.8	18.2	11.2	12.3	0.56	-14.50
500 ^f	10.8	15.7	9.3	12.6	0.53	-13.60

Reaction condition: CH₄ = 15 ml/min, CO₂ = 15 ml/min and N₂ = 3 ml/min, wt. cat. = 0.75 g, 3 wt% Ni loading.

^a 30 min on stream.

^b 540 min final on stream.

^c Average data during time on stream.

^d [(final CH₄ conversion - initial conversion CH₄)/initial conversion of CH₄] × 100.

^e Calcination temp. = 900 °C.

^f Calcination temp. = 600 °C.

For high surface area catalyst (3 wt% Ni/ γ -Al₂O₃), Fig. 1 shows the effects of calcination temperatures on CH₄ and CO₂ conversions at reaction temperatures of 500, 600, 700 and 800 °C. It is evident that at higher calcination temperatures such as 900 °C, the activity is enhanced at higher reaction temperatures. The conversions of CO₂ were higher than that of CH₄ for all reaction and calcination temperatures and the ratio of H₂/CO as given in Table 1 was always less than 1 indicating the occurrence of reverse water gas shift reaction. This led to reduction of carbon deposition on the catalyst. All calcined catalysts together with that of the un-calcined catalyst were examined by XRD in order to investigate the phase development. Fig. 2 presents similar pattern for catalysts calcined at 500, 600 and 700 °C. While the pattern for catalyst calcined at 900 °C was slightly different from those calcined at lower temperatures. The difference of pattern at low and high temperatures was due to the existence of two phases. Therefore, to choose the optimum temperature condition, further experiments are carried out and results are summarized in Table 1. In this case the favorable calcination temperature seemed to be either 900 °C or 600 °C. To support the choice 900 °C over 600 °C calcination temperature, time on stream stability tests were conducted at 500 and 700 °C reaction temperatures. The stability result shown in Table 1 indicates that 900 °C cal-

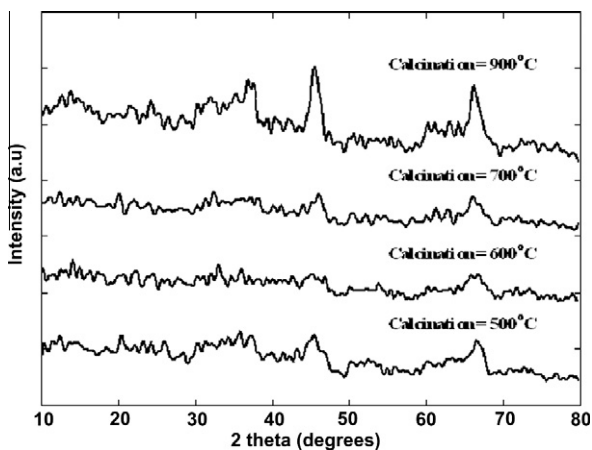


Figure 2 XRD patterns of catalyst calcined at various temperatures for 2 h with heating/cooling rates of 10 °C/min.

ination is better than 600 °C for both temperature reactions. At 700 °C reaction temperature better stability of the catalysts was observed than at 500 °C. On the other hand, calcination at 900 °C is above the highest reaction temperature (800 °C) and, therefore, there will be no phase change.

The specific surface area is one of the important parameters in heterogeneous catalysis; it must be taken into account especially in the case of supported catalysts. Table 2 presents the results of fresh and used BET surface area variation with calcination for high surface area support.

It is clear that the surface area of the support decreases with increase of the calcination temperature. The fresh BET surface area was as high as 211.8 m²/g when the catalyst sample was not calcined, but it dropped noticeably as the calcination temperatures were raised. The surface area became 149.7 m²/g when the catalyst sample was calcined at 900 °C. The used catalyst BET surface area was 160.0 m²/g when the catalyst sample was calcined at 500 °C and the reaction was conducted at 500 °C, but it dropped slowly as the calcination temperature was raised. The surface area became 132.5 m²/g when the catalyst sample was calcined at 900 °C and the reaction was conducted at 700 °C. It is evident herein that the value of surface area of the used catalyst is lower than the corresponding value for fresh sample. The relative reduction of the BET surface areas for the used and fresh catalysts is attributed to deposition of carbon. The BET value for used catalyst decreased with the increase of the calcination temperatures. The highest reduction in BET surface area occurred at reaction and calcination temperature of 600 °C.

From the results obtained regarding the calcination temperatures of high surface area alumina, it can be stated that high calcination temperature suits the dry reforming of methane with carbon dioxide which is an endothermic reaction that requires high reaction temperature to achieve acceptable conversions. Although the high calcination temperature reduces the BET surface area yet it has the benefit of securing the existence of a stable structure of the catalyst.

3.2. Effect of activation

The objective of activation or pre-reduction of all catalysts at different temperatures is to reduce nickel oxide to metallic Ni. The procedure started by heating the reactor while feeding N₂ at rate of 30 ml/min for 30 min primarily to remove water and

Table 2 BET variations with calcination for 3 wt% Ni/ γ -Al₂O₃.

Calcination temp. (°C)	BET ^a (m ² /g)	Reaction temp. (°C)	BET ^b (m ² /g)
No. calc. (fresh)	211.8		
500	197.1	500	160.00
600	197.2	600	124.2
700	183.9	700	140.1
900	149.7	700	132.5

^a Fresh sample.^b Used sample.

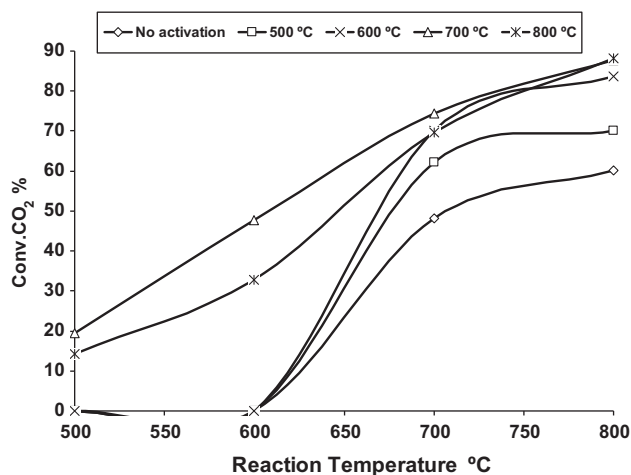
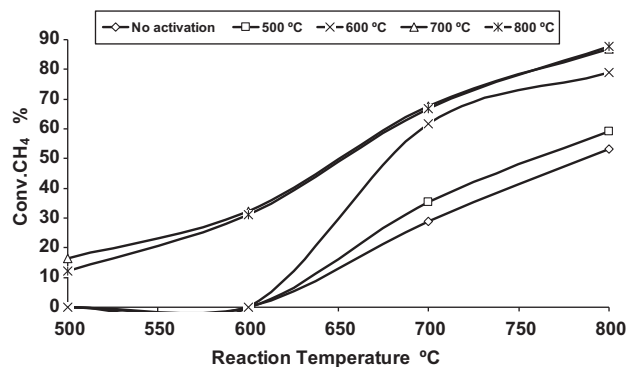
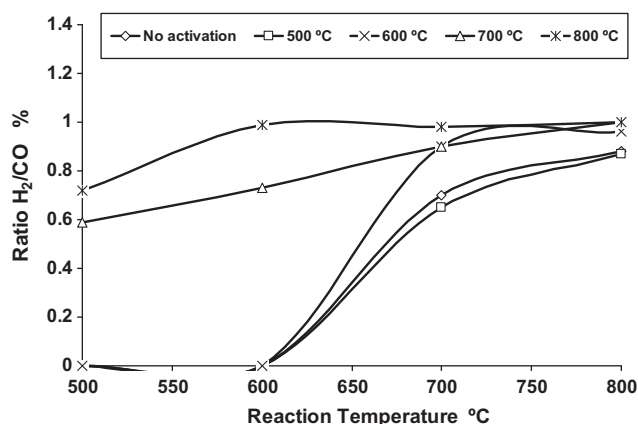
to establish the desired activation temperature followed by hydrogen (99.995% at 20 ml/min for 120 min). After termination of reduction, the catalyst was purged with flowing N₂ at 30 ml/min for 30 min to remove adsorbed hydrogen from the catalyst surface. 3 wt% of Ni loading for the high surface area (SA-6175) support was used. For all catalysts a fixed calcination temperature of 900 °C was applied. The procedure adopted for this investigation for each catalyst is as follows:

- No activation.
- Activation at 500 °C for 2 h.
- Activation at 600 °C for 2 h.
- Activation at 700 °C for 2 h.
- Activation at 800 °C for 2 h.

The activated catalysts were examined at different reaction temperatures (500, 600, 700 and 800 °C). The flow rates of feed gases were: CO₂ 15 ml/min, CH₄ 15 ml/min and N₂ 3 ml/min.

The results of this investigation are tabulated and presented in Figs. 3–5.

Results of 3 wt% Ni/ γ -Al₂O₃ support show that no reaction took place at 500 and 600 °C reaction temperatures when no activation or activation at 500 and 600 °C was applied as shown in Figs. 3–5. When the reaction temperature exceeds 600 °C, reaction started and products were generated. Indeed reaction took place at activation temperature of 600 °C when reaction temperatures of 700 and 800 °C were used. It was also

**Figure 3** Effect of activation temperature on % conversion of CO₂ using 3 wt% Ni/ γ -Al₂O₃.**Figure 4** Effect of activation temperature on % conversion of CH₄ using 3 wt% Ni/ γ -Al₂O₃.**Figure 5** Effect of activation temperature on H₂/CO ratio using 3 wt% Ni/ γ -Al₂O₃.

observed that reaction took place when activation temperatures of 700 and 800 °C were used for all reaction temperatures used (500–800 °C). It was also observed that 700 °C activation temperature gives better results than 800 °C activation temperature for all reaction temperatures.

3.3. Acid–base properties of the supported catalysts

The catalyst surface concentrations of acidic and basic centres were determined by temperature-programmed desorption of ammonia (NH₃-TPD) and carbon dioxide (CO₂-TPD), respectively, using a TPD/R/O 1100 Thermo Electron instrument. For NH₃/CO₂ TPD, a catalyst sample, weighing ~0.1 g, was pretreated in 20 ml/min helium (He) at 150 °C for 2 h before NH₃/CO₂ adsorption. Finally the sample was flushed with He in order to remove the excess NH₃/CO₂ gases. Analysis/desorption was done under constant He flow of 25 ml/min to the temperature of 500 °C with a ramp of 10 °C/min.

CO₂-TPD and NH₃-TPD measurements were performed to obtain information on the number of active acid and base sites in the prepared samples see Table 3. The table presents the results of CO₂-TPD and NH₃-TPD measurements for 3 wt% Ni/ γ -Al₂O₃ catalyst calcined at 900 °C. The non-activated fresh catalyst provided the lowest basicity and, therefore, the lowest CO₂ adsorption. On the other hand, the acidity and basicity changed as the H₂ activation temperature was increased. The

Table 3 Concentrations of acidic and basic sites in the 3 wt% Ni/ γ -Al₂O₃ calcined at 900 °C.

Sample type	Sample basicity	Sample acidity
	CO ₂ (μ mol/g)	NH ₃ (μ mol/g)
Fresh catalyst before activation	653.2	1309.2
Activation at 500 °C with H ₂	744.2	1350.8
Activation at 600 °C with H ₂	727.8	1182.6
Activation at 700 °C with H ₂	736.12	1316
Activation at 800 °C with H ₂	851	1320.7

Table 4 Concentrations of acidic and basic calcined at 900 °C.

Sample type	Sample basicity	Sample acidity
	CO ₂ (μ mol/g)	NH ₃ (μ mol/g)
Fresh catalyst before activation 3 wt% Ni/ γ -Al ₂ O ₃	653.2	1309.2
Used catalyst at Tr = 600 °C 3 wt% Ni/ γ -Al ₂ O ₃	785.1	1202.1

increased adsorbed amount of CO₂ due to activation would provide more oxygen species on the surface of the catalysts, which is helpful for the gasification of intermediated carbon from CH₄ dehydrogenation and would result in a coke-free reforming process. The results show that the catalyst possesses more surface acidic sites than basic sites, irrespective of activation temperature, and activation agent. Similarly, Table 4 compares the results of CO₂-TPD and NH₃-TPD measurements for 3 wt% Ni/ γ -Al₂O₃ catalysts calcined at 900 °C. It is evident herein that the catalysts have more surface acidic sites than basic sites, irrespective of support type.

4. Conclusions

Dry reforming of methane to produce CO-rich synthesis gas with a more suitable H₂/CO ratio was studied. The research effort focused on catalyst development to improve catalyst activity and resistance to carbon formation so as to achieve stable long-term operation. The requirement to acquire a desired active catalyst for dry reforming of methane and carbon dioxide encouraged the effects of principal parameters that influence the performance, activity, stability and resistance to carbon deposition. For this purpose, Ni was supported on high surface area γ -Al₂O₃. The activation process and calcination were experimentally studied using reaction temperature ranges of 500–800 °C, atmospheric pressure and total feed gas flow rate of 33 ml/min. The results of this work lead to the following conclusions:

- It is found that activating and calcining the catalyst promotes activity and enhances performance.
- The catalysts must be activated once before they are used for the first time. The optimum activation of the catalyst occurs under reaction condition by fast reduction of NiO with hydrogen at temperature 700 °C.
- It is noted that at any calcination temperature the conversions of both methane and carbon dioxide increase as reaction temperature is increased as well as hydrogen to carbon

monoxide ratio. The highest conversion is obtained at 800 °C reaction temperatures when the catalyst is calcined at 900 °C.

- The non-activated fresh catalyst provided the lowest basicity and, therefore, the lowest CO₂ adsorption. On the other hand, the acidity and basicity changed as the H₂ activation temperature was increased. The increased adsorbed amount of CO₂ due to activation would provide more oxygen species on the surface of the catalysts, which is helpful for the gasification of intermediated carbon from CH₄ dehydrogenation and would result in a coke-free reforming process.
- The deactivation factor at reaction temperature of 700 °C is lower than that at 500 °C which indicates lower carbon formation and longer stability of the catalyst activity.

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