# Cobalt Impregnated Alumina: Nitrogen Adsorption Study at 77 K

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Alumina powder is impregnated with cobalt in the concentration range 5% to 20% (w/v) and is characterized by nitrogen adsorption at 77 K by continuous flow method using the Quantasorb sorption system. It was observed that cobalt metal on impregnation does not contribute any extra surface to alumina. Values of BET surface area determined from nitrogen adsorption data follow the sequence Co (20% w/v) - $Al_2O_3$ < Co (10% w/v) - $Al_2O_3$ < Co (5% w/v) - $Al_2O_3$ < Pure $Al_2O_3$. Pore size distribution curves demonstrate the mesoporous nature of cobalt impregnated alumina.

## Introduction

Alumina ($Al_2O_3$) is a porous material and is extensively used as an adsorbent and catalyst support. It is especially used for chromatographic purposes i.e. for the identification and separation of organic and inorganic substances. Due to its high adsorption capacity and surface area, it is widely used to remove metal ions[1−2], dyes[3−4] and organic acid and solvents[5−6] from solutions. The importance of alumina as a support or catalyst has also been widely recognized and it is used in many industrially important catalytic processes. The chemical properties and the structure of alumina play an important role in the catalytic process. These properties can be modified by the addition of impregnate, which has a profound effect on both the reactivity and the selectivity of the surface in the catalytic reactions and that functions as an adsorbent[7−8]. Few reports have been published in recent years in which researchers have modified alumina with metal ions by the impregnation technique and characterized them by various physical and chemical methods[9−12]. We modified the alumina by impregnation with cobalt in the concentration range of 5% to 20 % w/v and characterized the resulting materials by nitrogen adsorption at 77 K to investigate the effect of cobalt ion impregnation on the different pore parameters of alumina.

## Experimental

The chemicals used were alumina 60 G neutral (E-Merck; item No. 2316260) and cobalt nitrate (BDH; item No. 27795 4B). Solutions were made in distilled and deionized water.

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Cobalt impregnated alumina samples were prepared by soaking 10 g of alumina in 100 mL of 5% w/v, 10% w/v and 20% w/v cobalt nitrate solutions. An impregnation period of 16 h was allowed and the solutions were then heated at 100 °C until slurry formed. The slurries were then dried at 473 K under vacuum for 6 h. A blank alumina sample was also prepared by applying the same treatment except that distilled water was used in place of the cobalt nitrate solutions.

A Quantasorb sorption system, manufactured by the Quantachrome Corporation, New York, was used to measure the amount of nitrogen adsorbed on cobalt impregnated alumina samples by means of the continuous flow method[13]. Nitrogen gas was adsorbed on the sample, degassed previously at 100 °C, at liquid nitrogen temperature from a gas stream of nitrogen (adsorbate) and helium (carrier) at a fixed $N_2$/He ratio. It was then desorbed and the liberated nitrogen was measured using a thermal conductivity detector placed before and after the sample cell, and the volume of nitrogen adsorbed was calculated. The experiments were repeated with different $N_2$/He flow gas ratios, and the volume of nitrogen adsorbed was calculated at the respective $N_2$/He flow gas ratio. Details of the nitrogen adsorption method can be seen elsewhere[14].

## Results and Discussion

The nitrogen adsorption isotherms of cobalt impregnated alumina shown in Figure 1 depict the amount of nitrogen adsorbed plotted versus the relative pressure P/P°. These isotherms may be classified as type II according to the BDDT classification[15]. Such isotherms represent unrestricted monolayer-multilayer adsorption. The specific surface area of the cobalt impregnated alumina was determined by applying the BET equation to the physical adsorption data for nitrogen at 77 K. A convenient form of the BET equation[16] may be written as

$$1/X[(P°/P) - 1] = 1/X_m C + (C - 1/X_m C).P/P° \tag{1}$$

where X is the amount of gas adsorbed at relative pressure P/P°, $X_m$ is the monolayer capacity and C is the constant. The BET equation gives a linear relationship between $1/X[(P°/P)-1]$ and P/P°, and the range of linearity is usually restricted to a limited part of the isotherm. Herman and Emmett[17] indicated that the BET equation gives reasonable values of the surface area over the range of relative pressure extending from 0.05 to 0.35. They concluded that within this relative pressure range a monolayer is formed, with BET C values usually corresponding to the heat of adsorption. Thus, for the majority of the isotherms, the relative pressure range of 0.05 to 0.35 apparently corresponds to those conditions where very high energy sites have been occupied and extensive multilayer adsorption has not yet commenced. It is within these limits that BET equation is generally valid, with deviation from linearity over this range reflecting unusual surface properties that are quite difficult to ascertain. BET plots for nitrogen adsorption on pure and cobalt impregnated alumina are shown in Figure 2, the slopes and intercepts of these plots allowing $X_m$ to be calculated. Such values are listed in the Table 1. The values of $X_m$ also allowed the surface area of the samples to be calculated using the known molecular cross-sectional area of the nitrogen molecule (16.2 $\overset{'}{\text{Å}}^2$ at 77 K). These values are also listed in the Table 1. It can be seen from the table that BET surface areas of cobalt doped alumina decrease in the order

Co (20% w/v) - $Al_2O_3$ < Co (10% w/v) - $Al_2O_3$ < Co (5% w/v) - $Al_2O_3$ < Pure $Al_2O_3$

This shows that the impregnation of cobalt does not contribute any extra surface area to alumina, and that doping with a metal (cobalt) with a higher concentration reduces the surface area to greater extent than does a metal (cobalt) with a lower concentration. Hence, the cobalt metal resides preferentially at the alumina pore entrances, leading to appreciable pore blockage that impedes the flow of nitrogen to the alumina lattice. As a consequence of the presence of metal residues, the empty space available for nitrogen adsorption is reduced, resulting in lower surface area values of metal doped alumina.

**Table 1.** Determined values of $X_m$ and BET surface area for alumina and cobalt impregnated alumina by nitrogen adsorption.

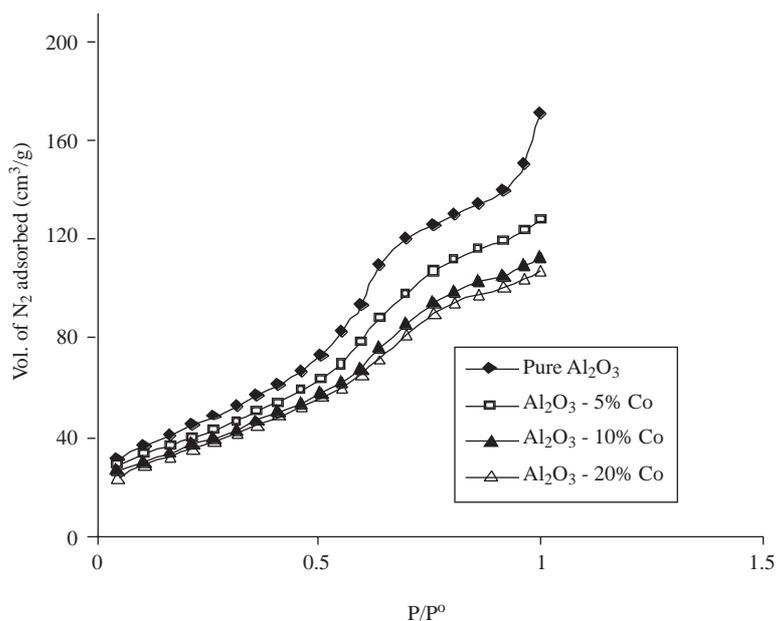| Sample | $X_m$ (g/g) | BET Surface Area $(m^2/g)$ | Correlation Coefficient, $R^2$ |
|---|---|---|---|
| Pure $Al_2O_3$ | 0.0511 | 177.98 | 0.9979 |
| Co (5% w/v) - $Al_2O_3$ | 0.0443 | 154.30 | 0.9976 |
| Co (10% w/v) - $Al_2O_3$ | 0.0412 | 143.50 | 0.9986 |
| Co (20% w/v) - $Al_2O_3$ | 0.0396 | 137.90 | 0.9978 |



**Figure 1.** Nitrogen adsorption isotherms for pure $Al_2O_3$ and cobalt impregnated $Al_2O_3$ samples at 77K.

The pore size distribution curves for pure alumina and cobalt impregnated alumina calculated by applying the BJH method[18] are shown in Figure 3. The pore size distribution curve for pure alumina indicates 1 peak (maximum) at a pore radius of ca. 50 Å. This demonstrates both the mesoporous nature of alumina and the fact that the major contribution to the total pore volume comes predominantly from mesopores of radius ca. 50 Å. The cobalt impregnated alumina samples also exhibit broader maxima at virtually the same pore radius, but the peak height as well as the percentage of total pore volume located in the mesopore region were significantly smaller in all cases than they were in the parent alumina. It is concluded that the relatively small surface areas observed for cobalt impregnated alumina may be almost totally attributed to the decrease in the mesoporosity in the ca. 50 Å range. This is probably due to the residence of the cobalt metal at the mesopores entrances, leading to an appreciable pore blockage that

impedes the flow of nitrogen in the mesopores. Pore volume and pore surface area distribution curves of pure and cobalt impregnated alumina are given in Figures 4 and 5, which are self-explanatory.
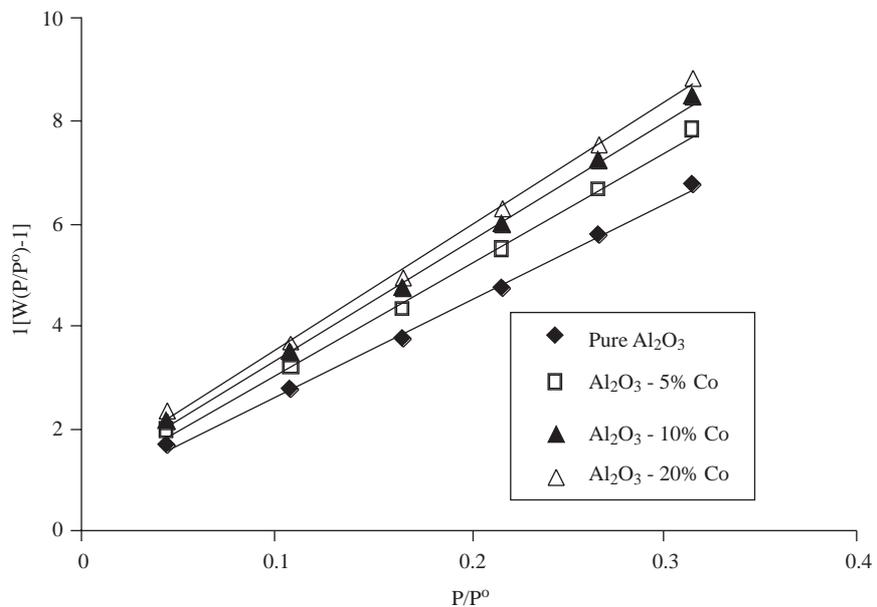


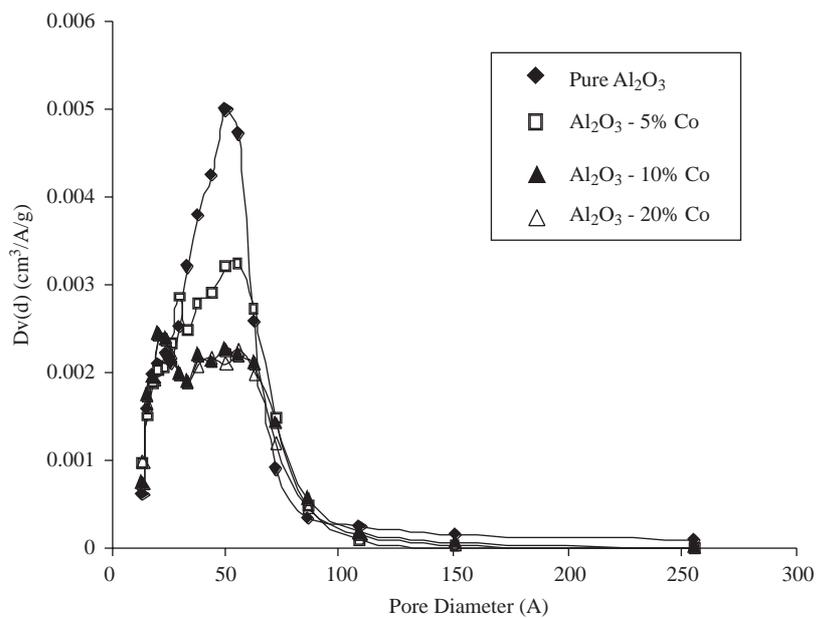**Figure 2.** BET plots for nitrogen adsorption on pure $Al_2O_3$ and cobalt impregnated $Al_2O_3$ samples.



**Figure 3.** Pore size distribution curves for pure $Al_2O_3$ and cobalt impregnated $Al_2O_3$ samples.
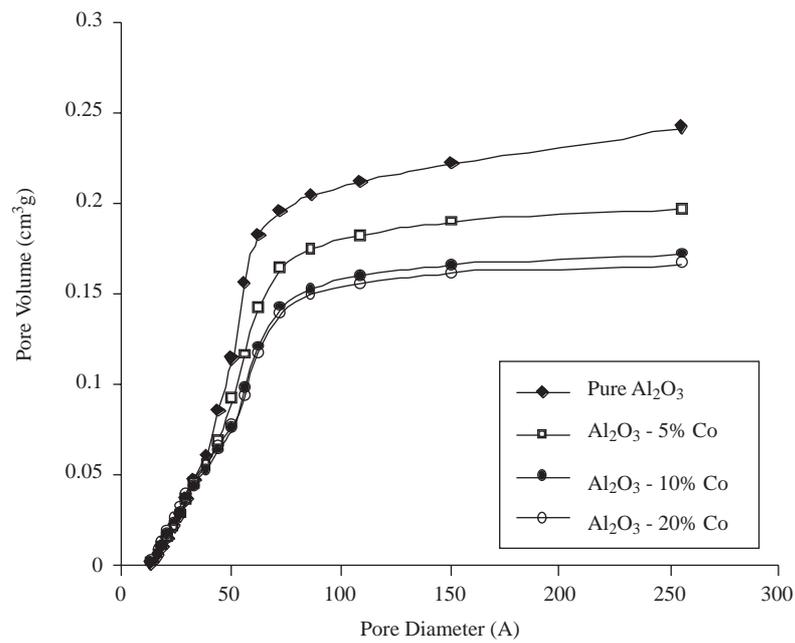
**Figure 4.** Pore volume distribution curves for pure $Al_2O_3$ and cobalt impregnated $Al_2O_3$ samples.
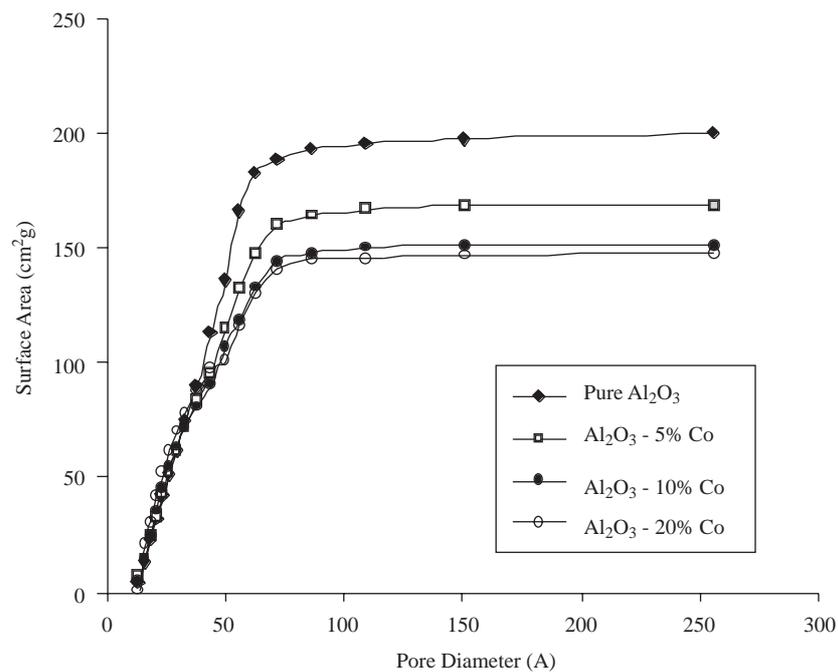
**Figure 5.** Pore surface area distribution curves for pure $Al_2O_3$ and cobalt impregnated $Al_2O_3$ samples.

## Conclusion

This study reveals that the impregnation of cobalt does not contribute any extra surface area to alumina, and that doping with cobalt with a higher concentration reduces the surface area to greater extent than does cobalt with a lower concentration. The determined BET surface areas of cobalt doped alumina lie in the order

Co (20% w/v) - $Al_2O_3$ < Co (10% w/v) - $Al_2O_3$ < Co (5% w/v) - $Al_2O_3$ < Pure $Al_2O_3$

Similar trends were also observed in the pore size, pore volume and pore surface area distribution curves. The study also reveals that the major contribution to the total pore volume comes predominantly from mesopores of radius ca. 50 Å.

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