COMPACTION VERSUS SURFACE PARAMETERS OF CERTAIN SOLID CATALYSTS

THESIS

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By

ANWAR MAHMOUD IBRAHIM

B.Sc. & Ed. (Physics and Chemistry) 1987
G. Diploma, Chemistry 1988
Sp. Diploma Physical Chemistry 1989

To

Ain Shams University
Faculty of Education
Chemistry Department

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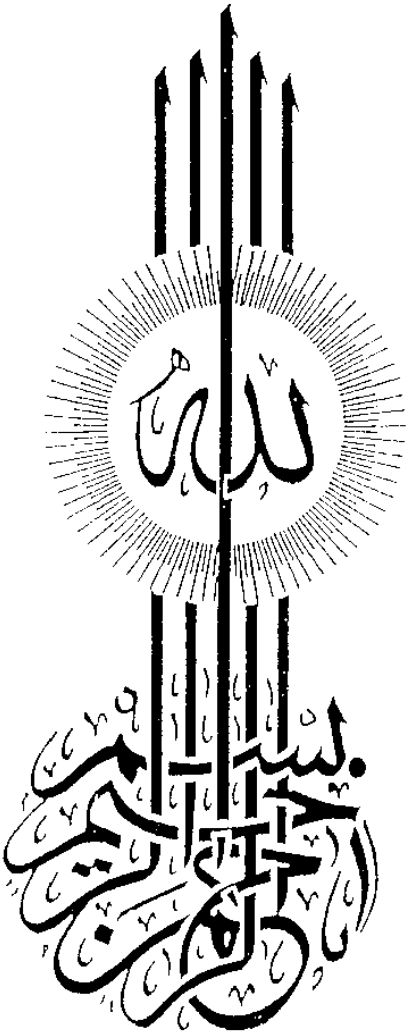
الله

بسم الله الرحمن الرحيم

قالوا سبحانك لا علم لنا إلا ما
علمتنا إنك أنت العليم الحكيم .

صدق الله العظيم
البقرة - ٣٢ -



بسم الله الرحمن الرحيم

TO
MY PARENTS

COMPACTION VERSUS SURFACE PARAMETERS OF CERTAIN SOLID CATALYSTS

SUPERVISORS	**APPROVED**
1. *Prof. Dr. FIKRY M. EBEID*	
2. *Dr. ANWAR A. IBRAHIM*	Anwar Amin Ibrahim
3. *Dr. LAILA IBRAHIM ALI*	Laila I. Ali

Head of Chemistry Dept.
Prof. Dr. BASHIER A. EL-SHETARY

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   Assistant Professor of Physical Chemistry, Faculty of Education,
   Ain-Shams University.

3. ***Dr. Laila Ibrahim Ali,***
   Assistant Professor of Physical Chemistry, Faculty of Education,
   Ain-Shams Univeristy.

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CHAPTER (1)

INTRODUCTION

CHAPTER (I) INTRODUCTION

I. I. Surface Study:

Mixed oxides, especially binary systems, have been employed successfully in many industrial catalytic processes.(1,2) Linnett and Rahman,(3) have focussed attention on a type of such systems in which both metal ions play a part in the geometry of the crystals. These systems are spinels with the formula $M_x''M_{3x}O_4$. Binary systems in which Al and Mg form the trivalent and divalent metal ions, respectively, have lately attracted some attention.(4-7)

Some surface properties and structural changes accompanying the calcination of the mixed hydroxide system were investigated(4). However, in view of the oxide/oxide interaction in the mixture at suitably varying temperatures, the effect of compaction becomes an essential pre-requisite to understand further studies on certain surface properties. The present work represents essensially a study on the effect of compaction prior to thermal treatment of the aluminium - magnesium hydroxide mixture on the phase and structural changes upon dehydration, by means of XRD, DTG and DTA.

(I-A) Historical review of the effect of compaction on the surface texture of mixed hydroxides and oxides:

S. Nashed and A. Amin (8) studied the structure and phase changes in the thermally mixed hydroxides and oxides of Zn and Al. The mechanically mixed hydroxide was 1:1 mole ratio of ZnO : Al_2O_3 were prepared in the powder form and as compacted pellets under a compaction pressure of 100 kg/cm^2. Two series of dehydration products were obtained by isothermal heating of powder and compact mixed hydroxide samples, at temperatures between 200° and 1000°C. Certain interesting phase changes are reported on calcination, e.g., the formation of spinal ($ZnAl_2.O_4$) at 600°C, and phase transformation of β-aluminium hydroxide to β-alumina via an amorphous phase. The compaction pressure applied seems not sufficiently effective to enhance the spinal formation at a lower temperature than in the powder mixture, viz, 600°C.

Sorption of nitrogen in porous compacts of silica and zirconia powders was studied by Avery, R.G., Ramsay J.D.F.(9) SiO_2 and ZrO_2 (yttria stabilized) powders with an exteremely small particle size ($<$ 40 A°) and a narrow size distribution were prepared by a vapour-phase condensation process which gave no strong particle agglomeration. The effect of compaction at pressures $\leq$ 100 ton/inch^2 on the specific surface area and pore structure of these powders was studied by measuring N_2 adsorption isotherms. The results are of regularly packed spherical particles with a coordination number contrrolled by the extent of compression. At the highest pressures of compaction the isotherms obtained indicate that with pores below some critical radius as $<$ 7A° estimated from Kelvin equation no capillary condensation is observed.

S.A. Selim et al.(10), studied the structure and phase changes in thermally treated mixed hydroxides of Mg and Al. Mechanically mixed (I) and coprecipitation (II), hydroxides of magnesium and aluminium were investigated in both powder and compact forms in the temperature range 200 - 1000°C using DTG, DTA and X-ray techniques. Upon thermal treatment of the mechanically mixed hydroxide, the solid material gives rise to products which at first become poorly crystalline and then gradually pass into crystalline state indicating a mixture of MgO, θ, δ and α-alumina together with a new spinel. Coprecipitation hydroxides (II) proved to constitute a new species probably a hydrated spinel. The spinel $MgAl_2O_4$ commences to form at a temperature as low as 200°C. Compaction with either 10 or 30 ton/in^2 decreases $\leqslant$500°C whereas it favours crystallization for the products from (II). Above $\sim$ 500°C, compaction has no appreciable effect on crystallization.

A. Amin et al.(11) investegated the effect of compaction on the surface area of mechanically mixed and coprecipitated hydroxides of aluminium, magnesium and the thermally dehydrated products obtained in the temperature range 200 - 1000°C were studied by N_2 adsorption. Precompaction treatment was found to increase the surface area of mechanically mixed hydroxide (I) below (400°C) the maximum specific surface area was obtained at 100°C lower than for powder oxides. The behaviour of coprecipitated mixed hydroxide (II) is not regular due to interfering factors which invariably influence the surface structure. At higher temperature, precompaction accelerates crystallization and sintering due to an increased number of solid-solid interfaces, complete pore structure analysis showed mixed hydroxides (I) and (II) to be mesoporous. Narrowing of pores commenced with thermal treatment the maximum micropore fraction was obtained at 500 and 400°C for mixed hydroxides (I) and (II) respectively. Precompaction treatment increased microporosity below 500°C and favoured the formation of mesopores at higher temperature.

Nitrogen adsorption-desorption isotherms at 77 k were determined by W. Mourad(12) who studied the specific surface area of powder and compacted samples (2 and 4 tons/in^2) of bentonite clay and three acid-activated preparations of different normalities. Analysis of the adsorption isotherms using the α_s method of Sing revealed that micropores were present in the original bentonite clay and that the microporosity developed progressively with acid activation. The presence of mesopores in addition to micropores in the samples studied was demonstrated by the occurrence of high pressure hysteresis loops. The observed changes due to acid treatment in various surface parameters of bentonite were correlated with corresponding chemical changes. Compaction at 2 tons/inch^2 of the four unactivated and acid-activated powder samples invariably produced a marked upward shift in their adsorption isotherm compared with the samples compacted at 2 tons/in^2 and even over that for the original powder samples. This effect is indicative of the occurrance of plastic deformation of the clay involving an increase in the surface area and void volume parameters. The response to plastic deformation is greater in acid-activated clay than in unactivated clay.

The porosity of compacts of 2 MgO. 3 SiO_2 was determined by Stanley-Wood(13), N.G. at low temperature N_2 adsporption and Hg intervsion. The total porosity of the compacts initially decreased rapidly with increasing compaction pressure then become slower.

I. II. Catalytic Study:

Catalyst becomes of its great applications in many catalytic processes, either in the chemical laboratory or in industry. Among the various reactions catalyzed by alumina are the dehydration of alcohols, alkylation and deamination of amines, cracking and isomerization of hydrocarbons and polymerization. It is also used as a carrier or modified by the addition of other constituents such as, nickel or platinum catalysts in hydrogenation reactions and silica in cracking process.

The dehydration of alcohols to ether and for olefins has been investigated by many workers(14-17). In the dehydration over solid catalysts, ether formation takes place at lower temperatures, whereas at higher temperatures hydrocarbons are main products of alcohol dehydration. The selectivity and activity of a given sample of alumina could be determined through knowledge of the type of active centers present on its surface. Such a study is of a great importance from both scientific and industrial points of view. A knowledge of the type of active centers involved in a certain reaction helps in understanding the nature of the adsorbed state of the reacting molecules and consequently the reaction mechanism.