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Investigation the activity of Pd Loading on Commercial Monolithic Catalyst in Automobile Exhaust Gases

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ABSTRACT

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

The present work aimed to study the experimental performance of monolith reactor on the oxidation and reduction of exhaust gas (NO, CO, and HC) which emitted from gasoline generator. Commercial and modified commercial ceramic monolith catalyst was used in the present work. The modified commercial catalyst was obtained by loaded Pd metal .A laboratory unit was constructed for this purpose where a versatile stainless steel monolith 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, in a border range of gas space velocity(17.69 – 44.23$s^{-1)}$, reaction temperature(373 – 673 K), bed length(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 and HC are slightly changed with the bed length . The conversion of exhaust gas reactant enhances in presence of water, increases with the increasing reaction temperature and decreases with increasing gas space velocity. Monolithic catalyst which loaded with 0.4% Pd gives high conversion compared with an commercial catalyst (unloaded) for the HC oxidation reaction more than CO oxidation and NO reduction.

Key Words: Three Way Catalyst, Pladium , Wash Coat, Catalytic Monolith Reactors.

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دراسة تأثير تحميل البلاديوم على اداء العامل المساعدالتجاري المونوليثي في ازالة الغازات الملوثة من عوادم السيارات

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 عمليةلكفاءة اداء المفاعل المونوليثي (Monolithic Reactor) لمعالجة عمليات الأكسدة والاختزال لغازات الأحتراق (NO, CO and HC) الناتجة من ماكنة احتراق الكازولين .

ان عملية المعالجة تمت باستخدام العامل المساعد السيراميكي التجاري والعامل المساعد المحمل على العامل المساعد السيراميكي(0.4 % بلاديوم) .

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 – 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 and HC) لا تتأثر بشكل ملحوظ بتغير طول فرشة العامل المساعد المستخدم .وتزداد نسبة التحول بزيادة درجة حرارة التفاعل وتنخفض بزيادة السرعة الفراغية.أعطى العامل المساعد المحضر 0.4 % بلاديوم أعلى نسبة تحول لأكسدة الهايدروكاربون من أكسدة أول أوكسيد الكاربون.

INTRODUCTION

Catalytic converters(TWC , three way catalyst) have been used for about thirty-five years to reduce the toxicity of exhaust emissions from the internal combustion engine to meet the requirements of government mandated emission limits. These converters are heterogeneous catalytic reactors that comprise a solid phase containing the catalyst and a fluid phase containing the reactants and products.The converter is comprised of a monolith type substrate, the surface of which is coated with a thin catalytic washcoat[1-2].The catalytic converter is used for simultaneous abatement of CO, NOx and hydrocarbons present in the exhaust gases [3]. The active component of the converter (washcoat) is supported on a cordierite monolith in two or three layers. The top layer contains rhodium deposited on a ceria–zirconia composition. The bottom layer contains palladium or platinum traditionally supported on alumina [4] . On the other hand, Pd-based materials are well-known highly active catalysts for a wide range of heterogeneous reactions, from fine chemical synthesis to partial or full oxidation reactions [5]. The use of Pd as the only active metal component in TWC has received considerable attention on the basis of economical aspects (the high cost and scarcity of Rh) and the availability of cleaner fuels. Despite limitations for

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NOx reduction reactions, this component exhibits remarkable activity for HC and CO oxidation reactions [6-8].

Boehman and Niksa, [9] measured oxidation rates of synthetic automotive exhausts over an aged palladium(Pd) catalyst during simulated cold-start conditions.

Eguchi et al [10], studied Pd catalysts supported on metal oxides, especially SnO_2 and Al_2O_3-36NiO were investigated in comparison with Pd/Al_2O_3 for developing catalyst materials for ignition of methane. The Pd/ SnO_2 and Pd/Al_2O_3-36NiO catalysts were found to have an excellent activity for the complete oxidation of methane‛ though the BET surface area of the SnO_2 support was far smaller than that of Al_2O_3.

Many research studied the effect of various precursors, supports and synthesis methods on the dispersity and oxidation state of supported Pd in Pd/Al_2O_3 catalysts have been published to date [11-14]. Meanwhile, there is very little knowledge on the relationshipbetween specific surface sites of the support (usually detectedby spectroscopic methods) and the properties of the stabilizedpalladium [8].

The main goal of Vedyagin et al [8], investigation of active sites of Pd/Al_2O_3 catalysts is to determine the role of special intrinsic surface sites of the support in stabilization of supported palladium.

In the present work , the performance of Pd/Al_2O_3 with Pd loading of 0.4 wt% on the treatment of exhaust gas emission from gasoline generator has been investigated experimentally .

EXPERIMENTAL ARRANGEMENTS

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.

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

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).

Table (2) Chemical and physical properties of monolith catalyst.

Chemical composition of monolith %	
$\gamma-Al_2O_3$	69.76
SiO_2	11.3

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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 / g	0.93
Surface area, m^2 / g	97

Catalyst Preparation

The sample of monolith commercial catalysts was loaded with 0.4 wt % Pd by impregnation with aqueous solution of palladium chloride . The palladium 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).

Table (3) The amount of reagents used for preparation of Pd loaded catalyst 0.4 % Pt catalysts

wt. of catalyst sample, g	Type of metal	wt. of metal g	wt. of salt g
14.39	Pd	0.0719	0.119

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.

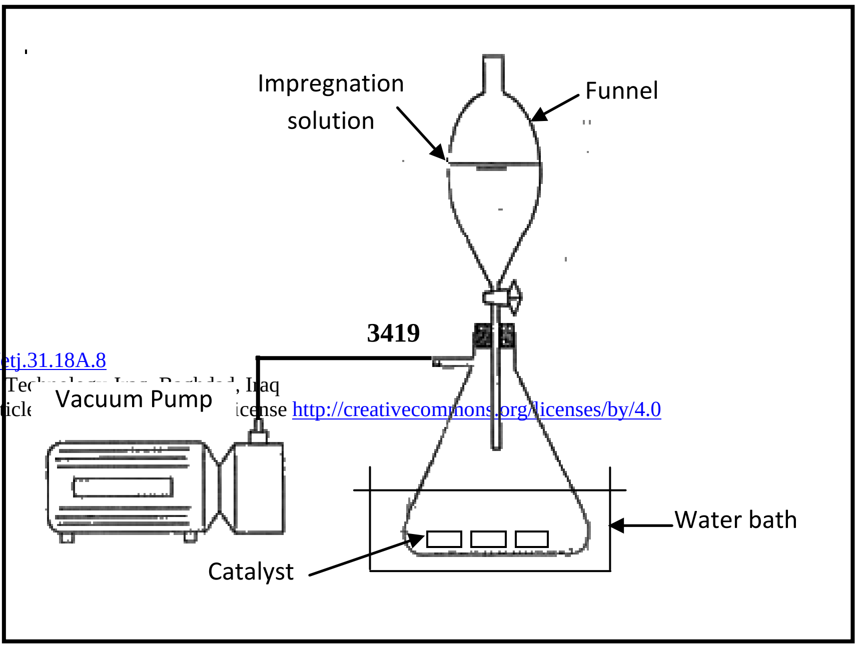

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Figure (1) Impregnation apparatus.

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.

Table (4) The properties of the prepared catalysts.

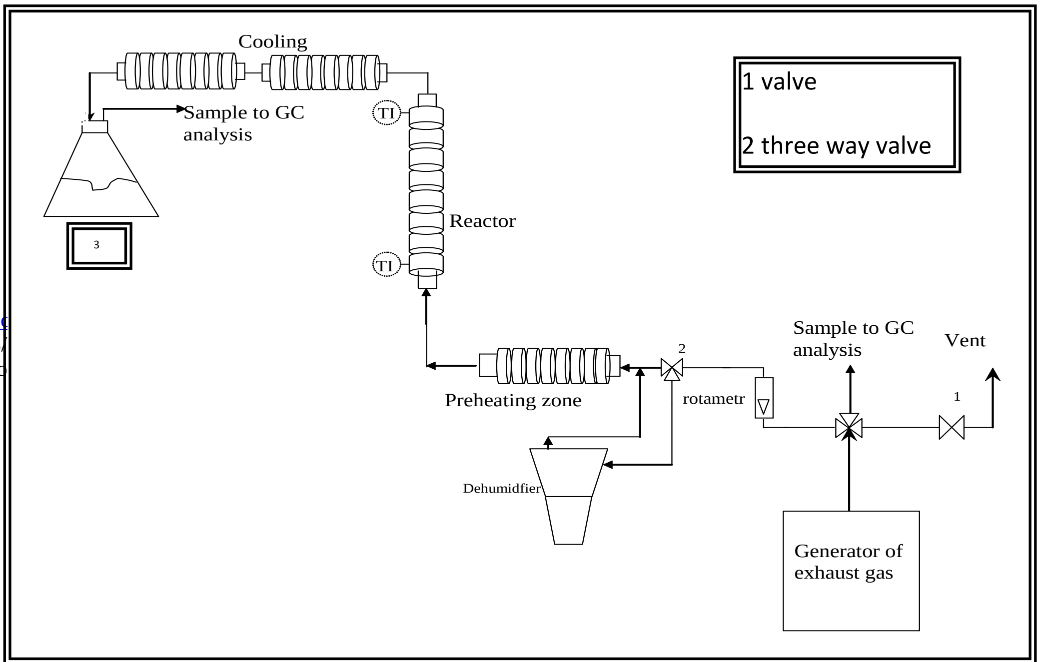
Catalyst Specification	Pd
Surface area, m^2/g	75
bulk density, g/cm^3	1.455
Porosity	0.43
Equivalent radius, nm	7.88

EXPERIMENTAL WORK

Equipments

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.



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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.

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 first column was porapaq N while the second one was porapaq Q. All the samples were trapped in a especial trap and sealed well, and analyzed in Abin Sina company. The operating conditions of the gas chromatography are shown in Table (5).

Table (5) 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

RESULTS AND DISCUSSION

Effect of Operating Variable on Monolith Performance

Effect of Temperature:

The effluence of temperature in the range of (373-673 K) on the exhaust gas conversion at a given gas space velocity (35.38 s^{-1}) for commercial monolith catalyst and 0.4% Pd loading catalyst, at bed length 10 cm is shown in Figure (3).

It can be seen from this figure, 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.

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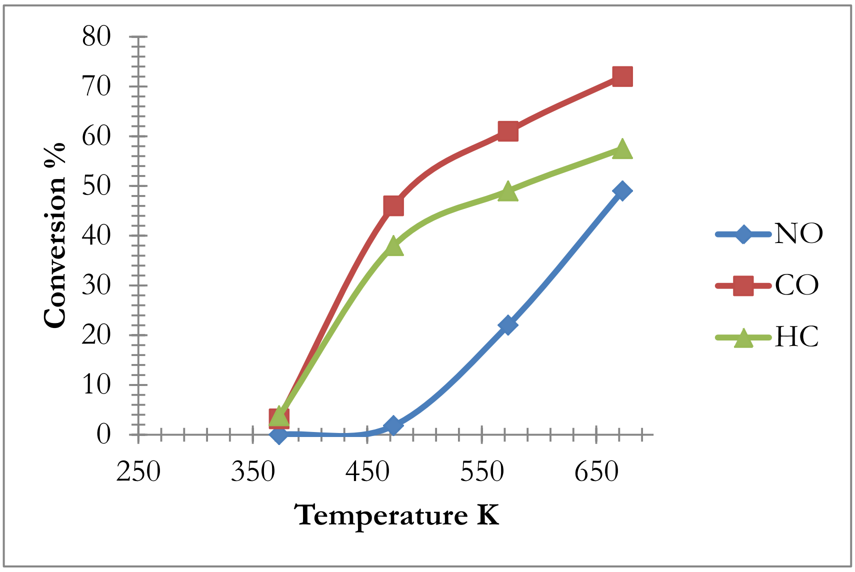

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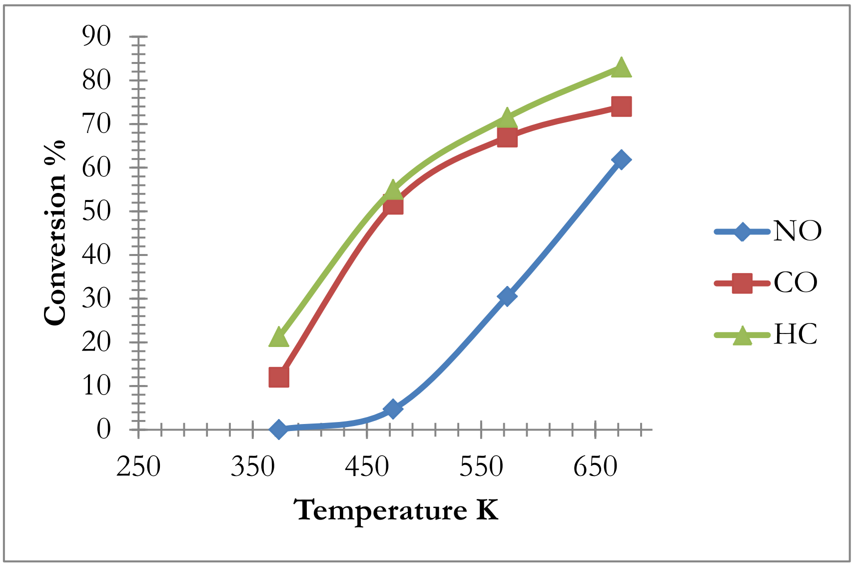

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Figure (3) Effect of temperature on conversion percentage, a: commercial catalyst , b:0.4wt%Pd at a given space velocity 35.38 S^{-1}.

Figure (3) also shows that the conversion of direct oxidation of $C_3H_6$and CO 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 (6). This indicates that NO reduction requires higher

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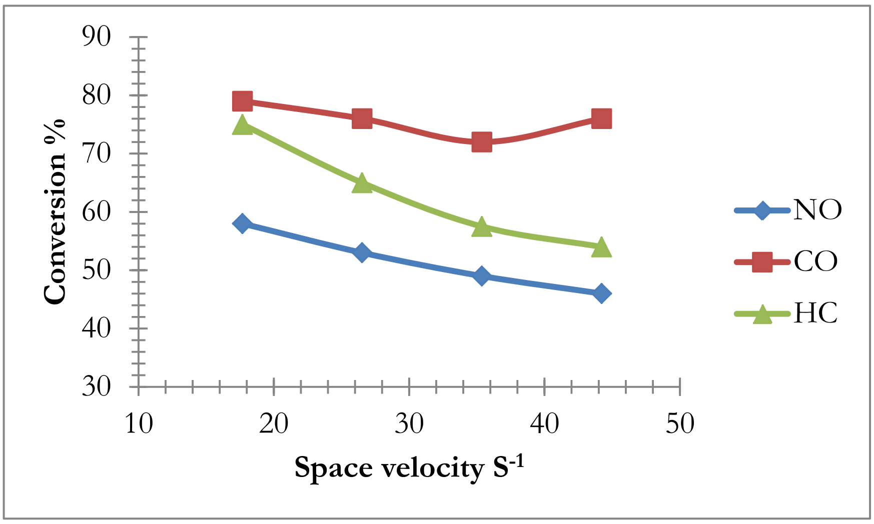
temperature to reach similar CO and C_3H_6 conversions. These results are in agreement with previous finding of Hoebink et al., [15] and Granger, et al., [16].

Effect of Gas Space Velocity

Figure (4) 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 (673 K) for commercial monolith catalyst and for 0.4wt%Pd loading catalyst.It can be noticed from this figure 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., [17], Tomasic et al., [18] and Fabiano et al., [19].



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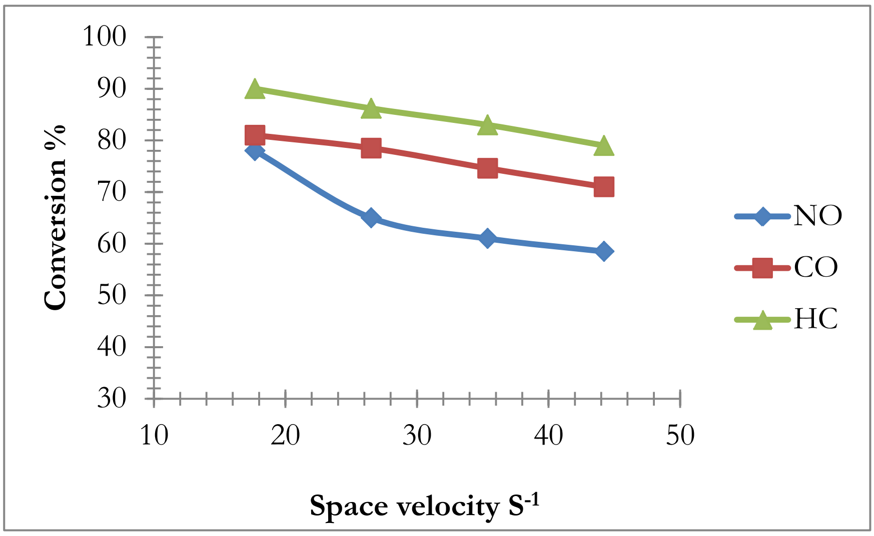

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B

Figure (4) Effect of gas space velocity on conversion percentage of components at wet condition at 673 K.

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Effect of Pd loaded on monolithic catalyst

Figures (5) show the effect 0.4% wt loading of Pd on the conversion of exhaust gas at a given temperature 673 K and different space velocities.

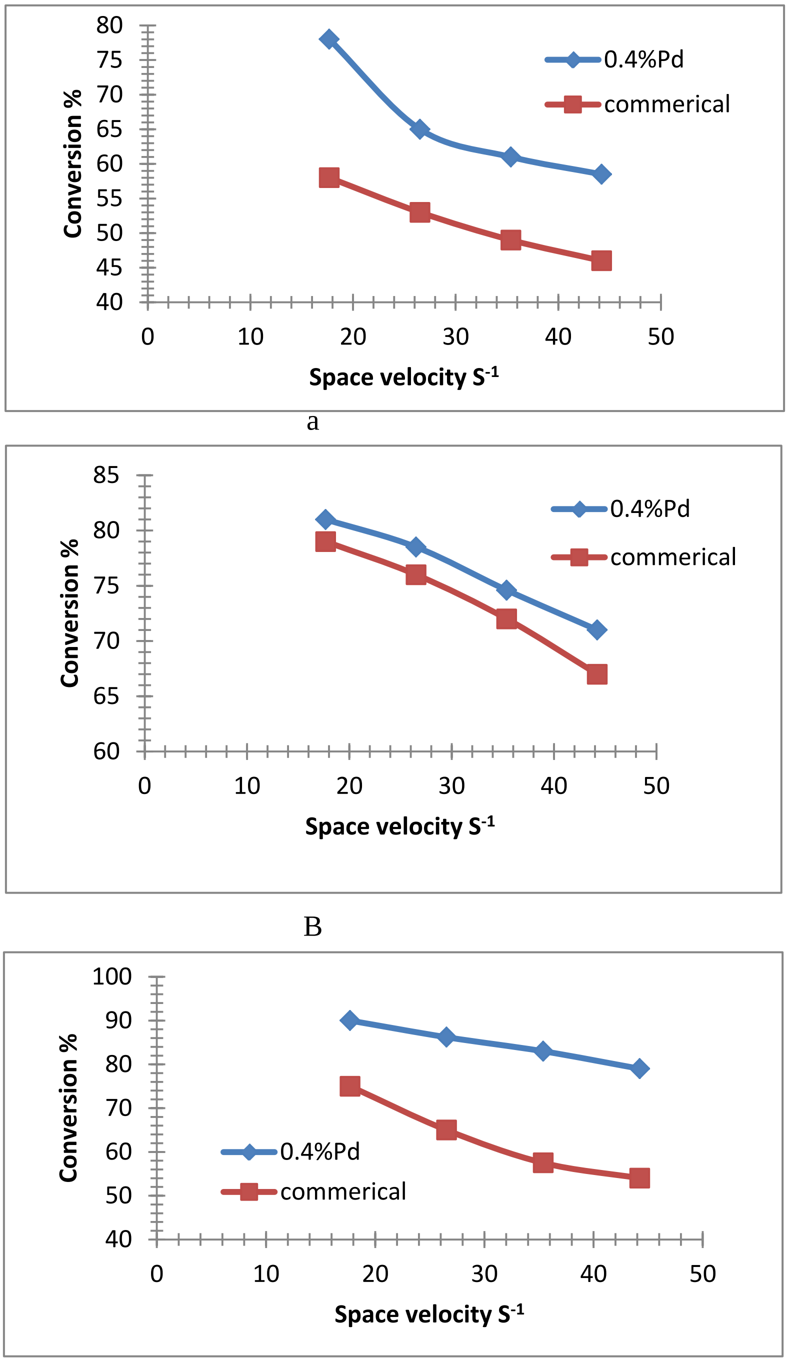

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Figure (5) Effect 0.4 % loaded of Pd metal on the conversionpercentage of a:NO component , b: CO component , c: HCcomponent at temperature of 673 K.

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From these figures, it can be seen that the conversion of NO reduction using Pd 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% Pd loading catalyst compared with the commercial catalyst (as can be seen in Table 6).

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 1, 2, 4 and 5 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[20].

$$2CO+O_2 \rightarrow 2CO_2 \qquad \dots (1)$$

$$4C_nH_m+(m+4n)O_2 \rightarrow 2mH_2O+4nCO_2 \qquad \dots (2)$$

$$2NO+2CO \rightarrow N_2+2CO_2 \qquad \dots (3)$$

$$CO+H_2O \rightarrow CO_2+H_2 \qquad \dots (4)$$

For each run in a differential reactor the performance equation becomes [20]:-

$$\frac{w}{F_{Ao}}=\int_0^x \frac{dx}{-r_A}=\frac{1}{(-r_A)_{av}}\int_0^x dx_A=\frac{\Delta x}{(-r_A)_{av}} \qquad \dots (5)$$

From equation (6) 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.

Figure (6) shows the results of the rate of reaction estimated for NO reduction, CO oxidation and C_3H_6 oxidation using commercial and 0.4%Pd loaded catalyst.

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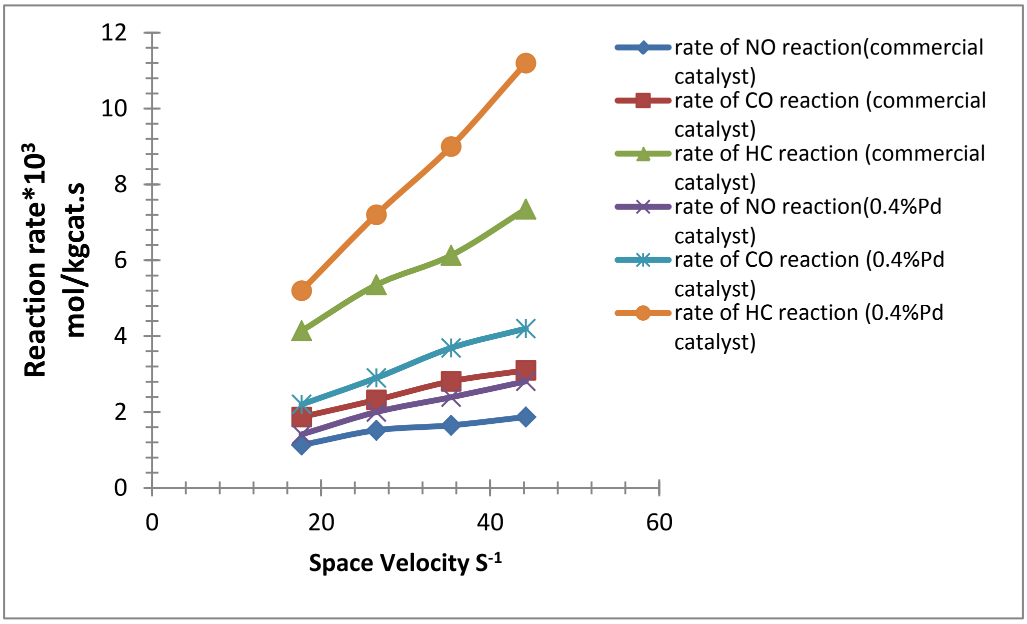

Figure (6) Effect 0.4 % loaded of Pd metal on the rate of reaction of NO, CO, and HCcomponents at temperature of 573 K.

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 Pd 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 (7) that satisfies the relationships between rate constant and reaction temperature.

$$K = A\, e^{-Ea/Rg\,T} \qquad \dots \quad (7)$$

A plot of ln (k) vs. $\left(\frac{1}{T}\right)$ is shown in Figure (6) which are used for estimation of E_a values, since (ln A) represents the intercept and the slope is represented by

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$\left(\frac{-E_a}{R}\right)$.Table (6) show the apparent activation and arrhenious factor for commercial catalyst and Pd loading .
Ba

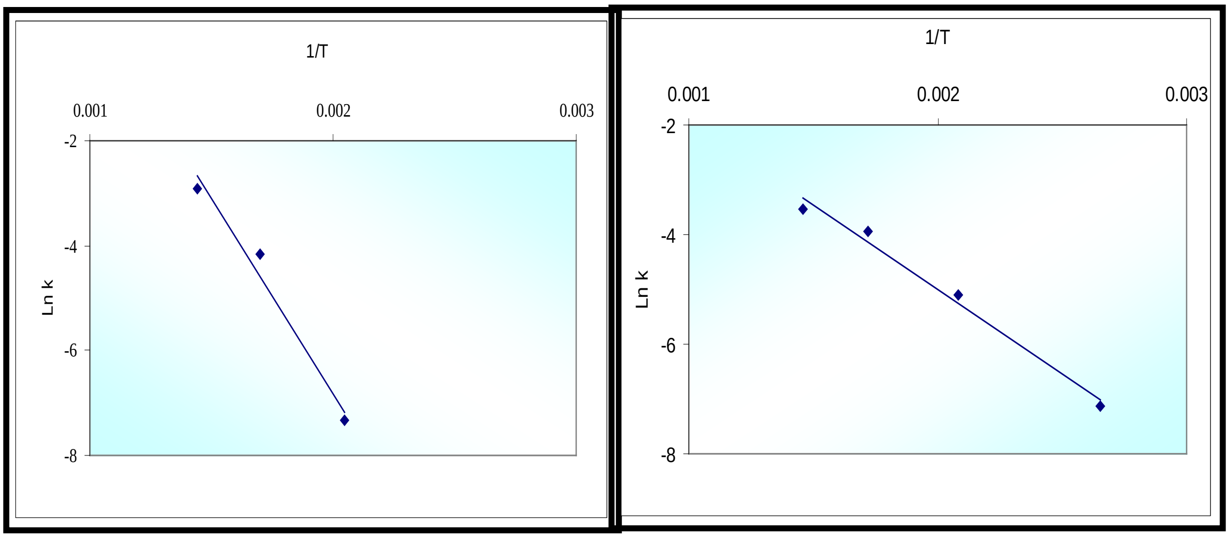

Figure (6) Arrhenious plot for a: CO + NO and b: C3H6 + O_2 for of commercial catalyst.

The results of the analysis of the parameters estimation are outlined in Table (6).

Table (6) apparent activation energy values and reaction order for commercial catalyst and Pt loading metal.

Reaction	E_a / R	E_a KJ / mol	Ao	Reaction order	
				a_i	b_i
Commercial catalyst					
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
0.4% Pd loaded catalyst					

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NO + CO	5340.0	44.4	1844.19	0.6	1.23
CO + ½ O_2	3033.4	25.2	15.879	0.6	1
CO + H_2O	1960.3	16.3	0.04746	1	0.6
C_3H_6 + 4.5 O_2	2865.8	23.8	12.558	1	0.5

CONCLUSIONS

The main points concluded from the present study are summarized as follows:-

- Pd loading over commercial ceramic monolith catalyst improves the HC oxidation rather than CO oxidation and NO reduction.
- The conversion of exhaust gas increases with increasing temperature, activation energies for the oxidation of HC and CO are lower than the reduction of NO.
- The conversion of the exhaust gas decreases while reaction rates increases with increasing space velocit

NOMENCLATURE

Ao	Frequency factor	(-)
Ai	Order of reaction	(-)
Bi	Order of reaction	(-)
Ea	Activation Energy	KJ/mol
FAo	Molar flow rate	Kmol/s
K	Reaction rate constant	$Kmol^{1-ai-bi}$ $(m^{3(ai-bi)}$ / kgcatalyst. s
Rg	Gas constant	$Kpa.m^3/kmol.K$
r_A	Reaction rate	Kmol /(kgcatalyst.s^{-1})
T	temperature	K
W	Weight of catalyst	Kg catalyst
X	Conversion	(-)

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