

CHAPTER 5
KINETIC ANALYSIS

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For many reactions , the rate expression can be written as a product of a temperature dependent term and a composition dependent term , or

$$\begin{aligned}r_i &= f_1 (\text{temperature}) \cdot f_2 (\text{composition}) \\ &= k \cdot f_2 (\text{composition})\end{aligned}\quad (1)$$

For such reactions the temperature dependent term , the reaction rate constant , has been found in practically all cases to be well represented by the Arrhenius' law ;

$$k = k_0 e^{-E/RT}\quad (2)$$

Where k_0 is the frequency or pre – exponential factor and E is called the activation energy of the reaction .

The temperature dependency of reaction is determined by the activation energy and temperature level of the reaction . as illustrated in Fig . (5.1).

These findings are summarized as follows :-

- 1- From Arrhenius' law a plot of $\ln k$ vs $1/T$ gives a straight line , with large slope for large E and small slope for small E .
- 2- Reactions with high activation energies are very temperature – sensitive ; reactions with low activation energies are relatively temperature – insensitive .
- 3- Any given reaction is much more temperature – sensitive at a low temperature than at high temperatures .
- 4- The value of the frequency factor k_0 does not affect the temperature sensitivity

The reaction rate constant itself can be found by studying the kinetics of a given reaction under different operating conditions to determine the form of the concentration dependent term in Eq .1. as will be given in the following section .

Testing for First Order Kinetics :-

At a given temperature the reaction rate is usually expressed as a function of reactant concentration in the form :-

$$-r = k C^n \quad (3)$$

Where n is referred to as the order of reaction .

If the reaction volume changes during reaction like for example in case of gas reactions then the final volume of the reactant + products for a reactant A is given by :-

$$V = V_0 (1 + \epsilon_A X_A) \quad \text{or} \quad X_A = \frac{V - V_0}{V_0 \epsilon_A} \quad (4)$$

Where V_0 = initial volume of reactants .

X_A = conversion .

ϵ_A = change in the system volume between no conversion and complete conversion thus and called expansion factor .

$$\epsilon_A = \frac{V_{X=1} - V_{X=0}}{V_{X=0}} \quad (5)$$

Noting that moles of A left unreacted .

$$N_A = N_{A0} (1 - X_A) \quad (6)$$

$$\text{and concentration of A} = C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \epsilon_A X_A)} \quad (7)$$

$$= C_{A0} \frac{(1 - X_A)}{(1 + \epsilon_A X_A)} \quad (8)$$

$$\text{Thus} \quad \frac{C_A}{C_{A0}} = \frac{(1 - X_A)}{(1 + \epsilon_A X_A)} \quad (9)$$

$$\text{or} \quad X_A = \frac{1 - C_A / C_{A0}}{1 + \epsilon_A C_A / C_{A0}} \quad (10)$$

The performance equation can be deduced as follows (Levenspiel ; 1999), for a plug flow reactor containing porous catalyst particle , take a thin slice of the PFR see Fig. (5.2).

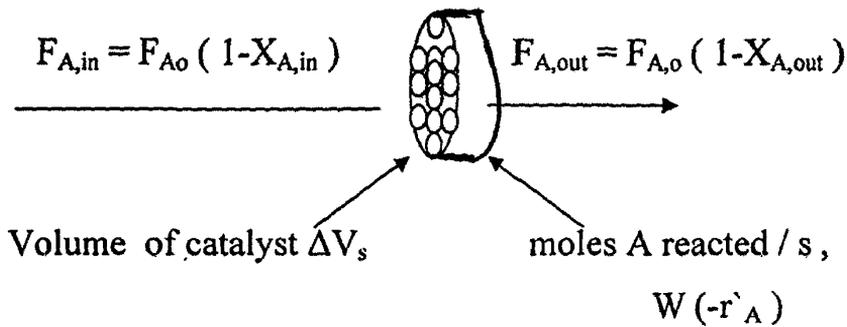


Fig. (5.1) . A thin slice of solid catalysed plug flow reactor .

At steady state a material balance for a reactant A gives :-

$$\text{Input} = \text{output} + \text{accumulation [mol A] / s .} \quad (11)$$

In symbols ;

$$F_{A0} - F_{A0} X_{in} = F_{A0} - F_{A0} X_{out} + (-r'_A) \Delta W \quad (12)$$

in differential form :-

$$F_{A0} dX_A = (-r'_A) \Delta W \quad (13)$$

Integrating over the whole reactor gives :-

$$\frac{W}{F_{A0}} = \int_0^{X_{Aout}} \frac{dX_A}{-r'_A} \quad (14)$$

$$\text{Let } \frac{WC_{A0}}{F_{A0}} = \tau \frac{\text{kg.s}}{\text{m}^3} \quad (\text{weight - time term}) \quad (15)$$

For a first order reaction :-

$$-r' = k' C_A \quad (16)$$

Substituting from (7) for C_A in (16) and integrating (14) taking into account the definition given in (15) .

The performance equation for a first order reaction in a plug flow reactor would be as given by Levenspiel ; (1999) as follows :-

$$k' \tau' = (1 + \epsilon_A) \ln \frac{1}{1 - X_{out}} - \epsilon_A X_{out} \quad (17)$$

A plot of τ' versus the r.h.s of Eq (17) should yield a straight line passing through the origin if the reaction obeys first order kinetics . The slope of the straight line is equal to k' , the reaction rate constant .

Reforming of methane using CO_2 can be expressed as follows :-



To calculate the expansion factor ϵ , one must consider the inert gas introduced with the reactants (Levenspiel ; 1999) . The reactant feed gas was CH_4 , CO_2 and N_2 in the ratio 1:1:4 respectively . The six volumes of entering gases will produce eight volumes of leaving product gases then expansion factor would be calculated as ;

$$\epsilon = (8 - 6) / 6 = 1 / 3$$

Equation (17) was investigated for each of the reacting species , namely CH_4 and CO_2 for the three types of catalysts prepared $\text{Rh} / \gamma\text{-Al}_2\text{O}_3$, $\text{Ru} / \gamma\text{-Al}_2\text{O}_3$ and $\text{Ir} / \gamma\text{-Al}_2\text{O}_3$.

The conversion X is calculated from the mole % and partial pressure of the reacting species . The calculation procedure and the calculated results are given in appendix A.

The assumption of first order kinetics with the reactants CH_4 and CO_2 was found to be obeyed in all cases studied . Least squares regression analysis was used to fit the data according to Eq.(17) , k' is calculated as the slope of the fitted straight lines as shown in Fig . (5 . 3 - 5) . These values together with the correlation coefficients are given in Table (5 .1).

Table (5.1) . Reaction rate constant as determined by least squares regression analysis.

Catalyst Type	Temperature	CO ₂		CH ₄	
		k'	c.c	k'	c.c
Rh / γ -Al ₂ O ₃	600	5.74E4	0.96	3.80E4	0.981
	700	13.10E4	0.957	5.74E4	0.979
	800	19.1E4	0.99	8.13E4	0.911
Ru / γ -Al ₂ O ₃	600	2.28E4	0.945	2.1E4	0.964
	700	3.66E4	0.952	3.48E4	0.848
	800	7.22E4	0.881	5.44E4	0.761
Ir / γ -Al ₂ O ₃	600	1.66E4	0.897	1.64E4	0.936
	700	2.57E4	0.933	2.18E4	0.938
	800	5.20E4	0.918	3.49E4	0.968

For each catalyst type , the k' values thus calculated at different temperatures are fitted to Arrhinius' equation to calculate the activation energy by plotting $\ln k'$ versus $1/T$, the data are given in Table (5 .2) and shown in Fig. (5 . 2 A-C) .

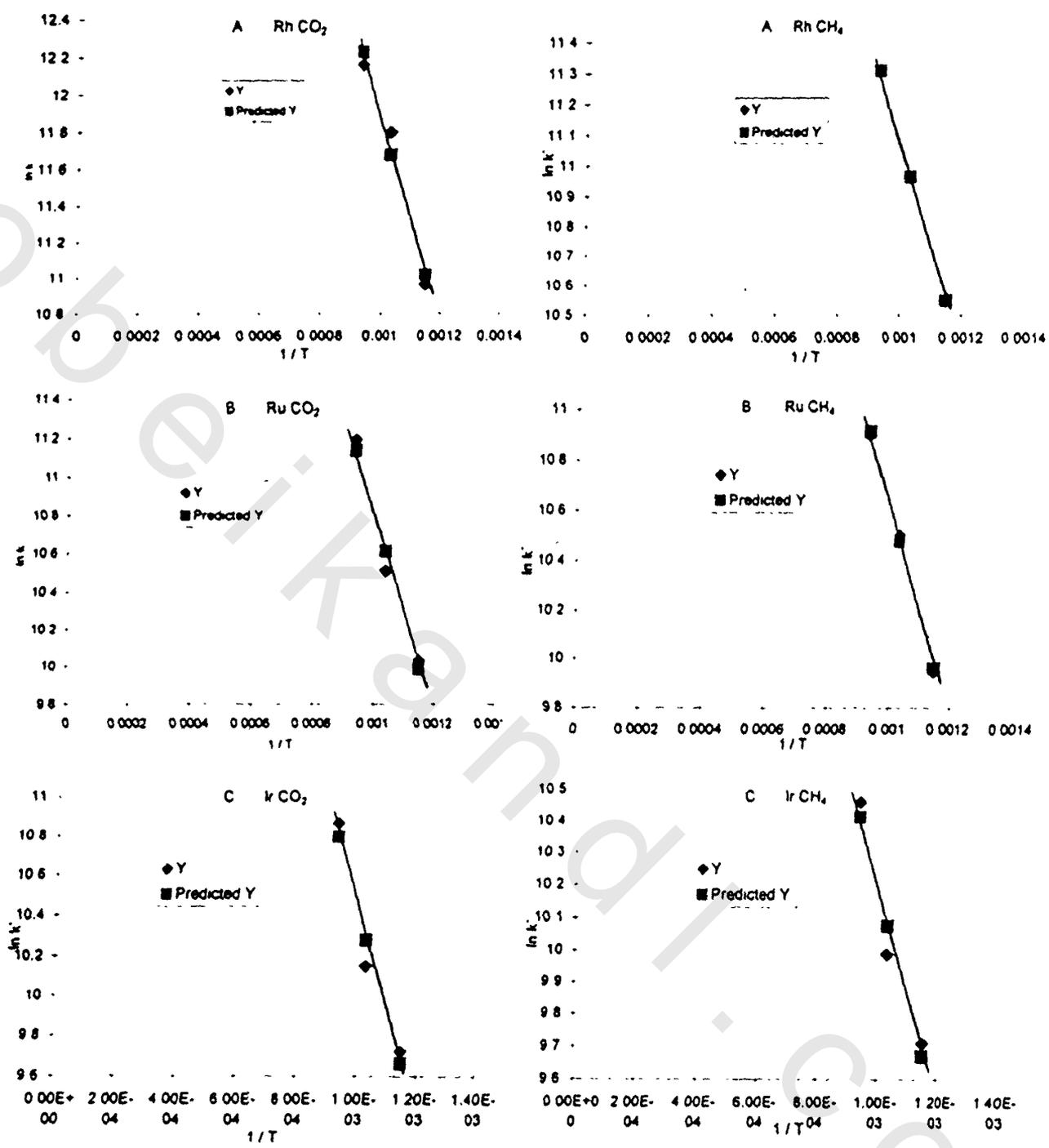


Fig (5.2 A - C) . Arrhenius' plot (A) Rh / Al_2O_3 , (B) Ru / Al_2O_3 , (C) Ir / Al_2O_3

Table (5.2). $\ln k$ and $1/T$ for 3- tested catalyst .

Catalyst Type	Temperature $1/T$	$\ln k'$	
		CO_2	CH_4
Rh / $\gamma\text{-Al}_2\text{O}_3$	0.00093	12.16	11.31
	0.001028	11.8	10.96
	0.001145	10.96	10.55
Ru / $\gamma\text{-Al}_2\text{O}_3$	0.00093	11.19	10.9
	0.001028	10.51	10.5
	0.001145	10.03	9.95
Ir / $\gamma\text{-Al}_2\text{O}_3$	0.00093	10.86	10.46
	0.001028	10.15	9.99
	0.001145	9.72	9.71

The results of the least squares regression analysis for k_0 (pre - exponential factor) , the intercept and $-E / R T$, the slope are given in Table (5.3) .

Table (5.3). Activation energy and pre-exponential factor from Arrhenius' equation

Catalyst	CO ₂					CH ₄				
	ln k ₀	k ₀	-E / R	E J / mol	c.c	ln k ₀	k ₀	-E / R	E J / mol	c.c
Rh / γ-Al ₂ O ₃	17.50	39.8E6	-5.66E3	47.06E3	-0.98	14.61	2.21E6	-3.55E3	29.51E3	-0.999
Ru / γ-Al ₂ O ₃	16.14	10.2E6	-5.38E3	44.65E3	-0.988	15.01	3.30E6	-4.42E3	36.24E3	-0.999
Ir / γ-Al ₂ O ₃	15.70	0.658E6	-5.27E3	43.81E3	-0.981	13.64	0.838E6	-3.47E3	28.85E3	-0.980

Discussion for each catalyst type is as follows:-

5.1. Rh / γ -Al₂O₃:-

Testing for the first order assumption for methane and CO₂ reaction over Rh / γ -Al₂O₃ catalyst is shown in Fig. (5.3). It is shown that the first order reaction kinetics assumption is valid for both reactants under almost all operating conditions investigated.

However, higher deviation is observed at the highest temperature investigated for the longest reaction time. This point was therefore excluded from the correlation.

A correlation coefficient (> 0.9) shown in Table (5.1) reflects the validity of the 1st order kinetics.

The deviation from first order equation observed for both reactants at the highest temperature and the longest reaction time may indicate a change in the reforming reaction mechanism or the onset of other reactions.

As shown in Table (5.1) the reaction rate constant for CO₂ is found to be approximately double that calculated for CH₄ at the same temperature, thus strongly suggesting a route other than reforming for the reaction of CO₂ for example the RWGS reaction.

This result is in confirmation with yields of CO which is higher than H₂ despite the equimolar volumes of the reacting gases as discussed in chapter 4. Arrhenius' plot for this catalyst is shown in Fig.(5.2 .A). The plot and Table (5.3) reveal that the activation energy for CO₂ reaction is (47.06E3 J / mol) which is more than that for CH₄ (29.51E3 J / mol) i.e. CO₂ is more temperature – sensitive than CH₄.

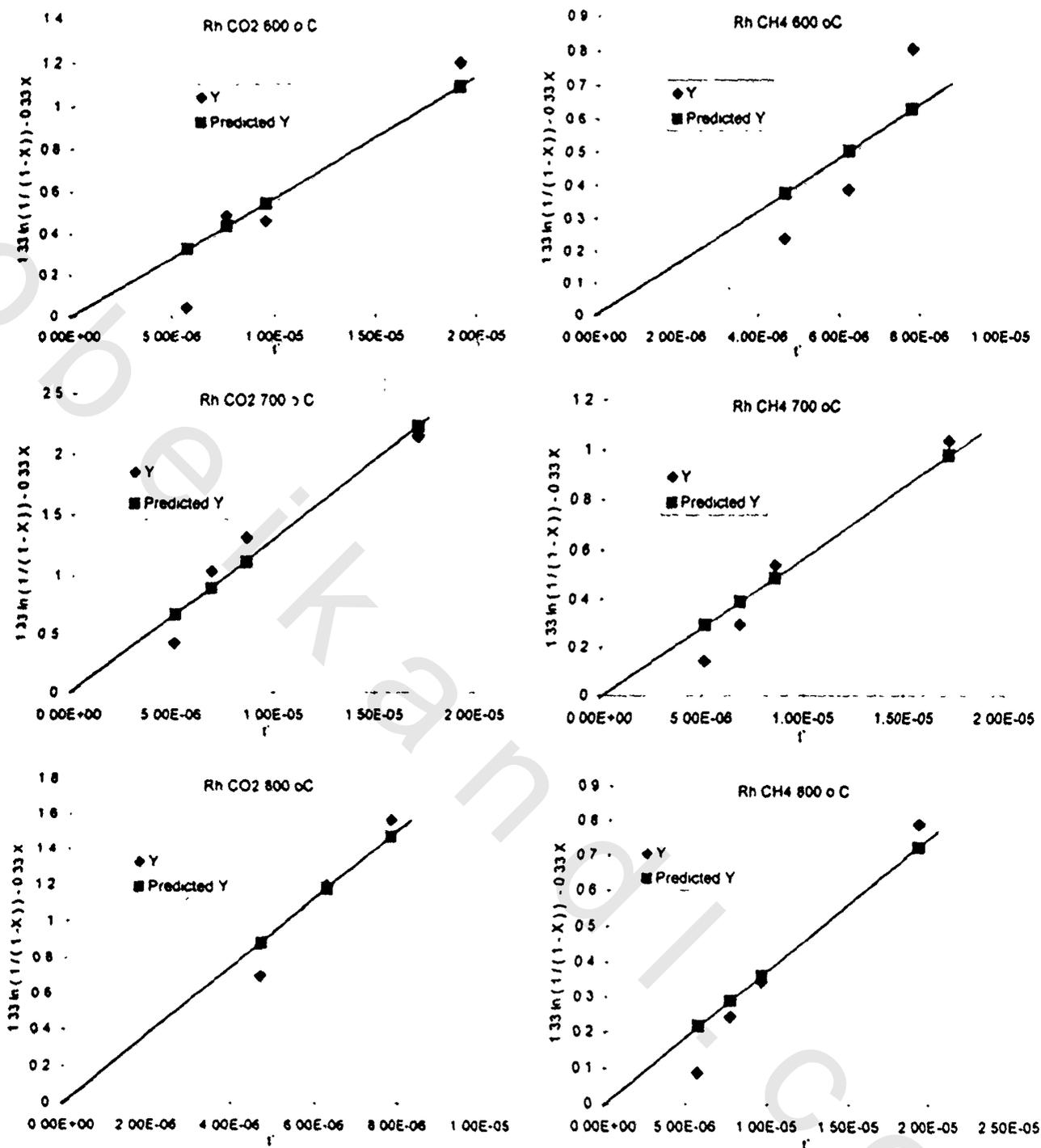


Fig (5. 3) . Test for First Order Reaction Kinetics w.r.t CO₂ and CH₄ Over Rh / Al₂O₃ Catalyst .

5.2. Ru / γ - Al₂O₃ and Ir / γ - Al₂O₃ catalysts :-

Testing for the first order assumption for methane and CO₂ reaction over Ru / γ -Al₂O₃ and Ir / γ - Al₂O₃ catalysts is shown in Fig. (5.4) & (5.5). It is shown that the first order reaction kinetics assumption is valid for both reactants on the two catalysts under almost all operating conditions investigated.

However, higher deviation is observed at the longest reaction time. These points were therefore excluded from the correlation. The correlation coefficient (≥ 0.9) in most of the cases as shown in Table (5.1) reflects the validity of the 1st order kinetics.

However ; Ir / γ - Al₂O₃ gave better correlation coefficient which are close to those of Rh / γ Al₂O₃.

The deviation from first order equation observed for both reactants at the longest reaction time may indicate a change in the reforming reaction mechanism or deactivation of both catalysts Ir and Ru / γ -Al₂O₃ with time, contrary to Rh / γ -Al₂O₃ which showed increased activation at the highest temperature with time.

As shown in Table (5.1) the reaction rate constant for CO₂ is found to be approximately equal to or slightly higher than those calculated for CH₄ at the same temperature, thus suggesting a route other than reforming for the reaction of CO₂ for example the RWGS reaction at the higher temperature, this result is in confirmation with those on yields of CO which are higher than H₂ despite the equimolar volumes of the reacting gases as discussed in chapter 4.

Arrhenius' plots for these catalysts are shown in Fig.(5.2.B,C). The plot reveals that the activation energy for CO₂ reaction is more than that for CH₄ i.e. CO₂ is more temperature – sensitive than CH₄. The activation energy for CH₄ dissociation is 28.85E3 J / mol while that for CO₂ is 43.81E3 J / mol for Ir/ γ - Al₂O₃ catalyst and 36.24E3 J / mol for CH₄ dissociation and 44.65E3 J / mol for CO₂ for Ru / γ - Al₂O₃ catalysts.

CONCLUSIONS

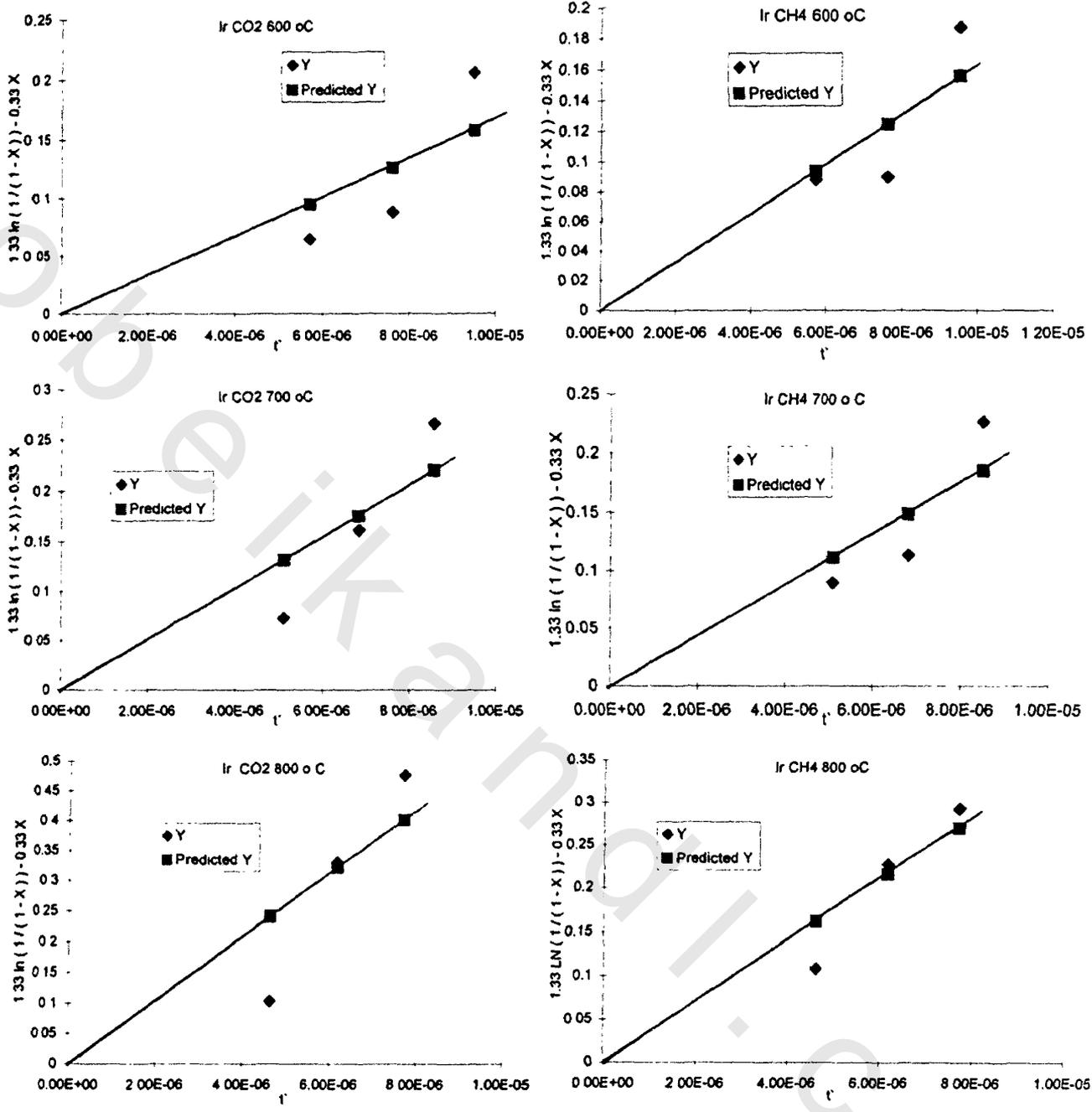


Fig (5 . 4) . Test for First Order Reaction Kineticses w . r . t CO₂ and CH₄ Over Ir / Al₂O₃ Catalyst .

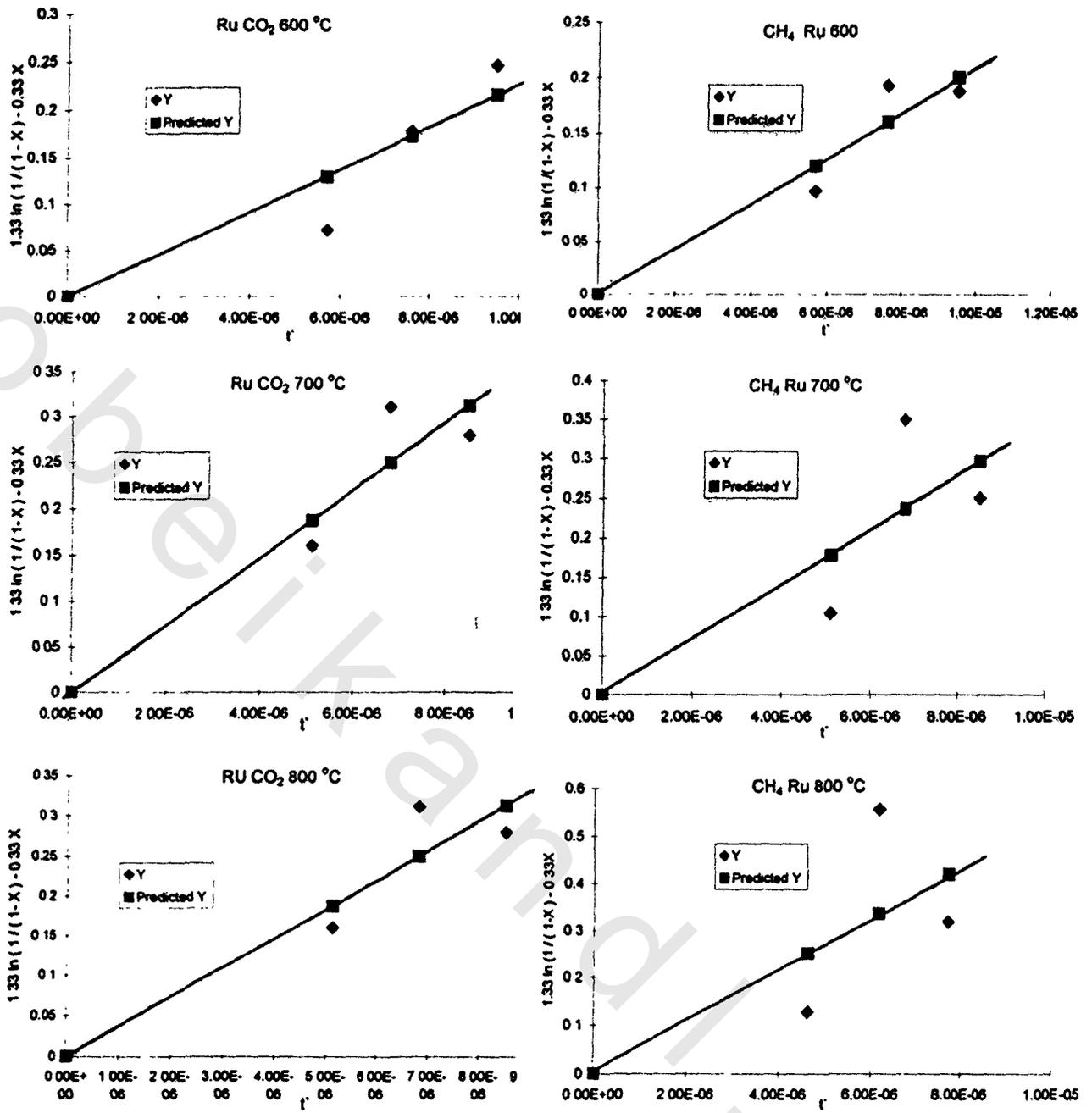


Fig (5 . 5) .Test for First Order Reaction Kinetics w .r .t CO₂ and CH₄ Over Ru / Al₂O₃ Catalyst .

CONCLUSIONS

The following conclusions can be drawn from the results of the present investigation:-

Generally ; for all the investigated catalysts the catalyst reactivity increased with increasing temperature and decreasing weight hourly space velocity .

a. For 0.5%Rh/ γ -Al₂O₃ catalyst:-

1. Rh/ γ -Al₂O₃ catalyst exhibits good reactivity within the whole temperature range and all the studied space velocities but with different degrees.
2. The space velocity 18000ccg⁻¹h⁻¹ and the temperature 800°C are the optimum condition resulting in the highest conversion of not only methane but also the other heavy hydrocarbons in the natural gas (ethane, propane, butanes, pentanes, hexanes, and heptanes).
3. The Rh / γ -Al₂O₃ selectivity with respect to H₂ and CO was achieved maximally at temperature of 800°C and space velocity 18000ccg⁻¹h⁻¹ .
4. (H₂ / CO) ratio was always less than one , however the highest ratio (0.65) was obtained at the optimum conditions, space velocity 36000 cc g⁻¹h⁻¹ and the temperature 700°C.
5. The first order kinetics assumption is valid for both CH₄ and CO₂ reactants under the operating conditions investigated . The reaction rate constant for CO₂ was higher than that of CH₄ (for example at 800°C reaction rate constants equal 19.1E4 and 8.13E4 J / mol) respectively .
6. The activation energy was calculated from Arrhinius' equation as 47.06E3 J / mol. and 29.51E3 J / mol. for CO₂ and CH₄ respectively .

b. For 0.5% Ru/ γ -Al₂O₃ catalyst:-

1. The space velocity 36000ccg⁻¹h⁻¹ and the temperature 800°C are the optimum condition resulting in the highest conversion of methane but , the space velocity 18000ccg⁻¹h⁻¹ and the temperature 800°C are the optimum condition resulting in the highest conversion of the other heavy hydrocarbons in the natural gas (ethane , propane, butanes, pentanes, hexanes, and heptanes).
2. The Ru / γ -Al₂O₃ selectivity with respect to H₂ and CO was achieved maximally at temperature of 800°C and space velocity 18000ccg⁻¹h⁻¹
3. Maximum (H₂ / CO) ratio was achieved at the optimum conditions, space velocity 18000ccg⁻¹h⁻¹ and the temperature 800°C.
4. The first order kinetics assumption is valid for both CH₄ and CO₂ reactants under the operating conditions investigated . The reaction rate constant for CO₂ was higher than that of CH₄ (for example at 800°C reaction rate constants equal 7.22E4 and 3.49E4 J / mol) respectively .
5. The activation energy was calculated from Arrhinius' equation as 44.65E3 and 36.24E3 J / mol for CO₂ and CH₄ respectively .

c. For 0.5% Ir/ γ -Al₂O₃ catalyst:-

1. The space velocity 45000ccg⁻¹h⁻¹ and the temperature 800°C are the optimum condition resulting in the highest conversion of methane but, the space velocity 18000ccg⁻¹h⁻¹ and the temperature 800°C are the optimum condition resulting in the highest conversion of not only methane but also the other heavy hydrocarbons in the natural gas (ethane, propane, butanes, pentanes, hexanes, and heptanes).

2. The Ir/ γ -Al₂O₃ selectivity with respect to H₂ and CO was achieved maximally at temperature of 800°C and space velocity 18000ccg⁻¹h⁻¹
3. Maximum (H₂ / CO) ratio was achieved at the optimum conditions, space velocity 36000ccg⁻¹h⁻¹ and the temperature 700°C.
4. The first order kinetics assumption is valid for both CH₄ and CO₂ reactants under the operating conditions investigated . The reaction rate constant for CO₂ was higher than that of CH₄ (for example at 800°C reaction rate constants equal 5.20E4 and 3.49E4 J / mol) respectively .
5. The activation energy was calculated from Arrhinius' equation as 43.81E3 and 28.85E3 J / mol for CO₂ and CH₄ respectively .

Finally 0.5% Rh/ γ -Al₂O₃ catalyst was the best as compared to the two other catalysts investigated . The optimum operating conditions were 18000 ccg⁻¹ h⁻¹ for the space velocity and 800°C for the reforming temperature . Maximum (H₂ /CO) ratio was obtained at 36000ccg⁻¹h⁻¹ space velocity and the temperature 700°C.

REFERENCES

REFERENCES

1. Alstrup , I. , Chorkendorff , I. , and Ullmann , S. , Surf. Sci. , **234** , 79 (1990).
2. Ashcroft , A. T. , Cheethan , A. K., Green , M. L. H. , and Vernon, P. D. F. ; Science, **352** , 225 (1991).
3. ASTM Designation (1996) Analysis of Natural Gas by Gas Chromatography , D 1945- 96 pp.51- 65.
4. Au , C. T. , Hu , Y. H. , and Wan , H. L. ; Catal. Lett. , **27** , 199 (1994).
5. Bhat , R. N. , and Sachtler , W. M. H. ; Appl. Catal. A : Gener. , **150**, 279 (1997).
6. Bitter , J. H. , Hally , W. , Seshan , K. , V. – Ommen , J. G., and Lercher , J. A. ; Catal . Today , **29** , 349 (1996).
7. Bitter , J. H. , Seshan , K. , and Lercher , J. A. ; J. Catal. , **171** , 279 (1997).
8. Bitter , J. H. , Seshan , K. , and Lercher , J. A. ; J. Catal. , **176** , 93 (1998).
9. Bodrov , I. M. , and Apel'baum , L. O. , Kinet. Catal. , **8** , 379 (1967).
10. Borer , A. L. , and Prins , R. , in Guzzi , L. , (Editor) ; 10th Symposium on Catalysis , Budapest , Hungary , (1992).
11. Bradford , M. C. J. , and Vannice , M. A. ; Catal . Rev . Sci . Eng . , **41** , 1(1999).
12. Bradford , M. C. J. , and Vannice , M. A. ; Catal . Today , **50** , 87 (1999).
13. Bradford , M. C. J. , and Vannice , M. A. ; Appl. Catal. A : Gener. , 223 (1997).
14. Brungs , A. J. , York , A. P. E. , and Green , M. L. H. ; Catal. Lett. , **57** , 65 (1999).
15. Bueno , J. M. C. ; Appl. Catal. A : Gener. , **193** , 173 (2000).

16. Buyevskaya, O. V., Wolf, D., and Baerns, M.; *Catal. Lett.*, **29**, 249 (1994).
17. Chang, J. S., Park, S. E., and Lee, K. W.; *Stud. Surf. Sci. Catal.*, **84**, 1587 (1994).
18. Che, M., Bennett, C. O.; *Advances in Catalysis*, **36** (1989)(a) Efstathiou, A. M., Bennett, C. O.; *J. Catal.*, **120**, 137 (1989).(b) Efstathiou, A. M., Bennett, C. O.; *J. Catal.*, **120**, 118 (1989).(c) Efstathiou, A. M., Chafik, T., Bianchi, D., and Bennett, C. O.; *J. Catal.*, **148**, 224 (1994).
19. Chen, X., Honda, K., and Zhang, Z.-G.; *Catal. Today* **93-95**, 87 (2004)
20. Chen, Z. X., Wu, J. L., and Zhu, M.; *Catal. Today*, **30**, 147 (1996).
21. Cheng, Z. X., Zhao, X. G., Li, J. L., and Zhu, Q. M.; *Appl. Catal. A: Gener.*, **205**, 31 (2001).
22. Cheng, Z., Wu, Q., Li, J., and Zhu, Q.; *Catal. Today*, **30**, 147 (1996).
23. Choudhary, V. R., Uphada, B. S., and Mamman, A. S.; *Catal. Lett.*, **32**, 387 (1995).
24. Claridge, B. J., Green, M. L. H., Tang, S. C., York, A. P. E., Ascroft, A. T., and Battle, P. D.; *Catal. Lett.*, **22**, 299 (1993).
25. Crisafulli, C., Scirè, S., Minicò, S., and Solarino, L.; *Appl. Catal. A: Gener.*, **225**, 1 (2002).
26. Effendi, A., Hellgardt, K., Honda, and Yoshida, T.; *Catal. Today* **77**, 181 (2002).
27. Effendi, A., Zhang, Z.-G. and Yoshida, T.; *ACS Symposium series* **809**, 275 (2002).
28. Efstathiou, A. M., Kladi, A., Tsipouriari, V., and Verykios, X. E.; *J. Catal.*, **158**, 64 (1996).
29. Erdöhelyi, A., Cresényi, J., and Solymosi, F.; *J. Catal.*, **141**, 287 (1993).

30. Erdöhelyi, A. Cresényi, J., Papp, E., and Solymosi, F.; *Appl. Catal. A: Gener.*, **108**, 205 (1994).
31. F. - Aparicio, P., G. - Ruiz, A., and R. - Ramos, I.; *Appl. Catal. A: Gener.*, **170**, 177 (1998).
32. F. - Aparicio, P., R. - Ramos, I., Anderson, J. A., and G. - Ruiz, A.; *Appl. Catal. A: Gener.*, **202**, 183 (2000).
33. Fischer, F., and Tropsch, H., *Brennstoff; Chemie*, **3**, 39 (1928).
34. Frusteri, F., Arena, F., Galogero, G., Torre, T., and Paratiana, A.; *Catal. Comm.*, **2**, 49 (2001).
35. Gadalla, A. M., and Bower, B.; *Chem. Eng. Sci.*, **43**, 3049 (1988).
36. Galuszka, J., Pandey, R. N., Ahmed, S.; *Catal. Today* **46**, 83 (1998).
37. Giapetta, F., G., and Plank, C. J., in P. H. Emmett (ed.), "Catalysis", Vol. 1. Chap. 7. Reinhold Publishing Corporation, New York, (1954).
38. Goldwasser, M. R., Rivas, M. E., Pietri, E., P. Zurita, M. J., Cubeiro, M. L., Gingembre, L., Leclercq, L., and Leclercq, G.; *Appl. Catal. A: Gener.*, **255**, 45 (2003).
39. Goula, M., Lemoidou, A., and Efstathiou, A. M.; *J. Catal.* **162**, 626 (1996).
40. Goula, M. A., Lemonidou, A. A., and Efstathiou, A. M.; *J. Catal.*, **161**, 626 (1996).
41. Gronchi, P., Centola, P., and Rosso, R. D.; *Appl. Catal. A: Gener.*, **152**, 83 (1997).
42. Gronchi, P., Mazzocchia, C., Tempesti, E., and D. - Rosso, R., in Genti, G., Cristiani, C., Forzatti, P., and Perathoner, S., (Editors). *Environmental Catalysis*, SCI, Rome, Italy, 1995, P.P.627-630.
43. Gronchi, P., Mazzocchia, C., and Del Rosso, R.; *En. Conv. Man.* **36** (6-9) 605-608 (1995).

44. Guo , J . , Lou , H . , Zhao , H . , Chai , D . , and Zheng , X . ;
Appl . Catal . A : General **273**(1-2) , 75-82 (2004).
45. Hashimoto , K . , Watase , S . , and Toukai , N . , Catal. Lett . , **80** ,
147 (2002).
46. Hayakawa , T . , Harihara , H . , Andersen , A . G . , York , A . P .
E . , Suzuki , K . , Yasuda , H . , and Takehira , K . , Angew . ;
Chem . , Int . Ed . Engl . , **35** , 92 (1996).
47. Hayakawa , T . , Suzuki , S . , Nakamura , J . , Uchijima , T .
Hamakawa , S . , Suzuki , K . , Shishido , T . , and Takehira , K . ;
Appl . Catal . A : Gener . , **183** , 273 (1999).
48. Hayakawa , T . , Harihara , H . , Andersen , A . G . , Suzuki , K . ,
Yasuda , H . , Tsunoda , T . , Hamakawa , S . , York , A . P . E . ,
Yoon , Y . S . , Shimizu , M . , and Takehira , K . ; Appl. Catal. A :
Gener . , **149** , 391 (1997).
49. Hickman , D . A . , Hauptfear , E . A . , and Schmidt , L . D . ;
Catal . Lett . **17** , 223 (1993) .
50. Hickman , D . A . , Hauptfear , E . A . , and Schmidt , L . D . ; Catal .
Lett . , **17** , 223 (1993).
51. Horiuchi , T . , Sakuma , K . , Fuku , T . , Kubo , Y . , Osaki , T . ,
and Mori , T . ; Appl. Catal. A : Gener . , **144** , 111 (1996).
52. Hou , Z . , and Yashima , T . ; Catal . Lett . , **89** , 193 (2003).
53. Hou , Z . , and Yashima , T . ; Appl . Catal . A : Gener . , **261** , 205
(2004).
54. Hou , Z . , Yokota , O . , Tanaka , T . , and Yashima , T . ; Appl.
Catal. A : Gener . , **253** , 381 (2003).
55. Huder , K . ; Chem . Ing . Tech . **63** , 376 (1991).
56. Ito , M . , Tagawa , T . , and Goto , S . ; Appl. Catal. A : Gener .
, **177** , 15 (1999).
57. J . - Juan , J . , R . - Martínez , and I . - Gómez , M . J . ; Appl. Catal. A :
Gener . , **264** , 169 (2004).
58. Kellner , C . S . , and Bell , A . T . ; J. Catal . , **67** , 175 (1981).

59. Kim, G. J., Cho, D. S., Kim, K. H., and Kim, H. J.; *Catal. Lett.*, **28**, 41 (1994).
60. Kim, J. - H., Jinsuh, D., Park, T. - J., and Kim, K.L.; *Appl. Catal. A: Gener.*, **197**, 191 (2000).
61. Kurz, G., and Teuner, S., *Erdöl and Kohle*, **43**, 171 (1990).
62. Lee, J. - H., Lee, E. - G., Joo, O. - S., and Jung, K. - D.; *Appl. Catal. A: Gener.*, **269**, 1 (2004).
63. Lemonidou, A. A., and Vasalos, I. A.; *Appl. Catal. A: Gener.*, **54**, 119 (1989).
64. Lemonidou, A. A., Goula, M.A., and Vasalos, I. A.; *Catal. Today*, **46**, 175 (1998).
65. Lercher, J. A., Bitter, J. H., Hally, W., Niessen, W., and Seshan, K.; *Stud. Surf. Sci. Catal.*, **101**, 463 (2001).
66. Mark, M. F., Maier, W. F.; *J. Catal.*, **164**, 122 (1996).
67. Martínez, R., Romero, E., Guimon, C., and Bilbao, R.; *Appl. Catal. A: General* **274**(1-2), 139-149 (2004).
68. Matsui, N. - O., Anzai, K., Akamatsu, N., Nakagawa, K., Ikenaga, N. - O., and Suzuki, T.; *Appl. Catal. A: Gener.*, **179**, 247 (1999).
69. McCarthy, T. J., Marques, C. M. P., Treviño, H., and Sachtler, W. M. H.; *Catal. Lett.*, **43**, 11 (1997).
70. Menad, S., F. - Aparicio, P., Cherifi, O., G. - Ruiz, A., R. - Ramos, I.; *Catal. Lett.*, **89**, 63 (2003).
71. Morterra, C., Bolis, and V., Magnacca, G.; *J. Chem. Soc., Faraday Trans.*, **92**, 1991 (1996).
72. Múnera, J., Irusta, S., Cornaglia, L., and Lombardo, E.; *Appl. Catal. A: General* **245**, 383 (2003).
73. Munera, J., Irusta, S., Cornaglia, L., and Lombardo, E.; *Appl. Catal. A: Gener.*, **245**, 383 (2003).
74. Nagaoka, K., Okamura, M., and Aika, K. - I.; *Catal. Comm.*, **2**, 255 (2001).

75. Nagaoka, K., Takanabe, K., and Aika, K.; *Appl. Catal. A: General* **255**, 13 (2003).
76. Nagaoka, K., Takanabe, K., and Aika, K.; *Chem. Commun.* **1006** (2002).
77. Nakamura, J., Aikawa, K., Sato, K., Uchijima, T.; *Catal. Lett.*, **265**, 25 (1994).
78. Oklay, J., Hon, K., and Hughes, R.; *Appl. Catal. A: General* **170**, 13 (1998).
79. Omata, K., Hottai, N. T., and Yamada, M.; *Catal. Comm.* **5**, 771 (2004).
80. Omata, K., Hottai, N. T., Showa, Y., and Yamada, M.; *Catal. Comm.* **5**, 775 (2004).
81. Paipatyadar, S. A., *Cyclic Operation of Sodium Heat Pipe, Solar Reformers*, Ph. D. Dissertation, Department of Chemical Engineering, University of Houston, Houston TX, May (1987).
82. Pant, B., and S. – Williams; *Catal. Comm.*, **5**, 305 (2004).
83. Paturzo, L., Gallucci, F., Basile, A., Vitulli, G., and Pertici, P.; *Catal. Today* **82**, 57 (2003).
84. Paturzo, L., Gallucci, F., Basile, A., Vitulli, G., and Pertici, P.; *Catal. Today*, **82**, 57-65 (2003).
85. Paturzo, L., Gallucci, F., Basile, A., Vitulli, G., and Pertici, P.; *Catal. Today*, **82**, 57 (2003).
86. Pessi, F., and Bonvicino, F., Thesis; Politecnico di Milano, Milan, Italy, 1994.
87. Petersen, K., Nielsen, C., and Jørgensen, S.; *Catal. Today* **46**, 193 (1998).
88. Pitsai, P., and Kleir, K.; *Catal. Rev. – Sci. Eng.* **28**, 13 (1986).
89. Portugal Jr., U. L., Marques, C. M. P., Araujo, E. C. C., Morales, E. V., Gitto, M. V.; *Appl. Catal. A: Gener.*, **193**, 173 (2000).

90. Prabhu , A . K . , Radhakrishnan , R . , and Oyama , S . T . ; Appl . Catal . A : Gener . , **183** , 241 (1999).
91. Quinalan , M. A . , Wood , B. J . , and Wise , H . ; Chem. Phys. Lett . , **118**, 478 (1985).
92. R . - Nielsen , J. R . ; Stud. Surf. Sci. Catal . , **81** , 25 (1994).
93. R . - Nielsen , J. R . ; J. Catal . , **31** , 173 (1973).
94. R . - Nielsen , J. R . ; J. Catal . , **31** , 184 (1974).
95. R . - Nielsen , J.R . , and B . - Hansen , J.H . ; J. Catal . , **144** , 38 (1993).
96. Raskó , J . , and Solymosi , F . ; Catal. Lett . , **46** , 153 (1997).
100. Richardson , J . T . , and Paripatyadar , S. A . ; Appl . Catal . A : Gener . , **61** , 293 (1990).
101. Richardson , J . T . , Garrit , M . , and Hung , J . - K . ; Appl . Catal . A : General **255** , 69 (2003) .
102. Richardson , J. T . , Garrait , M . , and Hang , J . -K . ; Appl . Catal . A : Gener . , **255** , 69 (2003).
103. Ruckenstein , E . , Wang , H . Y . ; J. Catal . **190** , 32 (2000).
104. Ruckenstein , E . ; and Wang , H . Y . ; Appl . Catal . A : Gener . , **204** , 257 (2000).
105. Ruckenstein , E . , and Wang , H . Y . ; Appl . Catal . A : Gener . , **198** , 33 (2000).
106. Ruckenstein , E . , and Hu , Y. H . ; J. Catal . , **161** , 55 (1996).
107. Rynkowski , J . , Samulkiewicz , P . , Ladavos , A K . , and Pomonis , P.J . ; Appl. Catal. A : Gener . , **263** , 1 (2004).
108. Sachtler , W . M . H . , and Zhang , Z . ; Adv. Catal . , **39** ,

- 129 (1993).
109. Shiozaki, R., Andersen, A.G., Hayakawa, T., Hamakawa, S., Suzuki, K., Shimizu, M., and Takehira, K.; *J. Chem. Soc., Faraday Trans.*, **93**, 3225 (1997).
110. Solymosi, F., Kutsán, G., and Erdöhelyi, A., *Catal. Lett.*, **11**, 149 (1991).
111. Solymosi, F., Erdöhelyi, A. and Cresényi, J.; *Catal. Lett.*, **16** (1992).
112. Somorjai, G. A.; *Introduction to Surface Chemistry and Catalysis*, Wiley, New York, 1994.
113. Soria, J., Coronado, J.M., and Conesa, J.C.; *J. Chem. Soc., Faraday Trans.*, **92**, 1618 (1996).
114. Stull, D. R., Edgar, F., Westrum, J., and Sinke, G. C.; *The Thermodynamic of Organic Compounds*, Princeton University Press, Princeton, N J (1984).
115. Suh, D. J., and park, T. - J.; *Chem. Mater.*, **8**, 509 (1996).
116. Suh, D. J., Park, T. - J., Kim, T. - H., and Kim, K. - L.; *J. Non - Cryst. Solids*, **225**, 168 (1998).
117. Swaan, H. M., Kroll, V. C. H., Martin, G. A., and Mirodatos, C.; *Catal. Today* **21**, 571 (1994).
118. Swaan, H. M., Kroll, V. C. H., Martin, G. A., and Mirodatos, C., *Catal. Today*, **21**, 571 (1994).
119. Takayasu, O., Soman, C., Takegahara, Y., and Mastsuura,

- I.; *Stud. Surf. Sci. Catal.* , **88** , 281 (1994).
120. Takehira , K. , Shishido , T. , Shoro , D. , Murakami , K. ,
Honda , M. , Kawabata , and Takaki , K. ; *Catal. Comm.* , **5** ,
209 (2004).
121. Tenner , S. ; *Hydrocarbon Process* , **64** , 106 (1985).
122. Tomishige , K. , Himeno , Y. , Matumoto , Y. , Yoshinaga ,
Y. , and Fujimoto , K. , *Ind . Eng . Chem . Res .* **39** , 1891
(2000).
123. Tomishige , K. ; *Catal. Today* , **89** , 405 (2004).
124. Tornaiainen , P. M. , Chu , X. , and Schemidt , L. D. ; *J. Catal.* ,
146 , 1 (1994).
125. Trovarelli , A. ; *Catal. Rev. - Sci. Eng.* , **38** , 439 (1996).
126. Tsipouriari , V. A. , Efastathiou , A. M. , and Verykios , X.
E. ; *J. Catal.* , **161** , 31 (1996).
127. Tsipouriari , V. A. , Efstathiou , A. M. , Zhang , Z. L. , and
Verykios , X. E. ; *Catal. Today* , **21** , 579 (1994).
128. Turlier , P. , Pereira , E. B. , and Martin , G. A. ; *Proceedings
of the International Conference on Carbon dioxide Utilization
, Bari , (1993), P. 119.*
129. Valantini , A. , Carreño , N. L. V. , Probst , L. F. D. , L.
Filho , P. N. , Schreiner , W. H. , Liete , E. R. , and Longo , E
; *Appl . Catal . A : Gener .* , **255** , 211 (2003).
130. Verykios , X. E. ; *Appl . Catal . A : General* **225** , 101 (2003).
131. Verykios , X. E. ; *Appl. Catal. A : Gener.* , **225** , 101 (2003).
132. Wang , H. Y. , and Au , C. T. ; *Appl. Catal. A : Gener.* , **155** ,

- 239 (1997).
133. Wang , H. Y. , and Ruckenstein , E. ; Appl. Catal. A : Gener. ,
204 , 143 (2000).
134. Wang , L . , Murata , K . , and Inaba , M . ; Catal . Commun .
4 , 147 (2003) .
135. Wang , Lercher , J . A . , and Haller , G . L . ; J. Catal. , 88 , 18
(1984).
136. Wang , Q . L . , Giannetto , G . , Torrealba , M . , Perot , G . ,
Kappenstein , C . , and Guisnet , M . ; J. Catal . , 130 , 459
(1991).
137. Wang , S . , and Lu , G. Q. M. ; Appl. Catal. B : Envir. , 16 ,
269 (1998).
138. Wang , S . , and Lu , G.Q. ; Appl. Catal. A : Gener. , 169 , 271
(1998).
139. Wang , S . , and Lu , G.Q. ; Appl. Catal. B : Envir. , 19 , 267
(1998).
140. Wang , S . , Lu ,G. Q. M. , and Millar , G. ; J. , Energy and
Fuels , 10 , 896 (1996).
141. Wang , S . , Ph.D. Thesis , The university of Queensland ,1998.
142. Weckhuysen , B . , M . , Keller , D . E . ; Catal . Today 78 , 25
(2003) .
143. Wei , J . , and Iglesia , E . ; J . Catal . 225 , 116 (2004) .
144. Wei , J . - M . , Xu , B . - Q . , Li , J . - L . , Cheng , Z . - X . , and
Zhu , Q . - M . ; Appl. Catal. A : Gener. , 196 , L167 (2000).
145. Wei , J . , and Iglesia , E . ; J. Catal. , 225 , 116 (2004).

146. Weisz, P., *Physik, Z.; Chem. N. F.* **11**, 1 (1957).
147. Westheimer, F. H.; *Chem. Rev.*, **61**, 265 (1961).
148. Wie, J., and Iglesia, E.; *J. Catal.*, **224**, 370 (2004).
150. Winkler, A., Guo, X., Siddiqui, P. L., Hagans, P. L., and Yates, J. T.; Jr., *Surf. Sci.*, **201**, 419 (1988).
151. Wong, T. T. T., Stakheev, A. Y., and Sachtler, W. M. H.; *J. Phys. Chem.*, **96**, 7733 (1992).
152. Xu, G., Shi, K., Gao, Y., Xu, H., and Wei, Y.; *J. Mol. Catal. A: Chem.*, **147**, 47 (1999).
153. Xu, H. Y., Su, X. X., Fan, Y. M., L. – Xu, G., Liu, J. X., Yu, W. G., and Zhou, P. H.; *Petrol. Chem. Eng.*, **21**, 147 (1992).
154. Xu, L., Zhang, Z., and Sachtler, W. M. H.; *J. Chem. Soc., Faraday Trans.*, **88**, 2291 (1992).
155. Yamazaki, O., Nozaki, T., Omata, K., and Fujimoto, K.; *Chem. Lett.*, 1953 (1992).
156. Yao, C., and Yao, Y. F. Y.; *J. Catal.*, **86**, 254 (1984).
157. Yokota, S., Okumura, K., and Niwa, M.; *Catal. Lett.*, **84**, 131 (2000)
158. York, A. P. E., Claridge, J. B., Brungs, A. J., Tsang, S. C., and Green, M. L. H.; *Chem. Comm.* 39 (1997).
159. Zhang, Z., and Verykios, X. E., and Baerns, M.; *Catal. Rev. –Sci. Eng.* **36**, 507 (1994).
160. Zhang, Z., and Verykios, X. E.; *Catal. Today*, **21**, 589 (1994).

REFERENCES

161. Zhang , Z. , and Verykios , X.E. ; J. Chem. , Soc. , Chem. Comm. , 71 (1995).
162. Zhang , Z. , Verykios , X. E. , M. - Donald , S. M. , and Affrossman, S. ; J. Phys. Chem., 100 , 744 (1996).
163. Zhang , Z. L. , Tsipouriari , V. A. , Efastathiou , A. M. , and Verykios , X. E. ; J. Catal. , 158 , 51 (1996).

APPENDIX A

APPENDIX . A .

First Order Reaction Kinetic's Calculations :-

Given the volumetric analysis (percentage remained) of the reacting species in Table (A 1-3).

Table (A.1) . Remaining Concentrations of CO_2 and CH_4 for Rh / $\gamma-Al_2O_3$ at the studied conditions .

Temperature	600 °C		700°C		800°C	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
Space Velocity $ccg^{-1}.h^{-1}$						
18000	41.53	28.38	32.97	22.37	5.17	6.56
36000	66.04	58.03	53.38	40.51	41.06	33.99
45000	73.99	56.59	69.59	48.95	63.02	43.2
60000	89.21	94.85	83.29	74.94	74.44	62.26

Table (A.2) . Remaining Concentrations of CO_2 and CH_4 for Ru / $\gamma-Al_2O_3$ at the studied conditions .

Temperature	600 °C		700°C		800°C	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
Space Velocity $ccg^{-1}.h^{-1}$						
18000	88.26	91.04	87.44	81.62	85	69.91
36000	78.5	79.7	65.54	68.46	52.58	49.05
45000	78.95	73.69	73.38	70.95	67.83	59.35
60000	91.17	90.83	88.72	76.01	82.9	66.92

Table (A.3) . Remaining Concentrations of CO₂ and CH₄ for Ir / γ -Al₂O₃ at the studied conditions .

Temperature Space Velocity ccg ⁻¹ .h ⁻¹	600 °C		700°C		800°C	
	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
18000	89.26	91.43	89.04	90.99	87.02	87.48
36000	89.05	89.22	86.44	81.51	75.37	67.01
45000	79.03	77.25	75.44	72.02	69.89	57.12
60000	98.63	97.43	99.46	94.22	95.03	92.89

The following procedure was used to calculate the conversion and hence the r.h.s of Eq. (17) as well as the weight – time term of the l.h.s of the same equation

Take as an example Rh / γ - Al₂O₃ catalyst for the reaction of CO₂ .

The partial pressure of CO₂ in the entering gases = 1 / 6 atm.

The entering CO₂ concentration =

$$C_{CO_2, in} = \frac{N_{CO_2}}{V} = \frac{P_{CO_2}}{RT} = \frac{0.167 atm.}{(0.082 lit.atm./ mol.^{\circ} K \times 873^{\circ} K)}$$

$$= 0.0023 mol./l.$$

For a feed rate of 600 cc / min at 25°C :-

The volumetric flow rate flow rate =

$$600 \text{ cc / min} \times (\text{lit.} / 10^3 \text{ cc}) \times (60 \text{ min} / \text{h}) = 36 \text{ lit.} / \text{h} .$$

This flow rate is corrected for reaction temperature by :-

$$V_2 = V_1 \times T_2 / T_1 = 36 \times 873 / 298 = 105 \text{ lit.} / \text{hr} .$$

Then the entering molar flow rate :-

$$F_{CO_2} = C_{CO_2, in} \times V_2$$

$$= (0.0023 \text{ mol CO}_2 / \text{lit.}) (105 \text{ lit.} / \text{hr}) = 0.2415 \text{ mol.} / \text{hr} .$$

given the weight of catalyst utilized = 2 g , then the weight – time term in equation is calculated as :-

$$\frac{C_{CO_2, \alpha} W}{F_{CO_2, \alpha}} = \frac{0.0023 \times 0.002}{0.2415} = 1.9 \times 10^{-5} \text{ (kg .h} / \text{lit.)}$$

The conversion X_{CO_2} is calculated from equation :-

$$X_{CO_2} = \frac{C_{CO_2, in} - C_{CO_2, out}}{C_{CO_2, in} + 0.33C_{CO_2, out}}$$

Where ϵ = expansion factor = 1 / 3 in our case as shown in chapter 5.

$C_{CO_2, out}$ is calculated as $C_{CO_2, in} \times \% \text{ remained}$.

The same calculation procedure is repeated at each flow rate for a given temperature .

The calculations results are given in Tables (A .4-6) for the Rh / γ - Al_2O_3 , Ru / γ - Al_2O_3 and Ir / γ - Al_2O_3 respectively .

The value of $\{1.3 \ln 1 / (1 - X) - 0.3 X\}$ is plotted vs $\frac{C_{CO_2, ax} W}{F_{CO_2, o}}$ as shown in Fig (5.4-6) for each catalyst type .

The slope of the line = k' lit./hr. kg cat. the reaction rate constant .

For a first order reaction :-

$$- r'_{CO_2} = k' (\text{lit. / hr kg cat}) \times (C_{CO_2} \text{ mol / lit})$$

Table (A .4a) . The calculation needed to test the fit of Eq . (17) of CO_2 component for Rh / γ - Al_2O_3 .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	A - B	F_i	$C_i W / F_i$
$C_{i_0} = 0.0023 \text{ mol / lit.}$						
600 °C	0.0397	0.0539	0.0131	0.0408	0.805	5.7E-6
	0.3660	0.607	0.1210	0.486	0.605	7.6E-6
	0.3540	0.580	0.1168	0.463	0.483	9.5E-6
	0.6548	1.415	0.2161	1.199	0.242	19E-6
$C_{i_0} = 0.00209 \text{ mol / lit.}$						
700 °C	0.330	0.5326	0.1089	0.4237	0.8180	5.11E-6
	0.605	1.2354	0.1997	1.0357	0.6140	6.81E-6
	0.686	1.5406	0.2262	1.3142	0.4910	8.513E-6
	0.838	2.4208	0.2765	2.1443	0.2460	16.99E-6
$C_{i_0} = 0.0019 \text{ mol / lit}$						
800 °C	0.475	0.8569	0.1567	0.700	0.821	4.628E-6
	0.663	1.4466	0.2188	1.198	0.616	6.169E-6
	0.744	1.8122	0.2455	1.567	0.493	7.708E-6
	0.955	4.1245	0.3152	3.809	0.246	15.45E-6

Table (A .4b) . The calculation needed to test the fit of Eq (17) of CH₄ component for Rh / γ - Al₂O₃ catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33 C_o)}$	$A = 1.33 \ln (1 / 1 - X)$	$B = 0.33 X$	A - B	F _i	$\frac{C_i W}{F_i}$
$C_{i_0} = 0.002139 \text{ mol / lit.}$						
600 °C	0.08269	0.114795	0.027288	0.087507	0.74866	5.714E-6
	0.2056	0.31192	0.06899	0.24293	0.5615	7.619E-6
	0.278833	0.43476	0.09215	0.34274	0.44919	9.524E-6
	0.514226	0.96028	0.16969	0.79058	0.2245	19.056E-6
$C_{i_0} = 0.00194 \text{ mol / lit.}$						
700 °C	0.13107	0.18686	0.04325	0.1436	0.7601	5.1046E-6
	0.2473	0.37785	0.081611	0.29623	0.570	6.8062E-6
	0.3964	0.67139	0.13080	0.54086	0.456	8.5087E-6
	0.60453	1.2336	0.19949	1.03431	0.228	17.017E-6
$C_{i_0} = 0.00177 \text{ mol / lit.}$						
800 °C	0.20519	0.30544	0.067714	0.2377	0.765	4.628E-6
	0.30613	0.48608	0.101024	0.38586	0.574	6.1716E-6
	0.51907	0.97359	0.17129	0.8023	0.459	7.715E-6
	0.93239	3.58307	0.300769	3.27538	0.229	15.432E-6

Table (A .5a) . The calculation needed to test the fit of Eq (17) CO₂ component for Ru / γ - Al₂O₃ catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	$A - B$	F_i	$\frac{C_i W}{F_i}$
$C_i = 0.0023 \text{ mol / lit.}$						
600 °C	0.06890	0.094947	0.022737	0.07221	0.805	5.7E-6
	0.15931	0.230798	0.05257	0.178226	0.605	7.6E-6
	0.211635	0.316266	0.06984	0.24643	0.483	9.5E-6
	0.07055	0.097309	0.02328	0.074027	0.242	19.0E-6
$C_i = 0.00209 \text{ mol / lit.}$						
700 °C	0.144799	0.20803	0.0477836	0.16025	0.818	5.11E-6
	0.25728	0.39558	0.084903	0.310682	0.614	6.81E-6
	0.23538	0.35695	0.077678	0.27927	0.491	8.513E-6
	0.19179	0.28320	0.06329	0.21991	0.246	16.99E-6
$C_i = 0.0019 \text{ mol / lit.}$						
800 °C	0.24449	0.37289	0.03068	0.2922	0.821	4.628E-6
	0.43852	0.767646	0.14471	0.62293	0.616	6.169E-6
	0.33992	0.55248	0.112175	0.440308	0.493	7.708E-6
	0.27096	0.42032	0.08941	0.330901	0.246	15.45E-6

Table (A .5b) . The calculation needed to test the fit of Eq. (17)CH₄ component for Ru / γ - Al₂O₃ catalyst.

Temperature	$X = \frac{C_i - C_0}{(C_i + 0.33C_0)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	$A - B$	F_i	$\frac{C_i W}{F_i}$
$C_i = 0.002139 \text{ mol / lit}$						
600 °C	0.0901	0.12678	0.030003	0.096774	0.74866	5.714E-6
	0.17076	0.24904	0.056352	0.192691	0.5615	7.619E-6
	0.16699	0.2430	0.055108	0.1879	0.44919	9.524E-6
	0.06787	0.09348	0.022399	0.07109	0.2245	19.05E-6
$C_i = 0.00194 \text{ mol / lit}$						
700 °C	0.09747	0.13640	0.03217	0.10424	0.7601	5.1046E-6
	0.2833	0.44306	0.09349	0.34956	0.570	6.8062E-6
	0.21431	0.32078	0.07072	0.25006	0.456	8.5087E-6
	0.08725	0.12142	0.02879	0.09263	0.228	17.017E-6
$C_i = 0.00177 \text{ mol / lit}$						
800 °C	0.11714	0.1657	0.038657	0.12705	0.765	4.628E-6
	0.40489	0.68848	0.133348	0.555137	0.574	6.171E-6
	0.26286	0.405622	0.08674	0.31888	0.459	7.715E-6
	0.13468	0.191759	0.044308	0.14745	0.229	15.432E-6

Table (A .6a) . The calculation of needed to test the fit of Eq (17)CO₂ component for Ir / γ - Al₂O₃ catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	$A - B$	F_i	$\frac{C_i W}{F_i}$
$C_i = 0.0023 \text{ mol / lit.}$						
600 °C	0.061916	0.085008	0.020432	0.06457	0.805	5.7E-6
	0.08328	0.115647	0.02778	0.08817	0.605	7.6E-6
	0.18128	0.266026	0.05982	0.20620	0.483	9.5E-6
	0.01944	0.021197	0.006417	0.01970	0.242	19.0E-6
$C_i = 0.00209 \text{ mol / lit.}$						
700 °C	0.06929	0.095508	0.022867	0.07264	0.818	5.11E-6
	0.1457	0.20945	0.04808	0.161367	0.614	6.818E-6
	0.22607	0.34084	0.07460	0.26624	0.491	8.563E-6
	0.04409	0.05997	0.01455	0.04542	0.246	16.99E-6
$C_i = 0.0019 \text{ mol / lit.}$						
800 °C	0.09715	0.13593	0.03206	0.10387	0.821	4.628E-6
	0.27015	0.41885	0.08915	0.3297	0.616	6.169E-6
	0.36079	0.59521	0.11906	0.47615	0.493	7.708E-6
	0.05442	0.07442	0.01796	0.05645	0.246	15.45E-6

Table (A .6b) . The calculation of needed to test the fit of Eq (17) CH₄ component for Ir / γ - Al₂O₃ catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	A - B	F _i	$\frac{C_i W}{F_i}$
$C_{i_0} = 0.002139 \text{ mol / lit.}$						
600 °C	0.08296	0.11519	0.02738	0.08781	0.74866	5.714E-6
	0.08463	0.11760	0.02793	0.08968	0.5615	7.619E-6
	0.1663	0.2419	0.05488	0.18705	0.44919	9.524E-6
	0.01033	0.01382	0.00341	0.0104	0.2245	19.05E-6
$C_{i_0} = 0.00194 \text{ mol / lit.}$						
700 °C	0.08471	0.11772	0.027954	0.089769	0.7601	5.105E-6
	0.10550	0.14829	0.034817	0.113473	0.570	6.806E-6
	0.19664	0.291214	0.064892	0.22632	0.456	8.509E-6
	0.00414	0.05519	0.001366	0.00415	0.228	17.017E-6
$C_{i_0} = 0.00177 \text{ mol / lit.}$						
800 °C	0.10084	0.14137	0.033278	0.108096	0.165	4.628E-6
	0.1972	0.2922	0.06509	0.22711	0.574	6.171E-6
	0.2446	0.37319	0.080741	0.29245	0.459	7.715E-6
	0.0378	0.05129	0.01248	0.03881	0.229	15.432E-6

ARABIC SUMMARY

تحويل الغاز الطبيعي بواسطة ثاني أكسيد الكربون لإنتاج غاز التخليق

رساله مقدمه للحصول على
درجة ماجستير الفلسفة في العلوم

من

رضوى عباس مصطفى السيد السلاموني
بكالوريوس علوم - جامعة عين شمس

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أ. د. عقيله كامل المرسي
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إلى

قسم الكيمياء
كلية العلوم - جامعة عين شمس

القاهرة - ٢٠٠٥ م

تحويل الغاز الطبيعي بواسطة ثاني أكسيد الكربون لإنتاج غاز التخليق

مقدمه من :-

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القاهره - ٢٠٠٥ م

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٢- ١ . د . سهام علي التمتامي .

٣- ١ . د . عقيله كامل المرسي .

و أشكر كل من تعاون معي في هذا البحث وهما :-

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د . سلوى عبد الواحد غنيم .

و كذلك الهيئات الآتية :-

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٢- معهد بحوث البترول .

جامعة عين شمس
كلية العلوم

اسم الطالب :- رضوي عباس مصطفى السيد السلاموني

الدرجة العلمية :- ماجستير الفلسفة في العلوم " كيمياء "

القسم :- الكيمياء .

الكلية :- العلوم .

الجامعة :- عين شمس .

سنة التخرج :- ١٩٩٨ م .

سنة المنح :- ٢٠٠٥ م .

رسالة ماجستير

اسم الطالبه :- رضوى عباس مصطفى السيد السلاموني .

عنوان الرسالة :- تحويل الغاز الطبيعي بواسطة ثاني أكسيد الكربون
لإنتاج غاز التخليق .

اسم الدرجة :- ماجستير الفلسفه في العلوم " كيمياء " .

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لجنة التحكيم

الدراسات العليا

موافقة مجلس الكلية
/ / ٢٠٠٥ م

أجيزت رساله بتاريخ
/ / ٢٠٠٥ م

ختم الإجازة

موافقة مجلس الجامعة
/ / ٢٠٠٥ م

الملخص العربي

يلعب الغاز الطبيعي دوراً مهماً وحيوياً في حياة الإنسان ، إذ أنه من أهم المصادر الطبيعية النظيفة للحصول على الوقود و هناك العديد من الأبحاث التي تتم لتحويل الغاز الطبيعي الى غاز التخليق (هيدروجين + أول أكسيد الكربون) و الذي بدوره يشكل المصدر الرئيسي لصناعة العديد من المركبات الكيماوية مثل الميثانول و ثنائي ميثيل الايثر الذي يعتبر وقود القرن الحادي و العشرين باستخدام الحفازات ، كما أنه مصدر مهم لتفاعل Fisher – Tropsch الذي يحول الغاز الطبيعي الى وقود سائل و المعروف ب (GTL) أيضا يعتبر غاز التخليق المصدر الأساسي لكثير من العمليات الكيماوية كالهدرجة و الأختزال و غيرها .

اتجهت الأنظار في نهاية القرن الماضي لتحضير غاز التخليق من الغاز الطبيعي باستخدام غاز ثاني أكسيد الكربون كعامل مؤكسد و ذلك لما له من أضرار على البيئة فهو أحد العناصر الضاره المساهمه بشده في حدوث ظاهرة الاحتباس الحراري .

كذلك يعتبر ارتفاع المحتوى الحراري المرتبط بهذا التفاعل و تفاعله العكسي مصدرا مهما لتخزين الطاقة (للطاقة المتجدده) .

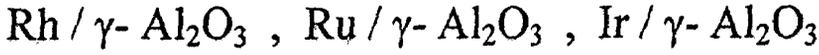
و كما هو معروف فقد تم اكتشاف كميات كبيره من الغاز الطبيعي في مصر خلال السنوات الأخيره مما يجدر بنا محاولة الاستفاده من هذا الكنز الذي أنعم الله به على هذه البلاد .

و لقد اعتمدنا في هذا البحث على دراسة الغاز الطبيعي المصري لانتاج غاز التخليق و ليس فقط الميثان و الذي يمثل المكون الرئيسي للغاز الطبيعي .

و قد استخدم المفاعل ذو المهد الثابت (Fixed Bed) والمكون من أنبوب زجاجي قطره ١٣ مم و طوله ١٢ سم حيث تدفع الغازات المغذيه (ثاني أكسيد الكربون ، الغاز الطبيعي ، النيتروجين) بنسبة ١ : ١ : ٤ في وجود ٢ جم من الحفاز تحت الاختبار.

الملخص العربي

و قد تم تحضير ثلاثة أنواع من الحفازات المحتوية على نسبة ٥،٠٠ % من معادن الروديوم ، الروثينيوم ، و الايريديوم المحمله على الجاما ألومينا



و قد تم دراسة تأثير درجة الحرارة عند ثلاث مستويات هي ٦٠٠، ٧٠٠، ٨٠٠ °م لسرعه الفراغية عند أربع قيم هي ١٨٠٠٠، ٣٦٠٠٠، ٤٥٠٠٠، ٦٠٠٠٠ سم^٣ جم^{-١} س^{-١} لتحديد الظروف المثلى للتشغيل .

و أخيرا ، تمت دراسة كيناتيكية التفاعل و تحديد الطاقه المنشطه باستخدام معادلة Arrhenius .

بصفه عامه فان نشاط هذا التفاعل يزيد مع زيادة درجة الحرارة حيث أنه تفاعل ماص للحراره ، و كذلك يزيد نشاطه مع نقصان السرعه الفراغية (يعني زيادة وقت بقاء المتفاعلات على الحافز أو وقت التقاء المتفاعلات) .

كذلك وجد أن درجة الانتقائيه (selectivity) تجاه مكونات غاز التخليق CO/ H₂ تزيد مع زيادة درجة الحرارة و نقصان السرعه الفراغية ، و كانت دائما نسبة الهيدروجين / أول أكسيد الكربون أقل من ١ و ذلك يفسر حدوث العديد من التفاعلات الجانبية أهمها تفاعل ثاني أكسيد الكربون مع الماء و الذي ينتج عنه مزيد من أول أكسيد الكربون (RWGS)



و قد تم تحديد الظروف المثلى للحصول على أعلى نسبة للهيدروجين/ أول أكسيد الكربون ووجد أنه بالنسبه للحافز Rh / $\gamma\text{-Al}_2\text{O}_3$ فان أحسن ظروف هي درجة حراره ٧٠٠ °م و ٣٦٠٠٠ سم^٣ جم^{-١} س^{-١} و بالنسبه للحافز Ru / $\gamma\text{-Al}_2\text{O}_3$ فان أحسن ظروف هي درجة حراره ٨٠٠ °م و ١٨٠٠٠ سم^٣ جم^{-١} س^{-١} أما بالنسبه

الملخص العربي

للحافز $\text{Ir} / \gamma\text{-Al}_2\text{O}_3$ فان أحسن ظروف هي درجة حراره 700°C و 36000 سم^2 $\text{جم}^{-1} \text{س}^{-1}$.

كذلك وجد أن جميع الحافزات تتبع سلوك تفاعل الدرجة الأولى $1^{\text{st}} \text{ order}$ reaction بالنسبه لكل من الميثان و ثاني أكسيد الكربون عند كل درجات الحراره المختبره ، و تم ايجاد العلاقه بين ثابت التفاعل k' و درجة الحراره باستخدام علاقه Arrhenius و كان متوسط الطاقه المنشطه للتفاعل بالنسبه الى ثاني أكسيد الكربون $46250 \text{ جول} / \text{مول}$ و بالنسبه للميثان كانت $31530 \text{ جول} / \text{مول}$.

في النهايه لوحظ أن الحافز $\text{Rh} / \gamma\text{-Al}_2\text{O}_3$ أظهر أفضل النتائج بالمقارنه بالحافزين الآخرين المستخدمين .

و كانت الظروف المثلى لاستخدامه هي $18000 \text{ سم}^2 \text{جم}^{-1} \text{س}^{-1}$ بالنسبه للسرعه الفراغيه و 800°C م بالنسبه لدرجة الحراره و أعلى نسبه للهيدروجين/ أول أكسيد الكربون كانت عند $36000 \text{ سم}^2 \text{جم}^{-1} \text{س}^{-1}$ و 700°C .