A THESIS
ENTITLED

ADSORPTION IN RELATION TO PORE STRUCTURE OF VARIOUS ALUMINAS

Presented By

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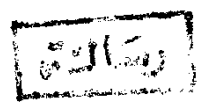

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ADSORPTION IN RELATION TO PORE STRUCTURE OF VARIOUS ALUMINAS

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To

My Dear Brother Mohammed

A C K N O W L E D G E M E N T

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General Introduction

The study of alumina is a subject of great importance because alumina is a large-volume product on the chemical market. Although the major part of it is used in the production of aluminium metal, an increasing amount is employed in other fields, e.g. ceramics, abrasives, medicinals, adsorbents and catalysts. Products of the last two applications are generally called "active alumina" and are the subject of this thesis.

Physical adsorption constitutes a very important means of investigating the properties of heterogeneous catalysts. Indeed, with the appearance and application of the BET theory the study of heterogeneous catalysis was given a significant impulse, because a reliable means of estimating the specific surface area (surface area per unit mass) of a wider range of industrial catalysts became available. Physical adsorption also forms the basis of most of the numerous methods of measuring the porosity of solids. Less widely appreciated is the fact that physical adsorption can also enable deductions to be made concerning the fractional amount of a solid surface which is energetically heterogeneous.

The importance of pore structure and surface area arises from the fact that the accessibility of a catalyst surface to reacting gases is of considerable importance in the selection of a solid material which is to function as an active catalyst for heterogeneous reaction. For a given catalyst, the greater the amount of the surface available to the reacting gases the better is the conversion to products.

The adsorption and catalytic properties of alumina have been studied for some time and by 1945 an impressive mass of empirical information about the preparation and properties of aluminas was available. Insight into the fundamental problems, however, was lacking almost completely. Many studies were devoted to developing reliable methods for the determination of "activity", which was found to differ considerably not only from the various known adsorptive or catalytic processes but also from the many natural and synthetic alumina products available. Some of these methods gained wide spread practical use; for instance, the classification of active aluminas for chromatographic purposes according to Brockmann and Schadder[1] (1941). This method, still used to day, was perfected and given a more rational base by Fortuin[2] (1955) and in recent years modified for use in thin layer chromatography (Hermanek et al[3], 1961).

At the same time much effort went into elucidating problems concerning the thermodynamic and mechanistic aspects of adsorption and catalysis on alumina. But the contradicting results of most of these studies must be due primarily to a back of detailed information about the origin and thermal history of the active alumina used. The title of Frary's paper[4] (1946). "Adventures with alumina", conveys a good idea of the situation at that time. But when strong interest for the more fundamental problems began, considerable knowledge was achieved, possible because of improvements in X-ray and electron diffraction and in infrared spectroscopic techniques. The development of the theory of physical adsorption has further stimulated deeper analysis.

It was shown that the important variables for the adsorptive and catalytic activities such as crystal structure, pore texture and the chemical nature of the surface were largely determined by other detailed points in the preparation of the alumina. Active alumina is prepared mostly by a thermal dehydration procedure because it is probable that the properties of the activated products are strongly related to the structure and morphology of the initial hydroxides.

I- A. Adsorption and Porous Textures of Aluminas:

Direct information on the porous texture could in principle be obtained by direct observation in an electron microscope. However, the very small quantity to be used, the necessary high vacuum and the changes produced by strong impact of high voltage electrons limit the applicability of this method and usually only quantitative results can be obtained. Similar difficulties are experienced with other "direct viewing" methods, such as field emission microscope studies, which can be used only for some very special materials.

One of the most powerful approaches has been to gradually fill the pore system with an adsorbate. Theories which can be used for the interpretation of adsorption phenomena are already available.

Small angle X-ray scattering has been used to study the particle size of the solids (Brindley and Nakahira[5] 1959). The broadening of X-ray diffraction lines can give information about crystallite size and lattice defects (Beretka and Lidga[6], 1967; Levy and Bauer[7], 1967). Optical methods have been used with success to study the orientation of the pore system (Steggarda[8], 1955, de Boer et al[9], 1956).

None of the above mentioned methods will in itself give an unequivocal description of the porous texture and the adsorption method remains the most successful method.

Nitrogen adsorption isotherms of the dehydration products of the aluminium trihydroxides were extensively studied to learn about their porous texture (e.g. for gibbsite: Steggerda[8], 1955, de Boer et al[9], 1956; for bayerite : Lippens[10], 1961, de Boer and Lippens[11], 1964, Lippens and de Boer[12], 1964; for nordstrandite : Alderoft and Bye[13], 1967).

The crystalline trihydroxides have a low surface area and pore volume; the shape of the isotherms is an agreement with a picture of loosely-packed non-porous particles with sizes of a few microns. When heated to just below the temperature at which the formation of low-temperature alumina starts, the adsorption isotherm shows that pores are formed. In this temperature region some well-crystallized boehmite is formed under intragranular hydrothermal conditions. In the case of gibbsite, which gives the highest quantity of boehmite, these pores have been described as "ink bottle" type pores, with a large volume and narrow openings. In the case of bayerite and nordstrandite these pores, as well as being much less abundant, are more slit-shaped in character.

Heated just above their decomposition temperature (250°C for gibbsite, 230°C for bayerite and nordstrandite) the nitrogen adsorption at low relative pressures increases enormously. If the Brunauer, Emmett and Teller theory is used to calculate the

adsorption
surface area, values of up to 700 m^2/g are obtained. From the/ desorption isotherms it can be concluded that only a small part of this surface area is present in pores wider than 20Å. The rest of the adsorbed nitrogen is present in micropore system.

When heated at much higher temperature (above 550°C) the shape of the adsorption isotherms changes drastically. The BET surface area drops to about half of its highest value and the calculation of the surface area and pore volume from the desorption isotherms shows that the micropore volume decreases to a very low value.

The isotherms of the various aluminas were the first ones to which the Lippens-deBoer method[14] was applied. This method is based on the experimental fact that, when dealing with the multimolecular adsorption the adsorbed volume per unit surface area as a function of the relative vapour pressure of the adsorbent can be represented by a single curve independent of the adsorbent. Necessary conditions for this to be valid are, no capillary condensation, no hindered adsorption in narrow pores at relative pressures higher than that required for a nearly full monolayers. The adsorbed volume per unit surface area in fact represents the average or statistical thickness t of the adsorbed multilayer, hence the name t-curve for this method.