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EFFECT OF CATALYST PREPARATION ON DRY REFORMING OF METHANE

Fakeeha A. H. *, Soliman M.A. * and Al-Fatish A. A. *

ABSTRACT

In this paper the effect of changing different supports, calcination temperature and Ni loading on carbon dioxide reforming of methane using Ni-based catalyst are explored experimentally. The supports used are alumina (with different surface areas), silica, titania and zirconia . Calcination temperature is ranged from 773 to 1073 K, while nickel loading is ranged from 0 to 22% .The results showed that calcination at 873 K led to an acceptable catalyst activity. High surface area alumina proved to be the best support in terms of both activity and stability. 12% nickel loading proved to be satisfactory.

KEYWORDS

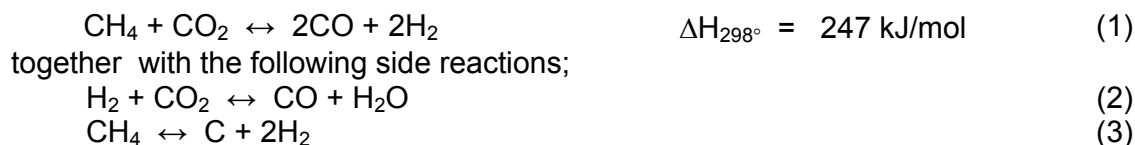
Dry reforming , Supports , Calcination temperature , Synthesis gas

* College Of Engineering, King Saud University, Saudi Arabia

1. INTRODUCTION

There is a rapidly growing interest in the catalytic conversion of CH₄ and CO₂ to synthesis gas (Dry reforming of methane) in recent years because this reaction has many potential incentives with economical and environmental benefits [1].

The reaction proceeds according to the following equation



Feed stock of this reaction can be obtained from waste gases e.g. ; biogas (agriculture waste, waste water treatment), fuel gas as well as rich oil or gas field in CO₂ gas,...

Dry reforming is slightly more endothermic than steam reforming. For this reason, dry reforming reaction is now being recommended for the chemical energy transmission system (CETS) to replace steam reforming. Another advantage of using dry reforming in CETS is that CO₂ is commonly present in gaseous phase, so no pipe heating is needed during transportation [2-6].

Wang and Max Lu [7] studied the effects of reaction parameters on catalyst activity and carbon deposition over Ni/ γ -Al₂O₃ catalyst. They found that the reduced Ni/ γ -Al₂O₃, nickel metal itself and active species of carbon were the active sites for the reaction. The carbon deposition on Ni/ γ -Al₂O₃ varied depending on the nickel loading and reaction temperature and was the major cause of catalyst deactivation and plugging of the reactor. At 5% Ni/ γ -Al₂O₃ the catalyst exhibited high activity and much lesser magnitude of deactivation in 140 h. The conversion increased with increasing reaction temperature and nickel content. When nickel loading was greater than 12 wt%, the conversion would reach the thermodynamic equilibrium. They found that CO₂ conversion was always higher than CH₄ conversions which indicated that the reverse water gas shift reaction occurred in the CO₂ reforming reaction [7].

Choudhary et al. [3] studied supported nickel catalyst prepared using commercial sintered low surface area porous catalyst carriers (containing SiO₂ and/or Al₂O₃) pre coated with MgO, CaO or rare-earth oxide, their results showed very much higher activity, selectivity and productivity in methane-to-syn gas conversion reaction, than the catalysts prepared using catalyst carriers without any pre coating. Among the pre coating metal oxides, the best performances was observed for MgO.

Gadalla and Sommer [2] characterized an industrial Ni catalyst supported on CaO – TiO₂ – Al₂O₃ that was used for methane reforming with carbon dioxide, and compared the results with that obtained from catalyst containing Ni on other support. Conversion close to 100% were achieved during 51 hours on stream for a CO₂ : CH₄ ratio of 2.64 : 1 using a weight hourly space velocity of 7.38 h⁻¹ despite the solid state reaction and sintering which decrease the surface area [8].

Conversion of CH₄ and CO₂ to synthesis gas approaching those defined by thermodynamic equilibrium can be obtained over most of the aforementioned catalysts as long as contact times are kept high enough. One of the major problems encountered toward application of this process is deactivation of the catalyst by carbon deposition [9].

Suhartant et al. [10], indicated that the conversion of natural gas to liquid fuel on a commercial scale can be found in Malaysia and South Africa, although smaller demonstration plants can also be found elsewhere.

Therefore a gas – to – liquids- (GTL) process, employing CO₂ reforming, offers another option for utilizing high CO₂ content natural gas produced from the natural gas field.

Quincoces et al. [11] studied the effects of Mo addition on the stability, the sulfur poisoning and carbon deposition over Ni based catalyst for CO₂ reforming of methane . The Ni catalysts promoted with small amount of Mo increases the stability of catalyst and decreases carbon deposition.

Bo-Qing xu et al. [12] studied nickel catalyst supported on Al₂O₃, SiO₂, TiO₂, and two ZrO₂ of different preparation at 1030 K .The activity and anti-carbon property of the nickel catalyst depend greatly on the nature of the support, while Zirconia is a good support for highly active and selective nickel catalyst . The preparation method of this support affects strongly the catalyst stability.

Potdar et. al. [13] prepared catalysts composed of Ni-Ce-ZrO₂ by one step co-precipitation technique. Their results indicate the superiority of technique in comparison with the impregnation technique having the same composition. Using 15% Ni (w/w) co-deposited with CeZrO₂ gave catalyst that had a yield of 97% CH₄ conversion at 800 °C and the activity was maintained for 100 hr, this indicated that the reason for this superiority is due to the nano-crystalline nature of cubic Ce_{1-x}-Zr_xO₂ producing strong interaction with finely dispersed nano-sized NiO_x crystallites

It is noticed that the previous studies differ in preparation methods, calcination temperatures, activation procedure, catalyst loading and or reaction temperature. This paper present experimental study that explore the effect of using different supports (Alumina , Silica, Titania, and Zirconia), calcinations temperature and nickel loading on the performance of Ni – based supported catalysts for dry reforming reaction.

2. EXPERIMENTAL

Preparation method:

Different supports have been used to prepare Ni - base supported catalysts. The supports used are high surface area alumina[γ -alumina (SA-6175)], low surface area alumina [α -alumina (SA-5239)], medium surface area alumina (SN-74707) silica (S151-10), TiO₂ , and ZrO₂ the surface area of the above supports are (230 – 290 m²/gm), (0.15 – 0.45 m²/gm), (80 – 120 m²/gm), (< 1 m²/gm), (11.8 m²/gm), (6.9 m²/gm) respectively. Impregnation of the supports was carried out with aqueous solutions of nickel-nitrate . After impregnation, the catalysts were dried for 13 hr. at 383 K and calcined for 5 hr at 873 °K in air atmosphere.

Experimental set-up:

The experimental equipment used in this study is AMI- 2000 ZETON-ALTAMIRA micro-reactor system which is shown schematically in Fig. 1. The system is composed of the following sections:

1. Feed Section: The feed section contains three gas cylinders for CO₂, CH₄ and N₂. Gases coming from the regulators pass through in-line filters are then introduced to the Mass Flow Controllers (MFC), obtained from Brooks. The gases are mixed and passed to the reaction section. On line samples from the feed gas mixture are directed to gas chromatograph for analysis.
2. Reaction Section: The micro-reactor overall length is 0.43m , with inside diameter of 6.35x10⁻³ m made of stainless steel and surrounded by three zones heater. Each zone temperature can be controlled separately. The temperature in the reactor is measured by a thermocouple located at three different location along the reactor height . The outlet from the reactor (bottom end) is passed through a back pressure regulator (BPR) to control the pressure in the reactor and the sample of product gases from the BPR were sent to analysis section .
3. Analysis Section : 3400-CX Varian gas chromatograph with TDC detector was used . The detector is equipped with Haysep A column.

Activation procedure

This pretreatment process was found to be essential for the reaction to take place.

The activation procedure was carried out according to the following:

- A. Introduce hydrogen to the reactor at 20 ml/min for 2.5 hr.
- B. Then hydrogen is stopped while N₂ is introduced at 40 ml/min for one hour.

Comparing catalyst A2 which was activated with catalyst A1 that was not activated, the conversion of both CH₄ and CO₂ as well as H₂ yield for the activated catalyst is much higher than the unactivated catalyst as shown in table (1)

Table 1: Conversion and yield with activated and unactivated catalyst

	Activated catalyst	unactivated catalyst
Conversion of CH ₄	34.7	2.51
Conversion of CO ₂	35.1	5.11
H ₂ yield	31.4	1.1

3. RESULTS AND DISCUSSION**1. Effect of the supporting material**

The six different types of supports used were prepared at two different calcinations temperature 773 and 1073 K and tested at 773, 823, 848 K. The results are presented in Fig. 2-5 and Tables 2-4 for conversion of CH₄. The results for most of

the catalysts prepared showed increased in conversion with the increased in tested temperature. Different supports gave different results at different calcination temperatures. The results for some catalysts prepared with calcinations temperature at 773 K is better than that obtained with catalyst prepared at calcinations temperature of 1073 K. It is noticed that when Zr-Oxide was used as support methane conversion is very low for catalysts prepared at both calcinations temperature used, so it will be excluded from further studies. No conclusive choice for the best support can be drawn from these results (conversion), so stability tests were conducted for all catalysts prepared and the results are shown in Table 5. Alumina with high surface area (SA-6175) shown high stability for 86h as can be seen in Fig.6 while the other catalyst prepared with other support show deactivation and or agglomeration so high surface area alumina will be selected for further studies.

2. Effect of the Nickel Loading

Fig. 7 show the effect of increasing nickel loading from 0- 22 % on CH₄ conversion. The results show that as temperature and nickel content increases the CH₄ conversion increases up to 12 % then slight increase occur which indicate that equilibrium was almost reached. At 22 % nickel loading, the catalyst agglomerate, similar results obtained for CO₂ conversion and hydrogen yield

3. Effect of the calcination temperature:-

Several catalysts supported on high surface area alumina were prepared using nickel loading of 12 % and calcined at 773 , 873 , 923 , 973 , 1073 K Testing these catalysts at atmospheric pressure and 773 , 823, 848 K indicated that both CH₄ and CO₂ conversion decreased as calcination temperature increased above 873 K . At 773K the conversion of CH₄ at the above selected calcinations temperatures are (17.1 % ,16.4 % , 14 % 1.3% , 0.61 %) , while the conversion of CO₂ at the above selected calcinations temperatures are (23.7% , 23.7% , 23.4% 2.8% ,1.1%) respectively Fig. (8) is sample of these results for conversion of CO₂. The results indicated increasing temperature above 873 K is not desirable.

4. CONCLUSION

From this experimental study the following conclusions can be drawn:

1. High surface alumina is the best support among the supports tested in our study
2. Calcination at 873 K is recommended
3. 12%. Nickel loading is quite satisfactory

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Table 2: conversion of CH₄, CO₂ and hydrogen yield using catalyst with different supports calcined at 773, 1073 °K and tested at 773 °K

Support Calcination °K	SA-6175		SN-74707		SA-5239		S151-10		Zr-Oxid		TiO ₂	
	773	1073	773	1073	773	1073	773	1073	773	1073	773	1073
Conversion CH ₄	17.2	0.61	20	18.1	31.6	39.8	12.2	24.1	0.13	1.12	18.4	25.1
Conversion CO ₂	22.7	1.1	20.4	27.1	17.4	19.2	18.4	18.3	0.83	2.8	19.9	15.4
Hydrogen yield	16.1	0.32	17.6	16.9	25.9	30.0	11.6	21.3	0.08	0.27	16.35	22.9

Table 3 : conversion of CH₄ , CO₂ and hydrogen yield using catalyst with different supports calcined at 773, 1073 °K and tested at 823 °K

Support Calcination °K	SA-6175		SN-74707		SA-5239		S151-10		Zr-Oxid		TiO ₂	
	773	1073	773	1073	773	1073	773	1073	773	1073	773	1073
Conversion	34.7	1.83	40.0	34.3	45.4	58.9	22.1	40.7	0.26	1.84	43.4	47.7
Conversion CO ₂	35.1	3.4	39.0	40.1	28.3	30.5	30.2	32.7	1.6	1.6	30.2	27.3
Hydrogen yield	31.4	0.93	35.4	31.4	46.9	46.7	20.5	36.0	0.17	0.50	38.0	41.5

Table 4: conversion of CH₄, CO₂ and hydrogen yield using catalyst with different supports calcined at 773,1073 °K and tested at 848 °K

Support Calcination °K	SA-6175		SN-74707		SA-5239		S151-10		Zr-Oxid		TiO ₂	
	773	1073	773	1073	773	1073	773	1073	773	1073	773	1073
Conversion CH ₄	46.2	2.2	50.0	47.5	63.5	64.7	22.5	47.6	0.33	2.53	58.0	58.0
Conversion CO ₂	43.0	4.64	47.6	44.0	40.1	41.9	31.6	42.6	2.9	6.10	35.7	38.2
Hydrogen yield	43.04	0.89	45.8	43.6	54.6	54.0	20.4	44.0	0.24	0.78	51.5	52.0

Table 5 . Comparison of conversions for both CH₄ & CO₂ as well as hydrogen yield during the stability studies

Support	CH ₄ conversion		CO ₂ conversion		H ₂ yield		H ₂ / CO		Time on stream		Remarks
	First	End	Start	End	Start	End	Start	End			
SA-6175	16.9	16.1	26.2	25.8	15.3	15.3	0.60	0.61	86	h	Stable
SN-74707	17.4	16.3	25.3	24.9	15.6	15.2	0.63	0.61	58	h	Slightly agglomeration
SA-5239	24.6	6.5	17.5	11.6	21.5	5.2	1.42	0.45	31	H	Deactivation(black carbon & agglomerate)
S151-10	7.03	1.8	13.0	5.3	6.5	1.47	0.51	0.28	13	H	Deactivation(black carbon & agglomerate)
TiO ₂	17.6	8.9	24.7	14.4	15.4	7.7	0.65	0.55	55	H	Deactivation(black carbon & agglomerate)

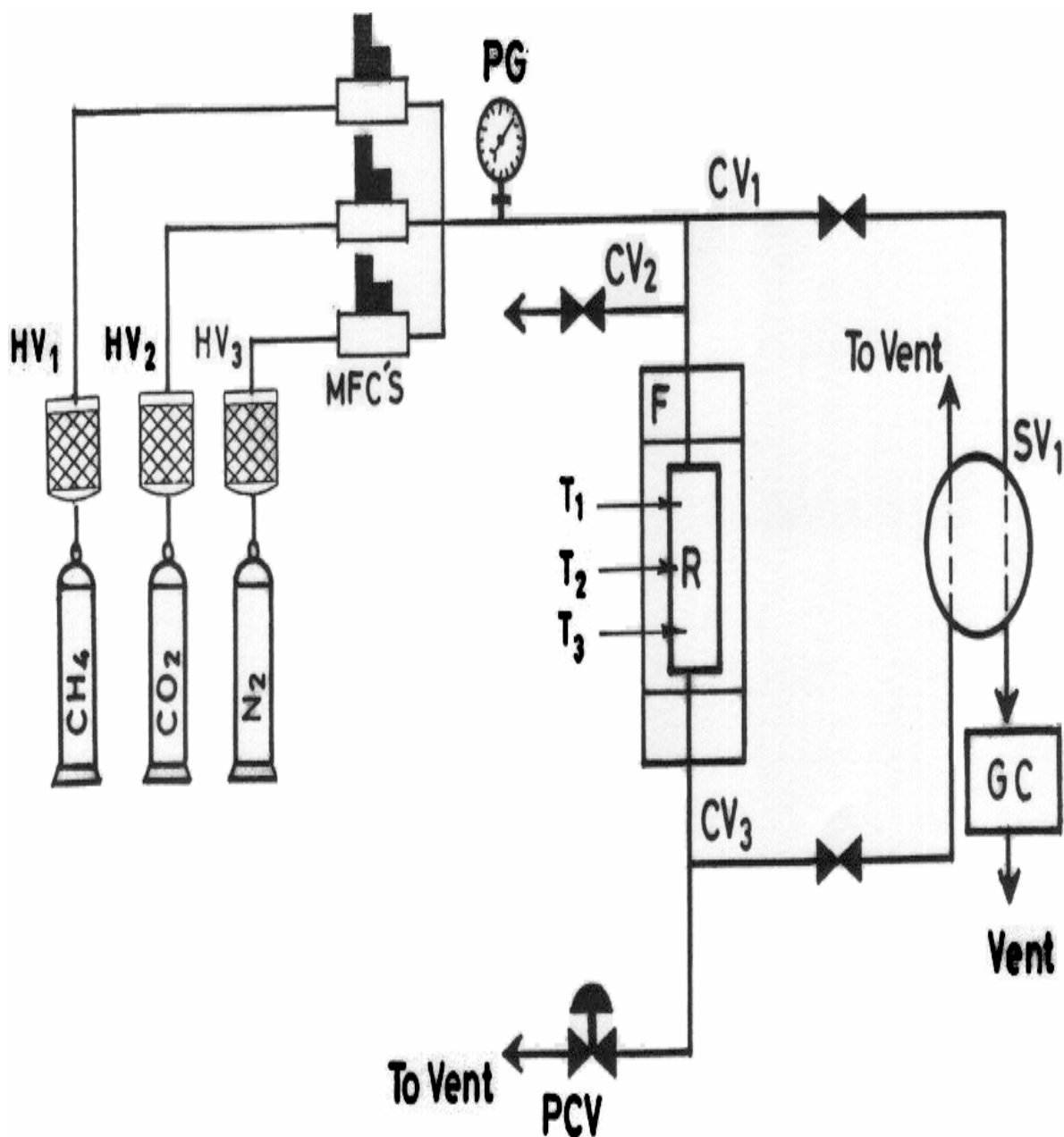


Figure 1: Schematic of experimental setup.(HV₁, HV₂ and HV₃ Filters , MFC's Mass Flow Controller, PG Pressure Gauge CV₁ , CV₂ and CV₃ Shut-off Valves, SV₁, Sampling Valve, F Furnace, R Reactor, T₁, T₂, T₃ Temperature Measurement (by Thermocouple), GC, Gas Chromatograph, PCV, Pressure Control Valve.)

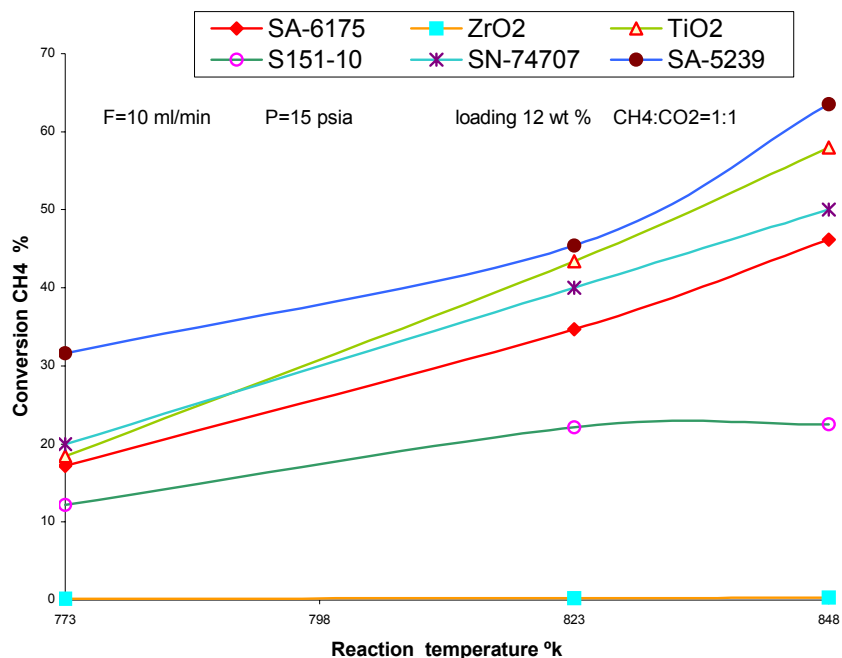


Figure 2. Effect of different types of supports on CH₄ conversion at calcination temperature of 773 °K

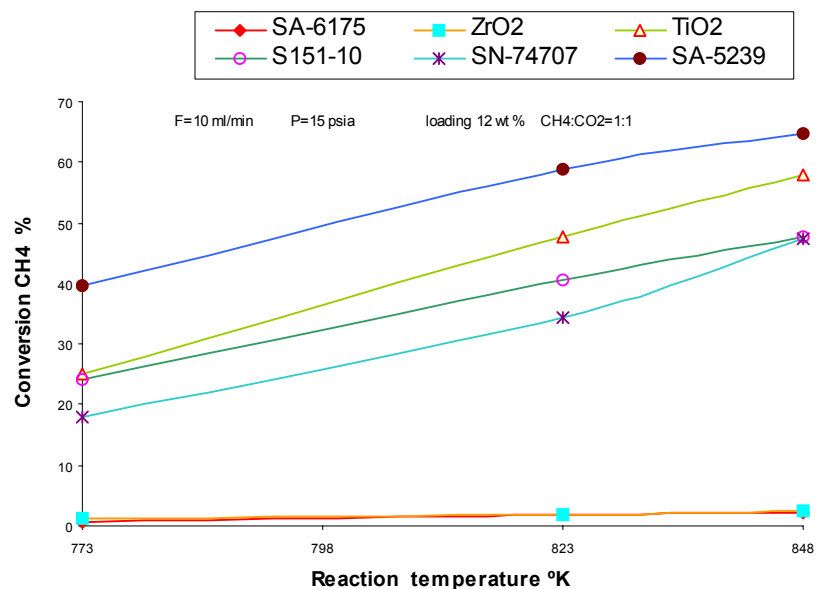


Figure 3. Effect of different types of supports on CH₄ conversion at calcination temperature of 1073 °K

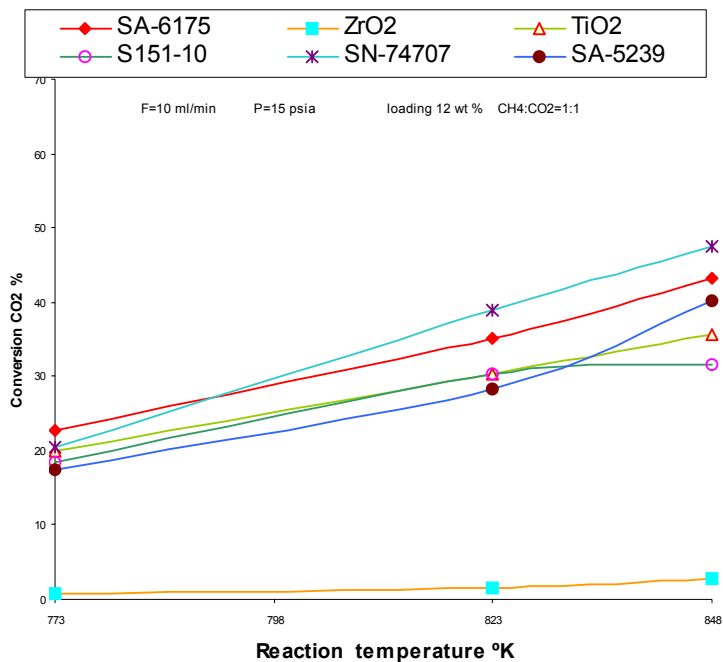


Figure 4. Effect of different types of supports on CO2 conversion at calcination temperature of 1073 °K

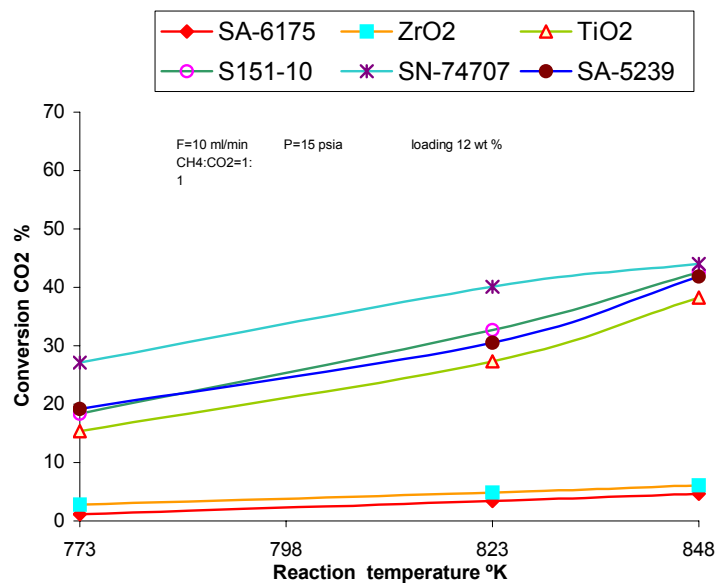


Figure 5. Effect of different types of supports on CO2 conversion at calcination temperature of 1073 °K

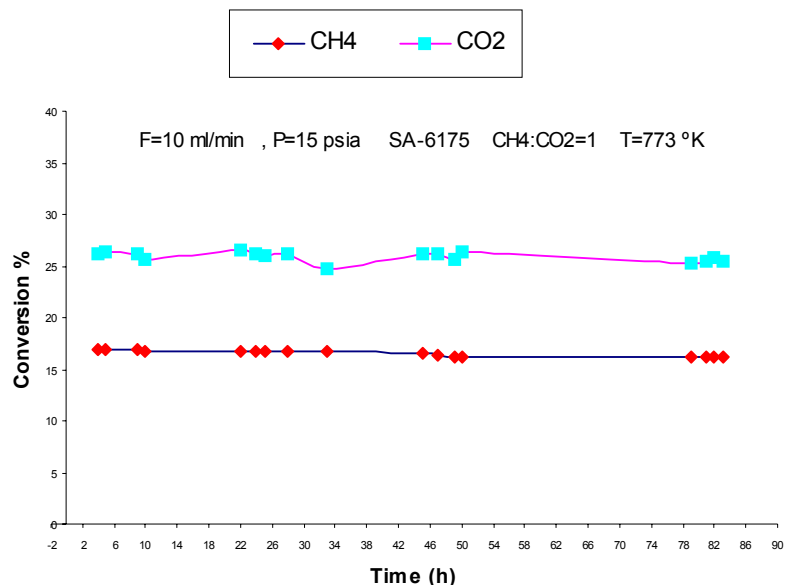


Figure 6. Variation of methane and CO2 conversion with time for Ni/SA-6175

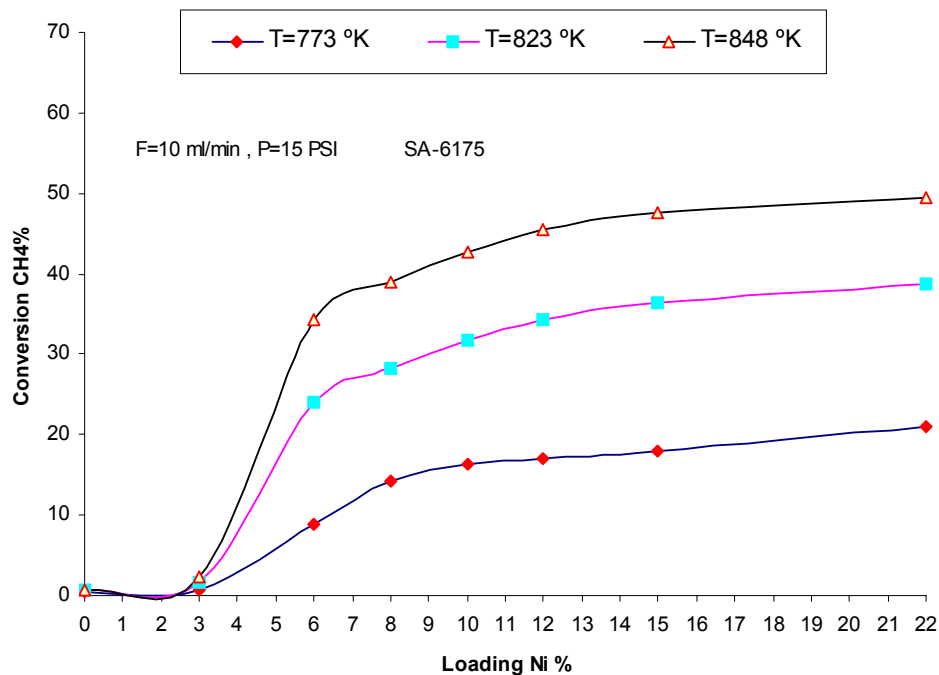


Figure 7. Effect of Ni Loading on CH4 Conversion

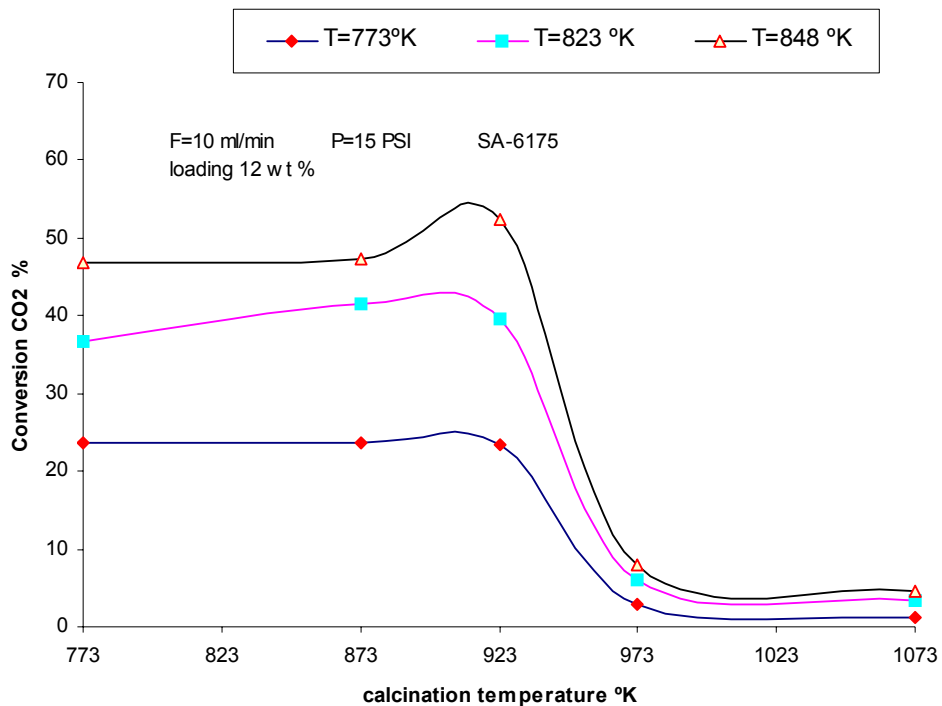


Figure 8. Effect of calcination temperature on CO₂ conversion