VOLUMETRIC CHEMISORPTION STUDIES OF REFORMING CATALYSTS

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ABSTRACT

Volumetric chemical adsorption was done in a volumetric apparatus using hydrogen gas at room temperature on eleven platinum catalyst, commercial catalysts (RG-412, RG-402, RG-432, RG-451, RG-482, and PS-10) and prepared platinum catalysts with 0.1, 0.2, 0.45, and 0.55% by weight of Pt supported with γ*-alumina. The results show that the metal crystallite area increases with increasing platinum content. The dispersion and particle size of metal crystallite located between 48.2-96.1% and 3.85-12.72 nm, respectively. For bimetallic catalysts, the hydrogen intake decrease in the following order: Re < Sn < Ir.*

INTRODUCTION

Chemisorption may be considered to be a chemical reaction between an adsorbate molecule and the surface array of metal atoms. The greatest interaction is with metal atoms in immediate contact with the adsorbed molecules, but the weaker interaction with all the other surface atoms is not negligible[1].

Gas-surface interactions may be complex and in many cases the fundamental mechanisms of the chemisorption process had to discern.(2)

Another point must be kept in mind with adsorption is that the stoichiometry of adsorption must be known in order to calculate surface concentrations.

Hydrogen adsorbed as M-H species over crystalline planes to form a "monolayer". The term "monolayer" is used here in the sense of referring to the hydrogen uptake in the saturation region of the adsorption isotherm. There are a number of factors, which in general influence the nature of gas chemisorption behavior on metals. The important factors are: adsorbed surface impurity, crystallographic, surface heterogeneity, surface reconcentration during adsorption, incorporation of solution of the adsorbate, intrinsic effect of metal particle size and the pressure of a support[3].

Condition of temperature and pressure to produce selective chemisorption on the metal might ideally be found from separate adsorption isobars for the metal and support. High temperature adsorption on supported metal catalysts was studied by several workers (4, 5). Frequently, high temperature about 500°C, are employed. Spenadel and Boudart (6) published a detailed paper in which H_2 was used as the adsorbate for chemisorption on Pt/Al_2O_3 catalyst. They concluded that hydrogen chemisorption is a useful and reliable tool to study dispersion of platinum on oxides supports. Each H atom adsorbed in a linear manner on each Pt atom. Atomic dispersions of Pt (<10Å) were demonstrated by H_2 chemisorption and for Pt particles between 50 and 1000 Å and good agreement between chemisorption of hydrogen an X-ray line broadening was obtained. At 250 OC, the isotherm was independent of pressure at 240 torr and application of the Langmuir isotherm equation gave a surface coverage of 96 %. These results show close agreement to those of Boreskove and Karankove [7].

Gruber[8] also successfully used volumetric system method to determine surface area of Pt. He selected temperatures between 250 OC and 300 OC. The surface areas of fresh and sintered catalysts were measured successfully, and a comparison for three different preparative techniques was made. From the amount of hydrogen adsorbed per Pt atom, the best dispersion was obtained for platinum hydroxide impregnations, followed by chloroplatnic acid. The poorest results were with a sulfided catalyst after chloroplatnic acid impregnation. Benis, Curtis, and Studer[9] similarly used hydrogen chemisorption for Pt catalysts prepared by ion exchange of $Pt(NH_3)_4$ on SiO_2 gel, which have almost atomic dispersions of Pt from 0.7 to 4.5 and aqueous impregnation of chloroplatnic acid, which have dispersions approximately 1/2 that of the ion-exchange procedures. Hydrogen uptakes were measured at 0°C, and monolayer coverage obtained at 1 torr. Chemisorption data was supported by X-ray line broadening and electron microscopy.

Adler and Kearney[10] studied the hydrogen chemisorption on Pt/ Al_2O_3 naphtha reforming catalysts. These authors monitored the effects of various changes incurred by the catalyst during and after operation. The quantity of hydrogen adsorbed before and after coking and after an attempt at regeneration, by burning off the deposited coke, was measured. Only 1/2 of the original H2 was adsorbed. Substantial loss of Pt surface area was found by H2 uptake after steam sintering at 1 atm, at 700 OC. No regeneration of steam sintered catalyst by O2 firing at 620 OC and 60 lb/psi, as measured by hydrogen uptake,was found.The pretreatment of the catalyst was quite similar to that of Spenadel and Boudart [6].

Hydrogen-Pt/Al_2O_3 isotherms were secured at 200°C with a monolayer taken at 8 to 9 torr. X-ray line broadening supported their results. Similar studies on Pt reforming catalysts using CO and H2 chemisorption were reported by Miller, Weller, and Cornelius [11] in which gas uptakes after treatments typically occurring during reforming were monitored.

The determination of Pt surface area via chemisorption of H2 has been useful in determining other important properties of catalytic system. Cusumano, Dembinski, and Sinfelt [12] investigated dispersion of Pt as influenced by the support finding higher dispersions on Al_2O_3 than Al_2O_3- SiO_2 .The greater catalytic activity of Pt/ Al_2O_3 toward cyclohexane dehydrogenation compared with Pt/ Al_2O_3- SiO_2 was attributed to the greater dispersion of the former. Their data were taken at 200°C and 300°C. Sinfelt et al[13] and Dorting et al[14] have also used H2 for measurements on Pt/ SiO_2 at room temperature; the latter temperature being acceptable for SiO_2 supported systems since minimum H2 adsorption occurs on the support under these conditions.

The chemisorption of bimetallic catalysts was first examined by Frell [15] who did not suggest a stoichiometry to relate his measured uptakes to surface metal.

A method for separate determination of Pt and Re in the bimetallic catalyst was proposed by Menon et al[16] .These authors did not determine a stoichiometry for adsorption by Re and later state that they were not able to determine a reliable chemisorption value for Re[17]. Bolivar et al[18] have also measured the uptake of H2 and O2 by Pt- Re/ Al_2O_3 catalysts and proposed a stoichiometry to relate their measured uptakes to the quantity of surface metal.

The uptake of H2 and O2 by P Al_2O_3t-Re/ Al_2O_3 catalysts has been examined by several research groups; one group has proposed a stoichiometry for surface area measurements. There are, however, significant differences in the results of these various groups, particularly with respect to H2 chemisorption by Pt and titration of O2 chemisorbed on Re.

Bruse and Eugene[19] studies the stoichiometry of hydrogen and surface area measurements on Pt-Re/ Al_2O_3, They concluded that the Re/ Al_2O_3 catalyst does not chemisorbed H2. Comparison of the gas uptakes expected based upon the sum of the monometallic catalysts with those experimentally found for the Pt-Re/ Al_2O_3 catalyst suggests alloy formation in the reduced bimetallic catalysts. The Pt-Re/ Al_2O_3 catalyst exhibits a suppression of H2 chemisorption. The gas uptakes also suggest that the overall dispersion of the bimetallic catalyst is larger than one would expect with no metal interaction, a stoichiometry value found experimentally equal to 0.56.

Rauof[20] studied physisorption and chemisorption at 25°C and other characterization of platinum catalyst at different zeolites supports types X, Y and Iraqi zeolite type A. She found that total surface area of Pt/exchanged zeolites Y is higher than those on X and A types, and that reduction temperature 350 OC causes an increase in the amount of metallic phase and higher dispersion.

This work includes chemisorption measurements, which is used to predict and monitor the reforming behavior catalysts, and to measure metal dispersion and area of metal.

EXPERIMENTAL WORK

Catalyst

Eleven prepared and commercial catalyst were used in this investigation.

Four catalyst were prepared by impregenation of g-alumina with aqueous solutions of the appropriated concentration of chloroplatinic acid to give catalysts of different weight percent of Pt (0.1, 0.2, 0.45, and 0.56). HCl was added in order to give a close value of chlorine concentration in all catalysts. The impregnation step takes place overnight. The alumina supported catalyst are dried at 110°C for 6 hr, and then calcined at 500°C in flowing dry air for 4 hr to convert the metal salt into a metal oxide. The metal oxide is reduced by hydrogen at 350°C, and for 3 hr to give zero-valent metal.

The commercial catalyst were RG-412, RG-402, RG-432, RG-451, RG-482, and PS-10.

Chemisorption Procedure

Hydrogen chemisorption was done by volumetric vacuum method. This method covers the determination of the chemisorption of hydrogen at 298 K on supported platinum catalyst.

Gas adsorption measurements were carried out in a conventional pyrex-glass volumetric adsorption apparatus capable of 10-6 torr as shown in Figure 1. The apparatus consists of sample bulb, gas bulbs, and vacuum system. The whole apparatus is evacuated to 10-4 torr using rotary and mercury diffusion pumps isolated from the adsorption system by a liquid nitrogen trap. The samples were first outgassed and heated by heating upto 250°C for 2h. The outgassing process was used for cleaning the surface of the catalyst sample and to remove all previously physisorbed material. After this pretreatment, nitrogen was used for purging oxygen by admitting nitrogen to the apparatus and nitrogen evacuating for 5 times. After that chemical adsorption of H2 on the metallic constituents of each catalyst was measured. Hydrogen adsorption was measured by using pirani gauge and digital pressure gauge.

A quantity of H2 was admitted to the reduced evacuated sample at room temperature and its pressure noted due to expansion into the sample chamber. The pressure monitored until no further variation with time is noted. The pressure over the sample is increased until the equilibrium is established (no longer gas uptake by the sample). Typical adsorption isotherms for H2 were determined by plotting the number of molecules of H2 or moles of H2 adsorbed versus pressure. The uptake due to chemisorption was then determined by extrapolating the straight-line portion of the isotherm to zero pressure.

Hydrogen gas purity was 99.99 % and is prepared by reaction of absolute ethanol 99.99 % with a pure piece of sodium metal 99.9 % .For this purpose, ethanol was frost by putting H2 chamber in liquid nitrogen and adding a piece of sodium metal. After liquid nitrogen trap removal, reaction is beginning gradually between sodium metal and ethanol. Hydrogen gas was then evolved and collected in a gas bulb.

Chemisorption Calculations

After evacuation the apparatus, the total volume Ve is measured at the end of the experiment. It is evaluated by expanding a dose volume Vd into the sample bulb and observing the pressure. The dead volume Vs is then calculated by subtraction.

$$V_s = V_e - V_d \tag{1}$$

The number of moles of the chemisorbed gas is calculated as follows. The number of moles contained in the dosing volume Nd is obtained from equation 2.

$$N_d = \frac{P_d\ V_d}{R\ T} \tag{2}$$

After expansion and at equilibrium, the number of moles of unchemisorbed gas Ne is calculated from equation 3.

$$N_e = \frac{P_e\ V_e}{R T} \tag{3}$$

Then the number of moles left from a previous expansion Ns is given by equation 4.

$$N_S = \frac{P_e'\ V_s}{R T} \tag{4}$$

Where Pè is the equilibrium pressure of the previous expansion.

The number of moles chemisorbed after each expansion ΔN is calculated by equation.

$$\Delta N = N_d + N_s - N_e \qquad (5)$$

By plotting ΔN against the equilibrium pressure, an isotherm is determined. Then the number of moles of the chemisorbed gas for a monolayer coverage Ns is determined by back extrapolation to zero pressure. Metal area, particle size, and metal dispersion were determined by equations 6, 7 and 8, respectively.

$$A = \frac{N_m^s X_m}{M} \qquad (6)$$

Where N_m^s is the monolayer coverage at zero pressure expressed in surface atoms per gm metal. M is the number of metal atoms per unit area of crystalline surface. Xm is the chemisorption stoichiometry which is to be taken to one.

Mean partical size $\bar{d}$ is determined from equation 7 assuming spherical metal atoms.

$$\bar{d} = 6\frac{V}{A} \qquad (7)$$

where V is the total volume obtained from the total mass of the metal and its density.

The percentage metal dispersion D is defined as the ratio of the number of surface atoms to the total number of metal atoms present in the sample. Metal dispersion can be calculated from the catalyst composition and the metal surface area by equation 8.

$$D = \frac{A\ W}{N\ a\ X} \qquad (8)$$

Where; W = the molecular weight of a metal, N = Avagadro's number = 6.02 x 1023, a = the area per surface pt atom=8.9 x 10-20m2, and X = the mass fraction of a metal.

RESULTS AND DISCUSSION

Chemisorption of eleven commercial and prepared reforming catalysts were carried out by hydrogen. The metal surface area, particle size, and dispersion of commercial and prepared catalyst were calculated from hydrogen uptake, assuming a chemisorption stoichiometry of 1:1 [18], i.e. one surface(s) platinum atom is associated with each one hydrogen atom(s) as shown below [19].

$$Pt_{(surface)} + \frac{1}{2}H_{2_{(gas)}} \rightarrow Pt-H \qquad (9)$$

By application the equations 6, 7 and 8 metal area, dispersion and partical size, and dispersion were calculated and presented in table 1.

The monolayer coverage of the hydrogen uptake was measured by back extrapolation of the chemisorption isotherm to zero pressure as shown in figure 2 for g-alumina.

Figures 3-8 show the hydrogen uptake for monometallic catalyst. It is clear from these figures that the hydrogen intake and metal area were increased with platinum content. This indicates that the velocity to made monolayer coverage on catalysts by hydrogen uptake is rapid, and ability to make a strong interaction between hydrogen atoms and the active sites of platinum particles is high [21].

Figures 9, 10, and 11 show the adsorption isotherm of bimetallic catalyst Pt-Ir/ Al_2O_3. These figures indicate that the Ir improve the hydrogen intake, and increases the metal area. This is may be due to a greater physical and chemical similarity of Ir and Pt [22].

Figure 12 shows that the hydrogen uptake of Pt-Re/ Al_2O_3 catalyst is slower compared with monometallic catalyst or with bimetallic catalysts Pt-Ir/ Al_2O_3, and Pt-Sn/ Al_2O_3. This is may be due to suppression for H2 intake when high Re content was used [19].

Figure 13, show that hydrogen intake slightly increases for Pt-Sn/ Al_2O_3 compared with monometallic catalyst Pt/ Al_2O_3, since the Pt-Sn interaction favors the stability of the metallic phase, and this is indicates that tin increases the dispersion of the Pt, furthermore a decrease in adsorption could considerably increase the particle size of the Pt [23].

CONCLUSIONS

For monometallic catalyst ,metal crystillate area increases with increasing metal content.

1. For bimetallic catalyst ,metal crystillate area increases with the following order Ir>Sn>Re
2. The dispertion and partical size of metal crystillate located between 48.2-96.1% and 3.85—12.73 nm, respectively.

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Table (1) Results of Chemisorption Calculation.

Catalyst	N_s (Monolayer Coverage of Molecule H_2)	Area (m^2/g)	Dispersion (%)	Particle Size (nm)
Al_2O_3 (support)	1.98×10^{20}			
0.1 Pt/Al_2O_3	3.30×10^{20}	26.40	96.10	12.73
0.2 Pt/Al_2O_3	3.73×10^{20}	29.84	54.30	11.26
0.35 Pt/Al_2O_3	7.40×10^{20}	59.20	61.56	5.68
0.45 Pt/Al_2O_3	7.74×10^{20}	61.92	50.10	5.43
0.55 Pt/Al_2O_3	9.10×10^{20}	72.80	48.20	4.62
0.6 Pt/Al_2O_3	10.2×10^{20}	82.40	49.99	4.08
RG-482	5.85×10^{20}	46.80	56.78	7.18
RG-422	10.9×10^{20}	87.20	52.90	3.85
RG-451	7.00×10^{20}	56.00	58.22	6.00
RG-432	7.52×10^{20}	61.16	62.60	5.58
PS-10	6.30×10^{20}	50.40	48.92	6.67

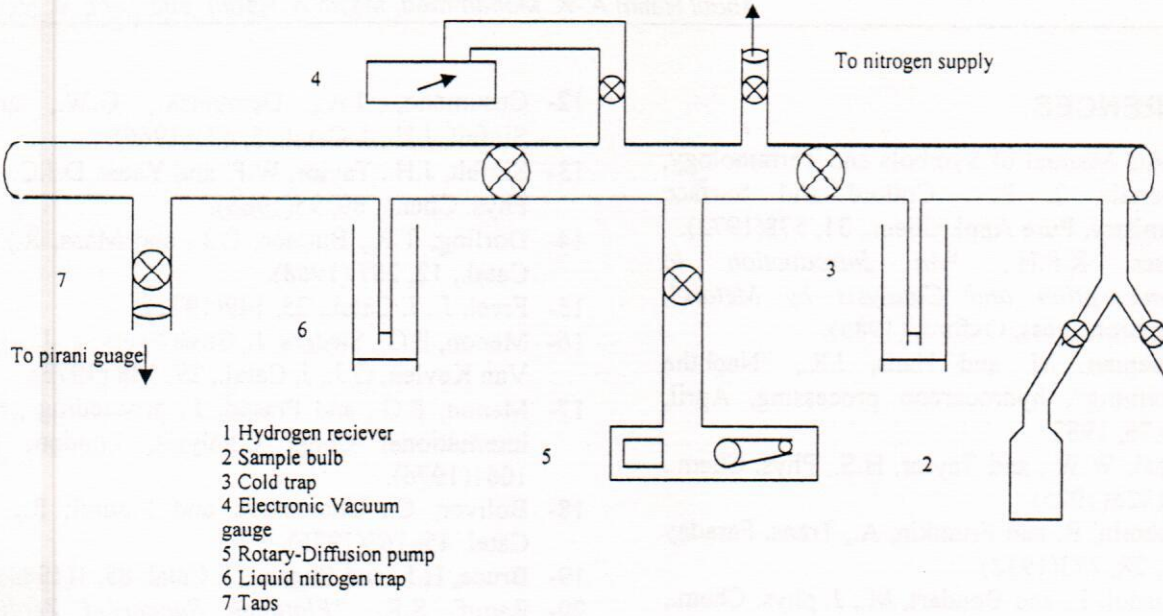

Fig. (1) Schematic Diagram of the Volumetric Apparatus for the Chemisorption

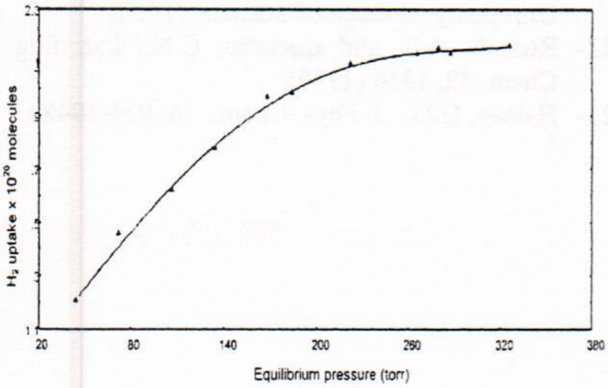

Fig. (2), Chemisorptions isotherm of alumina

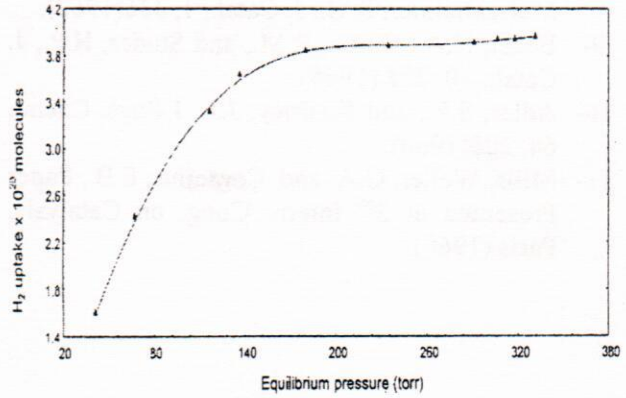

Fig. (4) Chemisorptioin isotherm of 0.2% Pt/alumina

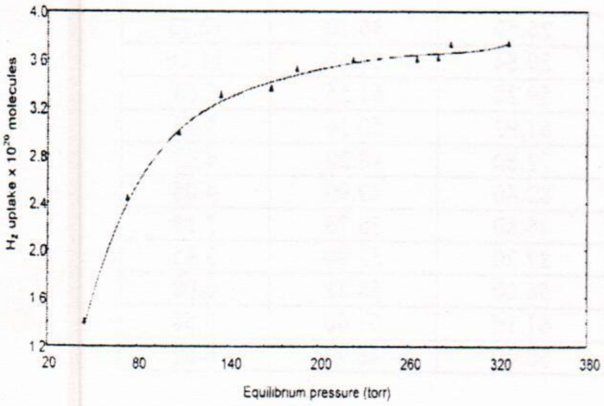

Fig. (3) Chemisorption isotherm of 0.1% Pt/alumina

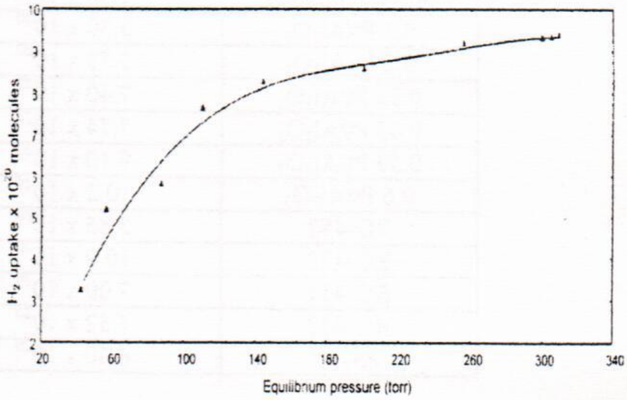

Fig. (5) Chemisorption isotherm of Rg-412 (Pt/Al_2O_3, extrudates)

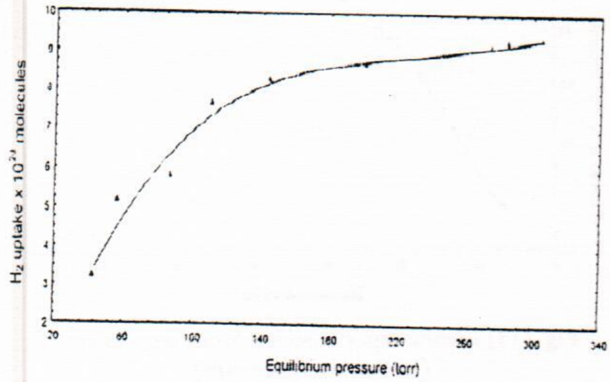

Fig. (6) Chemisorption isotherm of 0.45 Pt/alumina

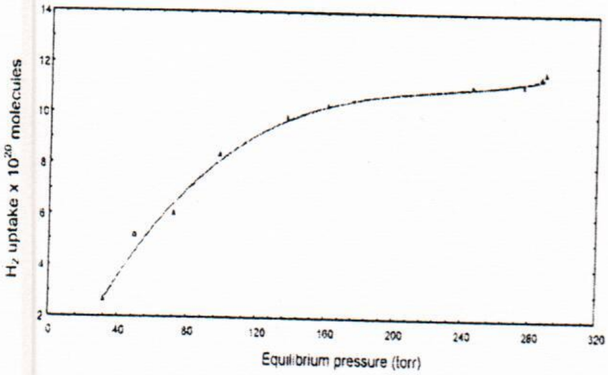

Fig. (7) Chemisorption isotherm of 0.55% Pt/alumina

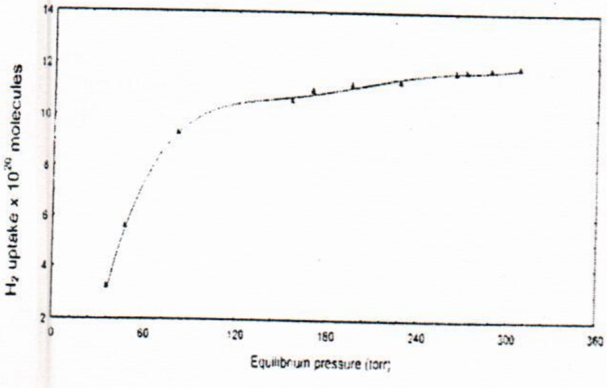

Fig. (8), Chemisorption isotherm of RG-402
(Pt.Al_2O_3, cylindrical)

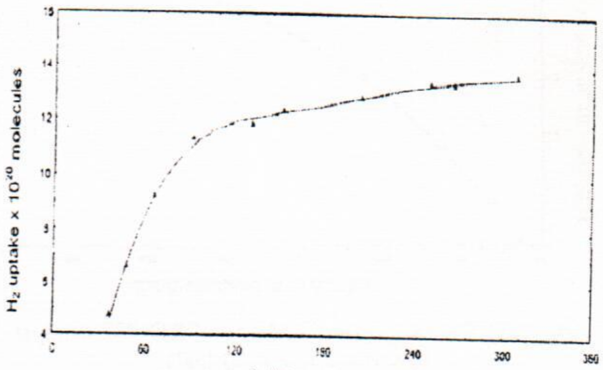

Fig. (9), Chemisorption isotherm of RG-422
(Pt-Ir/Al_2O_3, cylindrical)

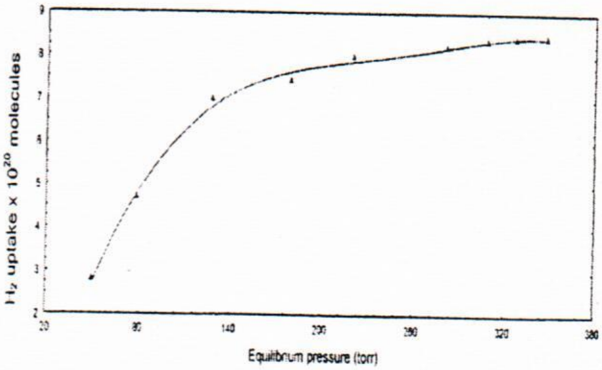

Fig. (10), Chemisorption isotherm of RG-451
(Pt-Ir-promoter/Al_2O_3, spheres)

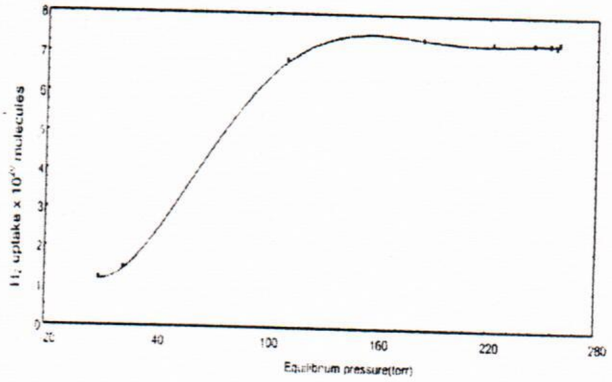

Fig. (11), Chemisorption isotherm of RG-432 catalyst
(Pt-Re/Al_2O_3, cylindrical)

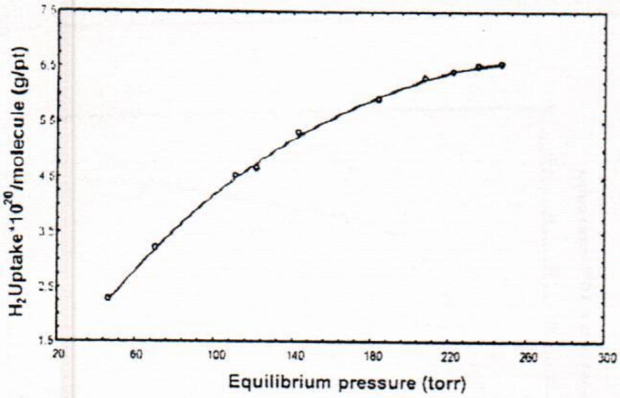

Fig. (12), Chemisorption isotherm of RG-482 catalyst
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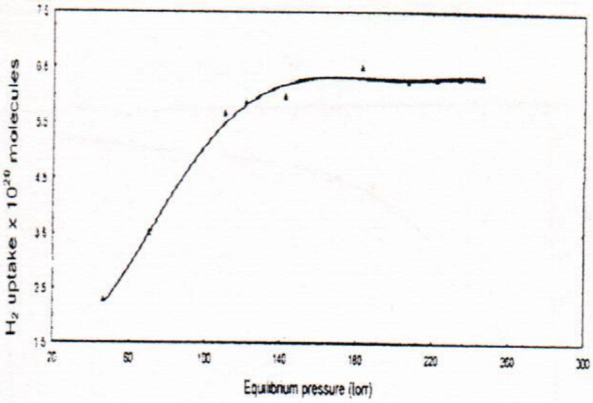

Fig. (13) Chemisorption isotherm of PS-10 catalyst
(Pt-Sn/Al_2O_3, spheres)