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Coproduction of Hydrogen and Carbon Filaments from Methane Decomposition over Fe/La₂O₃ Catalysts

[1]Ahmed. Sadeq. Al–Fatesh*, [2]Jehad Abu-Dahrieh**, [1]Ahmed Aidid. Ibrahim
[1]Anis Hamza. Fakeeha*** and [1]Wasim. Ullah. Khan

[1]*Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800 Riyadh 11421, Saudi Arabia.*
[2]*CenTACat, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, UK.*
aalfatesh@ksu.edu.sa* , j.abudahrieh@qub.ac.uk**

Summary: Clean hydrogen production from catalytic methane decomposition has attracted the attention of many researchers as an alternative fuel source. In the present work, the catalytic decomposition of methane into hydrogen and carbon filaments on La_2O_3 doped Fe catalyst was investigated using 25% iron loading. The effect of reaction temperatures (500-750°C) over 25% Fe/ La_2O_3 catalyst was studied. The catalysts before and after reaction were characterized by BET, XRD, H_2-TPR, TGA, TPO, SEM and TEM. Stability studies of 25% Fe/ La_2O_3 at 750 °C for 360 min for one cycle and 5 regeneration cycles were carried out. The 25% Fe/ La_2O_3 catalyst showed high stability for the six cycles with no reduction in activity. Hence, iron supported over La_2O_3 catalyst is an efficient catalyst for hydrogen production from catalytic methane decomposition. SEM and TEM images exhibited formation of carbon filaments with various diameters and lengths.

Keywords: Carbon filament, CO_x- free hydrogen, Decomposition, Methane.

Introduction

Hydrogen has an attractive alternative energy source which can be used to a large extent in the fuel cell without any emissions. Hydrogen does not exist alone in nature and it is currently derived from natural gas through steam reforming of methane (SRM). Despite the high efficiency of SRM process, it causes high CO_2 emissions. Moreover, hydrogen produced by this method needs to be further purified and even after the purification, the product stream contains large quantities of CO [1]. One interesting approach to produce clean or CO_2-free hydrogen is the catalytic decomposition of methane (CDM). Moreover, the carbon filaments produced from this process have attracted the attention of the scientists because of low production cost with extraordinary structural properties. CDM is an endothermic reaction and high temperature is favored thermodynamically and both hydrogen and carbon filaments are produced according to Eq. (1):

$$CH_4 \rightarrow 2H_2 + C \quad \Delta H^\circ = 75.6 \frac{kJ}{mol} \quad (1)$$
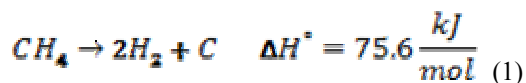
Higher temperature results higher methane conversion. It is also evident that methane decomposition is favored by decreasing pressure. This is due to the increase in volume during the decomposition. Although most studies are carried out at atmospheric pressure, Steinberg deduces that CDM is favored by lower pressures, but the reaction rate is favored by higher pressure and appears to be catalysed by the carbon particles formed by the reaction [2].

Different temperatures and catalysts produce CO_2-free hydrogen and carbon filaments with various textural and structural properties [3]. The use of metal-based catalysts produces highly graphitic carbon [3-5]. Carbon materials, especially carbon nanotubes, have attracted intense interest as a new carbon material. Zhang *et al* [5]. Produced from methane catalytic cracking hydrogen and broad spectra of graphitic carbon nano/micro materials over different catalysts with different combination of the metals Mo–Ni(Fe, Co)–MgO$_z$, Ni/Y and La$_2$NiO$_4$.

Ni, Co and Fe based catalysts supported over various metal oxides are widely used in the literature [4, 6-14]. Ni and Co catalysts are extensively used due to their high activity, and they favour the formation of carbon filaments [15]. Also supported Fe catalysts are reported in many literatures. Choudhary *et al* [16]. argued that Fe and Co have low carbon filaments formation rates/yields compared to Ni, however, the properties of the carbon filament depend on the employed metal. Pudukudy *et al.* [12], examined the catalytic activity and stability of silica micro-flakes supported monometallic Ni, Co and Fe based catalysts. They found that the catalysts showed excellent activity for the production of hydrogen, free of carbon oxides,

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and nano-carbon at reaction temperature of 800 °C. They obtained that Co and Fe based catalysts exhibited more stable activity performance than Ni based catalyst, though a maximum hydrogen yield of around 74% was attained for Ni based catalyst at the start of the reaction. Moreover, they reported that hydrogen yields around 43% and 46% were obtained for Co and Fe based catalysts for 300 min of time on stream, respectively. Beside this, Fe based catalysts are cheaper and more environmentally friendly than Co and Ni based catalysts [10]. Oliveira *et al* [17], presented a new two-step route to store and transport associated natural gas, promoted by Ni, Fe and Co supported catalyst. They found that Fe catalyst is the most active catalyst for converting CH_4 into carbon deposits, promoting mainly the formation of filaments.

In order to improve the performance of Fe-based catalysts, several iron to support ratio has been studied [11]. In our previous paper, Ibrahim *et al* [11], studied the effect of iron loading on Al_2O_3 support. They found that the hydrogen yield increased as the Fe loading increased and the maximum H_2 yield of 77.2% was obtained using 60% Fe/Al_2O_3 catalyst. Furthermore, they noticed that at lower Fe loadings, *i.e.*, 25% Fe, the hydrogen yield drops from 16.9% to 6.0% after 240 min of reaction time. At higher Fe loading, the drop in yield is less significant, *i.e.*, for 60% Fe, the yield drops from 77.2% to 74.5% for the same period of 4 h reaction time. Based on these facts, there is a need to improve the activity and stability of the iron based catalyst at lower loading. Several literatures are available where La_2O_3 has been used as a promoter for Raney type Fe catalysts in methane decomposition [18].

Herein we investigate the performance of co-production of CO_2-free hydrogen and carbon filaments from catalytic decomposition of methane, focusing on the influence of Fe based catalyst promoted with La_2O_3 at a temperature range of 500-800 °C. Follows, a detailed characterization of the iron based catalyst in order to check their activity and the carbon formation properties. Moreover, the effect of reaction temperatures on the activity of 25% Fe/ La_2O_3 will be studied. The stability of 25% Fe/ La_2O_3 catalyst will be tested for one cycle of 360 min and for 6 cycles of 900 min. Catalyst regeneration between cycles will be performed.

Experimental

Catalyst Preparation: Incipient wet-impregnation method was employed to prepare iron (Fe) based catalysts supported over lanthanum oxide

(La_2O_3). In this method, stoichiometric amount of the metal precursor *i.e.*, iron nitrate nonahydrate $[Fe(NO_3)_3.9H_2O]$ was dissolved in a double-distilled water in a crucible under magnetic stirring followed by the addition of the support (La_2O_3). The solution containing active metal and support was kept at 80 °C under constant stirring for 3 h to allow active metal impregnation over support. After the removal of water, impregnated catalysts were placed in the furnace for drying at 120 °C, overnight, followed by 3 h calcination at a temperature of 500 °C.

Catalyst Characterization: Powder X-ray diffraction (XRD) experiments of the catalysts were carried out using a Rigaku (Miniflex) diffractometer. This diffractometer equipped with a Cu Kα radiation operated at 40 kV and 40 mA. The diffractograms were collected between 10-85° and 0.02° respectively. The raw data file of the instrument was analysed by X'pert high score plus software. The peak intensity was measured and ASCI file was generated at granularity 8, bending factor 5, minimum, peak significance 1, minimum, peak width 0.40, maximum tip width 1 and peak base width 2 by minimum second derivatives. Further different phases with their scores were matched JCPDS data bank and X'pert high score plus software.

Brunauer-Emmett-Teller (BET) analysis was performed using Micromeritics Tristar II 3020 surface area and porosity analyser. The specific BET surface area of the catalysts was measured by N_2 adsorption-desorption isotherm on -196 °C. For each analysis, 0.3 g of catalyst was degassed at 300 °C for 3 h to remove moisture content from the catalyst surface as well as other adsorbed gases.

Micromeritics Auto Chem II apparatus was used to study the TPR measurements using 70 mg for each sample. The pre-treatment under high purity Argon flow was carried out at 150 °C for half an hour. Then the samples were cooled. Finally, furnace temperature was raised at 10 °C/min to 1000 °C under 40 mL/min flow rate of H_2/Ar mixture containing 10 Vol.% of H_2. The signal of H_2 consumption was monitored by a thermal conductivity detector (TCD).

The morphology and the composition of the catalysts were investigated using a scanning electron microscope (SEM), JEOL JSM-6360A, coupled to a Si/Li detector for energy-dispersive spectroscopy.

The quantitative analysis of coke deposition after 3 h reaction time over the catalyst's surface was carried out in EXSTAR SII TG/DTA 7300 analyzer

under air ambience. 10-15 mg of the used catalyst was heated from room temperature to 800 °C at a heating rate of 20 °C /min. Changes in weight were recorded during the ramping.

Catalyst Activity: CMD experiments over Fe based catalysts were performed at atmospheric pressure in a vertical stainless steel fixed-bed tubular (9.1 mm i.d. and 30 cm long) micro-reactor (PID Eng. and Tech micro activity reference). The reaction setup used in this study is shown in (Fig. 1). It consists of three main sections: feed gas delivery, catalytic reactor and products analysis section. A typical activity test was conducted over a fixed mass (0.3 g) of catalyst placed onto a quartz wool bed. In order to monitor the actual temperature in the reactor, a K-type stainless steel sheathed thermocouple was placed axially at the center of the catalyst bed. After loading the catalyst, a constant flow of N_2 (20 ml/min) was introduced to the reactor, to purge the moisture, air and other gases from the reactor. Prior to activity tests, the catalysts were subjected to a reduction treatment under a continuous flow of H_2 (40 ml/min) at 500 °C for 90 min. After reduction, the system was again flushed with N_2 about 15 min to purge any residual and physisorbed hydrogen from the reactor. Then, the reactor temperature was increased to the desired reaction temperature (*i.e.*, 700 °C) in the presence of N_2. Once the desired temperature was achieved a feed mixture of pure methane and N_2 gas was fed into the reactor to accomplish the methane decomposition. In a typical test, the volume ratio of the feed gas mixture, *i.e.*, methane/nitrogen was 3/1, whereas the total flow rate was 20 ml/min with a space velocity of 4000 ml/h.g_{cat}. The composition of the outlet gas was analysed online by gas chromatography (SHIMADZU) equipped with a thermal conductivity detector.

CH_4 conversion and hydrogen yield were calculated by using the following formulae:

$$CH_4 \text{ Conversion (\%)} = \frac{CH_{4\,in} - CH_{4\,out}}{CH_{4\,in}} \times 100$$

$$\% \text{ Yield of } H_2 : Y_{H_2} = \frac{\text{moles of hydrogen produced}}{2 \times \text{moles of } CH_4 \text{ in feed}} \times 100$$

Regenerated experiments for methane decomposition over 25% Fe/La₂O₃: The fresh 25% Fe/ La_2O_3 catalyst was tested using the same procedure described in Section 2.4. The catalyst activity was tested at 750 °C for 150 min in each cycle. In the first cycle, after 150 minutes of reaction, the pressure reached 1.8 bars. At this point the reaction stopped and the catalyst was regenerated by introducing 20 ml/min of pure oxygen for 20 minutes

at 800 °C. Then, the system was flushed with N_2 for 10 min to purge any residual and physisorbed gases. After that, the temperature was reduced to 750 °C again and the reaction of methane decomposition for the second cycle was resumed. The same steps were repeated for the five cycles as shown in (Table-1).

Results and Discussion

Catalyst

The surface areas and pore volumes obtained from BET measurements of fresh catalysts and used catalysts in the methane decomposition, for 180 min at 700 °C, are shown in (Table-2). The X-ray diffractograms of the fresh and used catalysts of 25% Fe/ La_2O_3 are shown in (Fig. 2). The fresh catalyst show diffraction lines that correspond to mixed oxide phase Lanthanum orthoferrite ($LaFeO_3$) (JCPDS card no. 00-037-1493), lanthanum oxide (La_2O_3) (JCPDS card no. 00-033-0020), burnt ochre phases (Fe_2O_3) (JCPDS card no. 00-033-0664) are formed chiefly. Maghemite (Fe_2O_3) (JCPDS card no. 00-039-1346), magnetite (Fe_3O_4) (JCPDS card no. 00-019-0629) and is also noticed. XRD for the spent catalyst after one cycle (3 h on stream) of 25% Fe/ La_2O_3 shows that there are two main sharp peaks at 26.3° and around 44° which correspond to (002) and (101) diffraction of hexagonal carbon graphite, respectively according to JCPDS 75-2078 and JCPDS 75-1621 [19].

H_2-TPR was used to investigate the reducibility behavior of the Fe based catalyst. Fig. 3 displays the TPR profile for the Fe based catalyst.. It is clear that there are three main reduction peaks. The Fig. 3 shows low temperature profiles at 224-350 °C, a medium temperature reduction profile in the temperature range 355-470 °C and a broad high temperature reduction profile in the temperature range 470-910 °C. The medium temperature peak can be attributed to the transformation of Fe_2O_3 to Fe_3O_4 and the high temperature peak for transformation of Fe_3O_4 to Fe [11, 20-22].

Fig. 4 shows SEM micrograph of the spent catalyst of 25% Fe/La₂O₃ after 3 h on a stream of methane decomposition at 700 °C. It is clear that carbon filaments have been formed on the catalyst surface with various diameters and lengths. This can be explained by increasing the length of these filaments with time on stream. A Similar result over Fe/Al₂O₃ catalyst was reported by Ibrahim *et al* [11] and over nickel based catalyst by Monnerat *et al* [23].
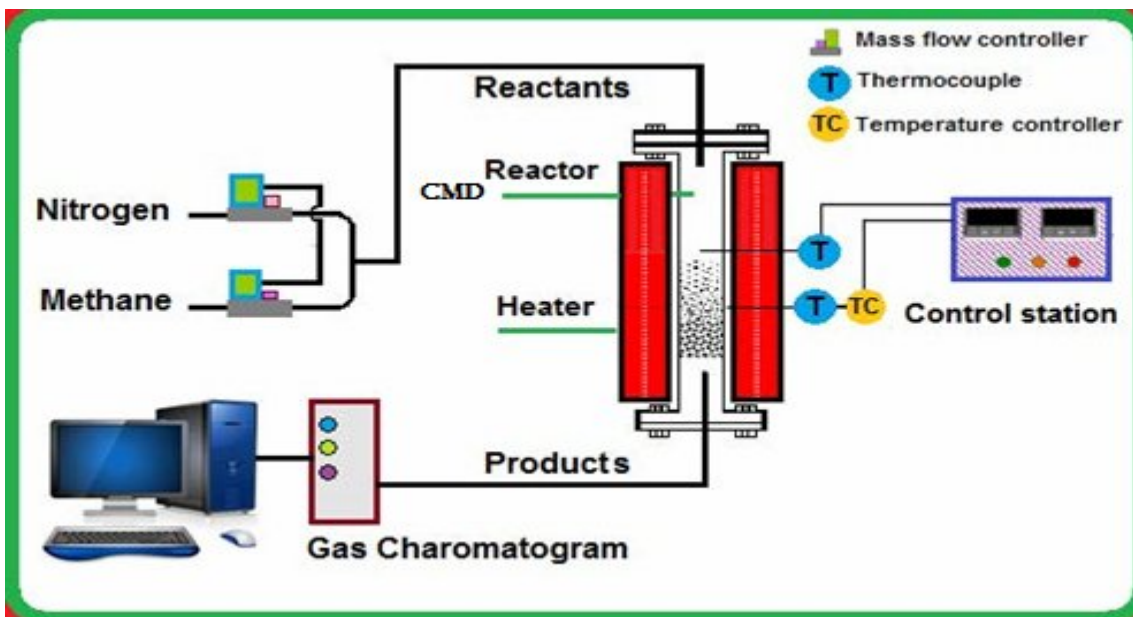
Fig. 1: Schematic diagram of experimental setup for catalytic CH$_4$ decomposition.
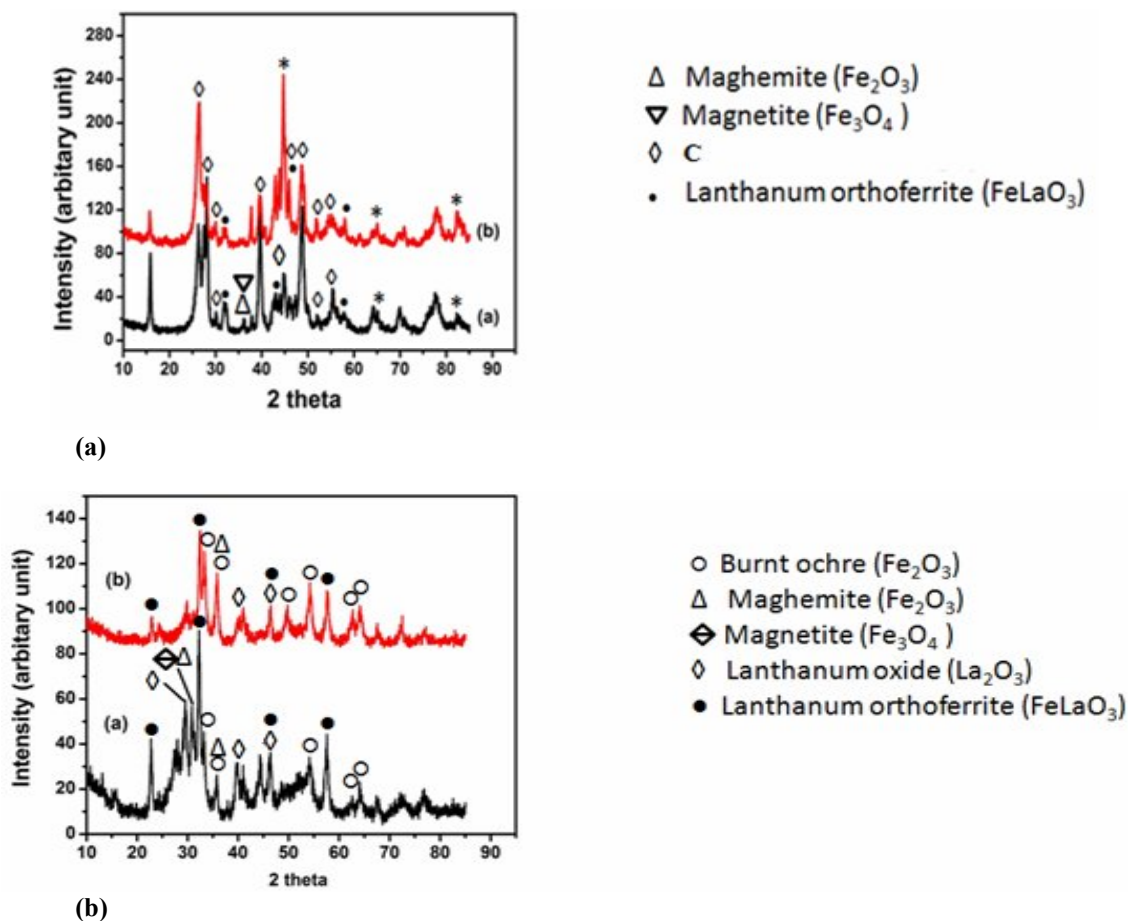

(a)

(b)

Fig. 2: XRD patterns of A) fresh catalyst (a) 25% Fe-La and (b) 60% Fe-La, B) spent catalyst (a) 25% Fe-La and (b) 60% Fe-La.

Table-1: Test cycles of methane decomposition over 25% Fe/ La2O3 catalyst at 750°C with time on stream 150 min in each cycle.

Cycle	Cycle 1 (Fresh)	Cycle 2 (R1)	Cycle 3 (R2)	Cycle 4 (R3)	Cycle 5 (R4)	Cycle 6 (R5)
Pressure after each cycle (bar)	**1.8**	**1.1**	**1.2**	**1.1**	**1.1**	**1.1**

Table 2: Characterisation of the Fe/La2O3 catalysts used for methane decomposition.

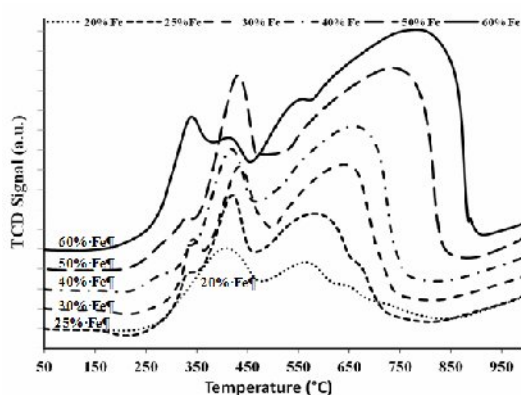| Catalyst	Fresh			Used after 700°C 180 min			TGA
	BET	P.V	P.D	BET	P.V	P.D	Coke % wt. loss
	m^2g^{-1}	cm^3g^{-1}	nm	m^2g^{-1}	cm^3g^{-1}	nm	68.1
25% Fe/La$_2$O$_3$	18.8	0.112	24.72	51.0	0.170	14.41	

Fig. 3: TPR profiles of iron based catalysts.

The carbon filaments formed from methane decomposition in the presence of 25% Fe/ La$_2$O$_3$ catalyst after 3h on stream at 700 °C was characterized by TEM as shown in **(**Fig.4b). It is clear that the carbon filaments have a high degree of heterogeneity with different length and diameter tubes which is in agreement with SEM micrograph. 25% Fe/ La$_2$O$_3$ catalyst is composed of metal particles of different sizes that give rise to carbon filaments of various diameters. The diameters of the carbon filaments range between 14 to 150 nm. The same results were found by Zhang *et al* [24] and Baldissarelli *et al* [25]. Alternatively, the interrelationship between the diameters of the carbon nanotube and the catalyst was demonstrated by Zhang *et al* [24]. The dark spots on TEM micrographs are due to the presence of amorphous carbon and metallic particles attached to the filaments and inside them [25, 26]. Moreover, it can be noticed that carbon formation followed tip-growth mechanism.

A temperature programmed oxidation (TPO) was conducted over the 25% spent catalyst to check the type of carbon filaments produced from methane decomposition at 700 °C for 3 h. In Fig. 5 the concentration of CO_2 is represented against experimental temperature. Clearly, there is a broad main peak for spent catalysts of 25% with a peak maximum of 690 ºC. The broad peak, at high temperature, can be attributed to the formation of carbon filaments [24, 27].

(a)

(b)

(c)
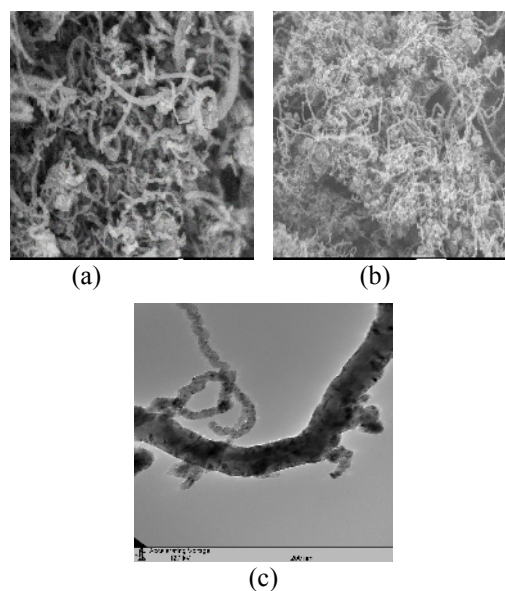
Fig. 4: SEM micrograph of the spent catalyst after 3 h time on stream of methane decomposition at 700 °C on a) 25% Fe/La$_2$O$_3$ catalyst and b) 60% Fe/La$_2$O$_3$ catalyst. c) TEM micrograph of the spent catalyst after 3 h time on stream of methane decomposition at 700 °C on 25% Fe/La$_2$O$_3$ catalyst.
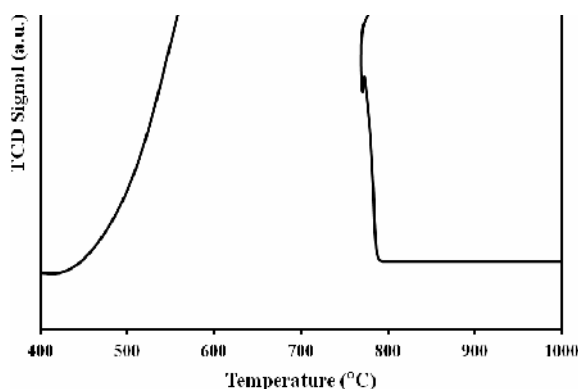
Fig. 5: TPO of spent catalyst after 3 h time on stream of methane decomposition at 700 °C on 25% Fe/La$_2$O$_3$ catalyst.
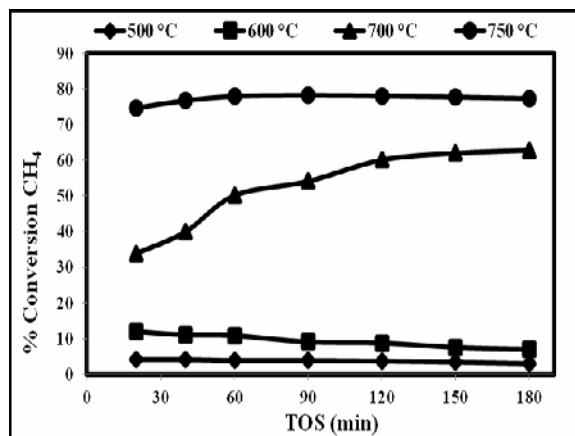
(a)
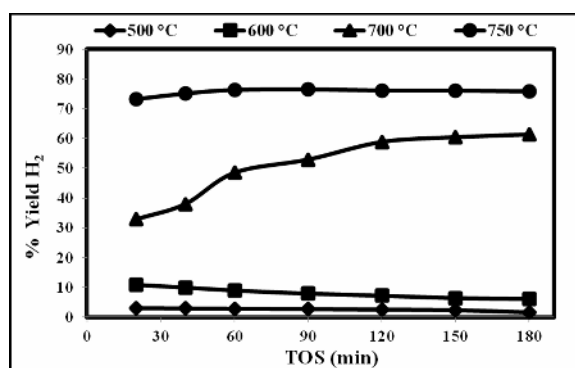
(b)

Fig. 6:   Effect of different reaction temperature on (a) % H_2 Yield, (b) % conversion of methane versus time on stream over 25% Fe/ La_2O_3 catalyst. The catalyst was reduced in H_2 @ 500 °C, catalyst weight: 300 mg, WHSV: 4000 ml g^{-1} h^{-1}.

Catalyst activity testing: Prior to catalytic testing, the reactor was exposed to reaction conditions without catalyst and methane conversion as low as 1% was observed at 800 °C. The effect of temperature on the conversion and the hydrogen yield of methane decomposition over 25% Fe/ La_2O_3 is shown in (Fig. 6). The methane conversion and hydrogen yield of methane decomposition over 25% Fe/ La_2O_3 catalyst was calculated at different time intervals for a total time of 180 min. It is clear that 25% Fe/ La_2O_3 catalyst was highly active with rapid methane decomposition. No CO and CO_2 by-products were noticed in the outlet stream. It can be seen that for all reaction temperatures, the methane conversion and hydrogen yield significantly increased throughout the duration of the experiment. This may be ascribed to the H_2 consumption in the reduction of the Fe_3O_4 to Fe. From TPR profile, Fe_3O_4 was reduced to Fe in the high temperature range of 470-

910 °C and therefore, it can be inferred that the catalyst reduction continued during reaction as well. The same behavior was noticed by Pudukudy *et al* [12]. It is also noticed that the catalyst did not deactivate during the 3 h time on stream. Moreover, the methane conversion and hydrogen yield increased as the temperature was increased. This is attributed to the fact that the methane decomposition is endothermic reaction and therefore as the temperature is increased, the conversion is increased and hence the yield. It can be seen that for reaction temperature of 750 °C the methane conversion didn't increase after 90 min and after that it maintained nearly constant at 78% until 180 min. This can be attributed to that the catalyst reached the equilibrium yield at 800 °C.
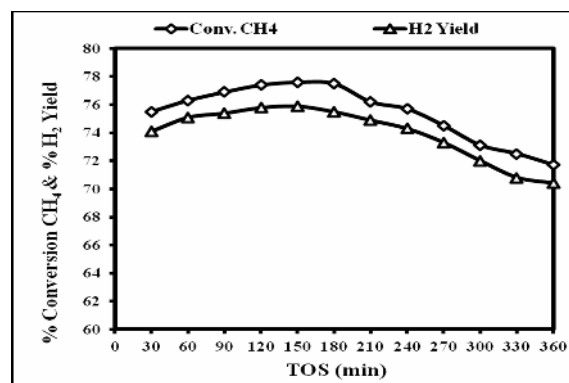

Fig. 7: CH_4 conversion and H_2 Yield versus time on stream for methane decomposition over 25% Fe/La_2O_3 catalyst at 750 °C. The catalyst was reduced in H_2 @ 500 °C, catalyst weight: 300 mg, WHSV: 4000 ml g^{-1} h^{-1}.

To study the stability of 25% Fe/La_2O_3 catalyst, the methane decomposition was studied at 750 °C for 360 min (Fig.7). It is noticed that the methane conversion and H_2 yield decreased from 78.1 to 71.7 and from 75.9 to 70.4 respectively. This slight deactivation could be attributed to the accumulation of carbon filaments on the active sites of the catalyst and the back pressure, which progressively increased to 20 bar at the end of the 360 min [28]. From the above results, it can be concluded that the Fe/La_2O_3 catalyst is a highly active catalyst for methane decomposition. Therefore, to study the stability of 25% Fe/La_2O_3 catalyst for H_2 production from methane decomposition, the catalyst has to be tested for 5 cycles after regeneration as described in Section 2.3.1. Fig. 8 displays that the H_2 Yield was maintained constant up to the second regeneration (R2). After that, it slightly increased in the successive regenerations. A maximum H_2 Yield of 86.6% was obtained in cycle 5 (R5). The 25%

Fe/La$_2$O$_3$ catalyst (in all cycles) showed high stability throughout the 900 min test time duration without any noticeable deactivation in each cycle. Moreover, no gaseous by-product was observed.
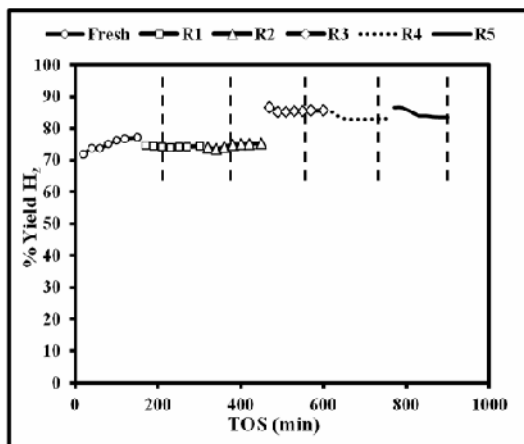

Fig. 8:　H$_2$ Yield versus time on stream for methane decomposition over 25% Fe/La$_2$O$_3$ catalyst at 750 °C for 6 cycles. The catalyst weight: 300 mg, WHSV: 4000 ml g^{-1} h^{-1}.

Conclusion

Iron based catalyst loaded on La$_2$O$_3$ was studied for hydrogen production from catalytic methane decomposition. Under reaction conditions studied in this work, 25% Fe/La$_2$O$_3$ catalyst showed high activity and stability for 5 regenerated cycles. Furthermore, SEM and TEM characterization of the spent catalyst after 3 h on stream for methane decomposition showed formation of carbon filaments with various diameters and lengths. The size of the nanofilaments was influenced by the duration of the time and the size of the active metal. Moreover, 25% Fe/La$_2$O$_3$ catalyst could be considered as a promising catalyst for COx -free hydrogen production from catalytic methane decomposition with high yield of 80% at 750 °C. The deactivation of catalysts during the investigation was partly due to the accumulation of carbon filaments on the active sites of the catalyst and the back pressure, which progressively developed from the deposition of the carbon.

Acknowledgements

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