Characterization of Metal Exchanged Zeolite-A using Quantasorb and Mercury Porosimeter

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Abstract

In this study, surface area and pore structure studies were carried out for cobalt, nickel, and copper-II-exchanged zeolite with the help of Quantasorb and Mercury Porosimeter techniques respectively. Values of surface area, micropore volume and characteristic energy for adsorbate-adsorbent system were calculated by using BET and D-R equations respectively. It was observed that surface area of metal-exchanged zeolite increases after outgassing at 300ºC and decreases at high levels of metal concentration due to partial collapse of the structure at the temperature of dehydration in vacuum. It was evident from the data of mercury porosimetery that micropore volume increases as metal concentration increases. Results showed that metal exchanged zeolites have good adsorption properties than parent zeolite-4A. Therefore, transition metals after exchange create a new surface with different thermodynamics and kinetics.

Keywords: Characterization, Metal Exchanged Zeolite-A, Quantasorb, Mercury Porosimeter

Introduction

Transition metal ion exchanged zeolites can be used as catalysts for a variety of chemical reactions, including dehydrogenation, oxidation, isomerization, and cracking of various organic feed stocks. The porous structure of the zeolites makes it possible to use them for the adsorption of gases and vapors at suitable temperatures if the dimensions of the channel and cavities are suitable. Owing to the rigid structure and the ease, with which the channels dimensions may be changed by varying the ionic form of the zeolite. Their specificity towards gaseous adsorption may be varied almost at will [1-3]. Adsorption studies of N_2 on pure zeolite-A were carried out by other workers [4-6]. But in this paper, N_2 adsorption is studied on metal exchanged (Co, Ni, and Cu) zeolite-A. Mercury porosimetry is a technique, which was originally developed to enable pore sizes to be determined in the macro pore range where the gas adsorption method breaks down for practical reasons [7]. A

well known method of determining the pore size distribution is the analysis of gas adsorption isotherms in the range where capillary condensation accompanies physical adsorption. The method originated by Barrett *et al.*[8] covered a limited range of pore radii from 15Å up to about 200 Å, so that for the study of the distribution above this upper limit other methods had to be found. Washburn and co-worker [9,10] were the first who suggested the utilization of the phenomenon of capillary depression for this purpose. In this method, an adsorbent is immersed into a non-wetting liquid and the liquid is penetrated into its pores by the action of external pressure.

Ritter and Drake [11] were first who put Washburn's concept to the practical use, using mercury as a penetrating liquid at pressure up to 1000 atm. They developed one of the earliest high-pressure porosimeters and measured the contact

angle between mercury and a variety of materials. They found that the angle of contact line lie between 135° to 142° with an average of 140° (which is close to the value for a wide range of materials) [12]. The present work was aimed to study the surface area and pore structure of cobalt, nickel, and copper-II-exchanged zeolite with the help of Quantasorb and Mercury Porosimeter techniques respectively.

Experimental

Zeolite-4A was supplied by Merck. It was ground by agate mortar and passed through U.S. standard sieve series no. 140 having an opening of 105 μm. Metal-II-chlorides used were supplied by Merck with the purity better than 99%.

Metal exchanged samples were prepared by magnetically stirring a predetermined amount of metal chloride and zeolite-4A in 100 ml distilled water at different temperatures and time intervals. Amount of metal exchange was determined by EDTA microtitration method. The metal exchanged zeolite samples are designated by the formula $M_x X$. Where M stands for Co, Ni, and Cu, x is the number of metal ions per unit cell and X is the residue. The exact number of water molecules was detected by using Shimadzu Thermal Analyzer.

The Quantasorb sorption system was used to determine the surface area and pore size distribution of zeolite samples by employing the technique of adsorbing an adsorbate gas from a flowing mixture of adsorbate and an inert non-absorbable carrier gas. The process of adsorption and desorption are monitored by measuring the change in the thermal conductivity of the gas mixture. An adsorbate to carrier gas ratio is established to give the required concentration and the recorder base line is adjusted to zero. Prior to the nitrogen adsorption, all the physisorbed species were removed from the surface of the sample by heating at 100°C and 300°C under a vacuum of 10^{-5} mbar respectively. Adsorption is started by immersing the sample cell containing a known amount of the sample in a liquid nitrogen coolant. The adsorption peak is produced by the change in the thermal conductivity of the gas mixture resulting from a decrease in adsorbate concentration due to adsorption on the sample surface. Adsorption

was completed when there was no longer any difference in the thermal conductivities of gas entering and leaving the sample cell. In this manner, the entire adsorption isotherms were obtained for a series of nitrogen concentration up to 99% adsorbate.

Before measurement, zeolite samples were dehydrated by keeping at 110°C overnight in an oven. A quantity 0.1-0.3g of dried sample was used for porosity measurement. The instrument used was Mercury Porosimeter, Autopore II 9220 from Micromeritics. Mercury surface tension 485 dynes/cm and contact angle 130° were used.

All the data was corrected for compression of mercury by taking 'blank' measurements with mercury.

Calculations and Results

Adsorption isotherms for zeolite-4A and Cobalt exchanged zeolite-A are given in Figs. (1-2). For surface area determination of zeolite samples, the value of V_m was calculated by using BET equation

$$P/V (P_o-P) = 1/V_m C + (C-1) P/V_m CP_o \qquad (1)$$

Where V is the amount adsorbed at relative pressures P/P_o and V_m is the monolayer capacity. The BET equation gives a linear relationship between $P/V (P_o-P)$ and P/P_o and the range of linearity is usually restricted to a limited part of the isotherm. The straight line obtained yields a slope $(C-1)/V_m C$ and an intercept $1/V_m C$, from which the monolayer capacity (V_m) and the value of constant C was determined. BET plots for zeolite-4A and Co-exchanged zeolite-A are given in Figs.(3-5). From the value of monolayer capacity, the surface area was calculated from the known molecular cross section of the nitrogen molecule (16.2 Å at 77K) which is generally considered to be the most suitable adsorbate for surface area measurement.

The surface area is calculated by using the following equation [7]

$$S = 0.269 A_m V_m \qquad (2)$$

where A_m is the area in square Angstroms which is occupied by one adsorbed molecule in the

monolayer (for nitrogen 16.2 $\overset{\acute{}}{A}$) and V_m is volume occupied by the molecules to form monolayer. Values of surface area are given in Tables (1-2).

A new way of treating the N_2 adsorption isotherm is developed which yields a more reliable estimation of the microporous volume and external surface of zeolites. This method is based on the assumption that the experimental adsorption isotherm results from two processes i.e., the adsorption on the external surface and to the adsorption in the micropores respectively, the former being governed by the BET equation [13] and the latter by the Dubinin-Radushkevich equation [14]. The correlation coefficient of the BET curve obtained from the experimental isotherms corrected for the adsorption in the micropores is optimized by adjusting the limiting adsorption volume and the adsorption energy of the DR-equation.

$$V = V_o \exp \{-B (RT/b)^2 \log^2 (P_o/P)\} \qquad (3)$$

where V represents the volume of adsorbate present in micropores at temperature T and at relative pressure P/P_o and V_o is the total volume of the micropores. B and b are specific constants depending respectively on the nature of the solid and the adsorbate [15].

In order to obtain the Dubinin-Radushkevich plot, eq (3) transformed into its logarithmic form as :

$$\text{Log } V = \text{Log } V_o - \{(RT/E)^2 \log^2 (P_o/P)\} \qquad (4)$$

DR-plots of zeolites samples are given in Figs. (6-8). By plotting $\log^2 (P/P_o)$ vs. Log V, we obtained value of V_o from intercept and E from slope. Where E, the characteristic energy for the given adsorbate-adsorbent system, is equal to b^2/B. Values of micropore volume and characteristic energy are given in Tables (1-2)

Discussion

The shape of the nitrogen adsorption isotherms of zeolite samples as shown in Fig. (1-2) is of type (I). The plateau represents complete filling of empty cavities and channels. Barrer [16] defined the term "surface area" when the area is

measured by filling the cavities by molecules. According to him, it is the estimate of the area, which would be covered by the number of guest molecules, which completely fill the intracrystalline pores of these molecules removed and placed in a close-packed monolayer upon an ideally smooth plane surface. This area has been termed the monolayer equivalent area. Such behaviour is characteristic of adsorption in narrow micropores followed by monolayer adsorption and interparticle capillary condensation [17]. The apparent surface areas of zeolite samples were determined by applying the BET equation to the physical adsorption data of nitrogen at 77K. The most convenient forms of the BET equation for the application to experimental data are given below.
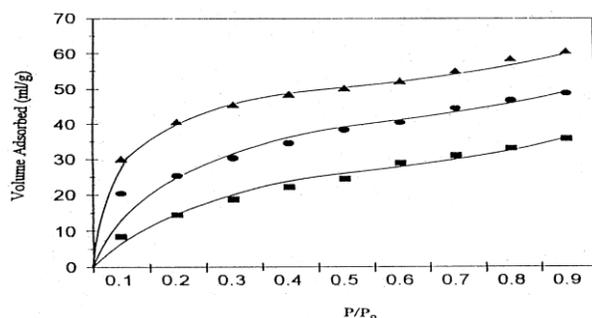

Figure 1. Nitrogen adsorption isotherms at 77K on NaA-zeolite (■); $Co_{3.73}A$ (●) and $Co_{5.27}A$ (▲) (after Out gassing at 100°C)
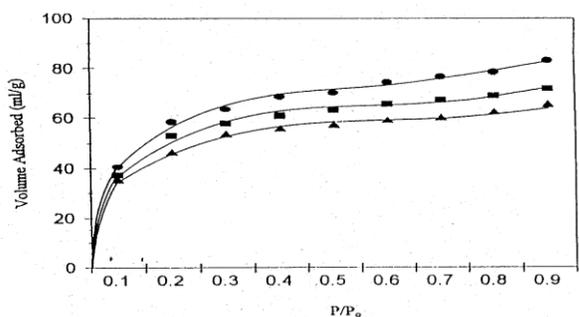

Fig. 2: Nitrogen adsorption isotherms at 77K on NaA-zeolite(▲); $Co3.73A$(■) and $Co5.27A$(●) (after Out gassing at 300°C)

The BET plots for zeolite-4A and Co-exchanged zeolites are given in Figs.(3-5) respectively which indicate that experimental points deviate from linearity with the increase in the relative pressure. This deviation from linearity is apparent at the relative pressure greater than 0.3, in other words BET equation breaks down for the less active points on the surface. It was shown by Brunauer *et al.* [13] that for P/P_o values greater than

0.3 the experimental points do not fall on the linear plots. It has been indicated by Herman and Emmett [18] that the BET equation is in good agreement with reasonable values in the range of relative pressures equals to 0.05 to 0.35. They concluded that in this range of relative pressure monolayer is formed and BET C values usually give heats of adsorption that are quite reasonable. Thus, for the majority of isotherms the range of relative pressures between 0.05 and 0.35, the linear BET range, apparently represents a condition in which the very high energy sites have been occupied and extensive multilayer adsorption has not yet commenced. It is within these limits that the BET theory is generally valid and the deviation from this range of linearity reflects unusual surface properties which is quite difficult to ascertain. In microporous substances, narrow pores exhibit high energy potentials due to overlapping potential from the walls of the micropores. Further, Hyness [19] investigated the measurement of surface areas by using krypton. He showed that BET equation contains several deficiencies, one of these relating to the value to be chosen for P_o. According to him, the value of P_o used influences the slope (and linearity) of a BET plot and hence affects both the values of V_m and the ease with which it is obtained. Lee and Basmadjian [20] investigated the adsorption isotherms of krypton in molecular sieve 4A and 5A. They showed that the adsorption isotherms of many conventional methods do not apply to zeolites. This behaviour appears to arise mainly from the small size of zeolitic adsorption cavities, the unique pore size distribution and the specific ionic properties of the zeolites. They further report that surface and layer adsorption (Langmuir and BET type) become meaningless when dealing with adsorption in "micropores". The adsorption field in this case extends over the entire pore space, and adsorption depends on the filling of the pore volume of the adsorbate. Breck [21] showed that the classical BET equation cannot be applied to zeolites. For zeolites it reduces to the Langmuir equation. According to Remy and Eberly [22,23] the presence of molecules blocking the pores of a zeolite or the partial destruction of its structure may drastically lower its activity by diminishing the microporous volume accessible to the reactants.

Values of surface areas obtained by the BET method for zeolite samples are given in Table

(1-2). From table (1), it is evident that the BET surface area of metal exchanged zeolite samples (outgassed at 100°C) decreases with an increasing amount of the metal, while Table 2 shows that metal exchanged zeolite samples (outgassed at 300°C) have greater surface area than parent zeolite. This may be due to water molecules, for transition metal ions are more hydrated as compared to sodium ion, as metal exchanged concentration increases number of water molecules also increase which is confirmed by thermal analysis technique.
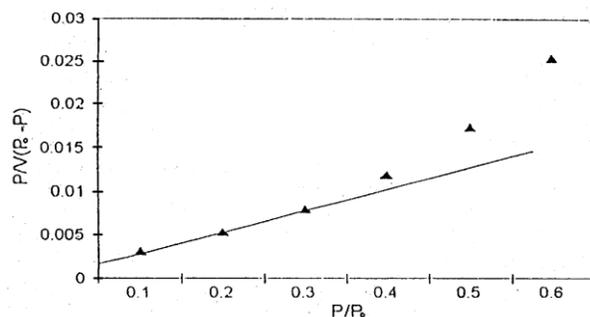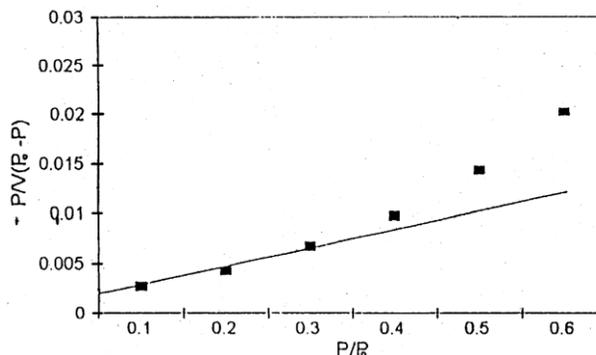

Figure 3. BET plot for NaA-zeolite
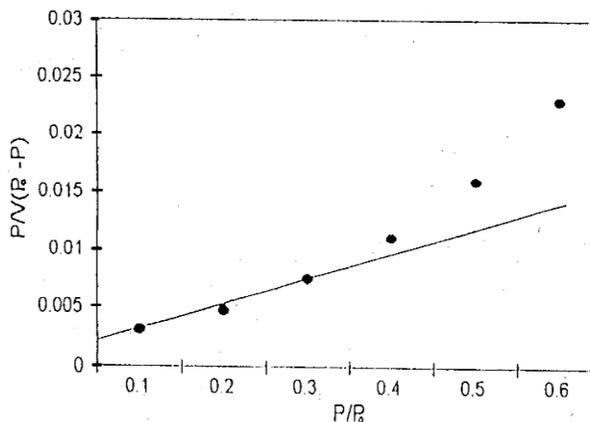

Figure 4. BET plot for Co$_{3.73}$A

Figure 5. BET plot for Co$_{5.27}$A

So as samples were out gassed for more time and at high temperature more space will be available for adsorbate molecule. As ionic radii of Na ion is greater than transition metal ions, so more space is vacant in zeolite cavities. Another reason may be that by increasing metal divalent cations, the number of free 8-rings increases. Therefore, adsorption of nitrogen increases with increasing the number of divalent metal ions per unit cell of NaA-zeolite. The pore opening of NaA-zeolite is 3.6-4.0 Å, depending on temperature. While in case of $Co_{5.27}A$, again surface area decreases, the most likely reason for this is the partial collapse of the structure at the temperature of dehydration in vacuum. The partial collapse of the structure for highly Co (II) exchanged zeolite-Barrer and Meier [24] have already showed A in an X-ray diffraction investigation. The results of surface areas of cobalt (II) exchanged A-zeolite in general confirmed their structural integrity after high temperature dehydration in vacuum. The low temperature adsorption of nitrogen also proved that cations prefer to be located in the 6-rings of dehydrated type A-zeolite. If there were more than 8 cations per unit cell, then those in excess of 8 would lodge in the 8-rings and partially block them. According to Yongan [25] the kinetic diameter of nitrogen is 3.6 Å. Thus the kinetic diameter of nitrogen is same as that of partially blocked 8-ring which is 3.6 Å at 77K. This is sufficient to prevent nitrogen from diffusion to the large, α-cavity through the 8-ring, at 77K. So surface area mostly depends on temperature and time of outgassing. The water molecules, which cannot move in the pores at 77K, impede the flow of nitrogen within the crystal lattice. The adsorption of nitrogen at 77K has occurred only in the α–cavities of zeolite, since opening into the β-cavities are too small to allow nitrogen molecules to pass through. The adsorption into β-cages is therefore omitted.

The values of total micropore volume and characteristic energies are given in Tables (1-2). From Table (1), one can see that the values decrease as metal concentration increases, because small amounts of water reduce the adsorption of nitrogen on metal exchanged zeolite. Energy values also decrease as metal concentration increases, because more active sites available

reduce as metal concentration increases. Initially more empty spaces are available inside the zeolite cavities and the tendency to enter in the cavities of these sorptive molecules are high and then decreases because the active sites of increasing activity occupied by metal cations. When samples were out gassed at high temperature for more time, the micropore volume and surface energy values increase for metal exchanged samples, because water molecules as well as other gases are removed, so more active sites are produced. Figure 6 shows the DR plots of nitrogen adsorption on zeolite-4A and metal exchanged zeolite. The DR plots for zeolite-4A and metal exchanged zeolites exhibit the long straight line and apparent upward deviation at higher relative pressure. This deviation from linearity shows that all samples have heterogeneous system of micropores [26]. The uncertainty in the extrapolation of straight line to $Log^2 (P_o/P) = 0$ to obtain V_o is very high for these zeolite samples. As shown in DR plots that at least two different values of V_o may be obtained. In fact, if experimental points at higher relative pressures were selected in the DR plots, the intercept would give larger values than those actually calculated from the straight line at lower relative pressure values. In the present work, the experimental points at relatively lower pressures are selected to obtain the V_o values.
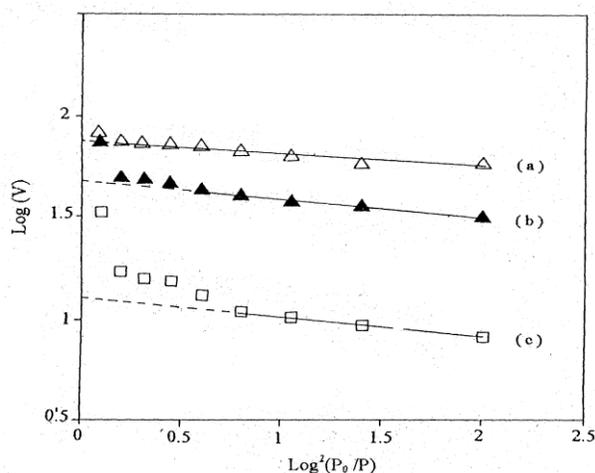

Figure 6. DR plots of nitrogen adsorption at 77K on (a) NaA (b) $Co_{3.73}A$ (c)$Co_{5.27}A$

**Table 1. Nitrogen Adsorption data for NaA-zeolite and metal exchanged zeolite (after outgassing at 100 ºC)**

System	Specific Surface Area	Specific Surface Area	Total Micro pore Volume	Activation Energy
	Single Point Method (m^2/g)	*BET Method* (m^2/g)	(cm^3/g)	(Joules mol^{-1})
NaA	38.61	115.05	5.96	2528
$Co_{3.73}A$	30.78	093.68	5.50	1954
$Co_{5.27}A$	27.33	063.98	4.83	1364
$Ni_{2.54}A$	29.67	076.63	5.17	2289
$Ni_{3.61}A$	29.63	046.76	4.65	1452
$Cu_{3.64}A$	28.45	030.85	3.71	1684
$Cu_{5.0}A$	25.99	027.85	3.28	1387

Table 2. Nitrogen Adsorption data for NaA-zeolite and metal exchanged zeolite (after outgassing at 300 ºC)

System	Specific Surface Area	Specific Surface Area	Total Micro pore Volume	Activation Energy
	Single Point Method (m^2/g)	*BET Method* (m^2/g)	(cm^3/g)	(Joules mol^{-1})
NaA	43.56	129.21	6.06	2624
$Co_{3.73}A$	98.64	185.82	6.94	2798
$Co_{5.27}A$	75.71	164.52	6.54	2362
$Ni_{2.54}A$	91.47	185.82	6.46	2887
$Ni_{3.61}A$	45.56	145.55	6.23	2807
$Cu_{3.64}A$	45.43	151.47	6.36	2702
$Cu_{5.0}A$	43.35	144.85	6.28	2544

In mercury porosimetry the volume of mercury taken up by the solid is measured as the applied pressure P (i.e.P^{Hg}-P^g) is gradually increased. The value V_i (Hg) at any value of applied pressure P_i, therefore gives the volume of all pores having a radius equal to or greater than r_i^P; and is termed as cumulative pore volume. Thus, in mercury porosimetry the cumulative pore volume decreases as pore radii increases [7]. The plots of intrusion volume, V_{int} vs pore diameter for zeolite-4A, $Co_{3.73}A$ and $Co_{5.27}A$ are given in Figs. (7-9). These plots show that there is a steep initial portion in the intrusion plot which gradually go slowly upward at higher pressure. Therefore, as the applied pressure further increases, there is again relatively sharp increase in the intrusion of mercury. The initial steep slope of the intrusion plot may be considered a consequence of penetration of mercury into the interparticulate spaces [27]. Once mercury has gained entry into the interparticulate

spaces, the slope of the plot flattens. As the pressure further increases, mercury is forced into the pores of zeolite samples having the restricted openings. The extrusion curves show that mercury extrusions do not follow the same path and after a small decrease in intrude volume at high pressure, no further mercury extrusion was observed. It is observed that after penetration and retraction, approximately 80% of the mercury remained in the pores of zeolite samples. The irreversibility of the hysteresis indicates that the pores of zeolite are not cylindrical in nature. It is believed that if a sample having only cylindrical pores with constant cross section, and providing the advancing and receding contact angles are equal, the point of penetration and retraction of mercury will fall on the same line. Emmett [28] reported that the mercury is not completely removed from the pores because the pore system deviates from the simple picture of cylindrical pores. According to Zhdanov [29] the fraction of mercury retained in the pores may amount 27-95% depending on the pore structure of the solid. The most extensive study of hysteresis in high-pressure porosimetry was made by Kamakin [30]. He believes that irreversibility of hysteresis is due to the fact that mercury cannot be reversibly retracted from pores with a minimum opening of r~75 Å. It is also observed that the samples showing the lower mercury hysteresis are those that exhibit little or no water hysteresis [31-32]. For metal exchanged zeolite samples, same behaviour is also observed except that the volume of intruded mercury is relatively high than that of the parent zeolite
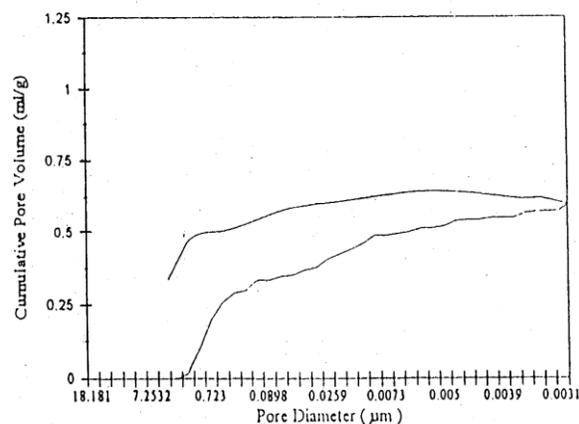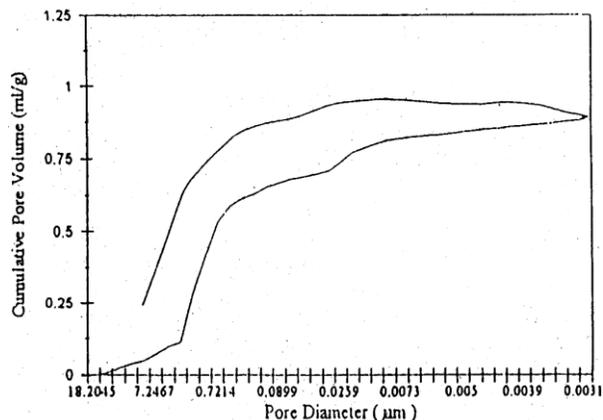

Figure 7. Mercury intrusion-extrusion curves for NaA.

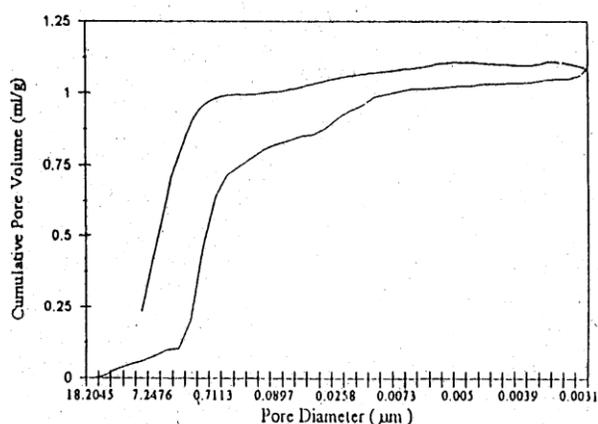**Figure 8. Mercury intrusion-extrusion curves for Co$_{3.73}$A**

Figure 9. Mercury intrusion-extrustion curves for Co$_{5.27}$A.

The results of pore size distribution in which volume of mercury is transferred to pores as the function of effective pore diameter are given in Fig. (10). Pore size distribution curve for zeolite samples indicates one maxima occurring at effective pore diameter of 0.0033 mm, and other small peaks are observed. The height of this peak shows that the contribution of pores of diameter 0.0033 mm is more significant to the total pore volume. For metal exchanged zeolite samples, the maxima occurred at the same pore diameter but the volume of intrude mercury is relatively high than that of parent zeolite. Plots of incremental volume Vs pore diameter for zeolite-4A Co$_{3.73}$A and Co$_{5.27}$A are shown in Figs. (11-13). The effective pore diameter is relatively at 1μm but incremental volume is high for metal exchanged A-zeolite than parent zeolite. The effective diameter of the window in the cavity and consequently, the adsorptive properties of dehydrated zeolite crystal depend substantially on

the nature of the ion-exchange cations, and on their number per elementry crystal cell [33,34]. This effect may be due to the arrangement of the cations in the centres of the windows, making the cavities inaccessible to relatively large molecules [35]. Presorption of small amounts of polar substances reduces the effective window diameters, and brings about considerable reduction in the adsorption of large molecules by zeolites. Fig. (14) shows three effective pore diameters with differential volume of NaA-zeolite and cobalt-exchanged A-zeolite.
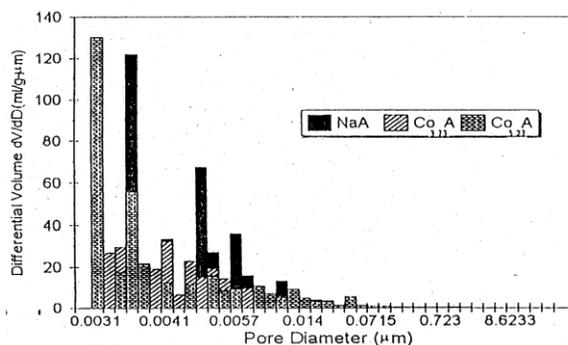

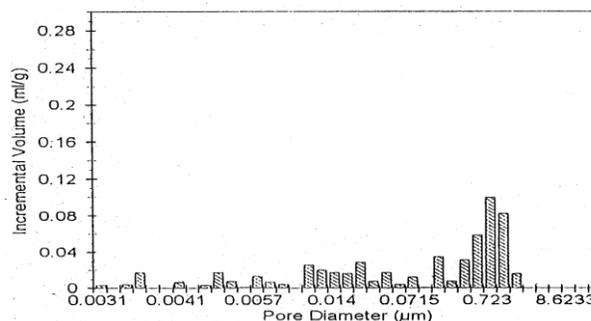**Figure 10. Pore size distribution plots for NaA-zeolite, Co$_{3.73}$A and Co$_{5.27}$A**
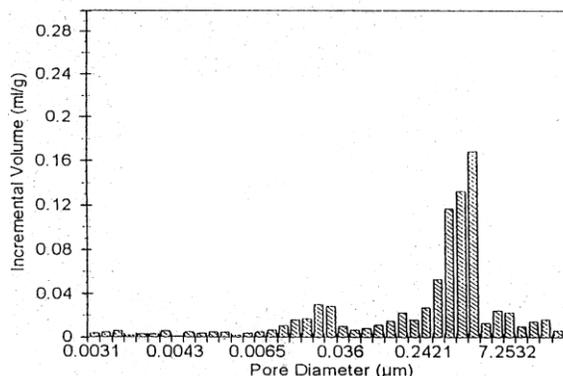

Figure 11. Pore size distribution plot for NaA-zeolite.

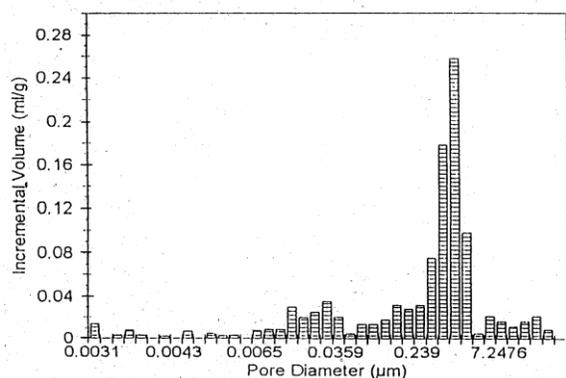**Figure 12. Pore size distribution plot for Co$_{3.73}$A**

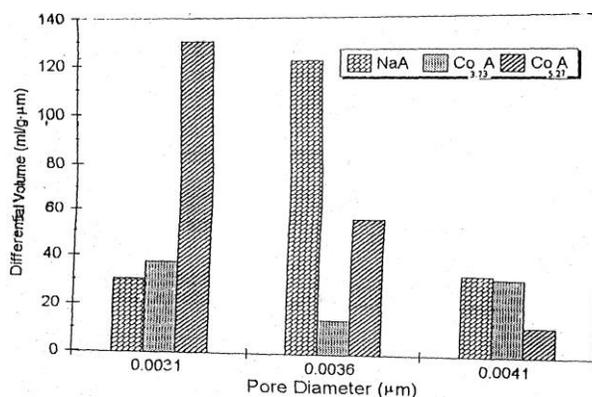**Figure 13. Pore size distribution plot for Co$_{35.27}$A.**

Figure 14. Change of pore volume of NaA-zeolite on cobalt exchange.

The values of pore volume and pore area are given in table (3). The value of pore volume as well as pore diameter increases as metal concentration increases. In type A zeolite with smaller pores, preadsorption of polar molecules such as water or ammonia affects the adsorption of another material by clustering about the cations, blocking the channels and reducing the pore size. Preadsorption primarily reduces the available pore volume [33]. As in this case, zeolite samples were out gassed at 300ºC, so more space is vacant for mercury.

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