

Catalytic Decomposition of Methane for Hydrogen Production Using Different Types of Catalysts

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Abstract

The main research objective is to study the hydrogen production and more particularly to examine in details the effect of reaction conditions on the catalytic processing of methane decomposition. The H₂ production were conducted in a quartz tube fixed bed reactor over three kinds of catalysts Fe/AC(Locally prepared), γ -Al₂O₃ and Activated Carbon(AC) (Commercial). The Fe/AC catalyst were prepared by a precipitation method and characterized by BET. The reactions were carried out under atmospheric pressure and at different temperature (800, 850, and 900 °C) with different VHSV(Volumetric Hourly Space Velocity), the outlet sample were measured using H₂ Analyzer. The results exhibit that the highest H₂ Production (26.3 %) was obtained over local AC ,when the CH₄ decomposition was (41.7%) at the following conditions: temperature: 900°C ,VHSV 3.6 and 6.0 l/h g.

Keywords : Hydrogen , Methane Decomposition , Catalyst Preparation.

التفكك المحفز للميثان لانتاج الهيدروجين باستخدام انواع مختلفة من العوامل المساعدة

الخلاصة

ان الهدف الرئيسي من هذا البحث هو لدراسة انتاج الهيدروجين عمليا مع اختبار تأثير ظروف التفاعل على العملية المحفزة لتفكك الميثان. اجريت عملية انتاج الهيدروجين بواسطة انبوب من الكوارتز باستخدام ثلاثة انواع من العامل المساعد Fe/AC (محضر محليا)، γ -Al₂O₃ و الكربون المنشط (تجاري). تم تحضير Fe/AC بطريقة الترسيب ووصفت بواسطة BET لاجاد المساحة السطحية . اجري التفاعل تحت الضغط الجوي وعند درجات حرارة مختلفة (800,850 و 900 م°) مع سرعة مختلفة للغاز في الفضاء لكل حجم(VHSV). النموذج الخارج من العملية تم قياس تركيزه بواسطة جهاز تحليل الهيدروجين.

النتائج اوضحت ان اعلى انتاجية للهيدروجين كانت (26.3 %) باستخدام الكربون المنشط، عندما كانت نسبة تفكك الميثان (41.7 %) عند الظروف التالية : 900 م° ، 3.6 VHSV ، و 6.0 لتر/ساعة.غم .

الكلمات الدالة: الهيدروجين ، تفكك الميثان ، تحضير العامل المساعد .

Introduction

Recently, people show great concern about the climate changes resulting from the emission of greenhouse gases in particular CO₂ and at the same time environmental

friendly energy source is strongly required. Hydrogen is the best choice because its combustion product is H₂O. However, Conventional hydrogen production methods,

such as methane steam reforming and methane partial oxidation, have disadvantages of hydrogen purification because of byproducts of CO, CO₂ and the consequence of CO₂ storage. While the direct thermal decomposition of methane has advantages over other methods because of the simple product of C and H₂ based on which the carbon black production has been industrialized. As it is known, methane is the most stable hydrocarbon having a high decomposition temperature without catalyst. So the activation of methane i.e., hydrogen production by catalytic decomposition of methane has been widely researched^[1].

Nowadays, hydrogen is considered to be one of the most promising alternative energy carriers and clean fuels. As the most abundant element in the universe, hydrogen is not available in elemental form and must be extracted from other compounds at low cost and without harm to the environment (no contamination by CO or CO₂).^[2]

However, the total CO₂ emissions from steam reforming process reach up to 17.5% CO₂ per 76.4% H₂ produced. Thus, the production of pure hydrogen from fossil fuels, in particular natural gas (NG), the main component being methane (CH₄), has great practical importance^[3].

Hydrogen will become a renewable and sustainable energy carrier of the future. Also the hydrogen is conventionally produced from steam reforming, partial oxidation or auto thermal reforming of hydrocarbons and alcohols^[4]. Worldwide statistics show that nearly 48% of hydrogen is produced from natural gas, 30% from petroleum, and 18% from coal, while only 4% of the hydrogen produced is obtained through water electrolysis. This high contribution of NG for the production of hydrogen is due to the fact that there are large methane reserves available in deep ocean beds or in some industrialized countries like the United States.

Approximately 49% of hydrogen produced is used for the manufacture of ammonia, 37% for petroleum refining, 8% for methanol production and about 6% for miscellaneous smaller-volume uses^[5]. In

addition to hydrogen as a major product, the hydrocarbon decomposition process produces a very valuable co-product, the carbon nanotube (CNT), considered a novel promising material for various technological applications. In recent years, filaments and nanotubes of various types have been synthesized and textural and adsorptive properties of this material, as well as kinetics and thermodynamics of formation over different catalysts, have been studied. Transition metals such as Fe, Co and Ni are well known to be effective for methane decomposition into hydrogen and carbon nanofibers. The nickel-based catalysts are active at low temperatures and provide a higher yield of CNT per mass unit of the active component^[6].

None catalytic thermal decomposition of methane requires quite a high temperature (1500–2000 K) in order to obtain a reasonable hydrogen yield. If the heat is supplied by burning a fossil fuel, overall CO₂ emission may not be reduced Corresponding author significantly. When concentrated solar–thermal energy is used, the CO₂ emission will be considerably reduced^[7]. The catalysts used in these researches are mostly based on transition metal such as Ni, Fe, Co etc., which show remarkable activity. Metal and carbonaceous catalysts have been widely used to reduce the methane decomposition temperature^[8].

Experimental Work

Different kinds of catalysts (AC, Fe/AC, and γ -Al₂O₃) were employed in methane decomposition. Fe/AC prepared locally by precipitation method. The characterization of catalysts are shown below in table (2.1). Methane (99.99%) with Argon (95.5) were used directly without further purification. The decomposition reaction was carried out in a quartz tube fixed bed reactor (1.5 cm inside diameter, 60 cm length and 1.2 mm wall thickness ,with a catalyst bed length of 20 cm) heated by an electric furnace. Fig.(1) illustrates the experimental setup.

The experiments were conducted at temperature ranges from 800 to 900 °C and the VHSV was from 3.6 to 6.0 l/ h g. Before introducing the reactant gas, the system was

heated up to the set temperature under Ar. All experiments were conducted at atmospheric pressure. The outflow gas was analyzed by H₂ Portable Analyzer (HITECH INSTRUMENT).

Catalyst preparation

Fe/AC (Locally prepared)

100 mg of Fe/AC catalyst with 2.1% of Fe was prepared. The activated carbon (Commercial) was impregnated with 1.25 g Ferric nitrate(FeNO₃)₃.9H₂O dissolved in 50 ml deionized water. The impregnated activated carbon is dried with air at 110°C overnight then calcinated at 200°C for 8 h with air and placed in a desicator..

Catalyst Characterization

The BET surface area of the catalyst was measured by N₂ adsorption at liquid nitrogen temperature of -196 °C using Varlo-Eroba Sorptomic(Series 1800).The metal elemental composition of the catalysts was determined by Atomic Absorption Spectrophotometer (PHONIX 986) .

Results and Discussion

Catalysts activities

Catalytic activity runs were performed in a quartz tube fixed bed reactor over different types of catalysts. All the experiments were carried out at similar conditions with Weight hourly space velocity of 3.6 l/h g. Figs. (2, and 3) represent the change in methane conversion and Hydrogen production as a functions of operating time over various types of catalysts at a temperature of 900 °C respectively. AC catalyst show high initial activity followed by a smooth decrease until the steady state because of the deactivation behavior of catalysts which was apparently due to the carbon deposition into the pores of the ACs produced by methane decomposition; were in good agreement with earlier reports^[3].

Effect of Temperature

The influences of temperature on methane conversion over AC, Fe/AC, and γ -Al₂O₃ are presented in Figs. (4,5,6 and 7). As can be seen, the initial rates of methane decomposition over the catalysts increase, this was because the methane decomposition is an endothermic reaction. However, a change was observed in the decaying rate of the catalytic activity as temperature

increases. In three types of catalysts a soft decaying rate of methane conversion is observed at low temperature i.e., 800 °C, whereas a rapid fall in methane conversion is observed at higher temperature ,which is especially apparent at 900 °C, agreed with^[9].

Effect of VHSV

Fig.(8) that shows percent methane conversion was strongly depend by an volumetric hourly space velocity (VHSV), whereas can be seen from Fig.(8), exhibit an initial methane conversion over AC at 900 °C was 41.7% with VSHV of 3.6 l/h g, but this percent decreases to 32.4% at same conditions bating VHSV of 6 l/h g. In all cases, the curves showed a gradual decrease in the methane conversion, indicating a progressive catalyst deactivation. Thus, it is clear that space velocity has a principal role in the CH₄ decomposition reaction due to its effect on the gas-solid contact. Agreed with^[10].

Conclusions

In summary, the test of the performance of the catalysts (AC, Fe/AC, and γ -Al₂O₃ on methane decomposition to produce the hydrogen (at 900 °C and VHSV= 3.6 l/h g), shows that the AC give the highest yield of H₂ than Fe/AC and γ -Al₂O₃. Also the decomposition of CH₄ increased with increasing of the temp. and decreasing VHSV.

References

1. Choudhary T.V., Sivadinarayana C., Chusuei C.C., Klinghoffer A., Goodman D.W.,Catal.199(2001) 9.
2. MuradovN. Catalysis of methane decomposition over elemental carbon. Catal Commun 2001;2:89–94.
3. Moliner R., Suelves I., Lazaro M.J., Moreno O., Int. J. Hydrogen Energ. 30 (2005) 293.
4. Thomas C.E., James B.D., Lomax F.D., Kuhn I.F., Int. J. Hydrogen D.W. Goodman, J. Catal. 199 (2001)9.
5. Stiegel GJ, Ramezan M. Hydrogen from coal gasification: an economical pathway to a sustainable energy future. Int J Coal Geol 2006;65:173–90.

6. Wang H.Y., Ruckenstein E., Carbon 40 (2002) 1911–1917.
7. Dahl J, Buechler K, Finley R, Tanislaus T, Weimer A, Lewandowski A, Bingham C, Smeets A, Schneider A. Rapid solar–thermal dissociation of natural gas in an aerosol Kow reactor. 11th Solar PACES International Symposium Concentrated Solar Power and Chemical Energy Technology, Zurich, 2002. p. 223–30.
8. Suelves I, La'zaro MJ, Moliner R, Corbella BM, Palacios JM. Hydrogen production by thermo-catalytic decomposition of methane on Ni-based catalysts: influence of operating conditions on catalyst deactivation and carbon characteristics. Int J Hydrogen Energy 2005;30:1555–67.
9. Kim M.H., Lee E.K., Jun J.H., Han G.Y., Lee B.K., Lee T.J., Yoon K.J., Int. J. Hydrogen Energy 29 (2004) 187.
10. Lee K K, Han G Y, Yoon K J, Lee B K. *Catal Today*, 2004,93-95: 81

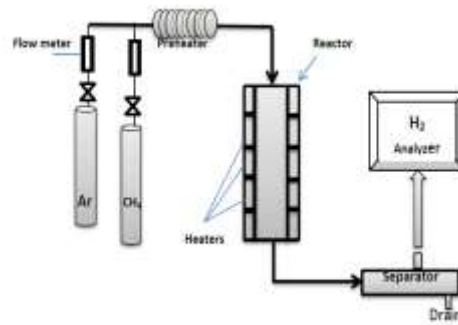


Fig. (1) Experimental setup for the Hydrogen production

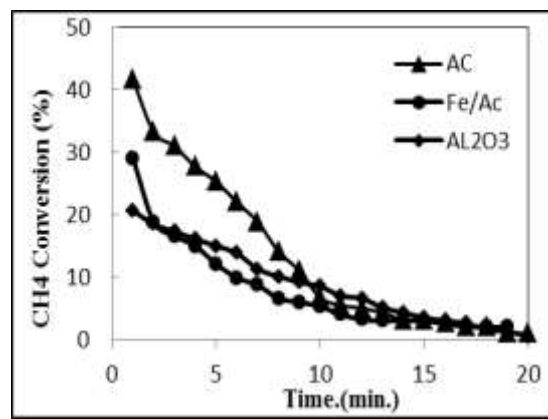


Fig.(2) Catalysts activity for H₄ decomposition, at temp. : 900 °C, VHSV= 3.6 l/h g

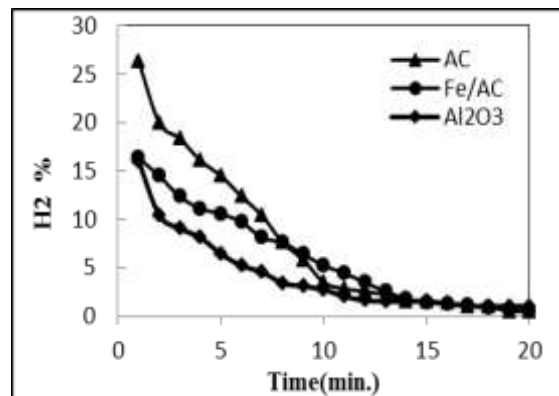


Fig.(3) Catalysts activity for H₂ production, at temp. : 900 °C, VHSV= 3.6 l/h g

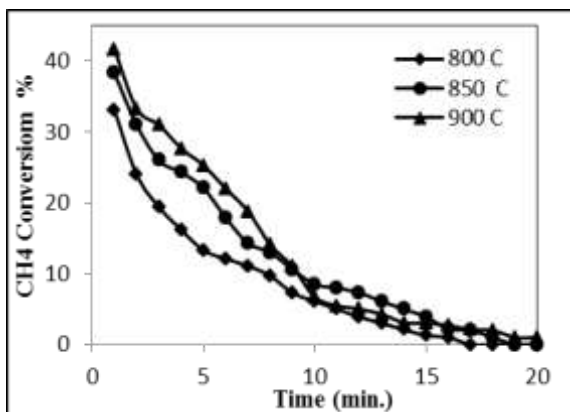


Fig.(4) Methane decomposition over AC, at various temperatures and VHSV= 3.6 l/h g

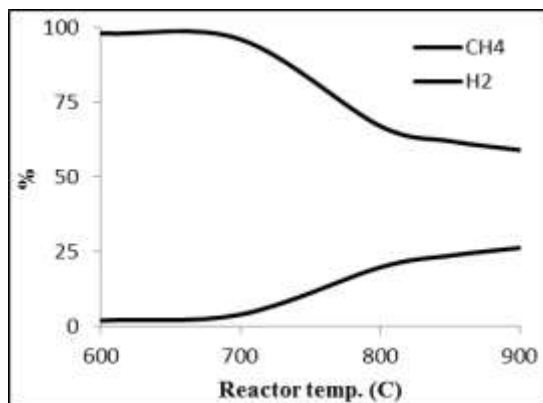


Fig.(7) Effect of temp. on CH₄ decomposition and H₂ production

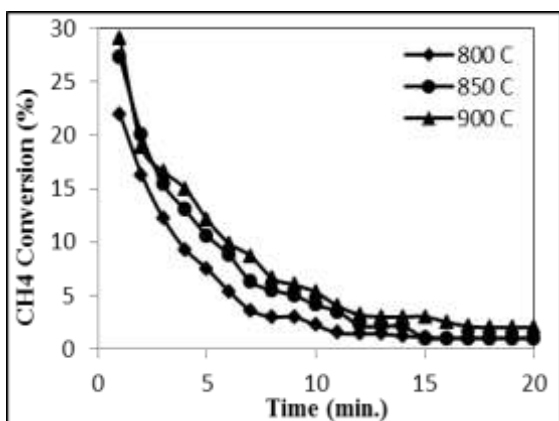


Fig.(5) Methane decomposition over Fe/AC (2.1% Fe), at various temperatures and VHSV=3.6 l/h g

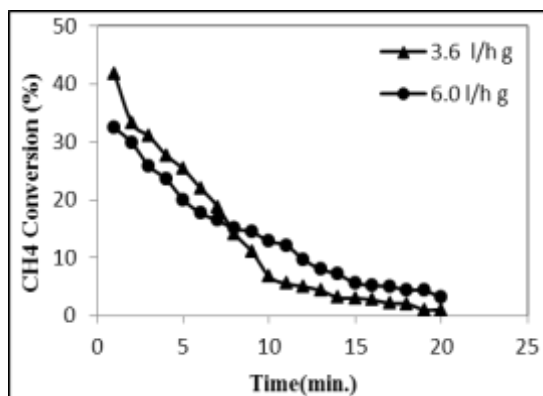


Fig.(8) Methane decomposition over AC at 900 °C with various VHSV

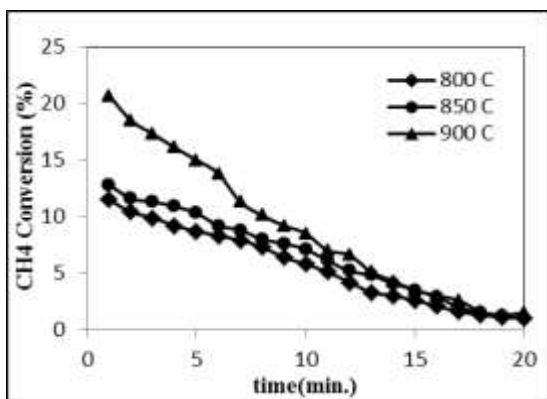


Fig.(6) Methane decomposition over γ -Al₂O₃ at various temp. and VHSV= 3.6 l/h g

Table(1):Catalysts characterization

Catalyst	γ -Al ₂ O ₃	AC	Fe/AC
Pore volume, cm ³ /g	0.364	0.434	0.375
Bulk density, g/cm ³	0.577	0.742	0.822
Surface area, m ² /g	289	974	890
Particle diameter, mm	1.6	0.3-0.7	0.3-0.7
Particle shape	Spherical	Granular	Granular
Production	Commercial	Commercial	Locally prepared