SURFACE AND CATALYTIC STUDIES OF SOME METAL OXIDES

T H E S I S

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OF THE REQUIREMENTS FOR
THE MASTER OF SCIENCE DEGREE

IN

PHYSICAL CHEMISTRY

BY

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SURFACE AND CATALYTIC STUDIES OF SOME METAL OXIDES

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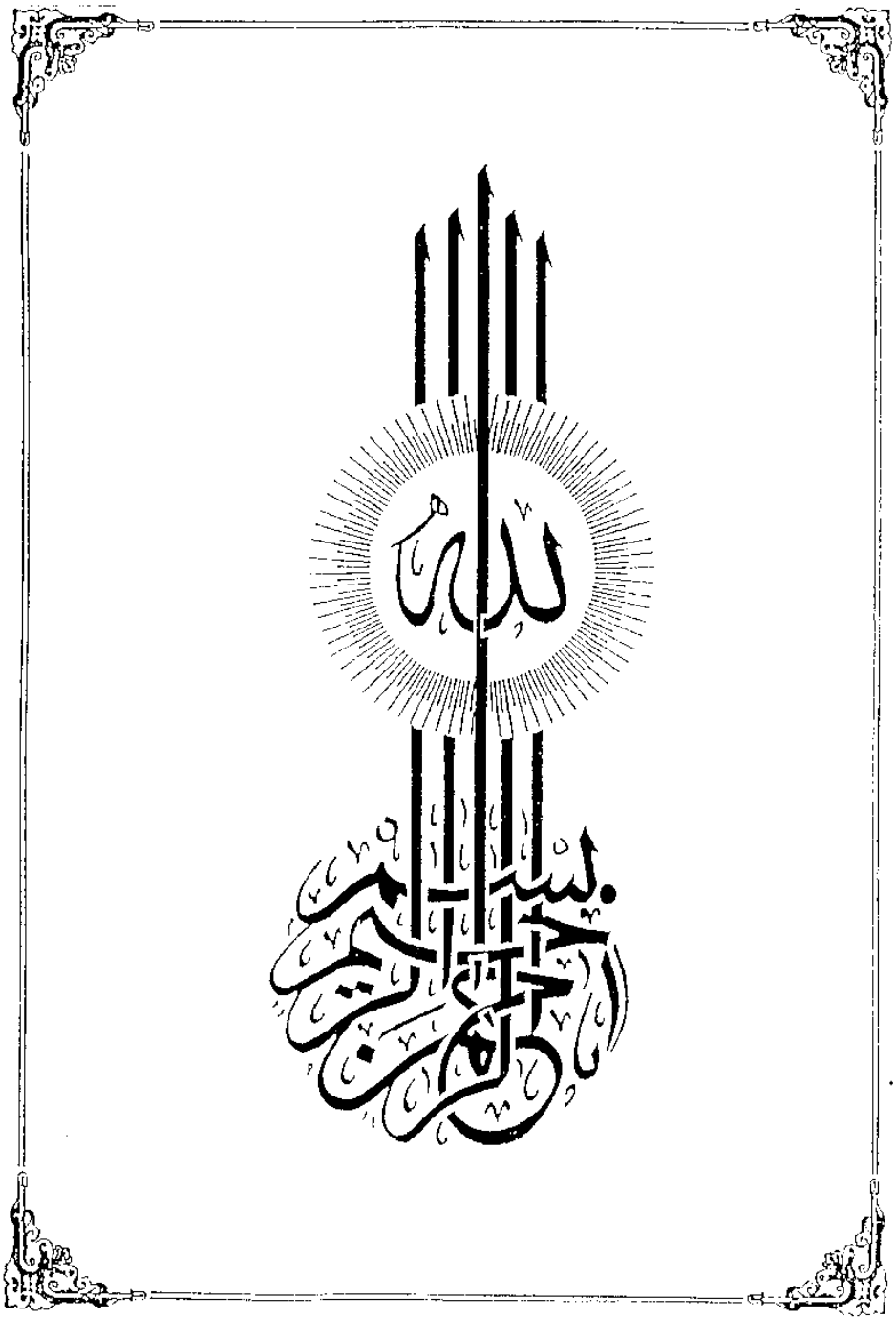

NOTE

Beside the work carried out in this Thesis, the Candidate has attended Post Graduate Courses for One Year in Physical and Inorganic Chemistry covering the following topics:

(1) Advanced Surface Chemistry.

(2) Advanced Electro Chemistry and Corrosion.

(3) Techniques of Inorganic Chemistry.

(4) Physical methods of Inorganic Chemistry.

(5) Nuclear Chemistry.

He had successfully passed a written examination in these courses.

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NOTE II

Also the Candidate has attended Higher Courses for One Year for the Degree of Diploma of Analytical Chemistry awarded in 1969 in the Faculty of Science Cairo University.
Covering the following Theoritical and Practical Study:

(1) Analytical Chemistry and Complexometry.

(2) Inorganic Chemistry, Gravimetry and Nuclear Chemistry.

(3) Physico Chemical Analysis and Quantitative Micro Analysis.

(4) Molecular spectrosoopy, spectrophotometry and spectro-chemical analysis.

(5) Thin layer and Gas Chromatography and Electrophoresis.

(6) Bibliography.

He had passed the examination in these courses with the Degree Very Good.

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

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C O N T E N T S

Object of Work

Ascertainment of the mechanisms of chemical reactions and in order to receive, in case of complicated processes, an information about the number and the nature of intermediate and the character of limiting stage is the main problem of chemistry. One of the fundamental methods of elucidation the mechanism of reaction is the kinetic study. At the same time the kinetic study discovers the way for prediction of optimum parameter for conduction of processes.

The study of the kinetics of heterogeneous catalytic processes in flow system is of great interest, since it can be applied in industry.

Nowadays there are no one view on the mechanism of dehydration of alcohols even on one and the same catalyst.

Consequently the kinetic study of well known monomolecular process of dehydration of alcohols by this method is of great interest. In this case it may be possible to obtain a new knowledge on the mechanism of the reaction under investigation. As starting materials ethyl, isopropyl, and tertiary butyl alcohols were taken, which differ, as known, by their reaction capability. Five types of aluminium oxide catalyst calcined in the temperature range 300-750°C were taken as catalysts.

This investigation was devoted in an attempt to follow the rôle of some textural properties, such as surface area, total pore volume and pore size distribution on the nature of intermediate catalytic complex formed during the process.

CHAPTER I.

L I T E R A T U R E

(1) The mechanism of heterogeneous catalytic dehydration of alcohols:

Although the dehydration of ethyl alcohol on aluminum oxide was discovered in 1797[1], passed one century, before the systematic study of conversion of alcohols on this catalyst[2-4].

Most of the uncertainities in the previous experimental data could be interpreted by three reasons:

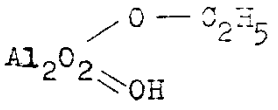
1) The importance of chemical nature of the used catalyst was not understood;
2) The absence of the accurate methods of analysis;
3) The field of using alcohols, nowadays, is much wide, therefore create new bases for understanding the mechanism of dehydration.

In the discussion of the mechanism of dehydration of alcohols, there is an openion to follow the data obtained in the conversion of one of the reagents e.g. ethanol on aluminum oxide were taken as reference. Most of these conclusions were based on the relations between ether and ethylene formation. Moreover many researchers had not taken into consideration the structure and the method of preparation of the catalyst and its changes during the

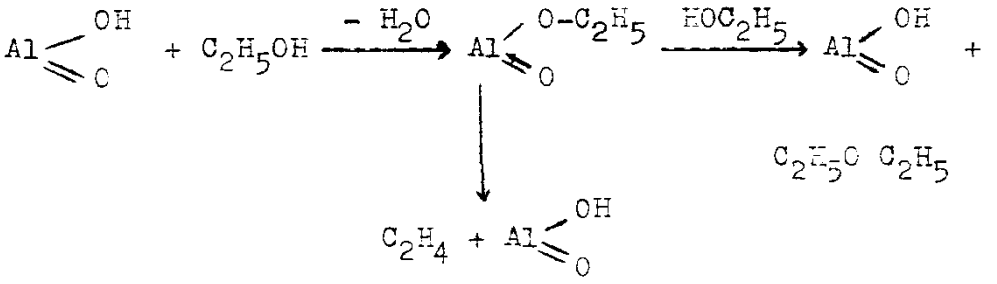
catalytic reaction which nowadays play the important rôle.

As a result of numerous processes of the dehydration of ethanol it was established that at temperature range 200 to 500°C the ethyl alcohol on aluminum oxide undergo dehydration with the formation of diethyl ether, ethylene and water. Ether, consequently can decompose to ethylene and water, the relation between the yeild of ether and ethylene depended on temperature at low temperature region the formation of ether was favoured[5-7], at the region of moderate temperatures ether and ethylene[9-11], at higher temperatures the alcohol gave practically only ethylene [12-14]. The boarder line of these regions depended on the activity and specific action of the catalyst[8]. The dehydration reaction of alcohols to ether was reversible[15] but the dehydration of alcohols to ethylene was practically irreversible[16]. In the dehydration of ethyl alcohol in flow system, the curve of yield of ethylene increased monotony with the increase of contact time, but the curve of yield of ether has a maximum[17, 18] the analogous dependence was observed for the yield of ethylene and alcohol for dehydration of diethyl ether[19].

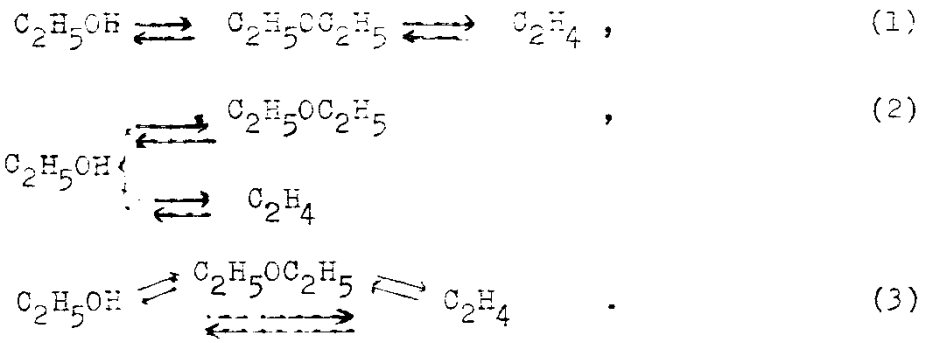
In 1904, Ipatieff[20] established, that ether and ethylene could be received as a result of consecutive reaction this proved the reversibility of the reaction of the dehydration of alcohols to ether and suggested that the catalyst of this reaction must contain some quantity of water. Then Senderens[21] suggested that the reaction proceeded through intermediate formation of surface complex



In 1936, Ipatieff[2] ascertained the following scheme



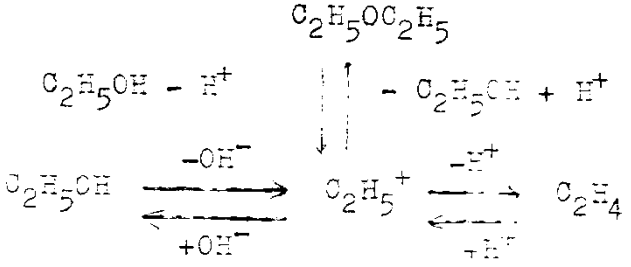
It may be conoluded, that ethylene can be obtained from alcohols by three different ways:



as shown from (1), ether is an intermediate product of dehydration of alcohol. However, this is not a general rule, hence the intermediate formation of ether is not observed by other catalysts[22].

Whitmore[23], on developing the idea of formation of carbonium ion, popularized the carbonium ion mechanism for the catalytic dehydration reaction. The use of the mechanism of sharing of carbonium ion in dehydration reactions of alcohols on aluminum oxide was supported by many other researchers[3-24, 25]. According to this mechanism the carbonium ion $C_2H_5^+$ can be formed at the adsorption of alcohol or ether on the catalysts.

It was shown[24], that in the limiting stage of this process a proton may be separated from the ethyl group of the adsorbed alcohol.

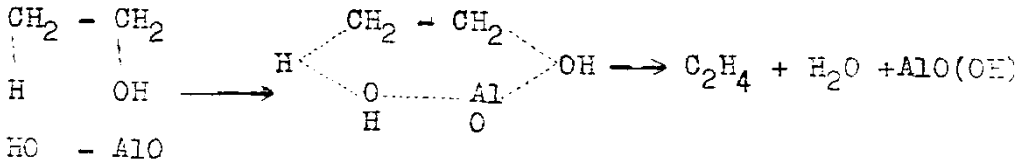


In 1951, Balaseani and Jungers[26] in the study of dehydration of ethanol and diethyl ether on aluminum oxide at 260°C to 400°C suggested the following scheme

$$2C_2H_5OH \xrightarrow{-H_2O} C_2H_5OC_2H_5 \longrightarrow C_2H_5OH + C_2H_4$$
$$\downarrow -\tfrac{1}{2} H_2O$$
$$\tfrac{1}{2}\ C_2H_5OC_2H_5$$

As shown in this scheme, the formation of ethylene is a second process.

Shulov[27], studied the probability of adsorption on centers of different types, which had polar bonds. In the case of dehydration of ethyl alcohol on alumina the reaction proceeded through the formation of active complex of alcohol on aluminum oxide catalyst, which has the form of six-membered ring with minimum strain of valency angle.

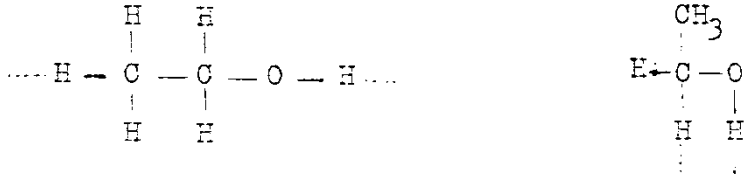


According to this scheme the coordination of unsaturated ion Al with polar hydroxyl group of alcohol, but the polar hydrogen of ethyl group interact with hydroxyl group of the surface of the catalyst. As a result in the process of dehydration the catalyst must exchange the proton with the reacted substance.

The dehydration reaction of alcohol has the index

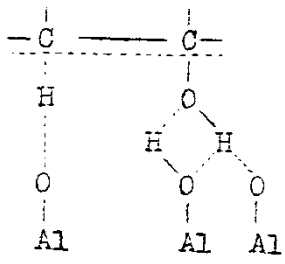
The process takes place, according to the multiplet theory of catalysis, through the formation of intermediate multiplet complex, analogous to the surface alcoholate[28],[81].

Schwab[29], on studying the dehydration and dehydrogenation of alcohol and formic acid on oxide catalysts, with the aim of ascertaining that the selectivity of oxides was independent on the porosity and method of preparation the following mechanism was suggested.



According to this mechanism, the dehydration proceeded mainly in the pores of the catalyst, on the other hand dehydrogenation on the surface. This conclusion was based on the observations, that the dehydration activity of aluminum oxide is lowered after heating at higher temperatures. When the disappearance of the defect of cristal lattice have occured.

According to Bucken and Wicke[30-32] the cyclic intermediate complex of the dehydration of alcohol on aluminum oxide has some different structure, than that suggested by Shulov [27].



here the donor was the electron pair of strong electronegative ion (the oxygen atom of aluminum oxide), but the acceptor is the weak negative —OH group of aluminum oxide. During the reaction the anion O^{2-} and hydroxyl OH^- exchange places.

Topshieva and Yun-Pin[8-11] established, that ether and ethylene could not be products of parallel reactions and they proposed the following scheme for dehydration of ethyl alcohol on aluminum oxide.

$$C_2H_5OH + HO\text{-}Al< \xrightarrow{-H_2O} \left[C_2H_5O\text{-}Al< \right] \xrightleftharpoons{+C_2H_5OH} (C_2H_5)_2O + HO\text{-}Al<$$

on the basis of this scheme there was an assumption about the formation of surface intermediate connections of the alcoholate type $\left[C_2H_5O\text{-}Al< \right]$ when the alcohol interacted with the active center of the surface >Al-OH. The surface connection could be decomposed at interaction with water or alcohol to give alcohol and ether. These processes were reversible. The active centers of dehydration on aluminum oxide were -OH groups.