ADSORPTION STUDY OF HYDRODESULPHURIZATION CATALYST

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Abstract

Physical and chemical adsorption analyses were carried out by nitrogen gas using ASTM apparatus at 77 K and hydrogen gas using volumetric apparatus at room temperature respectively. These analyses were used for determination the effect of coke deposition and poisoning metal on surface area, pore size distribution and metal surface area of fresh and spent hydrodesulphurization catalyst $Co\text{-}Mo\backslash Al_2O_3$.

Samples of catalyst (fresh and spent) used in this study are taken from AL-Dura refinery.

The results of physical adsorption shows that surface area of spent catalyst reduced to third compare with fresh catalyst and these catalysts exhibit behavior of type four according to BET classification ,so, the pores of these samples are cylindrical, and the pores of fresh catalyst suffers during the hydrodesulphurization .

The result of chemical adsorption shows that the metal surface area of fresh catalyst is 50.72 m2/g while it reduced to 39.04 m^2/g for spent catalyst.

الخلاصة

تم اجراء تحاليل الامتزاز الفيزياوي والكيمياوي باستعمال غاز النتروجين وبواسطة جهاز ASTM وبدرجة حرارة 77 K، وباستعمال غاز الهيدروجين بواسطة منظومة حجمية للامتزاز وبدرجة حرارة الغرفة على التوالي، هذه التحاليل تستعمل لحساب تاثير المواد الكاربونية والسمية على المساحة السطحية وحجم التوزيع المسامي والمساحة السطحية للمعدن للعامل المساعد $Co\text{-}Mo\backslash Al_2O_3$ الطازج والمستهلك المستعمل في عملية إزالة الكبريت .

جميع نماذج العامل المساعد (الطازجة والمستهلكة) تم أخذها من مصفى الدورة .تبين النتائج المستحصلة لعملية الامتزاز الفيزياوي بان قيمة المساحة السطحية للعامل المساعد المستهلك قلت للثلث مقارنة بالعامل المساعد الطازج وإن هذه العوامل المساعدة أظهرت النمط الرابع وفقا لتصنيف BET لمتساويات درجة الحرارة للامتزاز، لذا فان مسامات هذه المواد هي من النوع الاسطواني.وقد عانى العامل المساعد الطازج نتيجة الاستخدام إلى فقدان الكثير من مساميته ومساحته السطحية بسبب عملية السلفرة الهيدروجينية .

أظهرت نتائج الامتزاز الكيمياوي إلى ان المساحة السطحية للمعدن الطازج 50.72 م^2/غم بينما تقل لتساوي 39.04 م^2/غم للعامل المساعد المستهلك .

Keywords

Physical Adsorption, Chemical Adsorption, Surface Area, Pore Size distribution, HDS catalyst

Introduction

Catalysts are use in a variety of applications from the production of consumer goods to the protection of the environment. Optimum design and efficient utilization of catalysts require a thorough understanding of the surface structure and surface chemistry of the active material. Gas adsorption is extensively used in characterizations of micro – and mesoporous materials and is often considered as a technique accurately determines the amount of gas adsorbed on a solid material, which is a direct measure for the porous properties and structure (Francoise Rouquerol, 1999).

Since the catalytic phenomena occur in the internal surface of the solid, lying with the pores, optimizing of pore size becomes important for the mass transfer and diffusion of the reactant to the active sites .The pores are not only the path for the reactants and products also influence the incorporation of active metals during preparation of catalysts and coke deposition during deactivation (Wiwel, 1991).

Morphological characteristics like surface area, pore volume, pore size distributions have to meet the specification for a longer catalyst life time. Chemical adsorption (chemisorption) analysis techniques provide much of the information necessary to evaluate catalyst materials in the design and production phases. Hydrogen plays a very important role in catalysis; in addition to its applications as reducing agent and as reactant, and it is extensively used as a probe molecule. Its selective chemisorption on noble metals allows it to be used as an ideal probe to perform metal surface area measurement and catalyst characterization. (P. Ferreira-Aparicio,1997)

Hydrodesulphurization is a heterogeneously catalyzed reaction. Supported metal sulfides have been found to be the best catalysts for the hydrodesulphurization reaction. Alumina-supported CoMo catalyst structures of both precursor and final catalysts have been extensively studied and the nature of active sites have been proposed (H.Topsoe, 1984). Both molybdenum and tungsten sulfides are active catalysts in the hydrodesulphurization reaction. Nowadays however, mainly molybdenum-based catalysts are used worldwide in the processes connected with sulfur removal. Different promoters have been tested and nickel and cobalt were found to give the highest enhancement of the activity towards desired products. Alumina support has a very important role in the activity and stability of the hydrodesulphurization catalyst as well and the γ-phase is the most suitable for the operation (Mohamadbeigy, 2005).

Co-Mo\Al_2O_3 is superior hydrodesulphurization catalyst whose structure and activity have been studied extensively (Beather,1960), Richardson found that its activity varies with the concentration of metals, and that a Co/Mo weight ratio of 1/5 apparently is optimum (Richardson $_a$,1964) .Cobalt and Molybdenum are two of the more common metals that are used in HDS catalyst. When these two metals are used together as a HDS catalyst is more tolerate to the poisoning agent and is usually classed as being suitable for wide variety of feedstocks.

Studies of increasing the dispersion of the active metal on support catalyst were studied by (R.Prins, 1989, B.Delmon, 1996).The physicochemical properties of alumina-supported CoMo catalysts were studied by (Ch.Papadopoulou, 2003). Various efforts have been made to increase the activities of conventional CoMo-based alumina catalysts. These include loading of the active metals in greater amounts, improving dispersion of the active metals, and manipulating the acidity level of the alumina support. The first two objectives have been achieved by increasing the surface area of the support and also by using better metal loading techniques. (Mignard, 1996), and well-defined pore structures mesoporous materials have attracted much attention as supports for CoMo based HDS catalysts.(Turaga,2003,Song,2003).The higher surface areas allow loading of higher levels of the active metals without affecting dispersion.

This work deals with the study of physisorption and chemisorption of fresh and spent CoMo/Al_2O_3 catalysts.

Experimental Work

1- Materials

1-1 Catalyst

A fresh and its spent CoMo/Al_2O_3 HDS catalyst supplied from AL-Dura refinery are used in this study. Properties of fresh and spent catalysts are listed in Table (1).

1-2 Gases

1-2-1 Nitrogen

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

1-2-2 Helium

Helium was supplied from AL-Mansour plant with purity 99.9 %.

1-3 Liquid Nitrogen

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

2- Physical adsorption by ASTM BET method

BET method covers the determination of nitrogen adsorption and desorption isotherms of catalysts and catalyst carriers at the boiling point of liquid nitrogen. A static volumetric measuring system is used to obtain sufficient equilibrium adsorption points on each branch of the isotherm to adequately define the adsorption and desorption branches of the isotherm, provides data for establishing the pore shape and pore size distribution of catalysts.

The apparatus of physisorption shown in fig.1 consist measuring device, vacuum pump, two gas supplies, sample container, manometer and liquid nitrogen coolant. (ASTM, D4222-83, 1986).

Prior to determination of adsorption isotherm, all physisorbed material was removed from the surface of the adsorbent. This is achieved by exposure of the surface to high vacuum with heating at 250 C° for 3 h.

Then dead space volume is determined by adding helium gas into the system, and recording the pressure (P_{H1}) and temperature (T_{H1}),then opening sample valve to admit helium to the sample, recoding the pressure (P_{H2}) and temperature (T_{H2}) at equilibrium. The vacuum valve was open to remove the helium gas and to obtain the desired value of vacuum pressure.

The adsorption isotherm was determined by adding nitrogen, step wise to the system, and recording the pressure $P_{1(1+n)}$ and the temperature $T_{1(1+n)}$, where n= 0,1,2,3..etc ,then valve of sample container was open for admitting nitrogen to the catalyst, and $P_{2\ (1+n)}$ and $T_{2\ (1+n)}$, were recording at equilibrium . For recording multipoint of adsorption isotherm repeating the steps above.

After reaching to the saturation adsorption when there is no change in pressure noticed, the desorption isotherm procedure was started, which is summarized in recording pressure and temperature after each evacuated interval.

Method of Calculation

Volume of nitrogen in the dead – space *Vds(i)* calculated by equation 1. (ASTM,D4222-83,1986)

$$Vds(i) = (Vs + P_2)\left[1 + \frac{0.05P_{2(i)}}{760}\right] \qquad (1)$$

Where ,V_S Volumetric factor of dead space and was calculated by equation 2.

$$Vs = 273.2\frac{Vd}{760}P_{H2}\left[\left(\frac{P_{H2}}{T_{H1}}+273.2\right)-\left(\frac{P_{H2}}{T_{H2}}+273.2\right)\right] \quad (2)$$

Where,

Vd= Volume of manifold (cm^3)

P_{H1} = Initial hydrogen pressure (torr)

T_{H1} = Temperature of manifold at initial helium pressure (K)

P_{H2} = Helium pressure at equilibrium (torr)

T_{H2} = Temperature of manifold after equilibrium (K)

The quantity of gas adsorbed was calculated by equation 3.

$$Vad(i) = \frac{[Vt(i) - V2(i) - Vds(i)]}{Ws} \quad (3)$$

Where, V1(*i*) volume of N_2 in manifold + volume valve open and calculated by equation 4.

$$V1(i) = (Vd + Vx)\left[\frac{P_{1(1+n)}}{T_{1(1+n)}} \times \frac{273.2}{760}\right] \quad (4)$$

V2(*i*) =Volume of N_2 in manifold + volume of valve calculated by equation 5.

$$V2(i) = (Vd + Vx)\left[\frac{P_{2(1+n)}}{T_{2(1+n)}} \times \frac{273.2}{760}\right] \quad (5)$$

Where,

Vx = Volume of extra volume bulb (cm^3)

$P_{1(1+n)}$ = Initial N_2 pressure (torr)

$P_{2(1+n)}$ = pressure after equilibrium (torr)

$T_{1(1+n)}$ = Manifold temperature of initial N_2 pressure (K)

$T_{2(1+n)}$ = Manifold temperature after equilibrium (K)

Total inventory of nitrogen Vt(*i*) in the system calculated by equation 6 :

$$Vt(i) = Vt(i-1) + V1(i) - V2(i-1) \quad (6)$$

Where ; Vt $_{(0)}$ =0

Surface area by the BET plot was calculated by equation 7.

$$S_{BET}(m^2/g) = \frac{V_M \times N \times N_S}{22414 \times 10^{18} nm^2 \ / \ m^2} \quad (7)$$

Where, V_M Volume of adsorbate required to complete one statistical monolayer (cm^3/g), I intercept, and S, slop were calculated using equations 8, 9, 10, respectively (Richardson$_b$,1989).

$$V_M = \frac{1}{S + I} \quad (8)$$

$$I = \frac{1}{V_M C} \quad (9)$$

$$S = \frac{C - 1}{V_M C} \quad (10)$$

N= Avogadro's number (molecule/mole)

N_s= surface area of gas molecule (for N_2=0.168).

C = Constant, indicator of adsorbate – surface interaction.

Heat of adsorption (E_1-E_2) by nitrogen gas determined from equation 11 (S.Brunauer, 1938)

$$E_1 - E_2 = RT \ln C \quad (11)$$

Where,

E_1 = average heat of adsorption in monolayer (J/gmol).

E_2 = heat of condensation (J/gmol).

R= gas constant.

T= temperature of experiment (77 K).

Pore Size Distributions

Pore radius r_p obtained from equation12.

$$r_p = r_k + t \qquad (12)$$

Where r_k Kelvin radius was calculated by Kelvin equation 13, assuming zero wetting anglesθ. (K.S.W.Sing,1976).

$$\ln\left[\frac{P}{P^0}\right] = \frac{-2\gamma\overline{V}}{r_k RT} COS\,\theta \qquad (13)$$

P = equilibrium vapor pressure of liquid (torr)

P^0 = equilibrium pressure of the same liquid exhibiting a plane surface (torr)

γ =surface tension (N / m^2)

$\overline{V}$ = Molar volume (mol/ m^3)

θ = contact angle with which the liquid meets the pore wall

The film depth t (A^0) calculated from the Halsey equation 14(Lowell.S,1984):

$$t = \left[\frac{13.99}{0.03\,\gamma - \log\left(\frac{P}{P^0}\right)}\right]^{\frac{1}{2}} \qquad (14)$$

The actual pore volume V_p evaluated by recalling the volume evaporated out of the center cores plus the volume desorbed from the film on the pore walls was calculated by equation 15.

$$\Delta V_p = \left(\frac{\overline{r}_p}{\overline{r}_k}\right)^2 \left[\Delta V_K\right] \qquad (15)$$

Where, $\overline{r}_p$ and $\overline{r}_k$ are the mean two incremental values of r_p and r_k respectively.

ΔV_K ,the amount of the decrease in gas condensate in the pores calculated by equation 16.

$$\Delta V_k = \Delta V_{gas} - \Delta V_{liq} \qquad (16)$$

Where, ΔV_{gas} difference in interval gas adsorbed and ΔV_{liq}, Volume of liquid determined by equation 17 (Lowell,1984).

$$\Delta V_{liq} = 0.064 \times \Delta t \sum \Delta S_P \qquad (17)$$

Where, ΔS_P surface area of the pore walls calculated from the pore volume by equation 18. (K.S.Sing,1982).

$$\Delta S_P = 31.2 \frac{\Delta V_P}{\overline{r}_p} \qquad (18)$$

The total specific surface of catalyst calculated by equation 19.

$$S_{tot.} = S_{BET} + \sum \Delta S_P \qquad (19)$$

The percentage of the internal $S_{int.}$ and external $S_{ext.}$ surfaces calculated by equations 20 and 21 respectively.

$$\%S_{int.} = \frac{\sum \Delta S_P}{S_{tot}} \times 100 \qquad (20)$$

$$\%S_{ext.} = \frac{S_{BET}}{S_{tot.}} \times 100 \qquad (21)$$

Specific pore size V_P calculated from equation 22.

$$V_p = 0.00156 \times \sum \Delta V_p \qquad (22)$$

3-Chemisorptions by Volumetric Apparatus

Volumetric chemical adsorption was done in volumetric apparatus using hydrogen gas at room temperature on fresh and spent Co-Mo\Al_2O_3 catalysts .

The numbers of cobalt atoms exposed on the catalyst surface were evaluated by measuring the hydrogen adsorption at room temperature according to a procedure and method of calculation described in the literature (abdul-Halim 2002).

The amount of adsorbed H_2 covering the catalyst surface with monomolecular layer was obtained by extrapolating to zero the curve relating the amount of H_2 adsorbed to the adsorption equilibrium pressure of H_2.

Metal area was calculated by equation 23.

$$A=\frac{NmXm}{M} \qquad (23)$$

Where , Nm is the monolayer coverage at zero pressure expressed in surface atoms per gm metal determined by back extrapolation to zero pressure, M is the number of metal atoms per unit area of crystalline surface and Xm is the chemisorptions stoichiometry which is to be taken one (Geus.j.W,1971) .

The percentage metal dispersion D is defined as the ratio of the number of the surface atoms to the total number of metal atoms present in the sample.

Percentage metal dispersion can be calculated from the catalyst composition and the metal surface area by equation 24 .

$$D = \frac{AW}{NaX} \qquad (24)$$

Where ,W is the molecular weight of metal, N is Avogadro's number, a is the area per surface metal atom, X is the mass fraction of a metal.

Results and Discussion

Physisorption

1- Surface area

BET plots (P/P^0 Vs $P[V(P^0 - P)]$) are shown in Figures 2 and 3 for fresh and spent Co-Mo\$Al_2O_3$ catalysts, respectively. These plots used to calculate the volume of gas adsorbed at monolayer coverage. The results of surface area values for fresh and spent Co-Mo\$Al_2O_3$ catalyst show a decrease in the surface area of spent catalyst. This may be due to blockage a lot of pores or deformity of crystalline surface due to high temperature leads coke deposition and thermal deactivation caused by long time work at relatively high temperature of HDS process (J.Kiurski,1998) . These results well agreed with those obtained by Jim Linder (Jim Linder et al,1992).

The higher value of E_1-E2 for fresh catalyst compared with spent catalyst (Table 2) means that some fraction of surface is unoccupied in spent catalyst and the energy of the adsorption process on a surface located in a narrow pore would be different from that in a wide pore. The sizes of the pore can influenced both the poisoning characteristics of the surface of fresh and spent catalysts (S.H.AL-Khowaiter,1996). High value of E_1-E_2 in fresh catalyst also means higher affinity between nitrogen gas and catalyst surface (L.F.Jones,1977).

2. Pore Size Distribution

Tables 3 and 4 show the pore size distribution calculations of fresh and spent catalysts, respectively. The values of internal surface area in two samples occupied more than 50 % from the total surface area, and the reduction occur in both internal and external surface area of the spent catalyst .This means that a reduction in pore sites is occur and this lead to a reduction in the activity of catalysts and this is may be due to carbon deposition or blocking some pores leading into catalyst activity reduction.

Figures 4 and 5 show pore size distribution of fresh and spent catalyst, respectively. The adsorption curves exhibits behavior type four according to BET classification, so the pores of these samples are cylindrical.

Chemisorptions

Table 5 shows the results of monolayer coverage, metal area and dispersion of fresh and spent catalysts. It was noticed that metal surface area of spent catalyst reduced compared with fresh which indicates that the amount of hydrogen adsorbed on fresh catalyst is higher than that for spent catalyst. Lower percentage of dispersion for spent catalyst compared with fresh may be due to damage some of metal atom which play as active metal in catalyst (Satterfield,C.N,1969) .This is well agreed with the earlier study of Anderson and Dehghani (Anderson et al, 1949; A.Dehghani, 2009).The high temperature in reactor up to 673k may be the cause of poisoning some of the active sites of catalyst, so, the activity of catalyst decreased. Also the sintering and chemical deposition materials during operation leads to deactivation of spent HDS catalyst (S.Kressmann,1998).This results well agreed with those obtained by Mikhail (Mikhail,R,1973).

Figures 6 and 7 show hydrogen chemisorption isotherms of fresh and spent catalysts, respectively. The values of monolayer coverage obtained in the chemisorption curves show that the the amount of hydrogen chemisorbed in the smaller pore grows rapidly, and then becomes slower until reaching monolayer coverage.

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Table 1 Properties of Fresh and Spent $CoMo/Al_2O_3$ catalysts

Fresh $CoMo/Al_2O_3$ catalyst		**Spent $CoMo/Al_2O_3$ catalyst**	
Mo , wt%	12	Mo , wt%	12.6
CoO , wt%	4	CoO , wt%	5.2
NiO , wt%	0.06	NiO, wt%	0.13
Fe , wt%	0.03	Fe, wt %	0.06
SO_4 , wt%	1.5		
Al_2O_3	Balance		
Form	Extrudate		
Normal Size ,mm	2.5		
Surface Area , m^2/g	280		
Pore Size , Cm^3/g	0.55		
Porosity %	0.67	Porosity %	0.38

Table 2 Monolayer Capacity, Surface Area and heat of adsorption

Catalyst	V_m Cm^3/g	S_{BET} m^2/g	$E_1 - E_2$ J/gmol
Fresh Co-Mo\\Al_2O_3	62.88	273.76	2878.898
Spent Co-Mo\\Al_2O_3	28.169	122.625	878.766

Table 3 Pore Size Distribution of Fresh Catalyst

P/P^0	V_{gas}	r_k	t	r_p	$\bar{r}_p$	$\bar{r}_K$	Δt	ΔV_{gas}	ΔV_{liq}	ΔV_k	ΔV_p	ΔS_p	$\Sigma\Delta S_p$
0.964	300.8	259.3	18.2	277.5	237.6	220.4	2.1	1.1	0.0	1.1	1.3	0.2	0.2
0.949	299.7	181.6	16.1	197.7	178.1	162.6	1.2	0.3	0.0	0.3	0.3	0.1	0.3
0.936	299.4	143.7	14.9	158.6	123.1	109.7	2.9	5.5	0.1	5.4	6.7	1.7	2.0
0.828	293.9	75.7	12.0	87.7	74.6	62.8	0.4	3.4	0.1	3.3	4.6	1.9	3.9
o.827	290.5	50.7	11.6	61.6	53.9	43.3	2.1	5.3	0.5	4.8	7.4	4.3	8.2
0.772	285.2	36.7	9.5	46.2	41.7	23.6	0.8	10.7	0.4	10.3	16.8	12.5	20.7
0.717	274.5	28.5	8.7	37.2	34.1	52.7	0.6	29.6	0.8	28.8	50.7	46.4	67.1
0.661	244.9	22.9	8.1	31.0	28.8	20.9	0.5	59.5	2.1	57.4	108.9	117.9	185.0
0.607	185.4	19.0	7.6	26.6	24.8	17.4	0.5	41.5	5.9	35.6	72.3	90.9	275.9
0.550	143.9	15.9	7.1	23.0	21.6	14.7	0.3	21.5	5.3	16.2	37.9	50.4	326.3
0.496	122.4	13.5	6.8	20.3	19.1	12.5	0.3	13.6	6.3	7.3	17.0	27.7	354.0
0.439	108.8	11.5	6.5	18.0									

$\Sigma(\Delta S_P)=354.0\ m^2/g$,$S_{total}=273.76+354.0=627.76\ m^2/g$,$S_{ext.}$ %=43.7 ,$S_{int.}$ %=56.3 ,$V_p=0.5$ Cm^2/g

Table 4 Pore Size Distribution of Spent Catalyst

P/P^0	V_{gas}	r_k	t	r_p	$\bar{r}_p$	$\bar{r}_K$	Δt	ΔV_{gas}	ΔV_{liq}	ΔV_k	ΔV_p	ΔS_p	$\Sigma\Delta S_p$
0.964	260.2	259.3	18.2	277.5	245.8	228.4	1.6	0.6	0.0	0.6	0.7	0.1	0.1
0.953	259.6	197.5	16.6	214.1	187.6	171.8	1.6	0.3	0.0	0.3	0.4	0.1	0.2
0.937	259.3	146.1	15.0	161.1	124.8	111.2	2.9	5.2	0.0	5.2	6.5	1.6	1.8
0.883	254.1	76.4	12.1	88.5	74.6	63.3	1.6	11.6	0.2	11.4	15.8	6.6	8.4
0.828	242.5	50.3	10.5	60.8	53.4	43.5	1.1	32.9	0.6	32.3	48.7	28.4	36.8
0.772	209.6	36.7	9.4	46.1	41.7	32.7	0.7	58.3	1.6	56.7	92.2	68.9	105.7
0.718	151.3	28.7	8.7	37.4	34.3	25.9	0.6	40.1	4.1	36.0	63.1	57.4	163.1
0.663	111.2	23.1	8.1	31.2	28.9	21.1	0.5	21.4	5.2	16.2	30.4	32.8	195.9
0.608	89.8	19.1	7.6	26.7	24.9	17.5	0.4	9.9	5.0	4.9	9.9	12.4	208.3
0.552	79.9	16.0	7.2	23.2									

$\Sigma(\Delta S_P)=208.3\ m^2/g$,$S_{total}=122.625+208.3=330.925\ m^2/g$,$S_{ext.}$ %=44.9 ,$S_{int.}$ %=55.1 ,$V_p=0.417$ Cm^2/g

Table 5 Results of chemisorption calculations

Catalyst	N_S (Monolayer Coverage of Monolayer H_2)	Area m^2/g	Dispersion %
fresh Co-Mo\\Al_2O_3	6.34×10^{20}	50.72	88.76
spent Co-Mo\\Al_2O_3	4.88×10^{20}	39.04	57.13

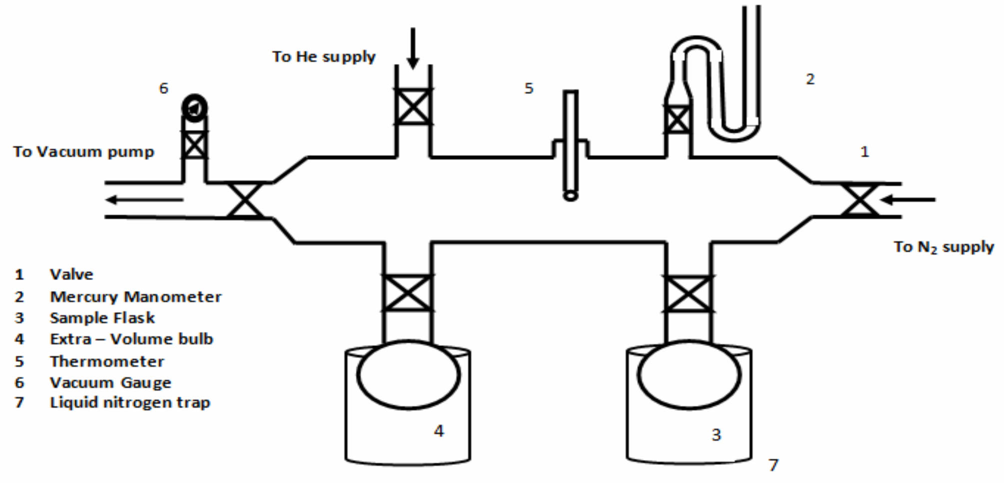

Fig. 1 ASTM apparatus of adsorption measurements

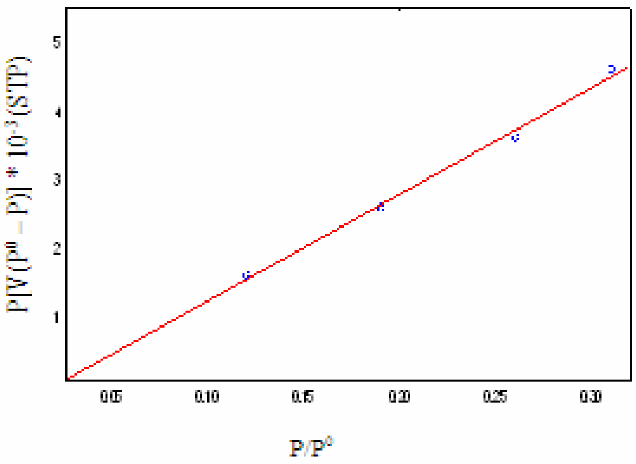

Fig.2 BET plot of adsorption data of Fresh Co-Mo\Al$_2$O$_3$ catalyst

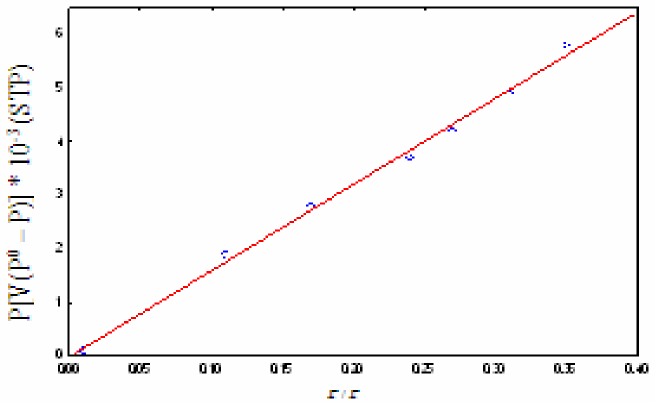

Fig.3 BET plot of adsorption data of Spent Co-Mo\Al$_2$O$_3$ catalyst

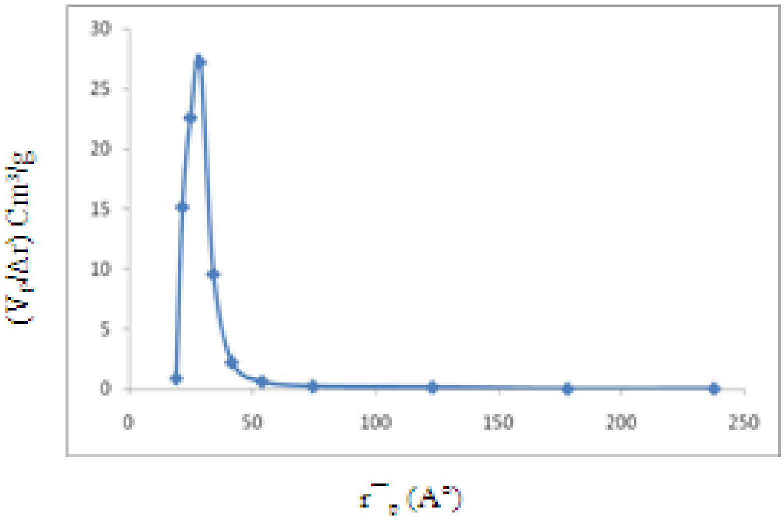

Fig. 4 Pore Size distribution of Fresh Co-Mo\Al2O3 catalyst

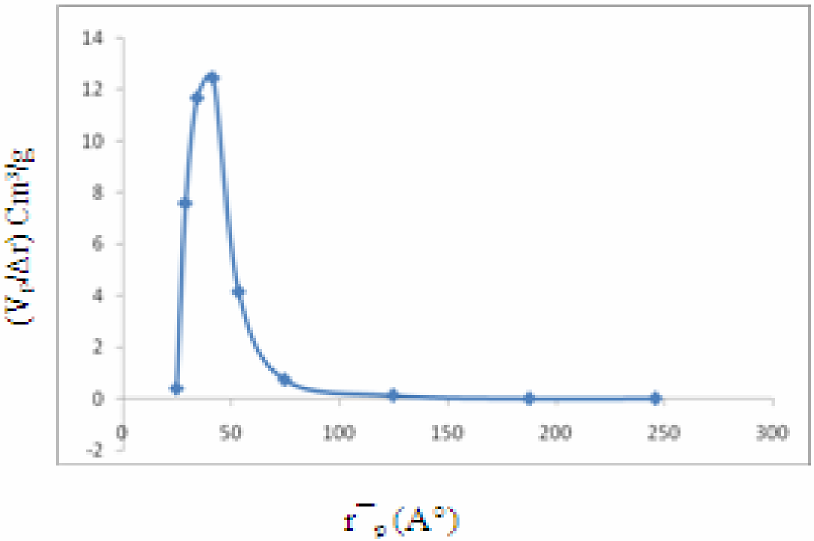

Fig. 5 Pore Size distribution of Spent Co-Mo\Al2O3 catalyst

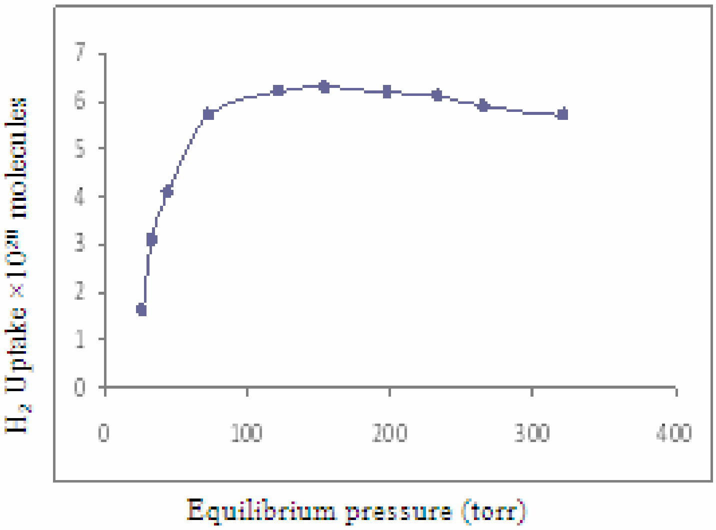

Fig.6 Chemisorption isotherm of Fresh Co-Mo\Al_2O_3

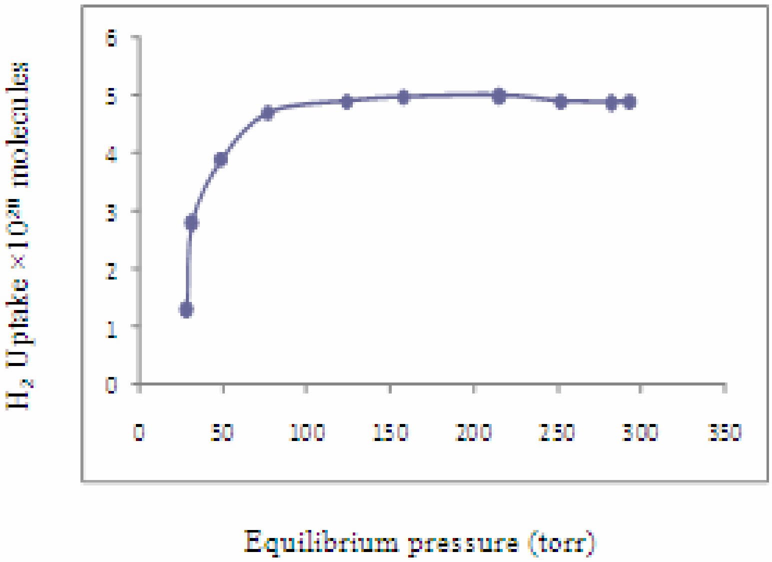

Fig.7 Chemisorption isotherm of Spent Co-Mo\Al_2O_3