Eng.& Tech. Journal ,Vol.27, No.10,2009

The Effect of Zr loading on the Performance of Honeycomb Monolithic catalyst for the Removal of NO , CO and Hydrocarbon from Exhaust Gas

Dr.Abdul Halim Abdul K.Mohammed* , Dr.Shahrazed R.Rauof* & Dr. Hussain Khalaf*

Received on: 10/6/2008
Accepted on:2/4/2009

Abstract

Catalytic monolith reactors have numerous applications in industrial processes and as technical devices, so the focus is set specially on automotive catalytic converters.

In present work the experimental and theoretical investigation has been carried out to study the performance of monolith reactor on the oxidation and reduction of exhaust gas (NO, CO, HC, O_2 and H_2O) which emitted from gasoline generator. Commercial ceramic monolith catalyst and catalyst loaded on the commercial with Zr were used in the present work. A laboratory unit was constructed for this purpose where a versatile stainless steel reactor of 0.02 m inside diameter and 0.2 m height was used.

The catalytic performance of the catalysts was studied in the following operating conditions: gas hourly space velocity in the range 17.69 – 44.23s^{-1}, reaction temperature in the range 373 – 673 K, bed length in the range 0.075 – 0.15 m and at atmospheric pressure and constant air / fuel ratio (14.6). The results show that the conversion of NO, CO, HC, O_2 and H_2O are slightly changed with the bed length, . The conversion of exhaust gas reactant enhances in presence of water (wet condition) rather than in the absence of water (dry condition) and increases with the increasing reaction temperature and decreases with increasing gas space velocity. Commercial catalyst loaded with 0.4% Zr gives the higher performance for all components reaction

Keywords: Three way catalyst, zirconia, washcoat

دراسة تأثير تحميل الزركونيوم على اداء العامل المساعد التجاري المونوليثي في ازالة الغازات الملوثة من الغاز العادم

الخلاصة

أن مفاعلات العوامل المساعدة المونوليثية لها أستخدامات متعددة في العمليات الصناعية وخصوصاً العمليات الحاوية على أجهزة تكنولوجية ولذلك فأنه بدأ التركيز خصوصاً على مفاعلات الحاوية على العوامل المساعدة في مكائن الاحتراق الداخلي . تضمن البحث دراسة عملية ونظرية) لمعالجة عمليات الأكسدة والاختزال لغازات Monolithic Reactorلكفاءة اداء المفاعل المونوليثي (الناتجة من ماكنة احتراق الكازولين . عملية المعالجة NO, CO, HC, O_2 and H_2Oالأحتراق تمت باستخدام العامل المساعد السيراميكي التجاري والعامل المساعد المحمل على العامل المساعد السيراميكي(0.4 % زركونيوم) . تم تصميم ونصب وحدة مختبرية ذات مفاعل من الفولاذ بقطر 0.02 متر وارتفاع 0.2 متر . تم دراسة اداء العامل المساعد التجاري المونوليثي والعامل المساعد المحمل بحدود السرع الفراغية الغازية 17.69 – 44.32 1/ثانية ، درجة الحرارة بحدود 373 –

---

* Chemical Engineering Department, University of Technology / Baghdad

https://doi.org/10.30684/etj.27.10.3
2412-0758/University of Technology-Iraq, Baghdad, Iraq

673 كلفن وطول فرشة العامل المساعد من 0.075 – 0.15 متر تحت ضغط جوي اعتيادي ونسبة ثابتة للهواء الى الوقود قدرها 14.6 . أثبتت النتائج العملية ان نسبة التحول لغازات الاحتراق NO, CO, HC, O_2 and H_2O لا تتأثر بشكل ملحوظ بتغير طول فرشة العامل المساعد المستخدم . عند دراسة تأثير السرعة الفراغية وجد بأن نسبة التحول تنخفض بزيادة السرعة الفراغية لكن نسب التحول تزداد بزيادة درجة حرارة المفاعل ، كما وجد ان نسبة التحول لغازات الاحتراق تتحسن بوجود الماءWet (condition) مقارنة بغياب الماء (Dry condition 0.4 أعطى العامل المساعد المحضر % زركونيوم أعلى نسبة تحول لغازات الاحتراق .

Introduction

Automobile exhaust gases are a major source of manmade emissions. Many improvements were made by engine modifications. However, 1975 U.S Federal and California limits could not met by engine modifications alone and the catalytic converter was shown to be the best forward. Considerable research into catalytic system was taken by both industry and academics. Catalysts using base metals such as nickel, copper, cobalt and iron seemed initially to be attractive on the basis of cost. However, these catalysts were adversely affected by sulfur and residual traces of lead in the fuel, and catalysts eventually chosen were based on the platinum – group metals. For a few years, the emission limit could be reached by oxidation of carbon monoxide and hydrocarbon emitted by the engine (Andrzej 1998), as in equations (1) and (2):-

$$2CO + O_2 \rightarrow 2CO_2 \qquad \text{.....(1)}$$

$$4C_nH_m + (m+4n)O_2 \rightarrow 2mH_2O + 4nCO_2 \qquad \text{.....(2)}$$

The most common catalyst called conventional oxidation catalyst (two ways catalyst) was based on platinum and palladium on the alumina support (Cybulski 1994). However, as legislation tightened further, it became necessary to control the NO_x emission. This brought two further requirements: closer around the stoichiometric air/fuel ratio, and the addition of a further catalytic metallic component, Rhodium, to the catalyst formulation to enable the NO_x to be selectivitely reduced to nitrogen as in equation (3) and (4) (Johnson 1996):

$$2mNO + 2C_nH_m \rightarrow (4n+m)N_2 + 2mH_2O \qquad \text{....(3)}$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad \text{....(4)}$$

Monolith catalyst research since 1987 has focused on reactor design, increasing efficiency and the search for more suitable catalyst. Thus the complete oxidation of *CO* and *HC* and reduction of *NO* can be found over either noble metal (*Pt*, *Pd* and *Rh*) or other metal oxide (*Ba* and *La*) (Kendal, 2003; Ismagilov, 1998). The investigation beyond 1997s on the addition of *CeO* and ZrO_2 to the monolithic catalyst shows that these components as stabilizers of the alumina surface area enhance the performance of the monolithic catalyst (Horiuchi et al., 1999; Tadashi et al., 2002; Vidal et al., 2001 and Priscila et al., 2005).

During the last years, extensive efforts were made to develop new formulations, reporting on the specific role of platinum, palladium and rhodium in single and multiple compositions on the total conversion under real conditions, and studied the aging resistance of the catalyst under oxidizing, reducing environments.

Furthermore, the Platinum / Rhodium three – way catalyst converter is an essential device in controlling the three regulated pollutant emissions (CO, NO_x and HC) (Granger et al., 2002; Peter et al., 2004). Also, a new generally three way catalyst using cerium – zirconium mixed oxide was under intensive research (Di Monte et al., 2002, Fabiono et al., 2007).

The aims of the present work is to prepare one type of metal catalyst on the commercial three way catalyst by impregnation method , study the catalyst performance in wide rang of temperatures , gas space velocity and bed length at atmospheric pressure and stochoimetry air/ fuel ratio .

Experiment

-Feed Gases

Average emission gases produced from commercial gasoline generator (Single piston Astra 2.5 kv) are used as feedstock in this investigation. Table (1) shows the chromatographic analysis of this feedstock.

-Commercial Monolith

Three-way monolith made from ceramic honeycomb substrate (cordierite) was used in this investigation. The chemical composition (analyzed by The State Company of Geological Survey and Mining / Ministry of Industry) and physical properties (determined by Petroleum Research and Development Center and Production and Metallurgy Department of University of Technology) are presented in Table (2).

-Catalyst Preparation

The sample of monolith commercial catalysts was loaded with 0.4 wt % Zr by impregnation with aqueous solution of zirconium chloride. The zirconium content of catalyst was calculated from the weight of sample of catalyst and amount of metal in impregnation solution and is presented in Table (3).

The impregnation was carried out in the apparatus shown in Figure (1) which consists of conical flask (500 ml) connected to a vacuum pump (Awelch 1402, one stage Germany) and funnel for impregnation solution addition..

The impregnation process was carried out under vacuum with shaking at room temperature for four hours. The impregnation solution was added drop by drop, and the impregnated sample was left in its solution over night followed by drying at 120 ^{o}C and calcined at 400 ^{o}C for four hours in an electrical furnace (W.C. Heraeus GMBHV) with dry air then stored in a porcelain crucible in glass desiccator over silica gel. Table (4) presents the properties of the prepared catalysts.

-Experimental Work Column System:

Sixty column experiments refer to table (5) were carried out at various initial conditions (reaction temperature, gas space velocity, bed length) at atmospheric pressure and air/fuel ratio (14.6).

-Equipment:

The schematic diagram of the unit employed is shown in Figure (2). The experimental setup consisted of preheating zone, tubular reactor, electrical heater, thermocouple, calibrated rotameter, condenser and gas analyzer. The isolated stainless steel reactor (20 mm inside diameter and 200mm length), is heated by external tape heater (HERAEUS type TM56, 2000 watt).

Calibrated gas rotameter was used to measure exhaust gas flow rate. The inlet exhaust gas temperature was measured by temperature indicator. The reaction temperature was measured and controlled by electrical controller type (Yang Ming C x TA 3000) with thermocouple (Ni-CrNi) which was placed in the reaction zone.

-The Procedure:

The flow rate of reactants (gas emitted from generator) was adjusted to the desired value for each particular experiment. The mixture of reactants was entered the preheating zone and then passed the catalyst bed after it was heated to desired temperatures. After 20 minutes, when steady state condition was obtained the samples were taken from the outlet condenser to be analyzed by gas chromatography. The above-mentioned procedure was used for wet condition study. During the dry condition, cyclone was placed before the reactor entrance to remove the humidity from the emission gases, therefore samples were taken from the outlet of cyclone analyzed by gas chromatography to insure that the gases were dried.

-Analysis System:

Reactants and products were analyzed by a gas chromatography (GC) (SHIMADZU – 14A) equipped with a thermal conductivity detector (TCD). The apparatus consists of two stainless steel columns, the length of each column is 2 m and of 0.317 cm internal diameter. The first column is open tube coated with porapaq N and the second with porapaq Q. The porapaq particle dimension is of 80-100 mesh. The temperature program for the column is shown in Table (6). The injection system is located at the head of the column, where the sample under consideration was injected inside column.

A syringe of 0.25 ml total capacity was used for this purpose. The sample analysis and the corresponding signals were recorded and integrated by a digital integrator (SHIMADZU – CR 4A). The analysis was done in Ibin Sina Company.

Results and Discussion

-Results and Discussion:

Sixty column experiments were carried out to study the effect of various initial conditions on the performance of monolithic reactor on the oxidation and reduction of exhaust gases (NO, CO, and HC).

-Effect of Operating Variable on Monolith Performance

- The Effect of Bed Length

Twelve experiments, as shown in Table (5), were carried out at different bed lengths (0.075 – 0.15 m) and different temperatures (373 – 673 K) at constant space velocity (23.61 sec^{-1}). Table (7), and Figures (3 to 6) show the effect of bed length on conversion of the exhaust gas reactants for NO reduction and C_3H_6 and CO oxidation.

From these figures, it can be noticed that the conversion slightly changes with the bed length, so there is no appreciable external mass transfer limitation for both NO reduction and CO and C_3H_6 oxidation. This observation is noted also by (Chalrabarti and Sharma 1993, George et al., 2004).

- Effect of Water:

Figures (7 to 9) show the effect of water in the exhaust gas of about 11% on the NO, CO and C_3H_6 conversion at a given temperature and different gas space velocities of exhaust gas on commercial monolith catalyst.

It has been observed that the conversion of exhaust gas reactants is enhanced in presence of water (wet conditions) rather than in the absence of water (dry conditions). This is attributed to two main reasons, the water reduces self poisoning of the metal surface by CO (Gonzales-Velasco, 1997), and contributes to the oxidation of ceria, being in much higher concentration than oxygen in the reaction environment. Oxygen from ceria is thought to contribute significantly to the oxidation of CO and C_3H_6 adsorbed on the metal (Bunluesin, 1998).

Also water weakens the adsorption strength, allowing the components to react continuously to high conversion (Botas, 2001). These results are in agreements with the finding of Gonzalez-Velasco (1997) and Chen (2004).

From these results all the experiments on 0.4 % Zr supported catalyst, were carried out all in wet conditions.

-Effect of Temperature:

The influence of temperature in the range of (373-673 K) on the exhaust gas conversion at a given gas space velocity (17.69 s^{-1}) for commercial monolith catalyst at wet and dry conditions and different types of loading catalyst at wet condition only, is shown in Figures (10 to 12).

It can be seen from these figures, the conversion of exhaust gas increases with increasing temperature. This is attributed to the increasing of diffusivity of molecular gases, thinner layer of gas film where the external resistance is neglected leading to direct access of gaseous to the catalyst.

Figures (10 to 12) also show that the conversion of direct oxidation of CO and C_3H_6 is higher than the conversion of the reduction of NO. This is due to higher value of activation energy of NO reduction compared with the activation energy of CO and C_3H_6 oxidation (see Table 8). This indicates that NO reduction requires higher temperature to reach similar CO and C_3H_6 conversions.

These results are in agreement with previous finding of Hoebink et al., (2002) and Granger, et al., (2002).

-Effect of Gas Space Velocity

Figures (13 to 15) illustrate the effect of gas space velocity in the range of (17.69 - 44.23 s^{-1}) on the conversion of exhaust gas at temperature (573 K) for commercial monolith catalyst at wet and dry condition and for Zr loading catalyst at wet condition only.

It can be noticed from these figures that the conversion of the exhaust gas components decreases with increasing gas velocity, owing to decrease in the residence time (decreasing contact time of the feed reactant) with the catalyst inside reactor, such trends are in agreement with the observation of previous finding of Williaamson et al., (1989), Tomasic et al., (1998) and Fabiano et al., (2007).

-Effect of Catalyst Type Loading

Figures (16 - 18) show the effect 0.4% wt loading of Zr on the conversion of exhaust gas at a given temperature 673 K and different space velocities.

From these figures, it can be seen that the conversion of NO reduction using Zr loading catalyst is higher than those obtained by commercial catalysts. This may be attributed to the lower apparent activation energy of the NO reduction over 0.4% Zr loading catalyst compared with the commercial catalyst (see Table 8). The presence of ceria oxide in Zr loaded catalyst may be the reason for increasing the conversion percentage and rate the reaction of NO reduction. These results agree with those obtained by Gonzales-Velasco et al., (1999); Granger et al., (2002) and Brinkmeier (2005).

-Estimation of Reaction Kinetic Parameters

The kinetic rate prediction is necessary for the reactor and monolith catalyst model simulation. The overall catalytic reactions that are important for controlling exhaust condition are given by questions 5 to 8 below. The kinetic reaction rate is considered to follow simple power law. Differential method analysis is used to estimate the reaction rate for small variation in the conversion or for shallow small reactor (Levenspiel, 1999).

$$2CO + O_2 \rightarrow 2CO_2 \qquad \text{…..(5)}$$

$$4C_nH_m + (m+4n)O_2 \rightarrow 2mH_2O + 4nCO_2 \qquad \text{….(6)}$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad \text{…..(7)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{.........(8)}$$

For each run in a differential reactor the performance equation becomes (Levenspiel, 1999):-

$$\frac{w}{F_{Ao}} = \int_{xA_{in}}^{x_{Aout}} \frac{dx}{-r_A} = \frac{1}{(-r_A)_{av}} \int_{x_{Ain}}^{x_{Aout}} dXA = \frac{X_{Aout} - X_{Ain}}{(-r_A)_{av}} \qquad \text{…….(9)}$$

From equation (5) the average rate for each run is found, thus each run gives directly a value for the rate of the reaction at the average concentration in the reactor.

From Figure (19 to 21) show the results of the rate of reaction estimated for NO reduction, CO oxidation and C_3H_6 oxidation using commercial and Zr loaded catalyst.

Non-linear regression analysis using Statistica (version 6) software is used to estimate reaction rate parameters (rate constant and reaction order) for each set of flow rate at a given temperature for each reaction component using commercial and Zr loading catalyst.

The statistical analysis gives correlation coefficients between (0.932-0.94) which is statistically significant.

The apparent activation energy was established from Arrhenious equation that satisfies the relationships between rate constant and reaction temperature.

A plot of *ln* (*k*) *vs.* $\left(\frac{1}{T}\right)$ is shown in Figures (22) which are used for calculation of E_a values, since (*ln A)* represents the intercept and the slope is represented by $\left(\frac{-E_a}{R}\right)$.

The results of the analysis of the parameters estimation are outlined in Table (8)

From Table (8), the apparent activation energy values are in the range of (17-56 KJ/mol), this indicates that the internal diffusion severely limits the reaction as mentioned also by Farrauto, (1997).

- Conclusions:

1. The conversion of exhaust gas reactants (NO, CO, HC, H_2O and O_2) increases with increasing reaction temperature from 373 to 673K and decreases with increasing gas second space velocity (17.69 – 44.23 s^{-1}).

2. The reaction rate of exhaust gas reactants increases with increasing reaction temperature and gas second space velocity .
3. The conversion of exhaust gas reactants is enhanced in presence of water (wet conditions) rather than in the dry condition.
4. The apparent activation energy values in the range of 16-56 kJ/mol, indicate that the internal diffusion severely limits reaction.
5. Conversion of exhaust gas on Zr loaded catalyst is higher than those obtained on commercial catalyst.

-Recommendations

1. The present work can be extended to study the treatment of exhaust gas in monolith reactor under periodic operation (unsteady state operation).
2. Another interesting feature that can be investigated further is to study the effect of air/fuel ratio on the performance of the monolith reactor.
3. The effect of loading / or bi-metallic loading on monolith reactor is another field for future study.
4. New mathematical model could be tested for the same process (3D model, 2D-axial dispersion model).

References

[1] Androzej C. and Jacob M. (1998); Structural catalysts and reactors, Marcel Dekker, Inc.,2.

[2] Botas J, Miguel A., and Pilar M. (2001); Kinetic consideration of three way catalyst in automobile exhaust converters, Applied Catalyst B: Environmental 32, 243-256.

[3] Brinkmeier C. (2005); Automotive three-way exhaust under transient conditions measurement, modelling and simulation. Ph.D thesis, University Stuttgart.

[4] Bunluesin T., Gorte R., and Graham G. (1998); Applied Catalyst B: Environmental 15, 107.

[5] Chen J., Wey M., and Liany Y. (2004); Simultaneous treatment of organic compounds CO and NOx in the flue gas by three way catalyst, Applied Catalyst B: Environmental 48, 25-35.

[6] Cybulski A. and Moulism A. (1994); Monolith in heterogeneous catalysis, Catalyst Revision Science Engineering, 36(2), 179-270.

[7] DiMonte R., Fornasiero P., Kaspar J., and Gomez-Herro A. (2002); Stabilization of nonstructured $Ce_{0.2}Zr_{0.8}O_2$ solid solution by impregnation on Al_2O_3: a suitable method for the production of thermally stable oxygen storage/release promoters for three way catalyst, Chemical Community, 2167.

[8] Fabiano S., Diego da S., Juan A., and Fabio B. (2007); The effect of $Pt/CeZrO_2/Al_2O_3$ catalysts for the partial oxidation of methane, Studies in surface science and catalysis, 167, 427-432.

[9] Fabiano S., Martenz D., Maltons L., Hori C., and Noronha, F. (2008); The effect of the use of cerium-doped alumina on the performance of $Pt/CeO_2/Al_2O_3$ catalysts on the partial oxidation of methane,

Applied Catalyst A: General 335(2), 145-152.

[10] Farrauto R. and Bartholomew C. (1997); Fundamentals of industrial catalytic process, Kluwer Scientific Publishers, Amsterdam, 8.

[11] George E., Evagelos A., and Iacovos A. (2004); Mechanistic and kinetic analysis of the NOx selective catalytic reduction by hydrocarbons in excess O_2 over Ir/Al_2O_3 in presence of SO_2 and H_2O, Applied Catalyst B: Environmental 48, 1-15.

[12] Gonzales-Velasco J., Jeam M., and Gilbert B. (1999); Contribution of Cerium/Zirconium mixed oxides to the activity of a new generation of TWC, Applied Catalyst B: Environmental 22, 167-178.

[13] Gonzalez-Velasco J., Botas J., and Gonzales-Marcos J. (1997); Influence of water and hydrocarbon processed in feed stream on the three way behavior of platinum-aluminum catalysts, Applied Catalyst B: Environmental 12, 61-79.

[14] Granger P., LeComete J., and Leclercq G. (2002); Kinetics of the CO+NO reaction over bimetallic platinum-rhodium on alumina, Effect of ceria in corporation into noble metals, Journal of Catalyst, 207, 202-212.

[15] Hoebink J., Van Gemert R., and Marin G. (2002); Modeling of the NOx conversion maximum in the light-off curves under net oxidizing condition, Chemical Engineering Science, 55, 1573-1581.

[16] Horiuchi T. Teshima Y., Suzuki K., and Mori T. (1999); Improvement of thermal stability of alumina by addition of zirconia, Catalyst Lett, 62, 107.

[17] Ismagilov Z.R., Long R.Q., Arendaeskii D.A., and Shikina N.V. (1998); Preparation of thermally stable waskcoat alumina for automotive catalyst, Catalyst and Automotive Pollution Control, Amsterdam. vol. IV, 507.

[18] Johnson M. (1996); Platnium-lnterim review, London

[19] Kendal T.(2003); Auto catalyst development and the use of platinum group metals, Platinum 2003, 25.

[20] Octave L. (1999); Chemical Reactor Engineering, John Wiley and sons, New-York.

[21] Petr K.(2005) ; catalytic monolith reactors with surface deposition of gas components – application in automobile exhaust gas conversation , PhD thesis , institute of chemical technology , Prague.

[22] Petr K., Milan K., and Milson M. (2004); Modeling of three way catalyst monolith converters with micro kinetics and diffusion in the washcoat, Industrial Engineering Research, 43, 4503-4510.

[23] Tadashi S., Akira M., Hideo S., and Toshihiro T. (2002); Alumina-Ceria-Zirconia composite oxide for three way catalyst, Research Report, R and

D review of Toyota CRDL, 37, 4.

[24] Tomasic V., Gomzi Z., and Zrncvic S. (1998); Catalytic reduction of NOx over Cu/25M.5 catalyst, Applied Catalyst B: Environmental 18,233-240.

[25] Tomasic V., Gomzi Z., and Zrncvic S. (2001); Development of the structured catalysts for the exhaust gas treatment, chemical biochemistry engineering, 3, 109-115.

[26] Vidal H., Kasper J., Bernal S., Cordon A., and Fally F. (2001); Redox behavior of CeO_2-ZrO_2 mixed oxide, Applied Catalyst B: Environmental 30, 75-85.

[27] Williamson W., Summers M., and Skowron J. (1989); Catalyst technology for future automotive emission system, SAE, 88-0103.

Table (1) Composition of the feedstock, % volume

CO %	***NO %***	***HC %***	***CO_2 %***	***O_2 %***	***H_2O %***	***N_2 %***
2.00	0.03	0.50	10.00	16.40	11.00	Balance

Table (2) Chemical and physical properties of monolith catalyst

Chemical composition of monolith %	
$\gamma - Al_2O_3$	69.76
SiO_2	11.3
Fe_2O_3	9.4
CeO_2	6.7
BaO	2.6
TiO_2	0.01
CuO	0.02
Pt	0.05
Rh	0.16
Physicals Properties	
Channel Structure	Circle
Number of channels, channel / cm^2	64
Channel spacing, mm	1.4
Wall thickness, mm	0.3
Wall porosity %	60
Bulk density, g / cm^3	1.4
Pore volume, cm^3 / gm	0.93
Surface area, m^2 / g	97

Table (3) The amount of reagents used for preparation of 0.4 % Zr catalysts

No.	wt. of catalyst sample, gm	Type of metal	wt. of metal gm	wt. of salt gm
1	13.8	Zr	0.069	0.24

Table (4) The properties of the prepared catalysts

Catalyst Specification	Zr
Surface area, m^2/gm	88
bulk density, gm/cm^3	1.45
Porosity	0.45
Equivalent radius, nm	7.23

Table (5) Operating condition of experiments

No.	GSV S^{-1}	Bed length cm	Set temperature °C	Observation
1	23.61	7.5	100	Effect of bed length for commercial catalyst.
2	23.61	10	100	
3	23.61	15	100	
4	23.61	7.5	200	
5	23.61	10	200	
6	23.61	15	200	
7	23.61	7.5	300	
8	23.61	10	300	
9	23.61	15	300	
10	23.61	7.5	400	
11	23.61	10	400	
12	23.61	15	400	
13	17.69	10	100	Effect of water (wet condition) on commercial catalyst.
14	17.69	10	200	
15	17.69	10	300	
16	17.69	10	400	
17	26.53	10	100	
18	26.53	10	200	
19	26.53	10	300	
20	26.53	10	400	
21	35.38	10	100	
22	35.38	10	200	
23	35.38	10	300	
24	35.38	10	400	
25	44.23	10	100	
26	44.23	10	200	
27	44.23	10	300	
28	44.23	10	400	
29	17.69	10	100	Effect of water (dry condition) on commercial catalyst.
30	17.69	10	200	
31	17.69	10	300	
32	17.69	10	400	
33	26.53	10	100	
34	26.53	10	200	
35	26.53	10	300	
36	26.53	10	400	
37	35.38	10	100	
38	35.38	10	200	
39	35.38	10	300	
40	35.38	10	400	
41	44.23	10	100	
42	44.23	10	200	
43	44.23	10	300	
44	44.23	10	400	
45	17.69	10	100	Effect of Zr loading on commercial catalyst
46	17.69	10	200	
47	17.69	10	300	
48	17.69	10	400	
49	26.53	10	100	
50	26.53	10	200	
51	26.53	10	300	
52	26.53	10	400	
53	35.38	10	100	
54	35.38	10	200	
55	35.38	10	300	
56	35.38	10	400	
57	44.23	10	100	
58	44.23	10	200	
59	44.23	10	300	
60	44.23	10	400	

Table (6) Temperature program and operating conditions of gas chromatography.

Temperature Program for the Column	
Initial Column temperature, K	303
Final Column temperature, K	393
Rate of temperature increasing °C / min	5
Other Condition	
Injection temperature, K	423
Detector temperature, K	523
Flow rate of Helium, ml / min	20

Table (7) The effect of bed length on % conversion at constant gas space velocity = 23.61 s^{-1} on commercial catalysts at different temperatures.

Bed length Cm	**T = 100 °C**			**T = 200 °C**			**T = 300 °C**			**T = 400 °C**		
	NO %	**CO %**	**C_3H_6 %**	**NO %**	**CO %**	**C_3H_6 %**	**NO %**	**CO %**	**C_3H_6 %**	**NO %**	**CO %**	**C_3H_6 %**
15	**0**	**8.1**	**7**	**30.2**	**58.5**	**54.9**	**53**	**74.9**	**65**	**65**	**79.8**	**76**
10	**0**	**7.5**	**6.5**	**29**	**56.7**	**53.8**	**51.1**	**73.7**	**62.8**	**63**	**77**	**74.8**
7.5	**0**	**6.6**	**5.7**	**27.8**	**55**	**51**	**49**	**69.5**	**61.1**	**62.4**	**76.4**	**73.5**

Table (8) Apparent activation energy values and reaction order for commercial cata

Reaction	**E_a / R**	**E_a KJ / mol**	**Ao**	**Reaction order**	
				a_i	**b_i**
Wet Condition					
NO + CO	6500.5	54.05	3008.8	0.5	1.25
CO + ½ O_2	3090.2	25.691	16.85	1	0.5
CO + H_2O	2194.4	18.24	0.0432	1	0.5
C_3H_6 + 4.5 O_2	3421.5	28.446	15.34	1	0.5
Dry Condition					
NO + CO	6809	56.61	47.002	0.5	1.25
C_3H_6 + 4.5 O_2	3708.4	30.82	3.265	1	0.5
Zr					
NO + CO	5250	43.64	1170.316	0.55	1.28
CO + ½ O_2	2800.7	23.28	13.206	1	0.45
CO + H_2O	1924.0	16.00	0.0556	1	0.56
C_3H_6 + 4.5 O_2	2848.9	23.68	10.320	1	0.55
CO + ½ O2	3427.6	28.49	10.580	1	0.5

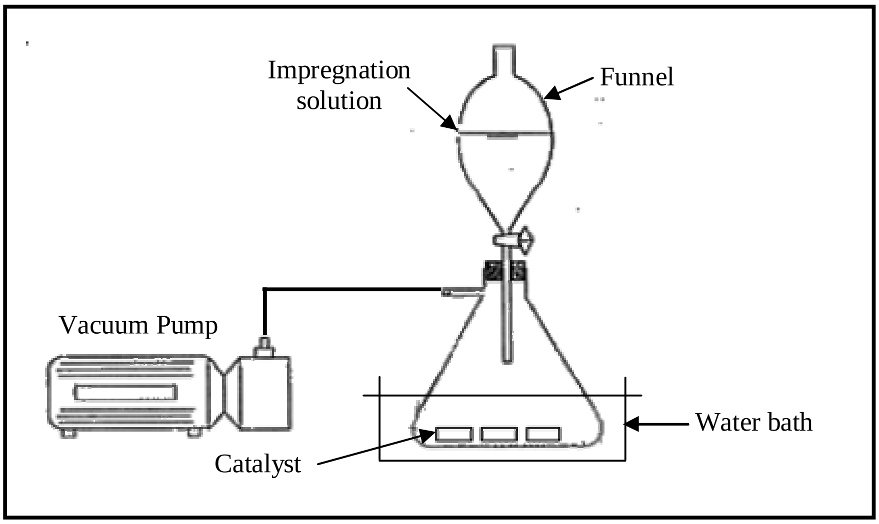

Figure (1) Impregnation apparatus

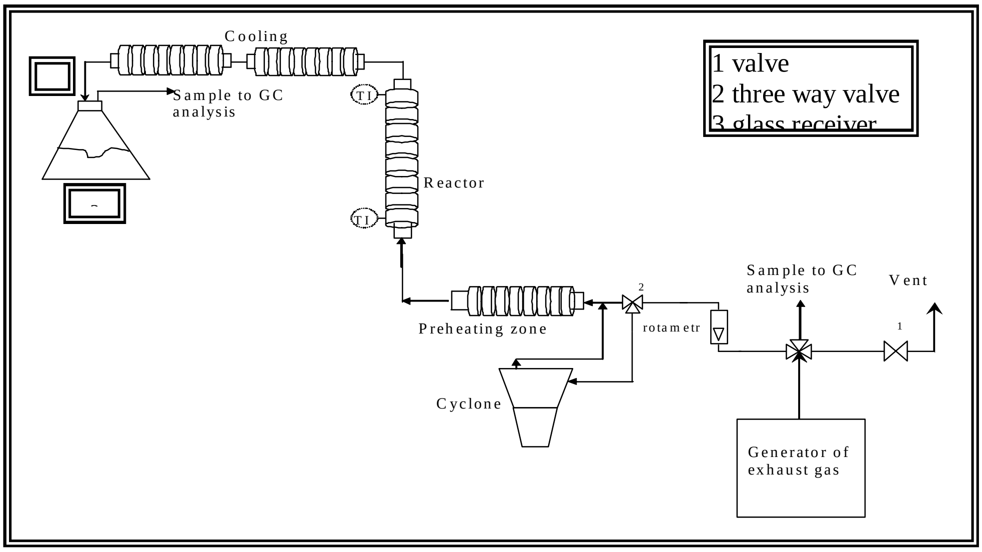

Figure (2) Schematic diagram of experimental setup

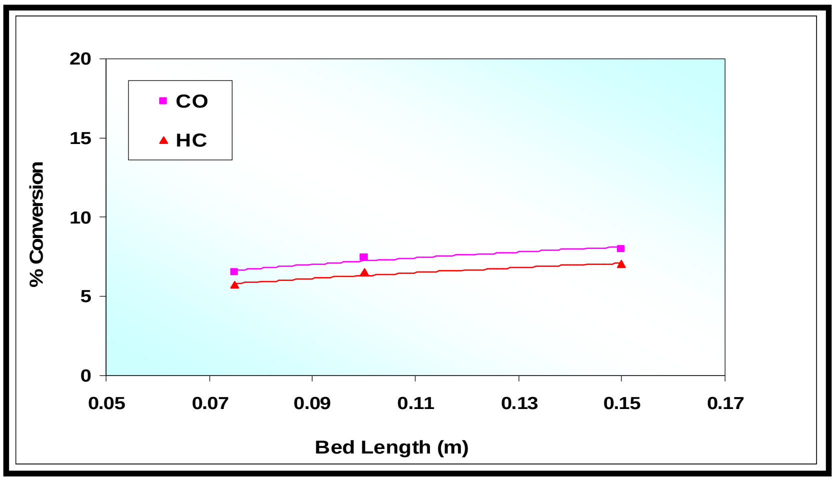

Figure (3) Effect of bed length of catalyst on conversion at 373K.

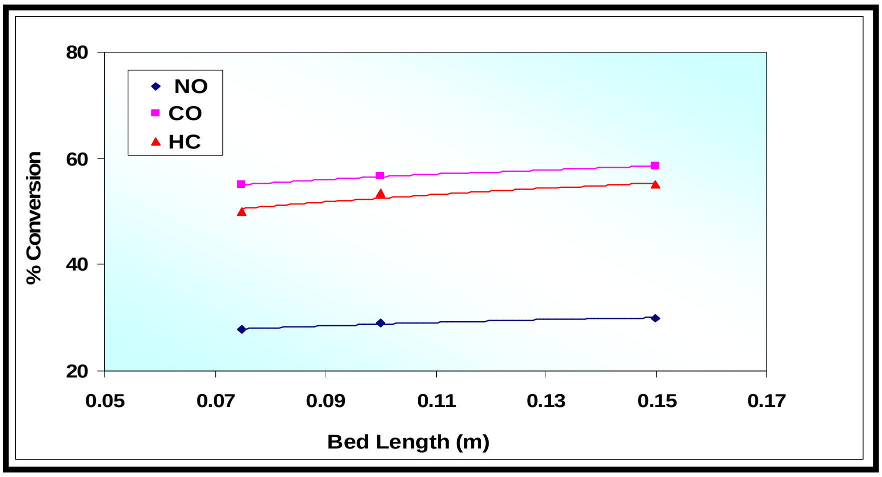

Figure (4) Effect of bed length of catalyst on conversion at 473 K.

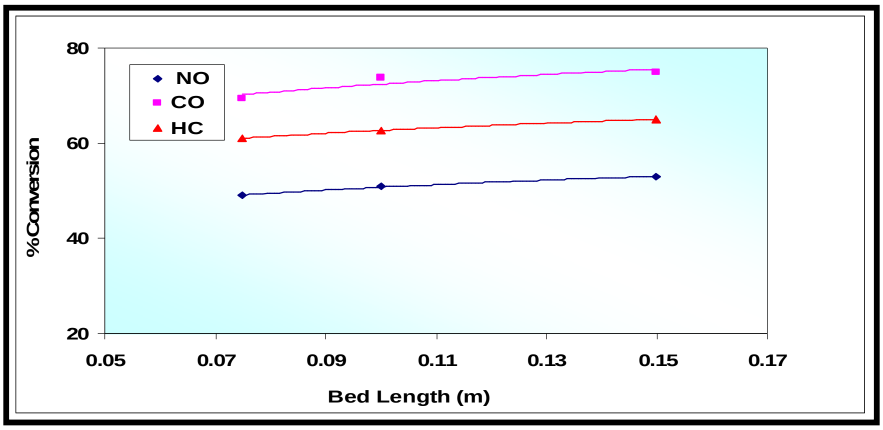

Figure (5) Effect of bed length of catalyst on conversion at 573K

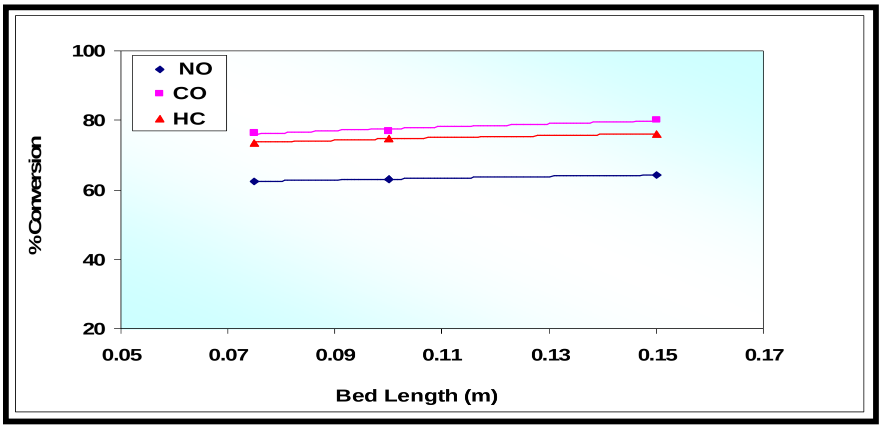

Figure (6) Effect of bed length of catalyst on conversion at 673 K

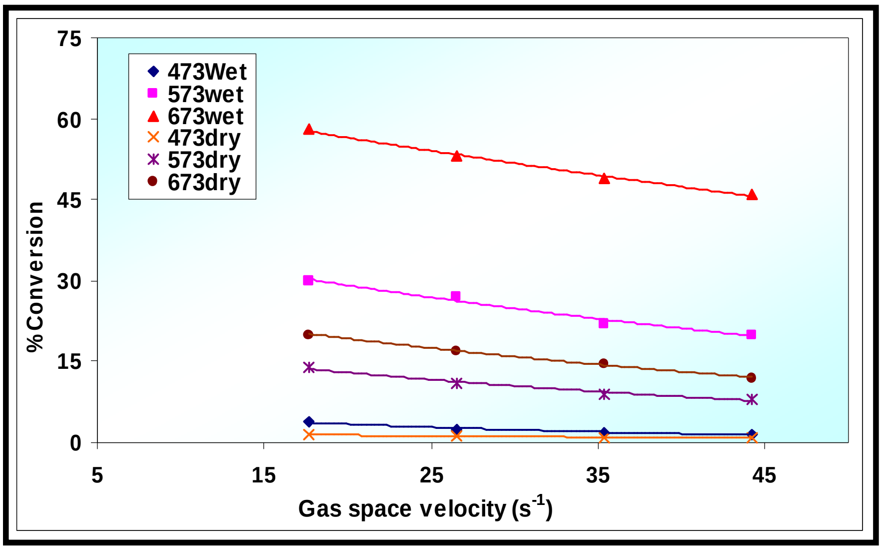

Figure (7) Effect of water on NO conversion

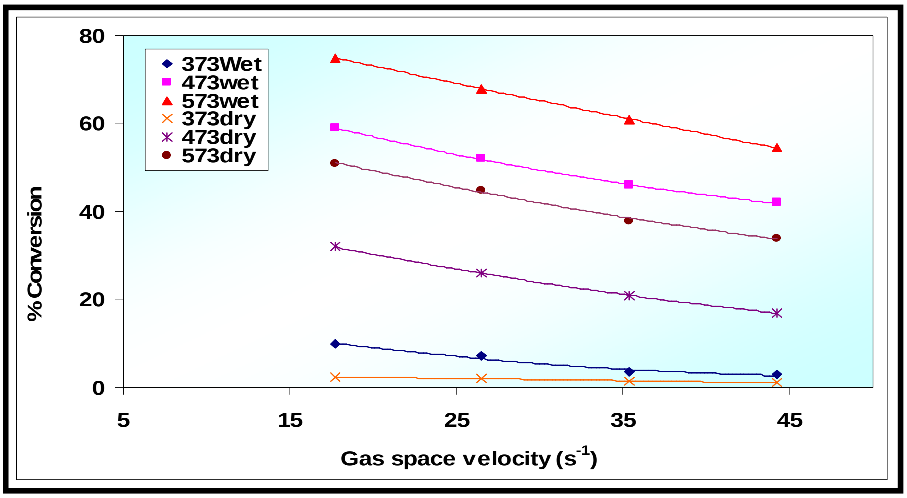

Figure (8) Effect of water on CO conversion.

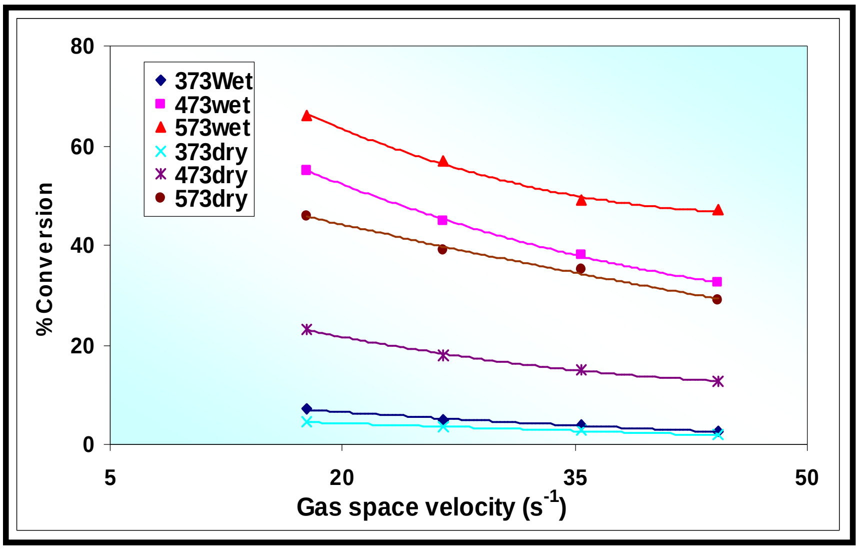

Figure (9) Effect of water on C_3H_6 conversion.

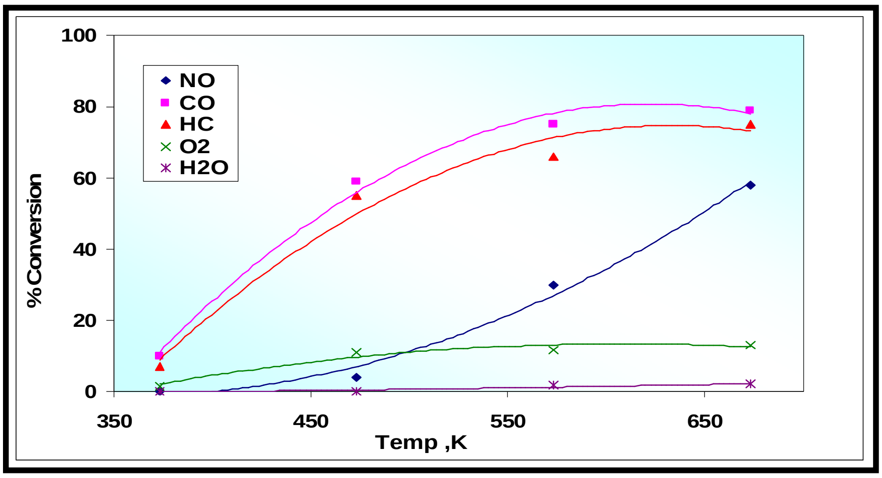

Figure (10) Effect of temperature on conversion percentage at space gas velocity (17.69 s^{-1}) using commercial catalyst for wet condition .

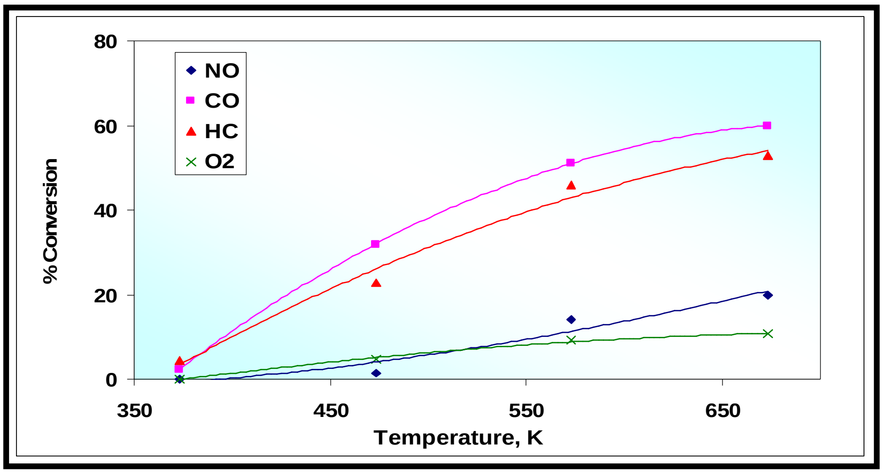

Figure (11) Effect of temperature on conversion percentage at space gas velocity (17.69 s^{-1}) using commercial catalyst for dry condition

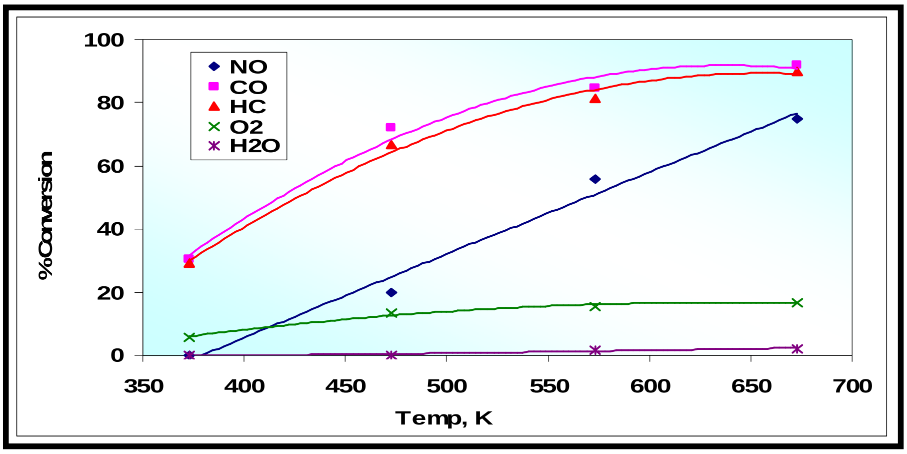

Figure (12) Effect of temperature on conversion percentage for Zr loading at gas space velocity (17.69 s^{-1}).

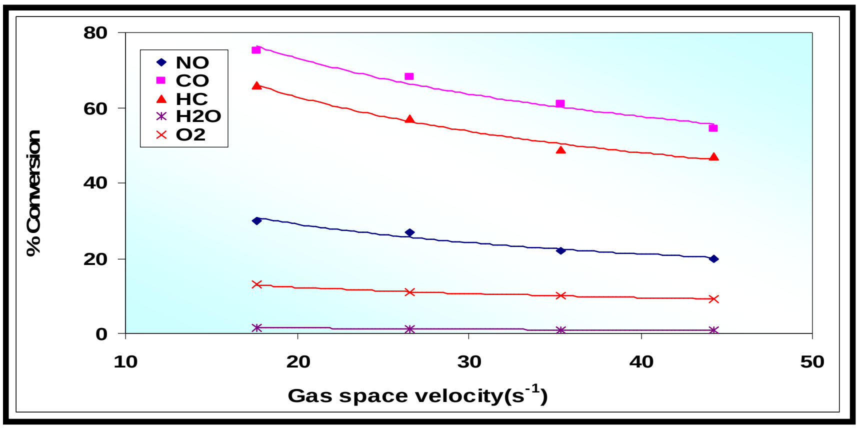

Figure (13) Effect of gas space velocity on conversion percentage of components at wet condition at 573 K.

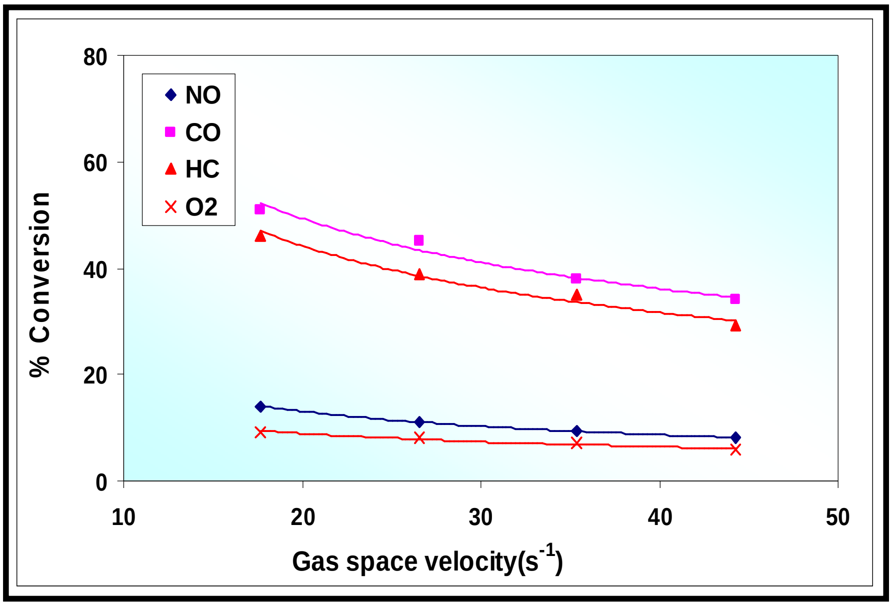

Figure (14) Effect of gas space velocity on conversion percentage of component for dry condition at 573 K.

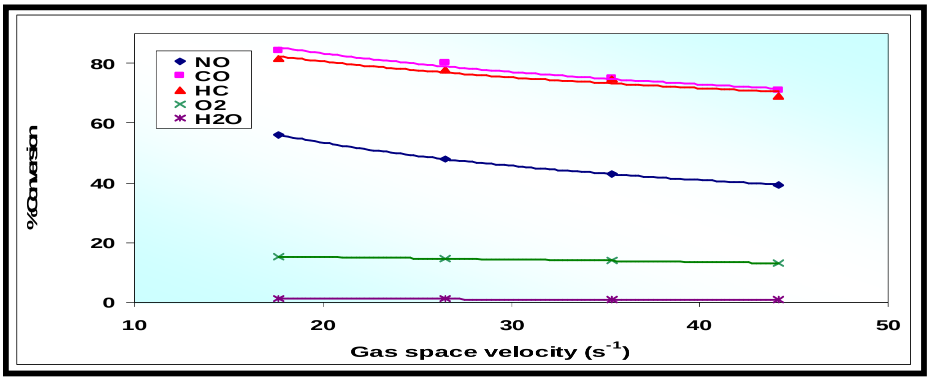

Figure (15) Effect of gas space velocity on conversion percentage of component on Zr loading at 573 K.

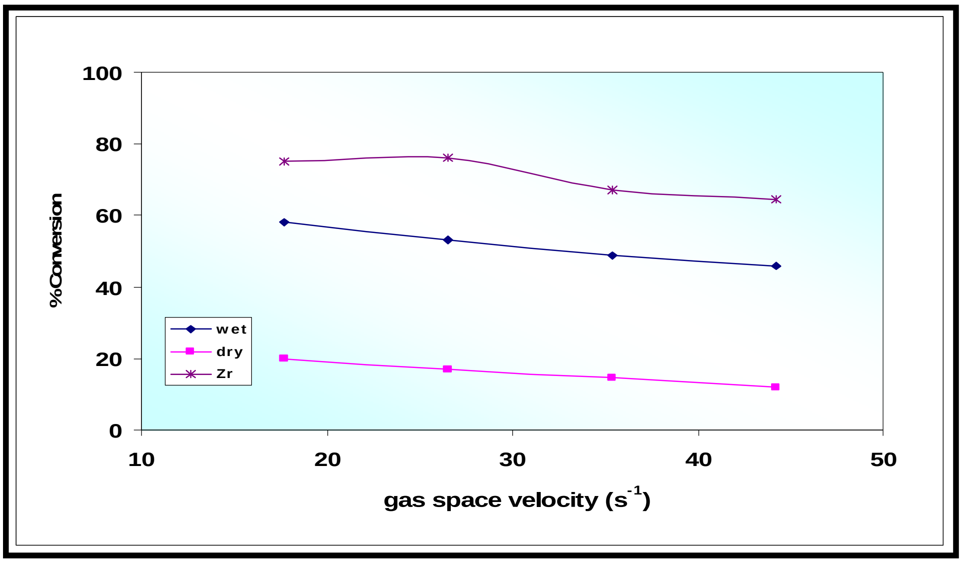

Figure (16) Effect 0.4 % loaded of Zr metal on the conversion percentage of NO component at temperature of 673 K.

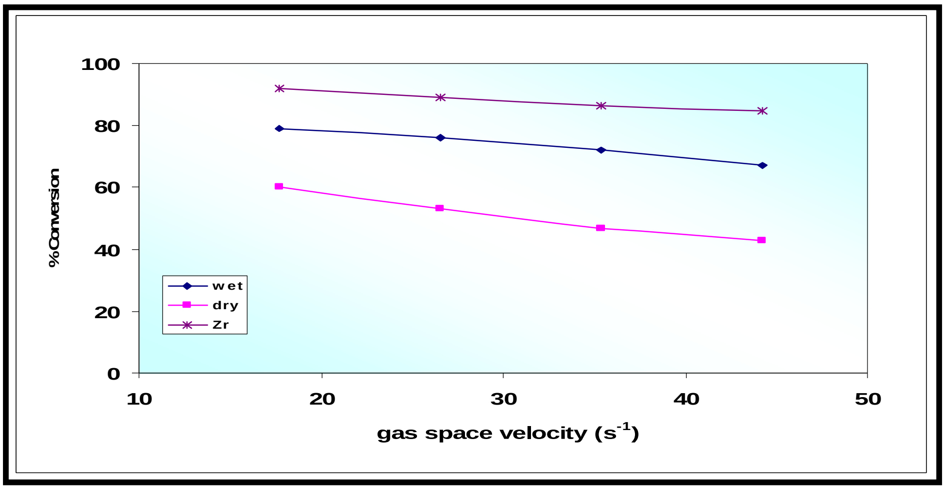

Figure (17):- Effect of 0.4 % loaded of Zr on the conversion percentage of CO at temperature of 673 K.

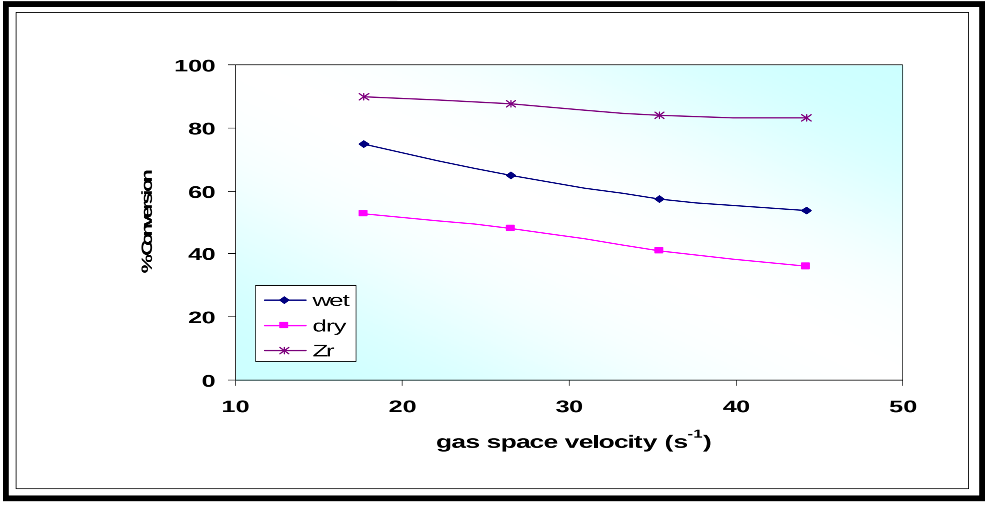

Figure (18) Effect 0.4% loaded of Zr on the conversion percentage of C_3H_6 at temperature of 673 K.

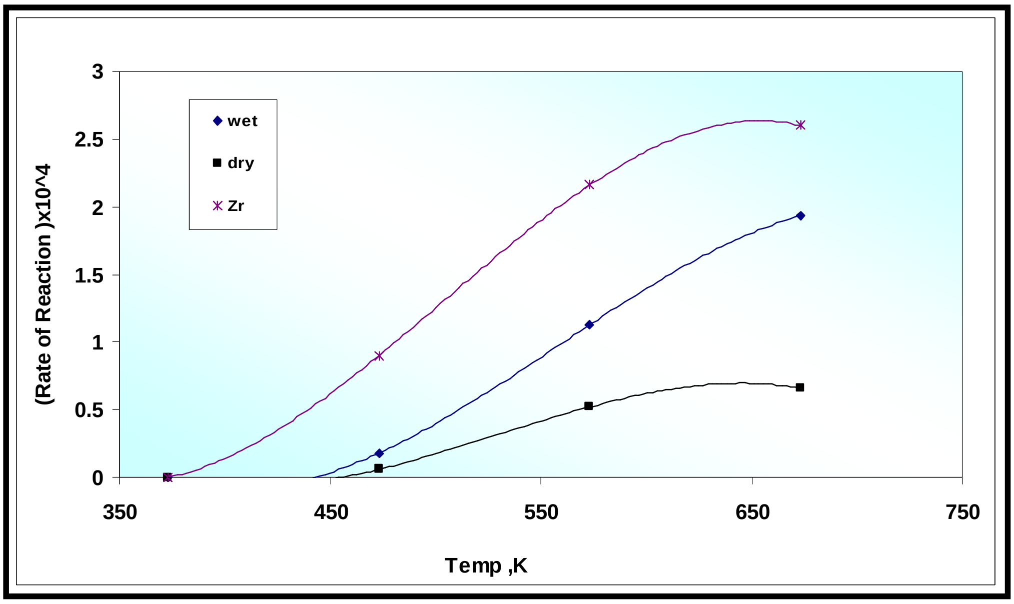

Figure (19) Effect of temperature on the rate of reaction for NO component at gas space velocity (17.69 s^{-1})

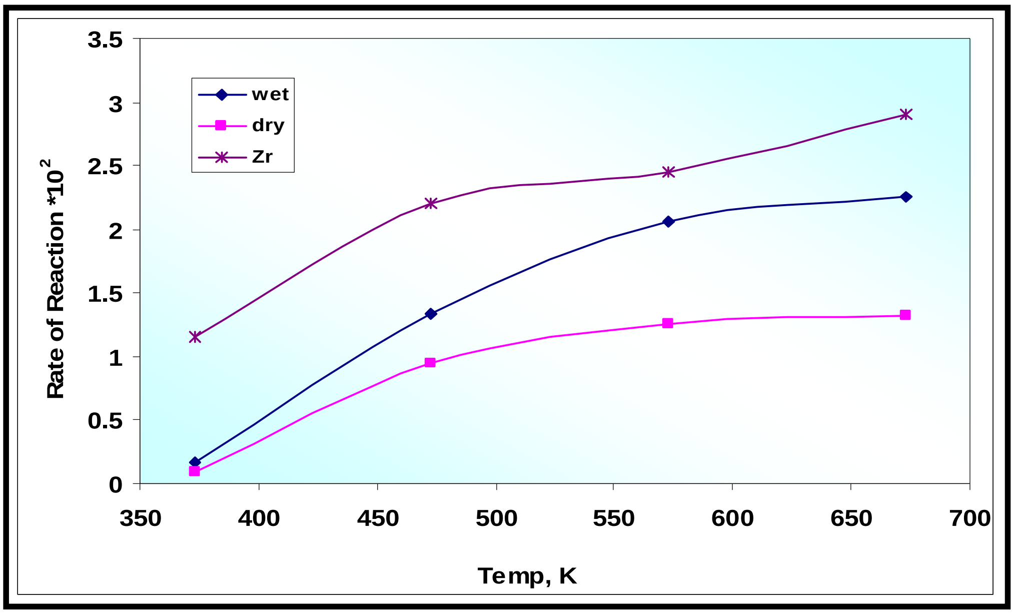

Figure (20) Effect of temperature on the rate of reaction for CO component at gas space velocity (17.69 s^{-1})

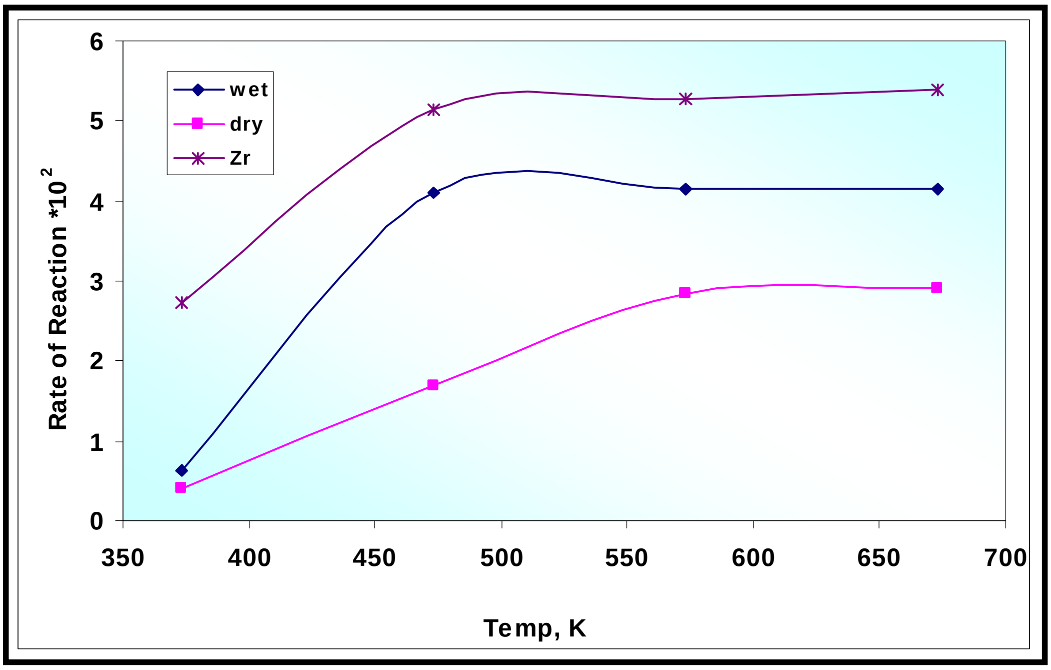

Figure (21) Effect of temperature on the rate of reaction for HC component at gas space velocity (17.69 s^{-1})

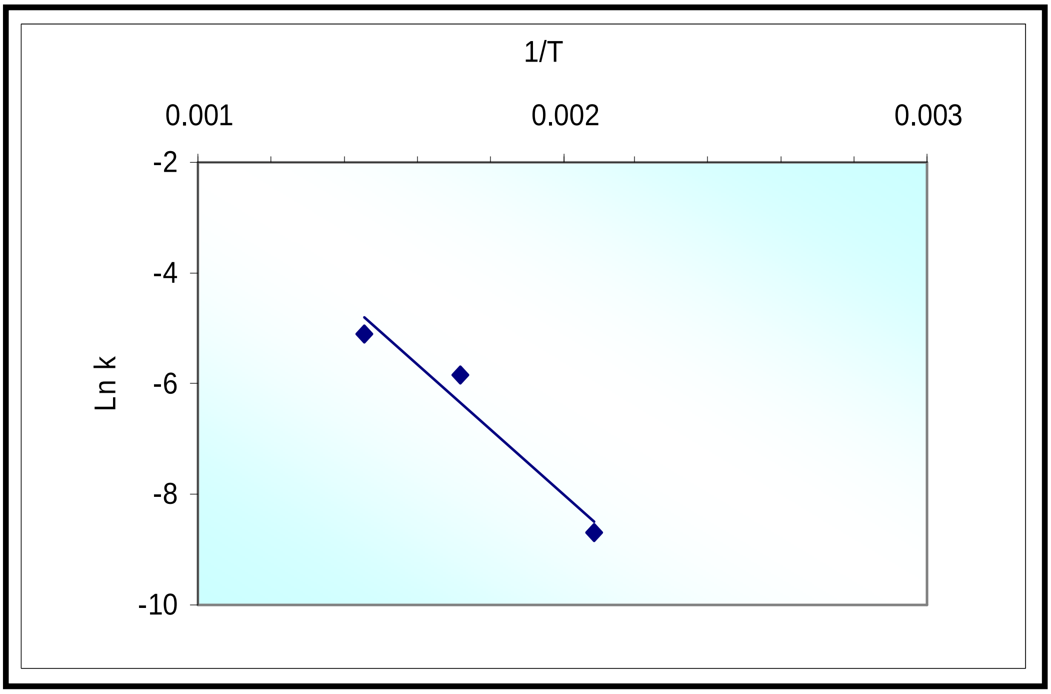

Figure (22) Arrhenius plot for CO + NO for dry condition of commercial catalyst.