NITROGEN ADSORPTION ON METAL IMPREGNATED ALUMINA BY CONTINUOUS FLOW METHOD

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SUMMARY: Alumina powder is impregnated with samarium (Sm), gadolinium (Gd) and erbium (Er) metals and is characterized by nitrogen adsorption at 77 K. It is observed that these metals on impregnation do not contribute any extra surface to alumina. The values of surface area and pore volume determined from nitrogen adsorption follows the sequence: Alumina > Sm-alumina > Gd-alumina > Er-alumina, and their behaviour is discussed in term of ionic radii of metal ions. It is also observed that meso and macropores contribute significantly to the total pore volume.

Key Words: Alumina, samarium, gadolinium, erbium.

INTRODUCTION

Alumina is frequently employed for adsorption of gases and liquids. It is especially used for chromatographic purposes i.e., for identification and separation of organic and inorganic substances. Moreover, due to high adsorption capacity and surface area, it is widely used to remove metal ions (1,2), dyes (3,4) and organic acids and solvents (5,6) from solutions. The importance of alumina as a support or catalyst has also been recognized and it is used in many industrially important catalytic processes. The chemical properties and the structure of alumina plays an important role in the catalytic process. These properties can be modified by the addition of metals which have profound effect on both the reactivity and selectivity of the surface in the catalytic reactions. In this work, we have modified the alumina with metals (Sm, Gd, Er) by impregnation technique and characterized them by nitrogen adsorption at 77 K to see the effect of metal ions impregnation on the adsorption capacity, surface area, pore volume etc of the alumina.

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EXPERIMENTAL

Chemicals

The chemicals used are alumina 60 G neutral (E-Merck; item No. 2316260) and nitrates of samarium, gadolinium, erbium (Rare Earth Products; 99.999 %).

Preparation of adsorbent (Metal impregnation)

Metal (Sm, Gd, Er) impregnated alumina were prepared by soaking 10 g of alumina in 100 ml of 10 % (w/v) metal nitrate solution. 16 hours impregnation period was allowed and then heated at 100 °C till the slurry was formed. The slurries were then dried at 473 K under vacuum for 6 hours. A blank alumina sample

was also prepared by giving the same treatment except that distilled water was used in place of metal nitrate solutions.

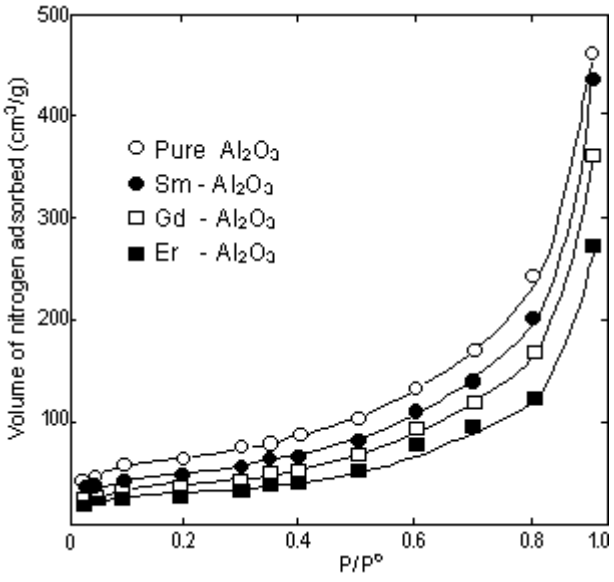
Nitrogen adsorption

The Quantasorb Sorption system, manufactured by Quantachrome corporation, N.Y., USA, was used to measure the amount of nitrogen adsorbed on the metal impregnated alumina samples by continuous flow method of Nelson and Eggertsen (7). Nitrogen gas was adsorbed on the samples at the liquid nitrogen temperature from a gas stream of nitrogen and helium at different N_2/He ratio. It was then desorbed and the liberated nitrogen was measured by thermal conductivity detector placed before and after the sample cell, and the volume of nitrogen adsorbed was calculated. The details of the nitrogen adsorption procedure can be seen elsewhere (8).

RESULTS AND DISCUSSION

The adsorption isotherms of nitrogen on impregnated and pure alumina were obtained by plotting the volume of nitrogen adsorbed against relative pressure P/P^0 and are given in Figure 1. Comparing these isotherm with the five types of B.D.D.T. classification

Figure 1: Nitrogen adsorption isotherms at 77 K.



(9), it was found that these isotherm are type II. This type of isotherms are associated with the multilayer adsorption. The specific surface area of the alumina and metal impregnated alumina was determined using B.E.T. equation in its usual form (8). The B.E.T. equation gives a linear relationship between $1/x\ [(P^0/P)-1]$ and P/P^0 and the range of linearity is restricted to a limited part of the isotherm. Herman and Emmett (10) indicated that B.E.T. equation give reasonable values in the range of relative pressure (P/P^0) from 0.05 to 0.35. They concluded that in this range of relative pressure,

Figure 2: B.E.T. plots for nitrogen adsorption on alumina and metal impregnated alumina.

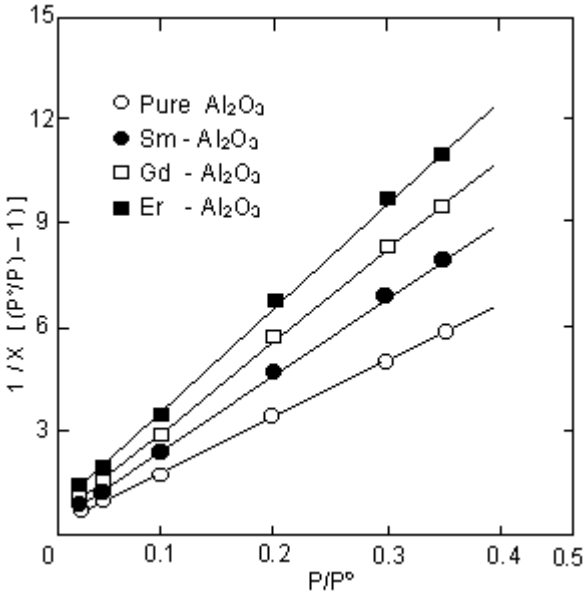


Table 1: Determined values of B.E.T. equation parameters and surface area for alumina and metal impregnated alumina by nitrogen adsorption.

Sample	Ionic radii of metal (A)	C	$X_m x10^{-2}$ (g/g)	B.E.T. surface area (m^2/g)
Alumina	-	103.07	6.075	211.60
Sm-alumina	0.964	95.23	4.518	157.36
Gd-alumina	0.938	67.40	3.773	131.41
Er-alumina	0.881	57.63	3.267	113.79

monolayer is formed and B.E.T. C values usually gives heat of adsorption.

B.E.T. plots for nitrogen adsorption on alumina and metal impregnated alumina are shown in Figure 2, where linear plots are obtained in the relative pressure range of 0.01-0.35. From the slopes and intercepts of these plots, the values of X_m and C are calculated and are given in Table 1. From the values of X_m, the surface area was calculated using known molecular cross section of the nitrogen molecule (16.2 Å at 77 K) and their calculated values are also given in Table 1. It is evident from Table 1 that the B.E.T. surface are metal impregnated alumina decreases and their values lie in the order of; alumina > Sm-alumina > Gd-alumina > Er-alumina.

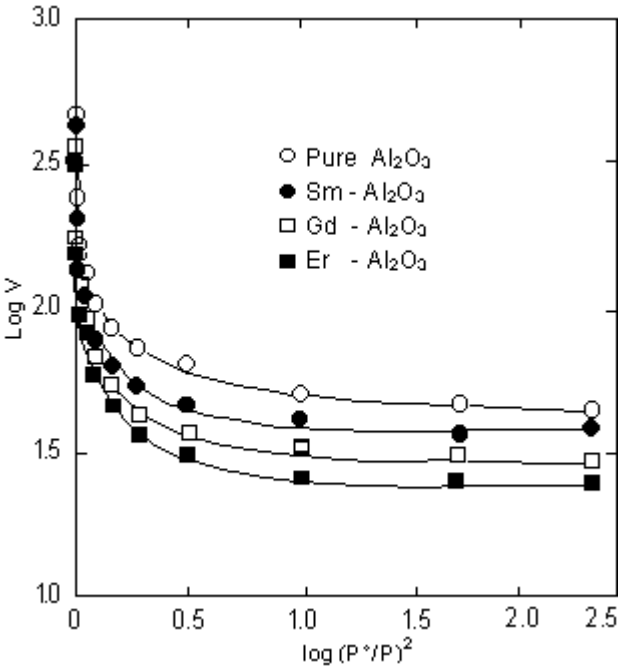
This shows that these metals on impregnation do not contribute any extra surface area to the alumina. The metal with smaller ionic radii on doping reduces the surface area more than that the metal with larger ionic radii; hence Er has greater tendency to penetrate deeper and resides preferentially at the alumina pore entrance, leading to an appreciable pore blockage, impede the flow of nitrogen in the alumina lattice. Therefore, due to the presence of these metals reside, the empty space available for the adsorption of nitrogen is reduced.

The total pore volume, which include all the varieties of pores, values of these powder samples determined from adsorption isotherms are given in Table 2. It is evident that the values of total pore volume of alumina and metals impregnated alumina follow a sequence similar to that of surface area and the charge in pore volume values is in line with the previous argument. The Dubinin-Radus kevich (DR) equation (11).

$$V = V_0 \exp - B(T/\beta)^2 \log^2 (P^0/P) \quad (1)$$

was used to calculate the micropore volume of the metal impregnated alumina. In equation 1, V is the volume of nitrogen at temperature T and at relative pressure P/P^0 and V_0 is the volume of micropores. B and β are specific constants depending respectively on the nature of the solid and on the adsorptive. To obtain

Figure 3: DR plots for alumina and metal impregnated alumina.



the micropore volume V_0, the adsorbate is assumed to be liquid like (11). The DR plots for alumina and metals impregnated alumina are obtained by plotting log V versus $\log^2 (P^0/P)$ according to equation 1 and are shown in Figure 3. The DR plot for the alumina exhibits the long straight line and apparent upward deviation at higher relative pressure. Same trend is observed for metals impregnated alumina powders. The deviation from straight line show that all the systems have het-

Table 2: Determined values of total pore volume, micropore volume and meso and macropore volumes of alumina and metals impregnated alumina.

Sample	Total pore volume (cm^3/g)	Micropore volume V_0(cm^3/g)	Meso and Macropore volume (cm^3/g)
Alumina	0.7099	0.1184	0.5915
Sm-alumina	0.6758	0.0850	0.5908
Gd-alumina	0.5629	0.0704	0.4925
Er-alumina	0.4231	0.0611	0.3620

erogenous systems of micropore (12). The uncertainty in the extrapolation of the straight line to $\log^2 (P^0/P) = 0$ to obtain V_0 is very high. As shown in DR plots that at least two different values of V_0 may be obtained. In fact, if experimental points at high relative pressures were selected, the intercept would give to larger value than those actually calculated from the straight line portion at low relative pressures values. In this work, the experimental point at relatively lower pressures are selected to obtain the V_0 values and its calculated values are given in Table 2.

The values of meso and macropore volume were obtained after subtracting the V_0 value from the total pore volume values and are also given in Table 2. This table indicate that the microporosity in alumina is weakly developed and contribution of micropores to the total pore volume is small. Therefore, major contribution to the pore volume comes predominantly from meso and macropores.

CONCLUSION

Based on the above data, it is concluded that the metals (Sm, Gd, Er) on impregnation do not contribute any extra surface to alumina and the values of surface area, and pore volume, determined by nitrogen adsorption, lies in the order of: alumina > Sm-alumina > Gd-alumina > Er-alumina.

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