

EFFECT OF SOME WATER SOLUBLE ORGANIC ADDITIVES ON THE SURFACE AND CATALYTIC PROPERTIES OF ALUMINA

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the Degree of
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In
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By

SAHAR AHMED ISMAIL

Chemistry Department

Faculty of Women

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سبحانك
لأعلم لنا إلا ما علمتنا إنك أنت العليم الحكيم
صدق الله العظيم



**I Dedicate This Thesis to
MY PARENTS, HUSBAND,
NADA AND AHMED**

AIN SHAMS UNIVERSITY
FACULTY OF WOMEN
CHEMISTRY DEPARTMENT

M.Sc. Thesis
(CHEMISTRY)

EFFECT OF SOME WATER SOLUBLE ORGANIC ADDITIVES ON THE
SURFACE AND CATALYTIC PROPERTIES OF ALUMINA

Thesis Supervisors:

- * Prof. Dr. ABD EL-FATTAH MOHAMED YOUSSEF *A. M. Youssef*
- * Ass. Prof. Dr. NADIA ABD EL-HAKEM YOUSSEF *N. A. Youssef*

Approved

Marguerite A. Wassef
Head of Chemistry Dept.

AIN SHAMS UNIVERSITY
FACULTY OF WOMEN
CHEMISTRY DEPARTMENT

COURSES

The student has passed the following courses in partial fulfillment of the requirement for the degree of M.Sc.

1. Thermodynamics.
2. Quantum Chemistry.
3. Instrumental Analysis.
4. Spectroscopy.
5. Photo-chemistry.
6. Chemical Kinetics and Catalysis.
7. Advanced Chemical Reactions.
8. Electrochemistry.
9. Surface Chemistry.
10. Polymer Chemistry.

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250 rue Saint Jacques
F-75005 PARIS

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Madame, Monsieur

Nous avons le plaisir de vous informer que votre mémoire intitulé :
MODIFICATIONS DE QUELQUES PROPRIETES CATALYTIQUES DE
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Professeur R. Schaal
Directeur Scientifique

CONTENT

<u>CHAPTER I</u>	Page
INTRODUCTION	1
Alumina gels	1
Adsorbent alumina	1
Alumina for catalysis	3
1.1 The nature and origin of pores	6
The control of pore size in alumina	9
The use of additive to control pore size	11
1.2 Acidity and catalytic activity of alumina	15
1.3 Catalytic properties of alumina	21
1.4 Aim of the work	26
REFERENCES	27
 <u>CHAPTER II</u>	
EXPERIMENTAL	34
II.1 Materials	34
II.2 Techniques	35
REFERENCES	41
 <u>CHAPTER III</u>	
Evaluation of Textural Properties and Determination of Catalytic Activity	42
III.1 Adsorption of vapours by solids	42
III.2 Estimation of surface area	45
III.3 Analysis of pores	52
III.4 Determination of the catalytic activity and kinetics of the catalysis	61
REFERENCES	65
 <u>CHAPTER IV</u>	
Structural and Textural Properties	67
IV.1 Thermal properties	67
IV.2 Nitrogen adsorption-desorption isotherms	71
REFERENCES	84

	Page
<u>CHAPTER V</u>	
Acidity and Catalytic Activity	86
V.1 Acidity of the aluminas investigated	86
V.2 Catalytic dehydration of Isopropanol	88
V.3 Relation between catalytic activity and some characteristics of the catalysts	91
V.4 Mechanism of decomposition of alcohol	92
REFERENCES	99
SUMMARY AND CONCLUSIONS	101
ARABIC SUMMARY	

CHAPTER 1

INTRODUCTION

CHAPTER I

INTRODUCTION

The system of the oxides and hydroxides of aluminum is of considerable interest from several points of view. In the first place, alumina itself occurs abundantly in nature, most often in the state of impure hydroxides which are the essential constituents of bauxites and laterites. In addition, this system is especially difficult to master, because there are so many structural varieties present, some of which can be obtained by synthesis^(1,2). The very diversity of these forms and their properties has led to the utilization of these products in a wide variety of fields.

Alumina gels:

The name gel is applied to preparations of alumina which are amorphous, or mainly amorphous, hydrated forms obtained by starting from solutions of aluminum salts or of alkaline aluminates according to the conditions under which these are prepared the products obtained differ widely in purity, in content of water of hydration, and in physical characteristics (texture and specific surface).

The main constituents of gels are the amorphous phase and colloidal boehmite (as the gel-type α -monohydrate). These two phases coexist very often and the crystallized trihydrates may also appear as additional constituents.

Adsorbent alumina:

The aluminas are very widely used in adsorption where their properties of large surface area and very fine pores play an essential

part. They are obtained from various hydrated forms by controlled heating, so as to eliminate most of the water of constitution. Currently they are known under the name of "activated aluminas". The oldest commercial method is known as Bayer process. In this process sodium aluminate solution is used. Activated alumina in the form of gibbsite. Alumina gels also serve as starting products for the manufacture of adsorbents. These gels are generally prepared from aluminum sulfate and ammonia, or from sodium aluminate on an acid.

The precipitate after being washed, is thoroughly drained to form a cake which embodies 8 to 20% of Al_2O_3 . This cake may be dried directly in order to be broken up afterwards or it can first be extruded in the form of cylinders. The gels are activated by heating to a temperature of around $400^{\circ}C$ in a current of air or other gas, to prevent it from remaining for long in the steam formed during dehydration. The adsorbent so obtained loses 6 to 8% on ignition and contains a specific surface area of 200 to 250 m^2/g and a pore volume of 0.2 to 0.25 cm^3/g . Essentially, this volume consists of two types of pores: The first, which are the most numerous have a diameter of less than 40; the second, a diameter of 50 A.

The most important industrial application of alumina as an adsorbent continues to be the drying of gases and liquids. Activated alumina is in fact one of the solids having the greatest affinity for water. In countercurrent drying, under suitable conditions, it permits drying to a residual moisture content of less than one part

(by volume) in million. Aluminas also find application in adsorption chromatography.

The adsorbing capacity of alumina (the amount of water fixed per 100 g of adsorbent at the point when the break point of the column is reached) depends mainly on the relative humidity of the gas. The flow rate and the time of contact. The adsorbing capacity may range from 6 to 15 g $H_2O/100$ g Al_2O_3 .

Alumina for Catalysis: Aluminas also find applications in catalysis, and in this context several special preparations are known⁽⁵⁾ catalysts are made either by impregnating the alumina support previously obtained or by introducing active compounds into the alumina. Active compounds may be introduced in the course of treating the alumina by coprecipitation, or they may be incorporated in a suspension. Activated alumina show high catalytic activity in dehydrating alcohols to olefins and in initiating other syntheses in which water may be either the reagent or the reaction product. The best aluminas for this purpose are those which have a large surface area and a low sodium content. In general, one is left with the use of essentially empirical recipe for the preparation of the various hydrated aluminas which themselves are used as precursors for dehydrated alumina. A variety of dehydration products have been characterized. Under all conditions α -alumina (corundum) is the high temperature ($147^\circ K$) and product of dehydration.

All of the others which results from dehydration at lower temperature approximate to a greater or lesser extent to a model in which the oxygens are arranged as in spinel, but in which not all the

cation positions are occupied, and in which there are varying doses of cation disorder. An order-disorder model was adopted by Ervin⁽⁶⁾ in agreement with the conclusion of Leonard⁽⁷⁾. There are however, two other factors which need recognition: one is the distortion away from the cubic symmetry of the spinel structure; the second is stacking disorder in the arrangement of the close-packed oxygen layers. In general terms, the dehydration products fall into two categories depending on the dehydration temperatures and the structure of the important product may be summarized as follows⁽⁸⁾: At low temperature (>720 K) the products are δ^- , η^- and κ^- alumina. Both δ^- and η^- are tetragonally distorted from cubic symmetry to an extent that decreases with decreasing residual water content. Both have cation disorder, particularly on the tetrahedral sites, and in addition η^- has stacking disorder. Both δ^- and κ^- are high temperature dehydration products (1070-1170 K) δ^- is monoclinically distorted with the cation mainly in tetrahedral positions while κ^- is rhombohedrally distorted, again with stacking disorder.

The dehydration sequence involved gibbsite, bayerite and boehmite (composition $AlO(OH)$) have been summarized by Lippens and Steggerda⁽⁸⁾:

