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Application of Aerosol Nanocatalysis Technology in Methane Steam Reforming

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Abstract

Steam Methane Reforming (SMR) is the main method to obtain synthesis gas in production of alcohol, ammonia, acids Fischer-Tropsch synthesis and other organic products. The study has investigated the reaction of SMR and it mechanism, explained the aerosol nanocatalysis (AnC) vibrated bed as alternative technology instead of using heterogeneous catalyst in bed. The research has proven that NiO is the best catalyst that could be used in the reaction of SMR by AnC after investigating catalysts: Fe_2O_3, K-905D2, GIAP-8, Co_2O_3 and NiO.

Introduction

Synthesis gas (syngas) is a gaseous mixture containing mainly hydrogen, carbon monoxide, and carbon dioxide in various amounts [1]. It could be defined in other resources such as [2], [3] and [4] as only mixture of hydrogen and carbon monoxide without carbon dioxide. In most cases, these three compounds constitute more than 90% of the syngas, but other components including methane and inert gases such as nitrogen and argon are often present in the mixture. In recent years, new areas have emerged that may open the way for an increased production and use of synthesis gas. One example is the large-scale production of syngas using synthetic hydrocarbon fuels, produced by the Fischer–Tropsch synthesis. Similarly, a considerable effort is currently being undertaken in the development and commercialization of various types of fuel cells for both small- and large-scale power productions [1].

Syngas are indispensable in chemical, oil, and energy industries. They are important building blocks and serve as feedstocks for the production of chemicals such as ammonia and methanol. Hydrogen is used in petroleum refineries to produce clean transportation fuels, and its consumption is expected to increase dramatically in the near future as refiners need to process increasingly heavier and sour crudes [4].

Natural gas is the largest source of syngas at present and its use for this purpose is growing. Methane is the chief constituent by far of natural gas. Petroleum fractions are the next largest syngas source at present and significant quantities of syngas are being made from coal[2].

Methane conversion is the main industrial method to obtain syngas for ammonia production, alcohol, acids, Fischer–Tropsch synthesis and other products. There are several ways of conversion: aerial, steam aerial, oxygenous, steam oxidation of methane…etc [5].

Natural gas is an odorless and colorless naturally occurring mixture of hydrocarbon and nonhydrocarbon gases found in porous geologic formations beneath the earth's surface, often in association with petroleum or coal. The principal constituent is methane (CH_4) and its composition is regionally dependent. In Iraq the composition of natural gas as the following: Methane 55.7%, Ethane 21.9%, propane 6.5%, H_2S 7.3%, and CO_2 3% [4].

Methane reacts with steam in the presence of a supported nickel catalyst to produce a mixture of CO and H_2 , also known as synthesis gas or syngas as represented by Equation (1) . This reaction is also referred to as steam methane reforming (SMR) and is a widely practiced technology for industrial production of H_2 . However, the SMR is not really just one reaction as indicated in Equation (1) but involves contributions from several different catalyzed reactions such as water - gas shift (WGS), reverse water - gas shift (RWGS), CO disproportionation (Boudouard reaction), and methane decomposition reactions as described in Equations 2 –5 :

$$CH_4(g)+H_2O(g)\rightarrow 3H_2(g)+CO(g) \qquad \Delta H^{\circ}_{298}=+205.9\ \mathrm{kJ/mol}, \qquad (1)$$

$$CO(g)+H_2O(g)\rightarrow CO_2(g)+H_2(g) \qquad \Delta H^{\circ}_{298}=-41\ \mathrm{kJ/mol}, \qquad (2)$$

$$2CO(g)\rightarrow CO_2(g)+C \qquad \Delta H^{\circ}_{298}=-172.4\ \mathrm{kJ/mol}, \qquad (3)$$

$$CH_4(g)\rightarrow C+2H_2(g) \qquad \Delta H^{\circ}_{298}=+74.6\ \mathrm{kJ/mol}, \qquad (4)$$

$$C+H_2O(g)\rightarrow CO+H_2(g) \qquad \Delta H^{\circ}_{298}=+131.3\ \mathrm{kJ/mol}, \qquad (5)$$

$$CO(g)+0.5O_2(g)\rightarrow CO_2(g) \qquad \Delta H^{\circ}_{298}=-283\ \mathrm{kJ/mol}, \qquad (6)$$

$$CO(g)+3H_2(g)\rightarrow CH_4(g)+H_2O(g) \qquad \Delta H^{\circ}_{298}=-205.9\ \mathrm{kJ/mol}. \qquad (7)$$

The process carries out in the pipe oven with heating and heterogenic catalyst. The properties of catalyst show the effect on productivity of pipe oven and its lifetime. This phase is one of the most expensive with high energy in modern technological schemes [6].

The mechanism of SMR reaction with catalyst can be expressed by the following [5]:

1. $CH_4 + Z \leftrightarrow Z\text{--}C^{\bullet}H_2^{\bullet} + H_2$
2. $Z\text{--}C^{\bullet}H_2^{\bullet} + H_2O \leftrightarrow Z\text{--}CO + 2H_2$
3. $Z\text{--}CO \leftrightarrow Z + CO$
4. $H_2O + Z \leftrightarrow Z\text{--}O + H_2$
5. $CO + Z\text{--}O \leftrightarrow CO_2 + Z$

Z – Active site of catalyst surface, $Z\text{--}C^{\bullet}H_2^{\bullet}$, Z--CO, Z--O chemisorptions of $C^{\bullet}H_2^{\bullet}$, CO and O- the first accepted stage for limited process

This research investigates the SMR using the technology of aerosol nanocatalysis (AnC). AnC is the effective direction in chemical technology field, as it allows us to obtain super active catalysts in virtue of permanent mechanical-chemical activation (mech-chem activation) on the surface of catalyst particles in situ, which allows us to yield nanoparticles from microparticles (powder of catalyst) after catalyst fragmentation by dispersed material (glass or ferrous bullets)[7]. The nanoparticles that formed during the process of mech-chem activation could be listed in top-down formation's nanotechnology by milling [8] the powder of catalyst inside the laboratory reactor. The size of nanoparticles that has been obtained is 8-100 nanometers according to Transmission Electronic Microscopy (TEM) method. Figure (1) illustrates the particle that obtained during the permanent mech-chem activation on the surface of catalyst.

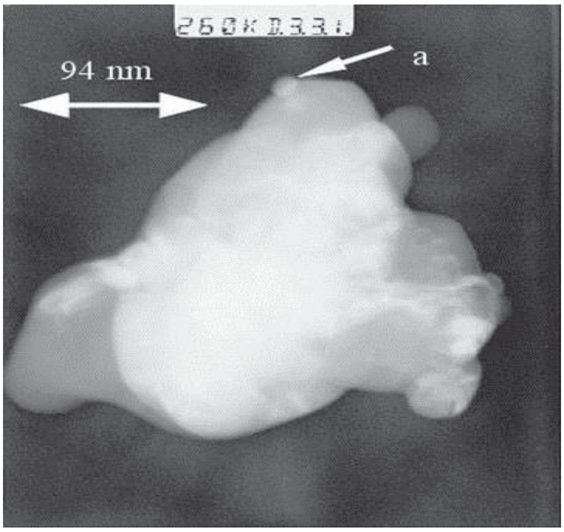
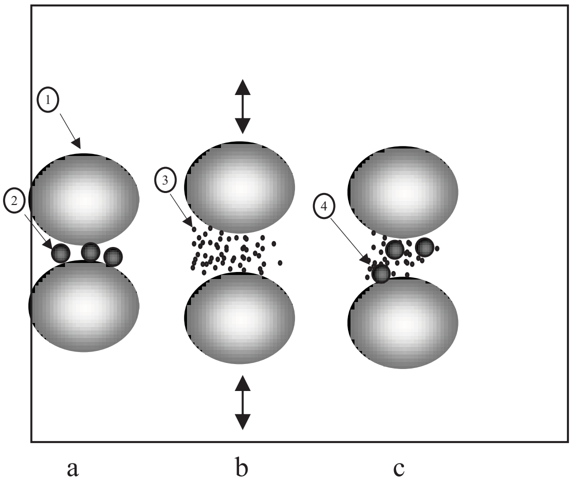


Fig. (1) The image of particle, has obtained by TEM

Nanoparticle defined as a small object that behaves as a whole unit in terms of its transport and properties. Particles are further classified according to size: in terms of diameter, fine particles cover a range between 100 and 2500 nanometers. On the other hand, ultrafine particles are sized between 1 and 100 nanometers [9].

In AnC technology, the catalytic system consists of glass bullets (d = 1.1 mm) that could be represents as a dispersed material and powder of catalyst (size for about 5×10^{-5} m). During vibration process appears catalyst abrasion till size of 10^{-7}-10^{-9}m. The changing of catalytic system structure is illustrated in the figure (2). As it has shown in (figure. 2 a) the catalytic system (without mechanical action (vibration)) is inert material and catalyst microparticles, under the vibration over the system appears fragmentation of catalyst by inert material to nanoparticles (figure.2.b). In the absence of mechanical action with determined time the nanoparticles would be suffering from agglomeration (figure2.c)[10]



Fi.(2) The changing of catalytic system in AnC by the time 1. Dispersed material, 2. Catalyst microparticles, 3. Catalyst nanoparticles 4. Agglomeration of catalyst particles.

Experimental

The aim of the research is: Using AnC technology vibrating bed to obtain economic and technological effectiveness method for syngas production. Figure (3) illustrates scheme of experimental setup for investigation of AnC technology by vibrated bed. Reactor (no. 3 in figure) is a cylindrical apparatus, works in the regime of mixing or milling. It performs reflexive-progressive motion through a vertical plane in electric furnace (2). The reactor has been designed to vibrate in diapason from 2 to 11 Hz. Reactor has branch pipes for inlet substances, outlet products of reaction, also pouch for thermocouple (11) which connected to control unit(1).

Catalytic system (particles of catalyst and dispersed material) is added to reactor before the experiment starts working. Their motions provide mech-chem activation on catalyst surface.

Water feed can be flow by dosator [9] or evaporator [10] or both of them. Particularity of this reactor is a filter [5] which been made from metal or specific net in order to retain the particles of catalyst and dispersed material. Thereby, the quantity of catalyst stays without changing after experiment.

By permanent vibration on the surface of catalyst, it would expose to mechanical influence of inert vibrated material. It is dispersed, arisen defect of structure, is changed properties of surface which determines its activity. In the reactor is added 0.0001 gm of catalyst which represents 2.38 gm/m^3 of reactor. Its easy to vary of quantity of catalyst, and change the substances. The technology of AnC has allowed obtaining syngas at temperature interval 600-800°C. The catalysts: Fe_2O_3, K-902 D2 (8-10% NiO, 0.01% SO_3), GIAP-8 (Ni-Al_2O_3), Co_2O_3 and NiO are investigated using different parameters (for example temperature change, vibration, rate of reactants).

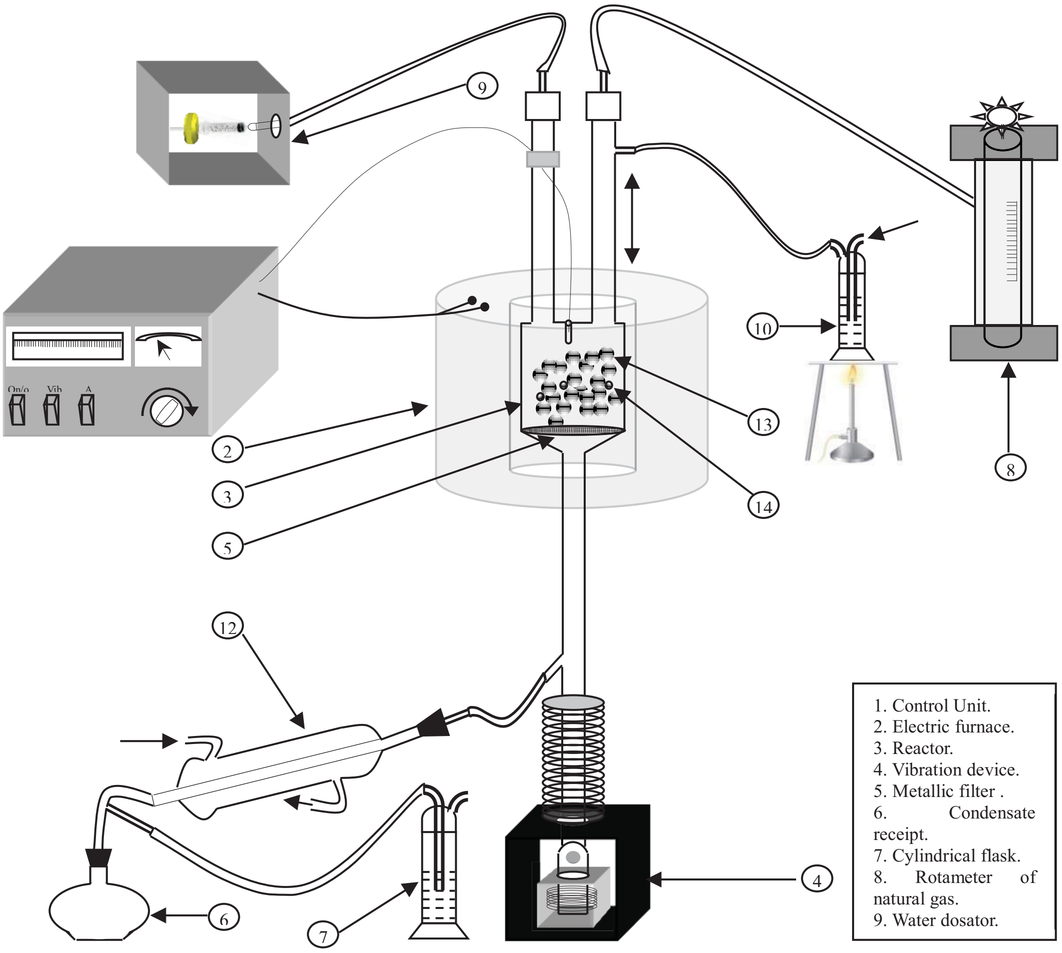


Fig. (3) Experimental set up of AnC technology vibrated bed

Analysis of SMR products

Chromatographer is used for products of SMR with chromatographic column filled with zeolite 5A. The conditions of chromatographic analysis to determine CH_4, CO, CO_2, and hydrogen are shown in Table (1)

Parameters	**Value**
CH_4, CO, CO_2	
Column, mm	1000
Diameter of Column, mm	4
Temperature of thermostat °C	50-180
Rate of temperature lifting °C/min	15
Detector's current mA	110
Rate of carrier gas (helium) ml/min	80
Rate of diagram tape's movements mm/min	10
Hydrogen	
Column, mm	1000
Diameter of Column, mm	4
Temperature of thermostat °C	50
Detector's current mA	110
Rate of carrier gas (nitrogen) ml/min	30
Rate of diagram tape's movements mm/min	10

The other parameters of chromatographic analysis could be determined in the preliminary calibration of chromatographer.

It's been investigated the following powder of catalysts in the reactor and their activities to do the reaction of SMR: Fe_2O_3, K-902 D2 (8-10% NiO, 0.01% SO_3), GIAP-8 (Ni-Al_2O_3), Co_2O_3 and NiO:

Table (1): Result of experimental research of SMR using Fe_2O_3 catalyst Volume rate of natural gas 18 l/h, volume rate of H_2O 0.02 l/h, frequency of bed: 8 Hz (vibration), Volume of glass bubbles in reactor: 20 cm^3, volume of glass bubble: 1.2 mm, mass of catalyst: 0.0001 gm, Concentration of catalyst in reactor 2.38 gm/m^3

№	T °C	Products of outlet, %vol.				H_2:CO (mol)	Degree of carbon conversion, %
		H_2	CO	CO_2	CH_4		
1	550	0.057	-		2.7	-	0.01
2	600	0.091	1.154	-	77.5	1/12	0.02
3	700	1.31	-	-	96.6	-	0.2
4	700	1.57	-	-	97.44	-	0.23
5	750	1.32	3.08	-	68.38	1/2.3	0.19
6	750	4.56	-	-	94.01	-	0.9

As its been shown in table No. 1, the results of products in %vol are not stable with a little H_2 in addition to that in rows No. 2 and No. 5 the %vol of CO is greater than H_2 and this is not compatible with the reaction of SMR that gives 3 mole of H_2 and only 1 mole of CO. therefore it could be determine that the catalyst of Fe_2O_3 couldn't not be used in SMR reaction by technology of aerosol nanocatalysis.

Table (2) Result of experimental research of SMR using K-905 D2 catalyst Volume rate of natural gas 18 l/h, volume rate of H2O 0.02 l/h, frequency of bed: 8 Hz (vibration), Volume of glass bubbles in reactor: 20 cm3, volume of glass bubble: 1.2 mm, mass of catalyst: 0.0001 gm, Concentration of catalyst in reactor 2.38 gm/m3

№	T °C	Products of outlet, %vol.				H_2:CO (mol)	Degree of carbon conversion, %
		H_2	CO	CO_2	CH_4		
1	600	0.42	-	-	94.01	-	0.02
2	600	0.9	-	-	96.6	-	0.04
3	650	0.26	-	-	94	-	0.01
4	700	0.74	-	-	72.6	-	0.03
5	750	1.32	3.08	-	68.38	1:2.3	0.14
6	750	6.3	-	-	89.7	-	0.9

K-905 D2 catalyst didn't give the reasonable results, this is what been shown in table No. 2, and its guide us to say after investigation that the catalyst of K-905 D2 couldn't not be used in SMR reaction by technology of aerosol nanocatalysis.

Table (3) Result of experimental research of SMR using Co_2O_3 catalystFrequency of bed: 8 Hz (vibration), Volume of glass bubbles in reactor: 20 cm^3, Temperature: 600 °C volume of glass bubble: 1.2 mm, mass of catalyst: 0.0001 gm, Concentration of catalyst in reactor 2.38 gm/m^3

№	Volume rate l/h		Vapor:gas (мol.)	τ,s	Products of outlet, %vol.				H_2:CO (mol)	Degree of carbon conversion, %
	Natural gas	Vapor			H_2	CO	CO_2	CH_4		
1	1.17	7.47	6.4	3.95	7.1	0	1.27	86.22	-	1.37
2	1.17	7.47	6.4	3.95	41.12	9.26	3.29	38.83	0.12	20.92
3	1.17	4.5	3.9	6.06	48.97	0	0.82	47.08	-	12.1
4	1.17	4.5	3.9	6.06	1.0	7.71	6.57	98.03	0.13	12.11
5	1.17	4.5	3.9	6.06	45.47	0	0.34	49.46	-	11.8

Its obviously that the results of Co_2O_3 catalyst better than previous catalysts that has been used, but still not stable, therefore this catalyst couldn't not be used in SMR reaction by technology of aerosol nanocatalysis.

Table (4) Result of experimental research of SMR using NiO catalystVolume of glass bubbles in reactor: 20 cm^3, mass of catalyst: 0.0001 gm Concentration of catalyst in reactor 2.38 gm/m^3

№	T,°C	f, Hz	Volume rate l/h		vapor/ gas (mol)	τ,s	Products of outlet, %vol.				H_2/CO (mol)	Degree of carbon conversion, %
			Natural gas	vapor			H_2	CO	CO_2	CH_4		
1	600	3	1.17	4.5	3.9	6.1	19.98	3.09	25.47	18.47	3.09	59.3
2	600	3	1.17	7.47	6.4	6.1	1.55	0	9.56	9.41	-	50.4
3	650	3	1.1	2.6	2.35	5.8	13.41	16.2	8.31	41.37	1.5	58.17
4	650	3	1.1	2.6	2.35	5.8	23.29	8.78	6.55	61.39	2.9	55.10
5	650	3	2.5	2.6	1.04	6.5	10.31	0	1.18	86.33	-	12.54
6	650	3	1.12	2.6	1.67	22	15.97	5.2	0	16.48	3.1	24.0
7	700	3	1.47	2.6	1.78	7.6	10.67	0	0.36	56.09	-	10.49
8	700	3	1.14	2.6	2.3	8.2	26.23	0.51	1.86	58.01	51.4	3.38
9	700	3	2.54	2.6	1.03	6.1	3.73	12.83	4.7	77.4	0.29	17.87
10	700	3	1.55	2.6	1.68	7.5	12.07	2.95	2.91	78.6	4.1	6.42
11	700	4	0.72	2.6	3.63	9.2	18.89	7.71	3.36	57.58	2.45	11.45
12	700	4	1.47	2.6	1.78	2.8	23.49	0.35	1.68	53.38	50	12.97
13	700	4	1.14	2.6	2.3	8.2	13.04	0.46	1.94	6.51	28.3	12.8
14	700	4	1.0	2.6	2.6	8.6	22.86	1.03	6.88	49.41	22.2	12.51
15	700	3	3.5	7.47	2.1	2.8	5.88	0	1.82	52.92	-	2.14

As its been shown in table no. 4, Its been found that NiO is the best catalyst which could be used in the technology of aerosol nanocatalysis, especially in row no. 1, 3, 4, 6, 10 and 11 using temperature 600 and 650 °C.

Conclusions

The research has shown the possibility to Apply the aerosol nanocatalysis vibrated bed as alternative technology in Methane steam reforming and it could be effective at 650 °C. Its very flexible to use the experimental setup and parameters changing such as temperature, vibration, volume rate…etc. NiO catalyst is an effective catalyst of methane steam reforming using AnC.

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