PHYSICAL ADSORPTION OF REFORMING CATALYST BY NITROGEN

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ABSTRACT

Physical adsorption by nitrogen gas was studied on seven commercial platinum reforming catalysts (RG-402, RG-412, RG-432, RG-451, RG 422,RG-482, PS-10), four prepared platinum catalysts (0.1%Pt/alumina, 0.2 %Pt/alumina, 0.45 %Pt/alumina and 0.55% Pt/alumina), and γ-alumina support.

Physical adsorption was carried out by using Accelerated Surface Area and Porosimetry (ASAP 2400 device) at 77 K .

The results indicate that the surface area in genaral decreases with increasing platinum percentage,high platinum loaded (0.45% and 0.55%) it was found that the percent increasing in surface area was lower than those obtained for low platinum loaded catalysts , and at very higher platinum loading 0.6 %Pt , some reduction in surface area was observed . The precipitation of Re and Ir metals with 0.35 % and 0.6 % platinum increases the surface area , while precipitation of 0.57% Sn with 0.375% Pt/ γ-alumina deceases the surface area catalyst .

الخلاصة

تم دراسة الإمتزاز الفيزياوي باستخدام غازالنتروجين للعوامل المساعدة التالية:

سبعة عوامل مساعدة تجارية (RG-402, RG-412, RG-432, RG-451, RG 422,RG-482, PS-10)

أربع عوامل مساعدة محضرة (0.1، 0.2، 0.45 و 0.55) % وزنا بلاتين (نسبة وزنية مئوية) محمل على الألومينا, اضافة الى كاما اوكسيد الالمنيوم.

تم إجراء الإمتزاز الفيزياوي في درجة حرارة النيتروجين السائل (77)كلفن باستعمال جهاز قياس المساحة السطحية والمسامية (ASAP 2400). أظهرت النتائج أن المساحة السطحية تنخفض مع زيادة نسبة البلاتين المحمل على الألومينا بشكل عام وفي نسب البلاتينيوم العالية (0.55,0.45)% وجد بأن نسبة الزيادة في المساحة السطحية هي أقل من التي تم الحصول عليها في نسب البلاتينيوم الواطئة للعوامل المساعدة ،وجد ايضا بانه عندما تكون نسبة البلاتين عالية جدا 0.6% لوحظ أنخفاض بسيط في المساحة السطحية.

أن ترسيب Re وIr للعوامل المساعدة الثنائية المعدن بنسبة 0.35 % و 0.6 % من البلاتينيوم أدى الى زيادة في المساحة السطحية مقارنة بالعوامل المساعدة الاحادية المعدن , بينما ترسيب Sn بنسبة 0.57 % للعامل المساعد 0.357%البلاتين / كاما-الومينا أدى الى أنخفاض المساحة السطحية.

KEY WORDS
Physisorption;Nitrogen adsorption;BET method;Surface area.

INTRODUCTION

Physical adsorption defined as adsorption in which the forces involved are intermolecular forces (Vander Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved[Lowell,1984].

Gas adsorption is of major importance for the characterisation of a wide range of porous materials.Many gases and vapours, which are readily available and could be used as adsorptives, nitrogen has remained universally pre-eminent. [Oscik,1982].

Physical adsorption or reversible adsorption is most sutaitable for surface area determinations. It is accompanied by low heats of adsorption with no violent or adsorption structural changes occurring to the surface during the adsorption measurement [Young,1962].The molecules physically adsorbed are not restricted to specific sites and are free to cover the entire surface.For this reason surface areas rather than number of sites can be calculated.[Van der Plas,1970].

During the adsorption,the increase of the pressure leads first to a monolayer coverage,then a multilayer coverage is generated .When the local condensation pressure is reached,a phase transition is produced and the pores are full with a liquid phase. This condensation pressure is an increasing function of the pore size. After the saturation, if the pressure is decreased gradually, the primary phenomena of the desorption is observed.On the contrary, if the desorption is started before the complete saturation, the secondary desorption was observed.[D.I Enach.2001].

Langmuir proposed equation 1 for monolayer adsorption on solid surface .

$$\frac{P}{V} = \frac{Po}{V_m C} + \frac{P}{V_m} \qquad (1)$$

Langmuir adsorption isotherm is based on the following assumptions, the surface contains a fixed number of adsorption sites(ϕ = fraction of sites covered; 1-ϕ= fraction of sites not covered), Each site can hold one adsorbed molecule,a monolayer is the maximum amount which can be adsorbed,the sites are independent and have no interaction and the binding energy is the same for each site and does not depend on ϕ.

The Langmuir isotherm makes no provision for more than one layer of gas adsorbing on the surface. Frequently however, the amount of gas adsorbed continuously increases as the pressure is increased indicating that gas sticks to the substrate and to gas already adsorbed.

Allowance for multilayer adsorption was introduced by Brunauer ,Emmett and Teller [Sing,1976 and Kenneth,2001]which develop the Langmuir equation, and they extended the monolayer coverage to multi-layer coverage as shown in equation 2.

$$\frac{P}{V(Po - p)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C Po} \qquad (2)$$

The BET isotherm was a generalization of the Langmuir isotherm and assumes the following,the surface is uniform and all sites are equivalent. (i.e., no pores, steps, etc.), molecules adsorbed on the surface sites are localized,each molecule in the first layer provides a site for adsorption of a second layer, each molecule in the second layer provides a site for adsorption of a third layer, and so on, there is no interaction between molecules in a given layer and molecules in the second and higher layers are held together by the forces in the bulk liquid whereas molecules in the first layer are different by virtue of being bound to the surface.

In spite of the perceived theoretical limitations of the BET model, the BET-nitrogen method soon became established as a standard procedure for surface area determination.

Empirical evidence indicated that the changeover from monolayer to multilayer adsorption occurred at the beginning of the middle, nearly linear section of the isotherm ,and was taken by them to indicate the completion of the monolayer .

The plot of $P/V(P^o-P)$ Versus P/P^o from equation 2 gives a straight line usually with range of P/P^o (0.05-0.35)[Loweel,1984] with slope S and intercept I which are calculated by equations 3 and 4 respectively.

$$I = 1/V_m C \qquad (3)$$

$$S = C-1/V_m C \qquad (4)$$

It is evident that the location and extent of the linear region of a BET plot is dependent on the adsorption system (both adsorbent and adsorptive) and the operational temperature. In view of this situation, it is strongly recommended [Gregg,1982] that the BET monolayer capacity(V_m) evaluted by equation 5.

$$V_m = 1/(S+I) \qquad (5)$$

Then surface area calculated by equation 6.

$$S_{BET}(m^2/g) = N_s * N * V_m \; / \; 22414 \; * 10^{18} \, nm^2/m^2 \qquad (6)$$

The evaluation of S_{BET} is,of course, dependent on the average area, N_s, occupied by each molecule in the completed monolayer. In the case of nitrogen at 77 K, N_s of nitrogen is usually taken as 0.162 nm^2, this value was originally proposed by [Emmett and Brunuaer ,1938] and was based on the assumption that the monolayer had the liquid form of close-packed structure.

High value of the parameter C, is an indication of strong adsorbent–adsorbate interactions. Typical C values in the range 80–150 for nitrogen at 77 K are consistent with the formation of well-defined monolayers on many non-porous and mesoporous adsorbents [Dubinin(1955)and Gregg1982].

Physical adsorption of gas or vapours is normally characterized by the liberation of between 10 to 40 kJ/mol of heat which is close to values associated with heats of liquification of gases . The heat evolved on adsorption of a gas or vapours onto solid from a liquid,however,is strongly dependent on the source and history of the solid adsorbent[Jhon and Barry,1998].

C value calculated by equation 7.

$$C = S + I/ I \qquad (7)$$

Heat of adsorption was calculated from constant C by equation 8 [Brunauer,1938].

$$C = \exp^{(E_1 - E_2)/RT} \qquad (8)$$

This work deals with preparation of platinum γ- Al_2O_3 catalysts wih different Platinum content and calculation of the surface area and heat of adsorption for γ- Al_2O_3 ,prepared and commercial catalysts by physical adsorption of nitrogen at 77K.

EXPERMINTAL WORK

Material

Commercial Catalysts:

Table (1) shows the properties of commercial catalysts and γ- Alumina support .

Symbol	Form	Pt Content (wt. %)	Cl Content (wt. %)	Diameter mm	Length mm	Bulk density g/cm^3	Pore volume cm^3/g	Porosity
γ- Al_2O_3	Extrudate	-	-	2.5	4-8	0.68	0.62	0.56
RG-412 0.35 % Pt/ γ- Al_2O_3	Extrudate	0.35	1	1.8	5	0.75	-	-
RG-402 0.6 % Pt/ γ- Al_2O_3	Cylindrical	0.6	1.02	1.5	7-9	0.75	-	-
RG-422 0.6 %Pt- 0.03 % Ir/ γ- Al_2O_3	Cylindrical	0.6	1.2	1.6	1.8	-	-	-
RG-432 0.35%Pt- 0.03 %Ir/ γ- Al_2O_3	Cylindrical	0.35	1	1.8	9	-	-	-
RG-451 0.35%Pt- 0.03%Ir- Promoter/ γ- Al_2O_3	Sphere	0.35	1.1	-	-	0.75	-	-
RG-482 0.3%Pt- 0.3%Re/ γ- Al_2O_3	Cylindrical	0.3	1	1.4	8-9	0.75	-	-
PS-10 0.375%Pt- 0.57%Sn/ γ- Al_2O_3	Sphere	0.375	1.02	-		-	0.82	0.75

Gases

a- Nitrogen:

It was supplied from Baghdad Factory for Drug Industry with purity 99.9 % and it is used as adsorbent.

b- Hydrogen:

It was supplied from AL-Mansour plant with purity 99.9 and it is used as a reduction material in preparation step.

c-Helium:

It was supplied from AL-Mansour plant with purity 99.9 and it is used in dead volume measurments.

d-Liquid nitrogen:

It was supplied from Baghdad factory for drug industry with purity 99.9 %.

e-liquid chloroplatinic acid:

It was supplied from Fluka Chemi AG with purity 99.9% and 40wt % platinum.

Catalysts Preperation

Four platinum supported with γ- Alumina catalyst containing different percentage of Pt were prepared .The impregnation method was applied for catalyst preparation.This includes preparations of hydrochloroplatinic solution with different concentration with a quantity just sufficient to fill the pores of γ- Alumina support as seen from **Table (2)** .

Table (2) Preparation of different Pt/ γ -Al_2O_3 percent

Catalyst with different Pt % loaded	Hydrochloroplatinic acid, g	H_2O, ml	γ -Al_2O_3, g
0.1 Pt/Al_2O_3	0.065	80	25
0.2 Pt/Al_2O_3	0.1375	92	26
0.45 Pt/Al_2O_3	0.283	84	29
0.55 Pt/Al_2O_3	0.345	98	27

Each sample of γ- Alumina was charged in 250 ml flask and connected to a vacuum pump in one side and from top side to a separation funnel where the impregnation solution was contained .The impegnation carried out at room temperture and 5 mmHg vacuum pressure for 4 h.The catalyst dried at 110 ° C for 6 h, and then calcined at 500 ° C in flowing dry air for 4 h to convert the metal salt into a metal oxide. The oxide was reduced by hydrogen at 350 C° and for 3 h to give zero-valent metal.

General description of the(ASAP) Instrument

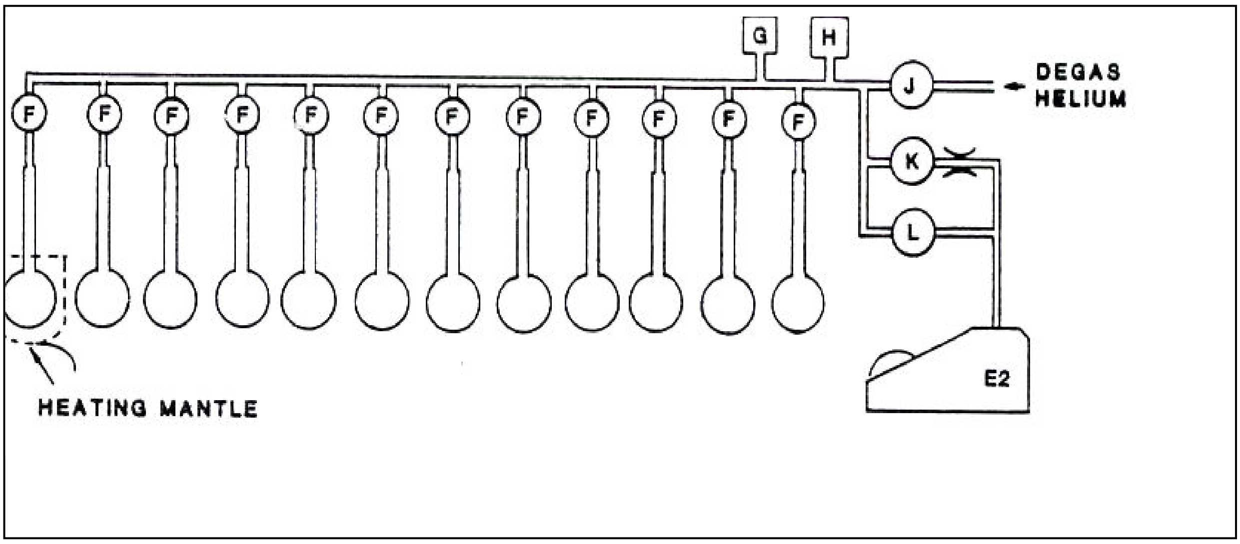
Accelerated Surface Area and Porosimetry instrument (ASAP-2400) is programmed to perform physical adsorption and desorption analysis completely under computer control. The (ASAP-2400) is actually two independent instruments in a single cabinet, one to degas samples and the other has to analyze sample.The specification of ASAP 2400 Instrument is shown in **Table (3).**

The sample degassing part of the (ASAP-2400) consists of a vacuum pump, a manifold with six degas ports , a vacuum transducer to monitor manifold pressure, a pressure limit switch, heating mantles and controls for heating samples, and individual sets of controls to govern the out gassing of each sample. Samples may be added to or removed from degas ports without disturbing the treatment of other samples sharing the manifold as shown in **Fig. (1).**

The analysis part of the (ASAP-2400) consists of vacuum pump, manifold with six sample ports and six Po tubes, an individual pressure transducer for each sample port, a master pressure transducer for the manifold, a precision volume to check the manifold volume calibration, a liquid nitrogen thermos flask and a status display panel a shown in **Figs. (2) and (3).**

Table (3) Specification of ASAP 2400 Instrument

Specification	Value
Minimum surface area ,m^2/g	5
Minimum pore volume ,cm^3/g	0.02
Pore size range ,Å	10-600
Environment temperature , °C	10-35
Pressure measurement range,mm Hg	0-950
Analysis manifold capacity, sample	6
Liquid N_2 system capacity ,(liter per one Dewar flask).	1.9
Minimum pressure ,mm Hg	0.005
Degas system capacity,sample	6
Temperature range , °C	Ambient to 350



E_2 Degas vacuum pump
F Degas port valve
G 1 psig pressure switch
H Degas vacuum Gauge
K Vacuum valve
L Vacuum valve

Fig. (1) Degassing part

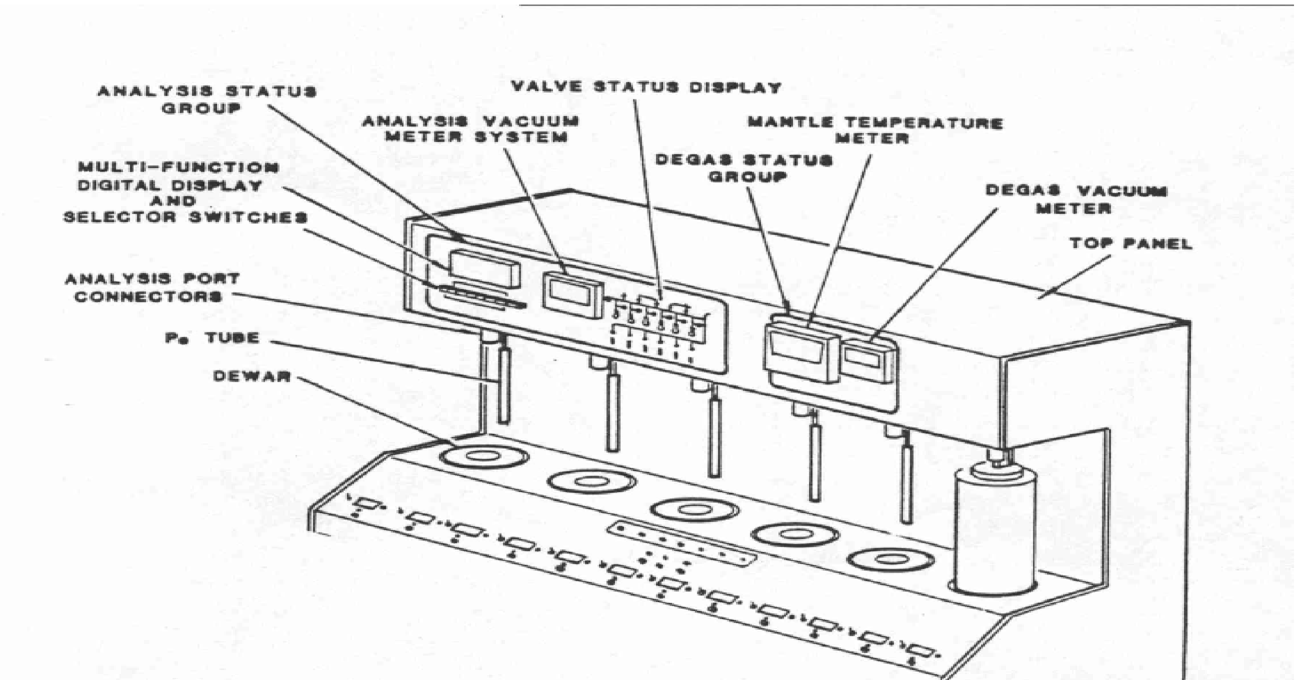


Fig. (2) Analysis part outside view

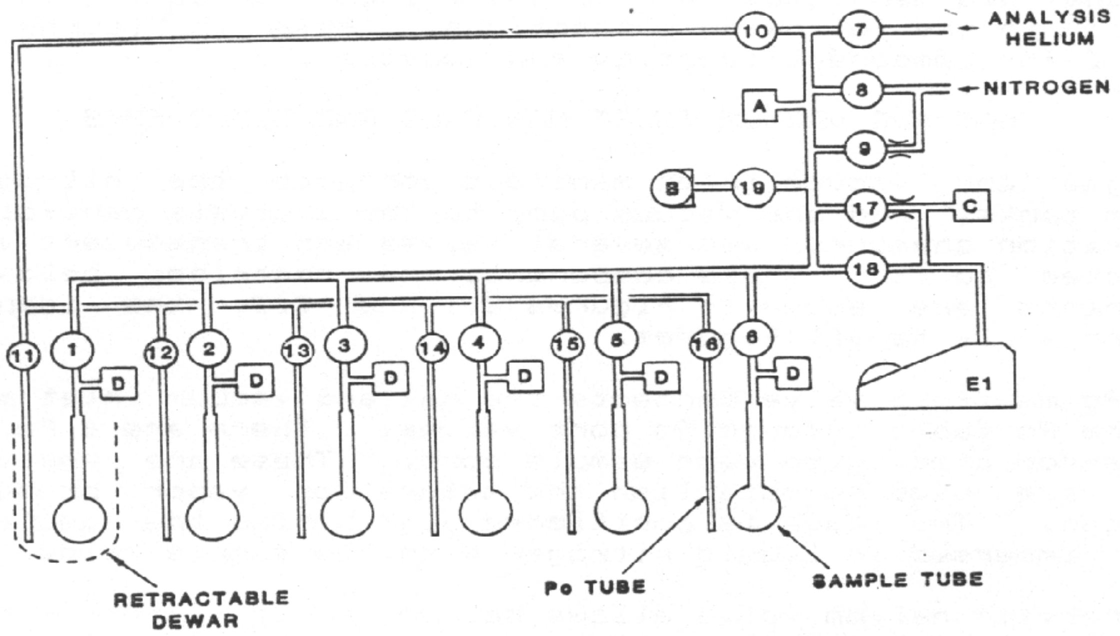


Fig. (3) Analysis part scheme .

Procedure

Appropirate quantities of samples loaded into sample flasks and then sample holders were mounted into degas ports.The sample flasks attached heating mantles to apply the degassing step. The degas vacuum meter set point 500 millitorr was mounted for each catalyst sample at 150 C° for 3 h.When degassing completed , the heating mantles were removed and allow the sample to cool to the room temperature,then the samples were weighted . For dead volume measurment the sample flasks were covered with isothermal jacket and attached to a liquid nitrogen thermas.Pulses of helium gas were admitted up to equilibrium pressure. For adsorption measurements pulses of nitrogen gas were admitted until reaching the different equilibrium pressure.

Results and discussion

The physisorption of nitrogen gas were carried out for γ-Alumina,prepared catalysts and commercial catalysts at 77 K and relative pressure (P/P^o) from 0-1.

Figs. (1-12) show the BET plot for γ-Alumina ,prepared catalysts and commercial catalysts.The slopes and the intercepts of the plotes of $P/V(P^o-P)$ verses P/P^o (BET plots) were used to calculate the volumes adsorbed at monolayer coverage (V_m) for all samples by Eq. 5 .The surface area of the samples were calculated by Eq. 6 .**Table (4)** showes the obtained values of the surface areas for γ-Alumina ,Prepared Catalysts and commercial catalysts.

γ-Alumina has higher surface area compared with all catalysts,because it has more porous structure.This is also observed by Savitzky and Golay[Savitzky and Golay,1964].The surface area of monometallic platinum catalysts genarally decreases by platinum content increasing from 0.1 to 0.35 %. This is presumably due to bulky platinum catalyst crystallites,which block up some pores and hence reduces the surface area as mentioned also by [Vanden,1979].Higher content than 0.3 % up to 0.55 % slightly promotes the surface area increasing. This is may be due to creation a new pore which increase the surface area .At very high platinum content 0.6 % there is some reduction in surface area and this may be due to slight reduction in the number of pores.

0.3% Pt-0.3% Re/ γ-Al_2O_3 catalyst has a high surface area compared with a monometallic 0.35% Pt/ Al_2O_3 catalyst .Addition of 0.3 % Re to Pt catalyst may be made a good alloy (Pt-Re) which could be create a new pores resulting in an increasing in surface area as mentioned by [Michael.1982].
The addition of 0.03 % Ir to Pt / γ-Al_2O_3 gave lower surface area compared with 0.3% Pt-0.3% Re/ γ- Al_2O_3 catalyst and slightly higher surface area compared with 0.35% Pt/ γ- Al_2O_3 catalyst.
The values of constant C in BET equation were calculated by by Eq.7 and presented in column 6 of **Table (4) .**
The constant C is an indicator of adsorbate -surface interaction [Loweel,1984].The value of C for 0.35 % Pt-Ir / γ-Al_2O_3 and 0.3 % Pt-0.3%Re higher than 100 and this means that higher interaction between nitrogen and catalyst surface took place.When the value of C approximate (100),this means, that some fraction of surface is unoccupied as observed for γ- alumina where C= 86.58.
The C values were used for the heat of adsorption calculation of nitrogen gas on γ- alumina, prepared catalyst and commercial catalysts according to Eq. 7 .The values of heat adsorption were presented in column 7. **Table (4) .**
The heat of adsorption represents the affinity between nitrogen gas and catalyst surface. [Sing,1982].As the heat of adsorption increases, the volume adsorbed at high relative pressure decreases which can be consider due to the increase in the temperature of catalyst surface.

Table (4) Monolayer Capacity, Surface Area , constant C and heat of Adsorption

Catalyst	V_m cm^3/g	S g/cm^3	I g/cm^3	S_{BET} cm^2/g	C	E_1-E_2 J/gmol
γ-Al_2O_3	63.857	0.01469	0.000893	277.889	86.580	2855.309
0.1 Pt/ γ- Al_2O_3	59.1160	0.01273	0.004185	257.344	115.060	3037.935
0.2 Pt/ γ- Al_2O_3	49.995	0.01634	0.002375	232.604	142.87	3176.52
0.45 Pt/ γ- Al_2O_3	59.948	0.017453	0.002242	221.022	127.67	3104.51
0.55 Pt/ γ- Al_2O_3	51.839	0.019142	0.000148	225.665	130.1184	3116.67
RG-412 0.35% Pt/ γ- Al_2O_3	49.2996	0.020097	0.000187	214.611	108.342	2999.42
RG-402 0.6 %Pt/ γ- Al_2O_3	46.6555	0.021290	0.000143	203.100	149.23	3204.4
RG-482 0.3 %Pt-0.3 % Re/ γ-Al_2O_3	52.759	0.018135	0.000225	238.428	138.35	3155.94
RG-432 0.35% Pt- 0.03% Ir/ γ-Al_2O_3	53.2874	0.018636	0.002406	231.971	144.424	3183.497
RG-422 0.6% Pt-0.03%Ir/ γ-Al_2O_3	55.229	0.017972	0.000134	240.423	134.547	3138.097
RG-451 0.35% Pt-0.03 %Ir-Promotor/ γ- Al_2O_3	49.127	0.020226	0.000129	213.860	157.9369	3240.706
PS-10 0.375 %Pt-0.57 % Sn/ γ- Al_2O_3	44.0147	0.022530	0.000189	191.605	119.877	3064.19

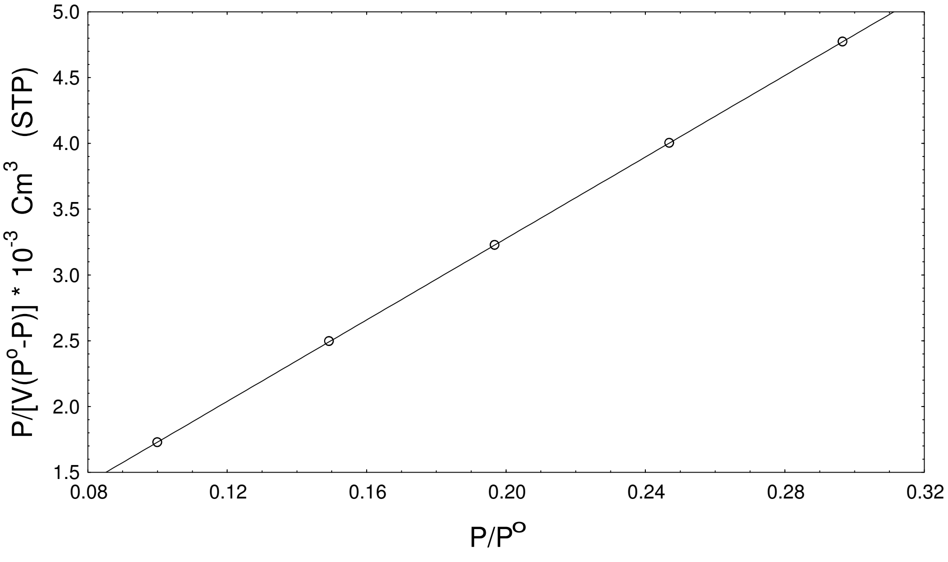


Fig.1 BET plot of adsorption data for Alumina

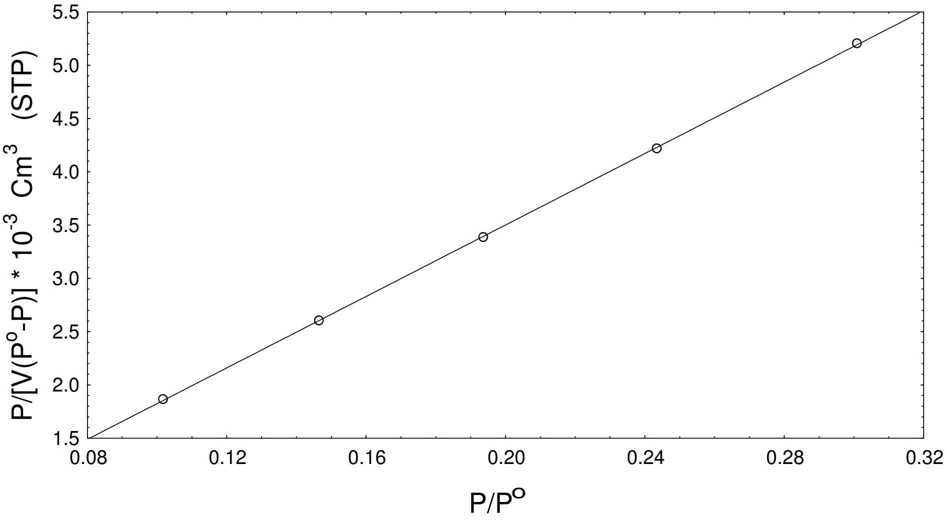


Fig.2 BET plot of adsorption data for 0.1 % Pt/Al_2O_3 catalyst

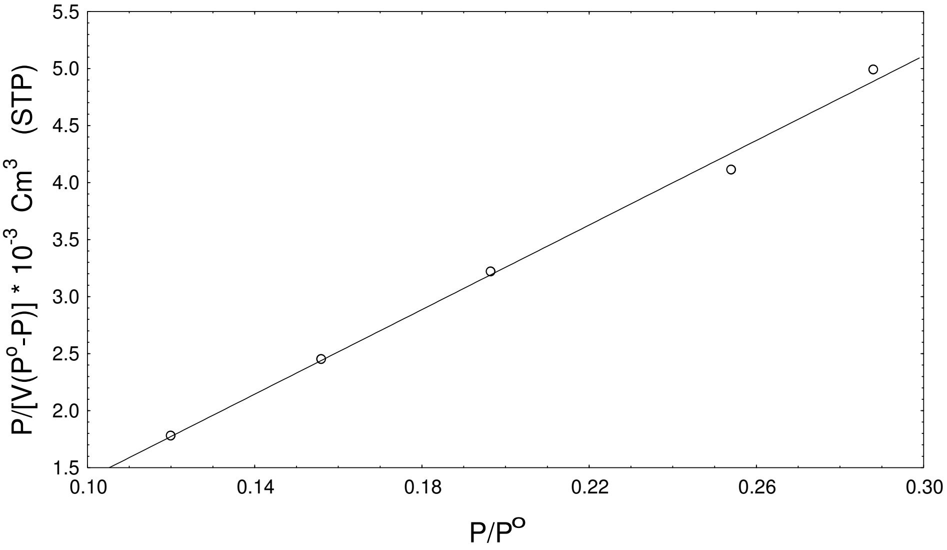


Fig.3 BET plot of adsorption data for 0.2 % Pt/Al_2O_3 catalyst

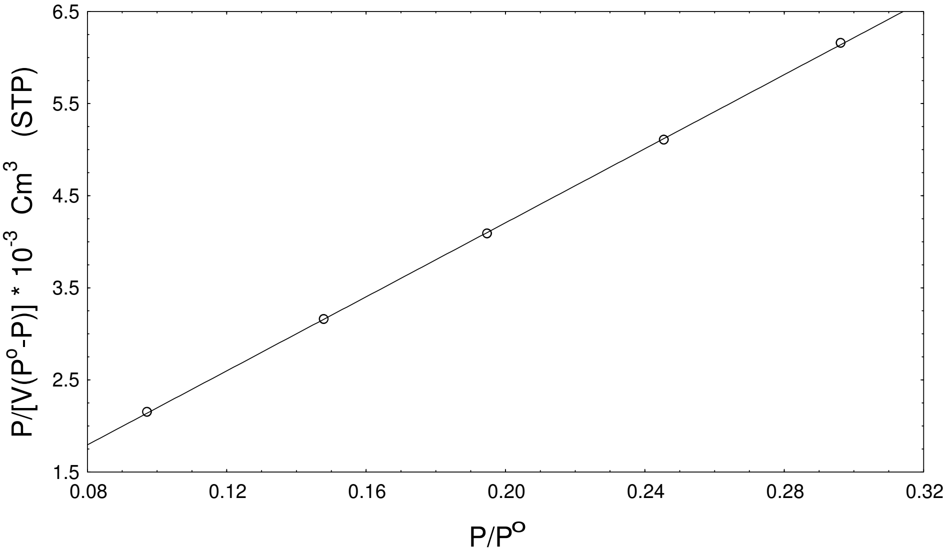


Fig.4 BET plot of adsorption data for RG-412 catalyst

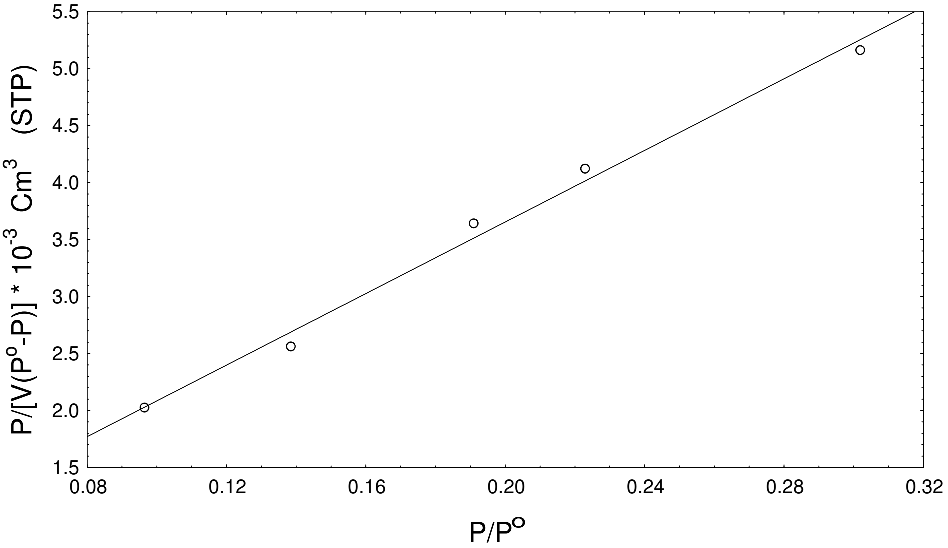


Fig. 5 BET plot of adsorption data for 0.45 % Pt/ Al_2O_3 catalyst

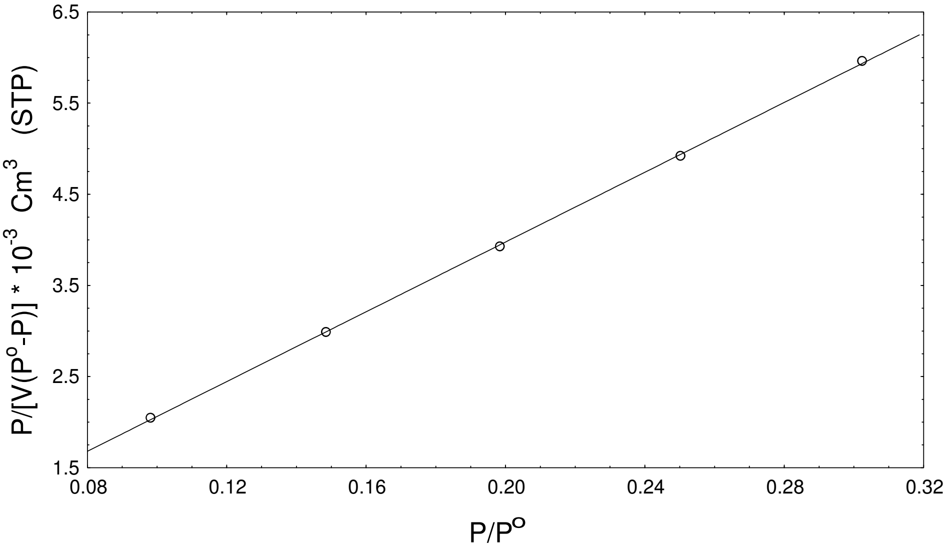


Fig. 6 BET plot of adsorption data for 0.55 %Pt/ Al_2O_3 catalyst

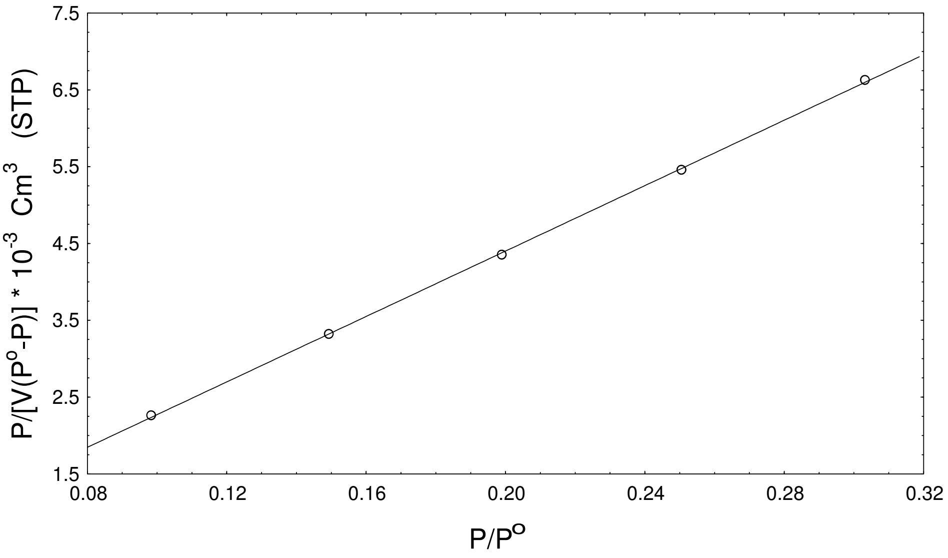


Fig. 7 BET plot of adsorption data for RG-402 catalyst

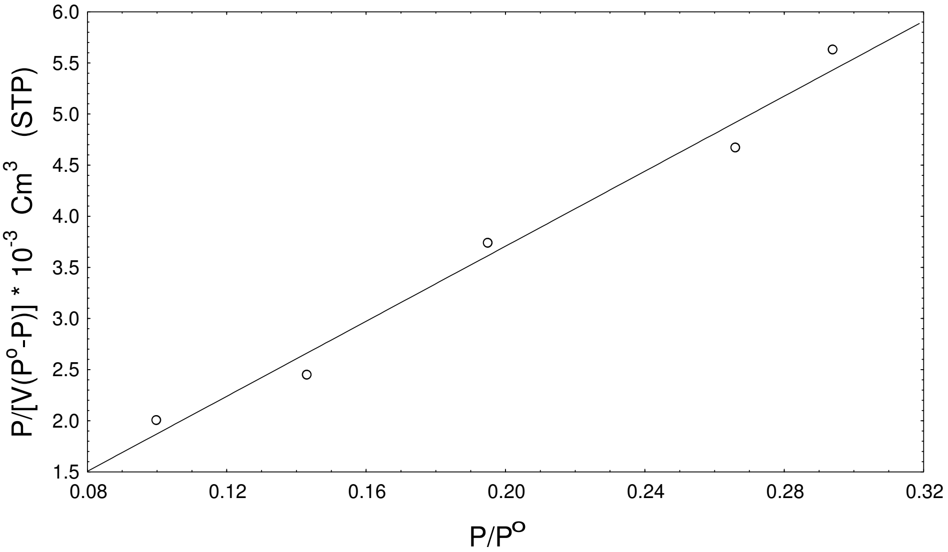


Fig.8 BET plot of adsorption data for RG-482 catalyst

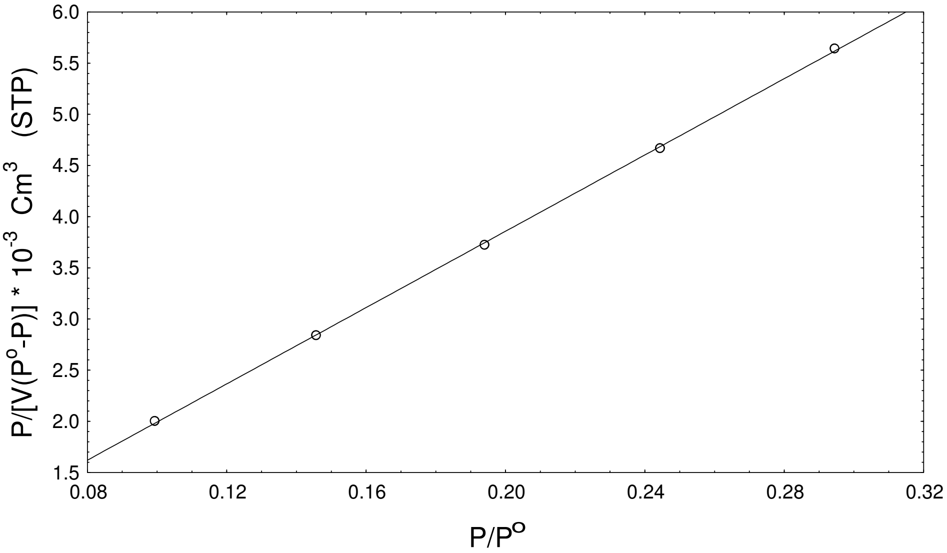


Fig.9 BET plot of adsorption data for RG-432 catalyst

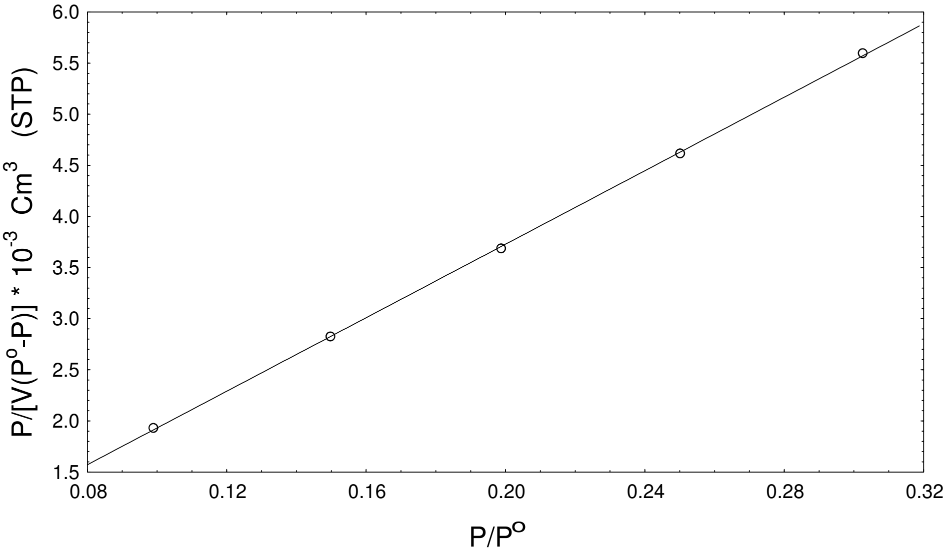


Fig.10 BET plot of adsorption data for RG-422 catalyst

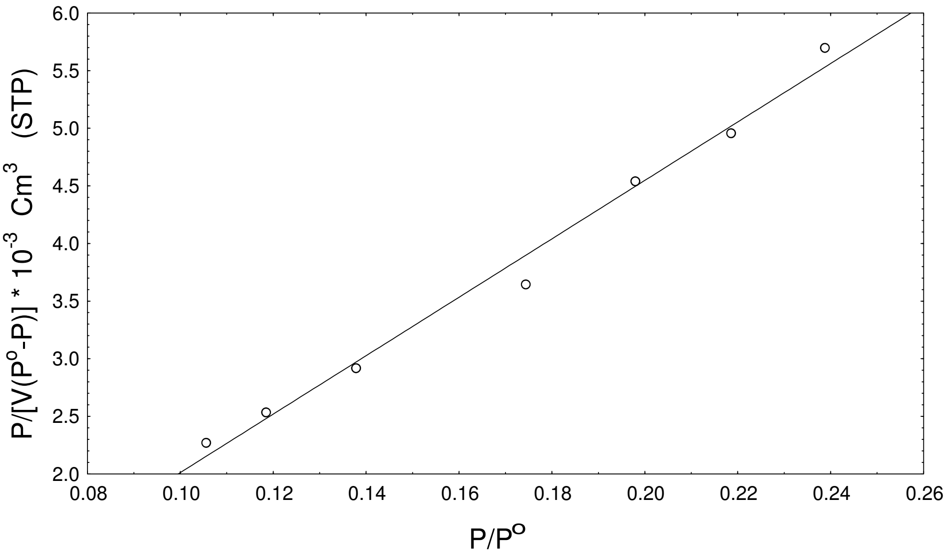


Fig.11 BET plot of adsorption data for RG-451 catalyst

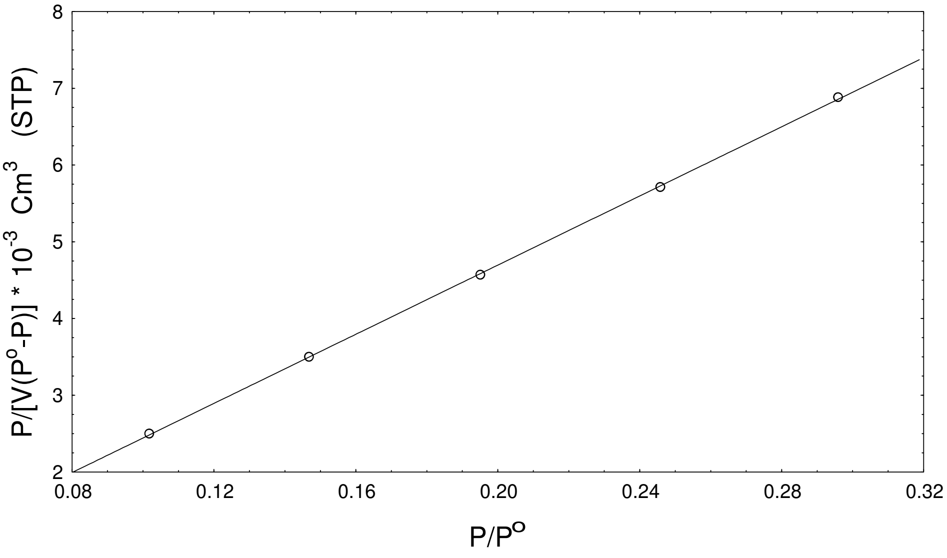


Fig.12 BET plot of adsorption data for PS-10 catalyst

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Nomenclature

C= Constant. Eq.7
E_1 = Average heat of adsorption in monolayer.(J/gmole) Eq.8
E_2 = Heat of condensation.(J/gmole) Eq.8
I=Intercept (g/cm^3) Eq.3
N= Avagadro number =6.023 *10^{23} (molecule/mole) Eq. 6
Ns= Nitrogen molecular cross sectional area= 0.162 nm^2 Eq.6
P= Equilibrium pressure (mmHg).
Po= Saturation pressure (mmHg).
R = gas constant = 8.314 (J/gmole.K) .
S= Slope(g/cm^3) Eq.4
T = Temperature (K)
V= Volume adsorbed (cm^3/g).
V_m= Monolayer coverage volume (cm^3/g)
ϕ = fraction of sites covered.
1-ϕ = fraction of sites not covered.