Petroleum and Coal

IMPROVEMENT OF METHANE DECOMPOSITION OVER A NI BASE CATALYST: PREPARATION, COMPARISON AND PERFORMANCE STUDY

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Abstract

The catalytic decomposition of methane (CDM) is investigated with a homemade nickel cobalt loaded on alumina (γ-Al_2O_3) catalyst for the production of COx-free hydrogen in a fixed bed reactor under moderate operating conditions (temperature from 773-873 K, atmospheric pressure, LHSV from 1 to 3 hr^{-1}, methane concentration from 70-90%). The catalyst is prepared using Co-Incipient Wetness Impregnation method (CIWI) of cobalt oxide and nickel oxide over gamma alumina (10% NiO-4%Co_3O_4/γ-Al_2O_3). The performance of the homemade catalyst is compared with a commercial 12% Ni-SiO_2/γ-Al_2O_3catalysts, The optimal design of experiments is studied to evaluate the effects of individual process variable such as, reaction temperature, concentration of methane and type of catalyst, their optimal values were found to be 813K, 90% and 10% NiO-4%Co_3O_4/γ-Al_2O_3 respectively. For conversion methane to pure hydrogen, the results indicates that the Co-Incipient Wetness Impregnation (CIWI) is suitable to prepare this type of the catalyst. Based on the experiments, kinetic models that represent a fixed bed reactor for describing the behavior of the CDM process are developed.

Keywords: Methane Decomposition; COx-Free Hydrogen; Ni Catalyst; Optimization.

1. Introduction

Methane can be thermally or thermocatalytically decomposed into carbon and hydrogen without producing CO_2, and this hydrogen production method has recently attracted the attentions of researchers [1].

Because the non-catalytic thermal cracking of methane requires a temperature higher than 1200°C to obtain a reasonable yield, metal and carbonaceous materials have been used as catalysts to reduce the methane cracking temperature [2]. Temperature, low space velocity, and high Ni loading enhanced the hydrogen concentration in the outlet gases. Additionally, SEM and TEM observations indicate that the size (diameter) distribution of the as-prepared became broader with increasing reaction temperature and Ni loading, respectively [3]. The CDM is shown possible to obtain in a single step both CO_2-free hydrogen and carbon nano-structures with a wide range of applications such as nano-composite reinforcements [4]. TCD of methane on Ni and Ni–Cu catalyst to produce hydrogen and novel carbon materials was first reported by Muradov [5] and Parmon *et al.* [6]. Although different metals are have been used in CDM such as Co [7-9], Fe [10] and mixed oxides [11-13]. However, most of the studies are conducted on Ni catalyst [9,14-18].

Simultaneous production of carbon nanofibers and methane conversion of 70% has been reported [19] using a Ni catalyst doped with Cu at higher temperature (1073 K). Production of carbon nano-tubes using bimetallic catalysts Fe–M (M = Pd, Mo, Ni) has been reported [20]. Production of filamentous carbon using ultra-high temperature solar reactors has been reported [21-22].

Ermakova [23] had extended those works by direct cracking of methane to produce hydrogen and filamentous carbon using very high concentration (up to 90 wt %) Ni catalysts. However, methane conversion was quite low -8% at 773 K, 15% at 823 K, and complete deactivation at 873 K. Li *et al.* [24] have also used high (>50 wt %) Ni catalysts prepared from hydrotalcite-like (HC) structure by co-precipitating mixed aqueous solution of nickel nitrate with Na_2CO_3 for production of hydrogen and nano-carbon from decomposition of methane and the maximum conversion of methane obtained was less than 70% at 1000K. This work contributes to a growing understanding of CDM to enhance methane conversion by using a novel catalyst design to produce hydrogen at mild conditions. The CDM reaction over two catalysts, commercial 12% $Ni-SiO_2/Al_2O_3$ and 10% $NiO-4\%Co_3O_4/\gamma-Al_2O_3$ catalyst prepared experimentally in-house, is studied to determine the methane conversion as well as to highlight operating issues that must be resolved in order to develop an industrially viable process.

2. Material and methods

2.1. Material

A. Commercial catalyst (CAT-1)

One commercial catalyst is used through the present work, $Ni-SiO_2/\gamma-Al_2O_3$, from UNICAT Catalyst Technologies Inc., the catalyst is obtained from to Northern Fertilizers State Company (NFSC). The specification of a commercial catalyst is presented in Table 1.

Table 1. Chemical and physical analyses of the catalyst

Chemical analysis		Physical analysis	
Ni, %	12	Bulk Density, kg/L	0.1
SiO_2, %	15	Holes	4
CaO, %	0.5	Radial crush strength, kg	60
MgO, %	0.20	Particle size diameter, mm	4.00-4.75
Al_2O_3,%	Balance		

The catalyst has been crushed by a jaw crusher and then sieved to have the mesh size of 4.00~4.75 mm which is the maximum particles diameter that does not stick in the reactor with minimum pressure drop throw catalytic bed while the reaction occurs and carbon deposited, the catalyst was used without any further shape reformation.

B. Homemade catalyst (CAT-2)

Specifications of the active compound used in the catalyst preparation are shown in Table 2. The specification of a commercial spherical shape alumina oxide type gamma alumina (γ) is presented in Table 3, which has been used as a carrier in the manufacturing of catalyst.

Ceramic balls of ¼″ in diameter from the North Refineries Company with crushing strength: 180 lbs, Bulk density: $1.4g/cm^3$, shape: Almost spherical with 6 mm particle diameter off-white color.

Table 2. Specifications of Active components

No.	Active component	Precursor	Wt. %	Catalyst	Supplying company
1	Co	$Co(NO_3)_2.6H_2O$	4	$Ni-Co/\gamma-Al_2O_3$	ALPHA
2	Ni	$Ni(NO_3)_2.6H_2O$	10	$Ni-Co/\gamma-Al_2O_3$	HIMEDIA

Table 3. Aluminum Oxide ($\gamma-Al_2O_3$) specifications

Properties	$\gamma-Al_2O_3$	Properties	$\gamma-Al_2O_3$
Particle diameter, mm	1.6	Bulk density, g/cm^3	0.577
Surface area, m^2/g	289	Pore volume, cm^3/g	0.364

2.2. Methods of catalyst preparation

The cobalt solution supported on alumina is prepared by incipient wetness impregnation (IWI). The preparation procedure is as follows: firstly 100 gm of the alumina is dried in the oven at 393K for 4 hour to remove the moisture from alumina before impregnation. Secondly, 3.8 gm of nickel nitrate is added to 50 cm^3 deionized water (pore volume of gamma alumina equal to deionized water volume), while the solution is being stirred (using magnetic stirrer) for one hour at room temperature. The pretreated gamma alumina in step one is put in the flask under evacuation condition (using vacuum pump) in order to remove gases out of support pores, then the solution prepared in the second step is added to gamma alumina at the rate of (15-20) drop per minute with continuous stirring until all the solution is impregnated. The temperature is kept constant at (373K) using a bath water. The impregnated gamma alumina is dried overnight in the oven at (393K). The aim of this step is to eliminate water. The calcination step is then applied for 5 hours in the oven at (823 K) under laminar flow of air. The purpose of this step is to convert the most of the metal salts loaded on the γ-Al$_2$O$_3$ into their corresponding metal oxides, which lead to deposit of active metal oxide over catalyst support as well as acquiring desired physiochemical properties of the catalyst. The same procedure is repeated with 1.6 gm of cobalt nitrate which is impregnated in nickel oxide on alumina. Calcination step is completed in *Fertilizer/Northern Company*- Baiji. The characteristics of prepared catalyst as shown in table 4.

Table 4. The characteristic of the prepared catalyst.

Catalyst issues	NiO$_2$-Co$_3$O$_4$/γ-Al$_2$O$_3$	γ-Al$_2$O$_3$
Particle shape	Sphere	Sphere
Particle diameter (d_p), mm	1.6	1.6
Surface area (S_g), m^2/g	251	289
Bulk density (ρ_B), g/cm^3	0.7014	0.671
Pore volume (V_g), cm^3/g	0.4897	0.5367
Calcinations temperature, K	823	-
Support	γ-Al$_2$O$_3$	-
Active phase Ni(NO$_3$)$_2$-Co(NO$_3$)$_2$.6H$_2$O%	10-4	-

3. Experimental procedure

The experiments of this work were conducted at high temperature, fixed bed system in chemical engineering department/college of engineering/Tikrit University. Process flow diagram of this system is presented in Figure 1.
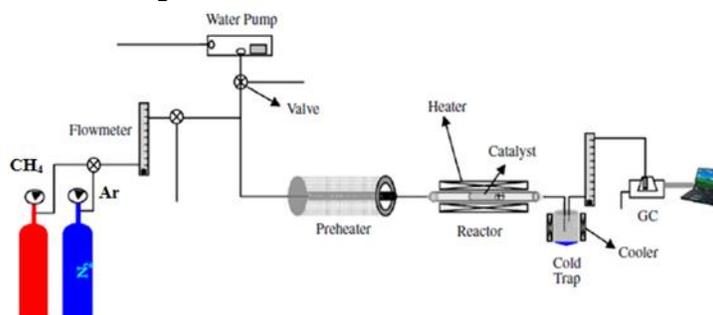

Figure 1. Experimental setup

In this work, various experiments are conducted with the following moderate operating conditions:
- Initial concentration of methane 70%, 80%, and 90%.

- Temperature: 773, 823 and 873K.
- Time on stream: up to 60 minutes
- Catalysts type: CAT-1= Ni-SiO$_2$/γ-Al$_2$O$_3$ and CAT-2= Ni-Co/γ-Al$_2$O$_3$.

A complete catalyst bed is made up of three main parts; two parts of ceramic balls and a part of the catalyst is loaded in between them. The purpose of the diluents as well as the ceramic balls is to provide complete catalyst wetting and to reduce radial dispersion and the bed porosity leading to minimization of any diffusion effects and thus providing plug flow conditions for isothermal reactions. The percent of inert layers (ceramic balls) in the catalyst bed is 70 % vol.

The running of experiments as follows:
1. The nitrogen gas is flown into the system to check leaks.
2. The temperature controller is turned on and set on the desired temperature.
3. Argon gas is flown for 20 min with a flow rate of 800ml/min to warm up the reactor bed from ambient temperature to 773K.
4. The preheater is warmed up to 573 K simultaneously with step 3.
5. The cooling water is turned on to cool the outlet gases.
6. Heating up of the reactor is started up to the desired reaction temperature (773, 823 and 873 K) with a rate of 283 K/min.
7. The feed gases, methane and argon, are flown into the reactor at the desired percentage of methane.
8. The portable hydrogen analyzer K6050 is turned on and the reading of hydrogen concentration is recorded every 1 minute up to 60 minutes.
9. The methane gas is turned off and argon gas continues in following through the bed.
10. The preheater and the vertical furnace are turned off.
11. When hydrogen concentration reaches 0, sampling is stopped and the portable gas analyzer K6050 is turned off.
12. Argon gas is kept flowing to purge the system, then the argon valve is closed.

4. Results and Discussions

A. Influence of Temperature on the Process Conversion

In order to study the influence of reaction temperature on catalytic behavior of the catalysts experiments were carried out at three different temperatures (773K, 823K and 873K). Figures 2 and 3 show the influence of reaction temperature on initial methane conversion at different feed gas concentration for CAT-1 and CAT-2.
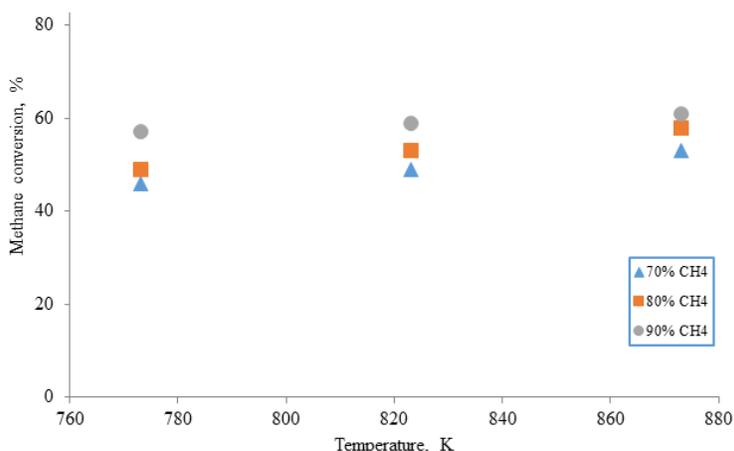

Figure 2. Influence of reaction temperature at different feed gas concentration over CAT-1

It can be seen that as reaction temperature rises, the initial conversion of methane increases for the two catalysts. It is realized that catalytic decomposition over CAT-2 is

significant at higher temperatures and methane decomposition exhibits stable activity rather than CAT-1. The catalysts effectively shift the conversion behavior toward substantially lower temperatures of decomposition, 773K, by reducing the activation energy of the methane decomposition reaction [20]. The higher activity of CAT-1 is attributed to the bimetallic function of the catalyst, the bimetallic supported catalysts were more active than a monometallic [20]. These results for conversion were in good agreement with other literature values [15,17,25-26].
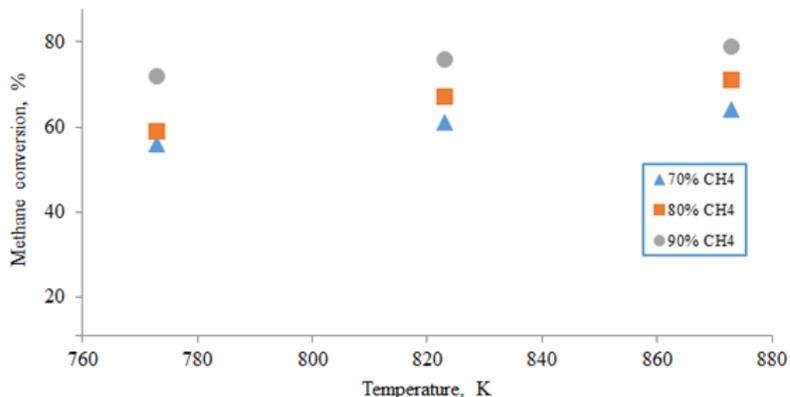

Figure 3. Influence of reaction temperature at different feed gas concentration over CAT-2

B. Influence of Methane Concentration on the Process Conversion

The influence of methane concentration on initial conversion via decomposition over CAT-1 and CAT-2 is shown in Figures 4 and 5 respectively. In Figure 5 it can be seen that all methane conversion curves show an initial conversion of methane until a maximum is reached at the highest methane concentration for CAT-1. An increase in the methane concentration in the gas phase leads to a boost in the diffusion–precipitation process through the Ni crystallites. This in turn causes the increase in the initial reaction rate [27]. The effect of concentration became less significant at higher temperatures, this attributes to the decay of CAT-1's activity, the deactivation rate is proportionally affected by methane concentration and temperature. In the reaction of CDM, the rate of carbon filament formation is in fact the reaction rate and therefore a measurement of the true catalyst activity. In most cases, the carbon formation corresponds to the deposition of coke through a secondary reaction, and the higher the coking rate is, the higher is the deactivation rate and the lower is the remaining activity.
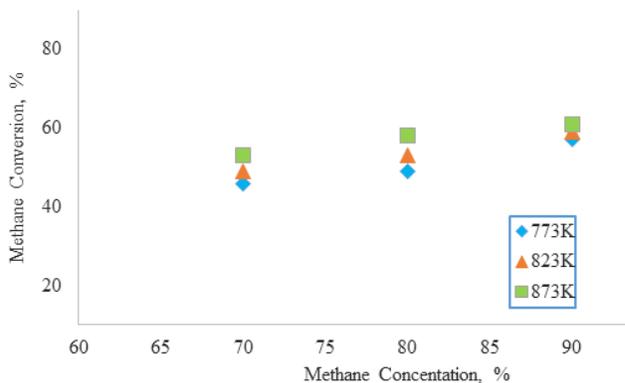

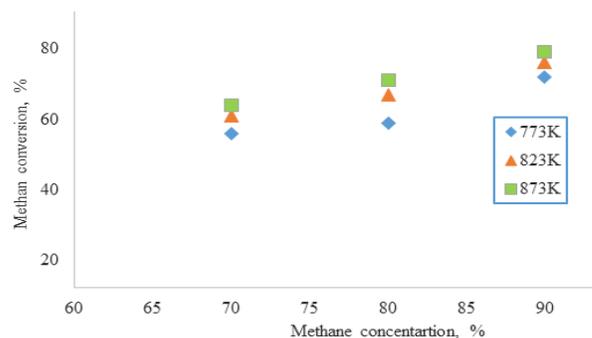Figure 4. Influence of methane concentration on conversion at different temperature over CAT-1

Figure 5. Influence of methane concentration on conversion at different temperature over CAT-2

Figure 5 shows a significant initial conversion of 56-64% at 70% for CAT-2 which is higher than the obtained conversion for CAT-1 initially (49-53%). The conversion increases

progressively with methane concentration and CAT-2 does not exhibit a significant deactivation due to increasing temperature.

C. Catalyst Deactivation

The initial activity for CAT-1 and CAT-2 is significant at different reactor conditions. It can be seen in Figure 6 that time on stream has a drastic effect on CAT-1 activity decaying, as a rapid fall is observed in methane conversion at 773 K and different methane concentration, whereas when temperature increases to 873K, methane conversion occurs with a soft decaying at high methane concentrations. As the temperature increased, the initial activity increased but the deactivation occurred more rapidly, the main reason for inactivation because the carbon covered the active site [28]. For CAT-2, Figure 7 shows a different behavior regarding decaying of catalyst activity. The activity decreases with time on stream due to carbon depo-sition gradually with time on stream and the deactivation stopped at a high catalyst activity which is an indication of a high sustainability for this catalyst. After certain time on stream, catalyst is deactivated as a result of carbon deposition.
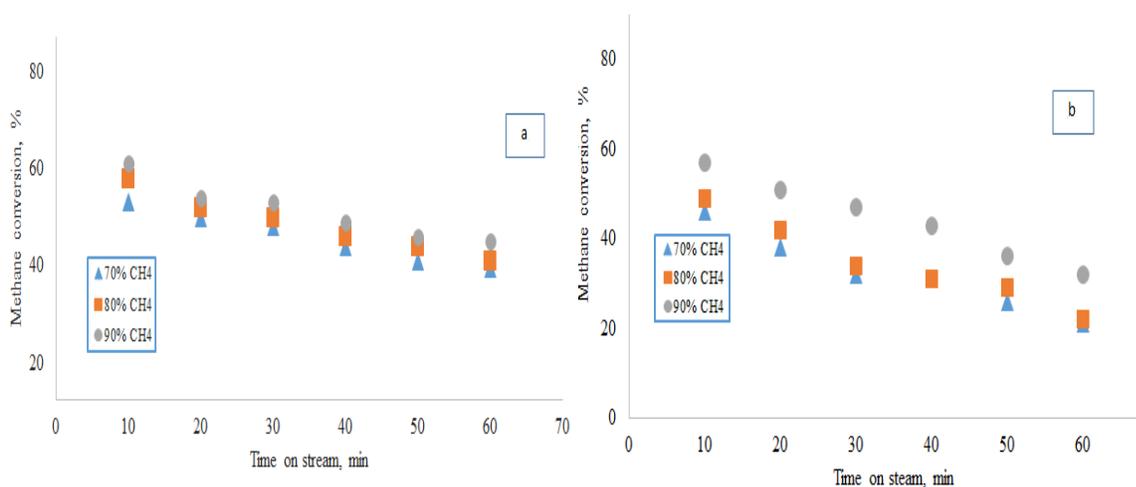

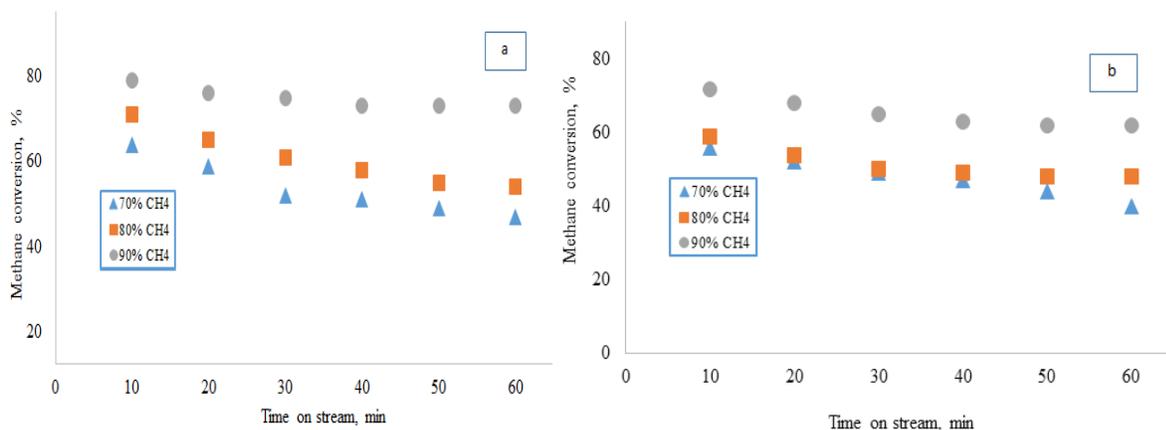Figure 6. Deactivation of CAT-1 a. at 873 K, b. at 773 K

Figure 7. Deactivation of CAT-2 a. at 873 K, b. at 773 K

D. Determination of the Most Active Catalyst and the Optimum Conditions

Figure 8 shows that the activity of these catalysts is related to the metal dispersion, BET surface area, porosity, and bulk density. The results exhibit initial methane conversions of

53.77% and 64.2%. However, the amount of carbon deposit is higher on CAT-2. The deactivation behavior of catalyst is apparently due to carbon deposition on pores of Ni produced by methane decomposition, which is proved by the weight gain of catalysts after the end of decomposition reaction. Based on the results presented in these Figures, the catalysts can be ranked as follows in terms of activity in methane decomposition:
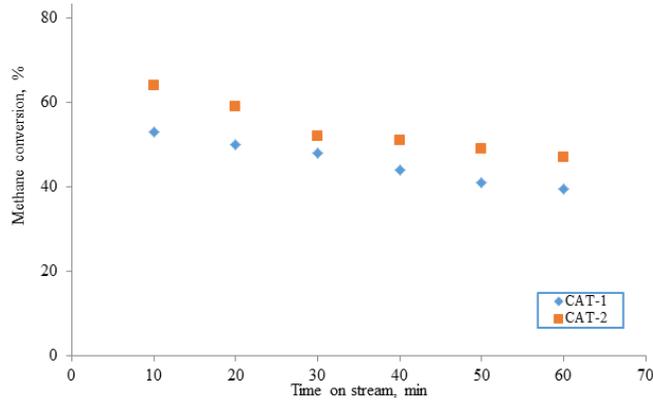
CAT-2 > CAT-1.

Figure 8. Reaction conditions (concentration of methane 70%, and T=873K) for the activities of the catalysts.

Also, it is clearly observed that the best conversion is obtained at the following operating conditions:
- The best catalyst is CAT-2.
- The initial concentration of methane of 90%.
- The best temperature is (873K).

The results show that the prepared CAT-2(10% Ni-Co/Al$_2$O$_3$), catalyst has a good activity in CDM over CAT-1(12% Ni-SiO$_2$/Al$_2$O$_3$) which is in agreement with the findings of Long *et al.* [29] and Ahmed Al-Fatesh [15]. The findings of the present work are compared with some recent studies as shown in Figures 9 and 10.
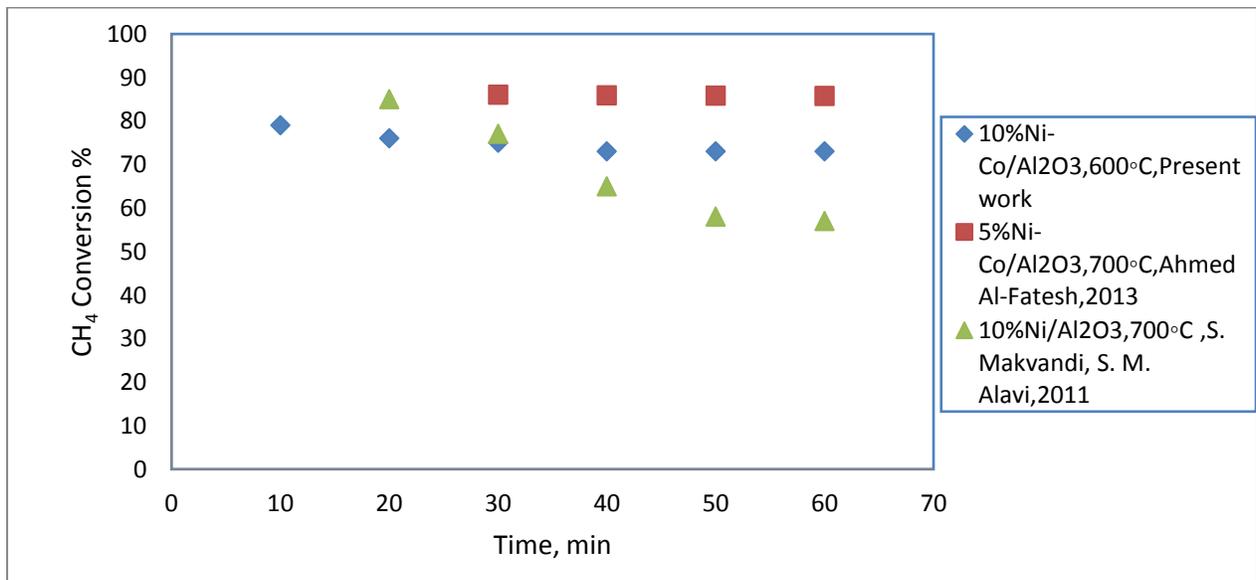

Figure 9. Comparison of the activity of CAT-2 (10% Ni-Co/A$_2$O$_3$) in the present study with some recent findings
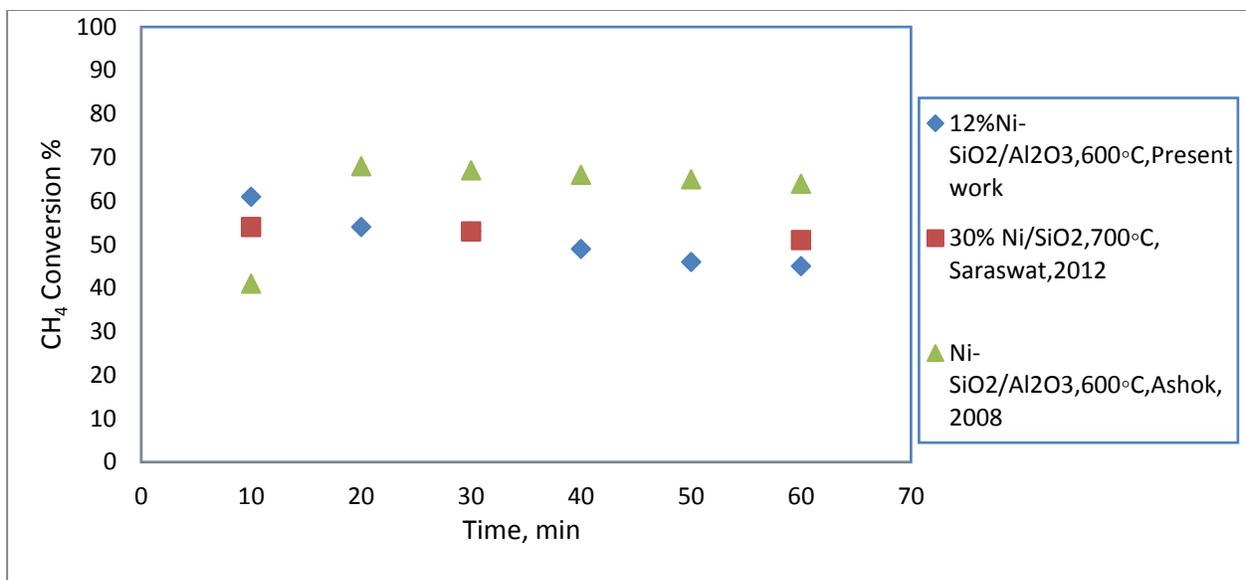
Figure 10. Comparison of the activity of CAT-1 (12% Ni-SiO$_2$/A$_2$O$_3$) in the present study with some recent findings

It is noted from Figure 9 that the activity and stability of CAT-2 is remarkable in comparison with Makvandi and Alavi [30] and Al-Fatesh [15]. This proves the higher activity of bimetallic catalysts over the monometallic catalysts. For the commercial catalyst, CAT-1, Figure 10 shows a high consistency of activities among the illustrative catalysts. Ashok [26] had used the same components of the present catalyst and Saraswat [18] had used a 30% Ni/SiO$_2$, the results of the present study are proven to be compatible with the recent published research.

E Estimation of sustainability factor

The sustainability factor is a measure of catalyst deactivation. It is defined as the ratio of the reaction rate after and the initial reaction rate upon reaching the desired temperature [31]. The sustainability factor is calculated for CAT-2 at different reactor conditions.

Because the catalyst deactivated quite rapidly, the initial activity at 0 min was estimated by extrapolation. The rate of deactivation by carbon deposition can often be represented, as a good approximation, by the following empirical expression [32].

$$R_t = R_o \exp \frac{t_t}{t_o} \qquad (1)$$

where R_0 and R_t are the initial rate and the rate at a given time in the unit of mmol/min gcat; t is the time on-stream, and to the time constant for deactivation. Ro can be estimated by plotting ln Rt versus t through extrapolating to zero time.

Its value ranges from 0 to 1 with 1 being the most stable. The highest sustainability factor obtained by using the parameters in Table 5 is 0.7911 at 773K and 80% methane for CAT-2.

Running at high temperatures have resulted in a decrease in sustainability factor, it is proven that an increase in temperature results in a fast deactivation. This is attributed to the formation of encapsulating carbon at high temperatures [4].

Table 5. Sustainability factor for Cat-1 and Cat-2 at different reactor conditions

Catalyst	Temperature, K	Methane concentration %	R_o (mol/min.g$_{cat}$)	R_1/R_o
CAT-2	773	70	0.735	0.1118
CAT-1	773	70	0.2936	0.3882
CAT-2	773	80	0.4902	0.7911
CAT-1	773	80	0.9796	0.2613
CAT-2	773	90	0.1161	0.5747
CAT-1	773	90	0.612	0.4084
CAT-2	823	70	0.4015	0.3686
CAT-1	823	70	0.8947	0.2302
CAT-2	823	80	0.839	0.2455
CAT-1	823	80	0.2405	0.6898
CAT-2	823	90	0.994	0.2776
CAT-1	823	90	0.5227	0.7040
CAT-2	873	70	0.3379	0.7576
CAT-1	873	70	0.341	0.6803
CAT-2	873	80	0.61	0.5639
CAT-1	873	80	0.99	0.4282
CAT-2	873	90	0.346	0.7052
CAT-1	873	90	0.5306	0.5126

5. Conclusions

CDM reaction on commercial and house made Ni catalysts has been studied at mild conditions and proved to proceed with a remarkable methane conversion. Among the two catalysts, the house made catalyst showed a good impregnation (Ni=10%), compared to the commercial catalyst (12% Ni-SiO$_2$/Al$_2$O$_3$). CDM reaction implemented based on different kinds of Ni catalysts and operation conditions from previous works gives low methane conversion and sustainability factor. Therefore, the newly prepared catalyst has been applied to obtain the best operation conditions and the highest conversion. The results of application of different temperatures, methane composition and time on stream give good conversion of 71% and sustainability factor of 0.7911 at 773K 80% methane within the first 10 minutes of reaction. It has been shown that time for catalyst deactivation depends on the operating conditions, so that, higher the temperature and methane flow, shorter the lifetime of the catalyst.

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