# STUDIES OF THE PHYSICAL AND CATALYTIC PROPERTIES OF METAL SUPPORTED CATALYST IN FLOW SYSTEM UNDER NORMAL PRESSURE

## THESIS

SUBMITTED FOR THE DEGREE OF
**DOCTOR OF PHILOSOPHY**
IN
**Physical Chemistry**

BY

**Maha Kamel El-Aiashy**
(B.Sc., M.Sc.)

PRESENTED TO

**Chemistry Department**
UNIVERSITY COLLEGE FOR GIRLS
AIN SHAMS UNIVERSITY

1987

# STUDIES OF THE PHYSICAL AND CATALYTIC PROPERTIES OF METAL SUPPORTED CATALYST IN FLOW SYSTEM UNDER NORMAL PRESSURE

THESIS ADVISORS

APPROVED

Dr. ESSAM MOHAMED EZZO

Professor of Physical Chemistry

E. M. Ezzo

Dr. NADIA ABD EL-HAKIM

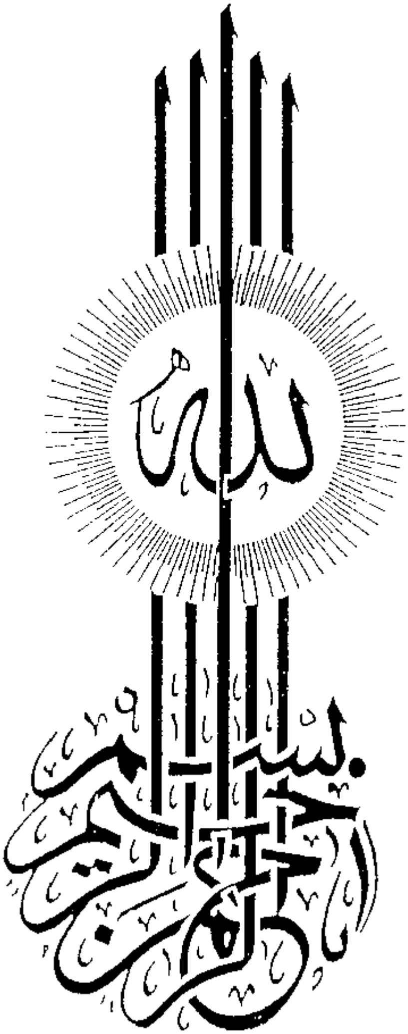
Assistant Professor of Physical Chemistry

N. A. Youssef

Dr. AISHA KASSAB

Lecturer of Physical Chemistry.

S. A. Awad


بسم الله الرحمن الرحيم

# ACKNOWLEDGEMENT

I which to express my deep sense of gratitude to **Dr. ESSAM MOHAMED EZZO,** Professor of Physical Chemistry, University College for Girls, Ain Shams University, for the helpfull supervision, his masterly guidance, suggesting the subject of this thesis and for discussing the results.

I am also grateful to **Dr. NADIA ABD EL-HAKIM,** Assistant Professor, Chemistry Department for her interest in the work and encouragement.

I am greatly indepted to Dr. **AISHA KASSAB,** Lecturer of Physical Chemistry, for her advice and encouragement.

I would like to offer my grateful respect to **Professor SALEH AHMED AWAD,** Head of Chemistry Department, University College for Girls, Ain Shams University, for his continuous co-operation.

Finally, I should not forget to express my sincere thanks to all members of Chemistry Department for their kind co-operation and friendship.

# CONTENTS

# AIM OF WORK

# AIM OF WORK

The chemical conversions, nowadays, play a considerable role in the industry processes, and their role increases with time. The catalytic processes, however, are the spinal column of the chemical industries for the activity and selectivity of these processes. Therefore, the synthesis of a new catalyst for new processes, and or the improvement of the used catalyst is one of the main factors for the technical success and the industry progress.

In the present investigation an attempt is made to prepare nickel alumina catalysts (with different dispersivity of metal), and to study the kinetics of the monomolecular model of heterogeneous catalytic dehydrogenation of cycloalkanes using a flow technique under normal pressure. Inspite of the intensive investigation of this subject, there is no general agreement on the nature of the intermediate even on one and the same catalyst.

The textural properties, thermal gravimetric analysis and X-ray diffraction are studied for the solid samples and also the nature of the intermediate heterogeneous catalytic complex formed during the catalytic action.

# INTRODUCTION

# CHAPTER I

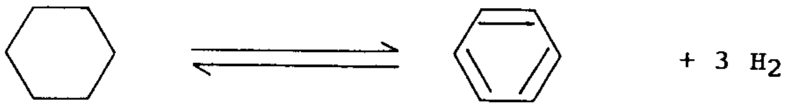
## INTRODUCTION

### I.A. The Mechanism of the Heterogeneous Catalytic Dehydrogenation

One of the most important problems, nowadays is the study of the kinetics of the heterogeneous catalytic reactions in order to throw the light on the mechanism of these processes. The heterogeneous catalytic hydrogenation and dehydrogenation,of different hydrocarbons on the metal supported catalysts, however, are of great interest, not only from the theoritical point of view, but also from the practical one. Besides, the determination of the optimum conditions for the proceeding of such reactions have great importance for the selectivity and activity of certain catalysts. It is well known(1) that the nickel alumina catalyst has a great value in petrochemical industries. Therefore, the study of dehydrogenation processes of conversion of cyclohexane over nickel supported alumina catalysts stimulates many investigators.

The conversion of cyclohexane (I) is one of the catalytic reactions with numerous contradictory statements(2).

Dehydrogenation catalysts are, in principle, the metals of Group VIII in the periodic table, copper oxides and sulphides of metals which are active in hydrogenation reactions. It is known(3) that the dehydrogenation process takes place at a temperature higher than that of hydrogenation. The catalysts of dehydrogenation are prepared by such methods to be active at a temperature range from 400°C-500°C.



**cyclohexane (I)** **benzene (IV)**

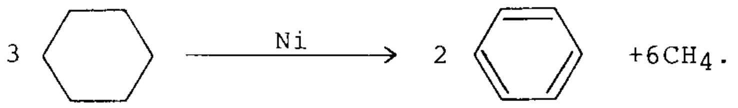
Since dehydrogenation reactions are endothermic reactions, then according to Le chatelier principle the decrease of pressure and increase of temperature should accelerate the rate of dehydrogenation reactions.

The first study of catalytic dehydrogenation was discussed by **Berthelot**(4) **in (1866)** and by **Sabatier et al.**(5) **in (1897)**, on studying aliphatic compounds:

$$nCH\equiv CH \xrightarrow{Fe} C_{2n} + nH_2;$$

$$H_2C= CH_2 \xrightarrow{Ni} HC\equiv CH + H_2.$$

The catalytic dehydrogenation of six-membered cyclic hydrocarbons using various catalysts, was discussed, by **Zelinskii**(6,7). On studying the dehydrogenation of cyclohexane over nickel catalyst, Zelinskii proposed the dissociation of C-C bond besides the dehydrogenation reactions:-



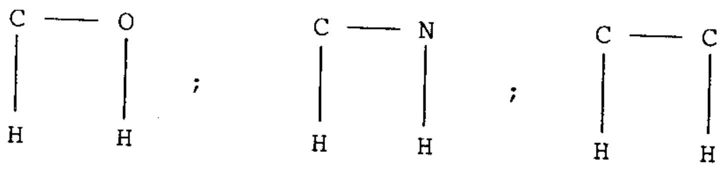
I IV

However, the conversion of cyclohexane was studied on nickel/glinsa catalyst at 330-350°C by **Zelinskii**(7,8) and **Shuiken**(8,9). The products were benzene, methane, toluene, xylene, methylcyclohexane and dimethylcyclohexane. Zelinskii and Shuiken proposed the formation of methyl radicals among the intermediate compounds, and gave the following reaction scheme:-

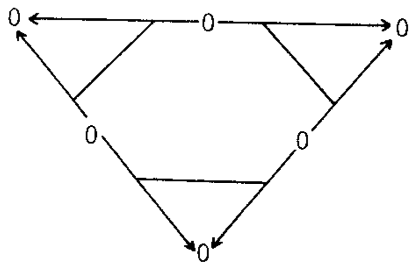
1. $C_6H_{12} \rightarrow \begin{cases} C_6H_6 + 3H_2 \\ 6\ CH_2; \end{cases}$
2. $CH_2 + H_2 \longrightarrow CH_4;$
3. $C_6H_6 + CH_2 \longrightarrow C_6H_5 - CH_3;$
4. $C_6H_6 + 2\ CH_2 \longrightarrow C_6H_4 - (CH_3)_2;$
5. $C_6H_{12} + CH_2 \longrightarrow C_6H_{11} - CH_3;$
6. $C_6H_{12} + 2\ CH_2 \longrightarrow C_6H_{10} - (CH_3)_2.$

The radical mechanism was supported by **Kiperman** et al.(10-12).

According to the multiplet theory of heterogeneous catalysis proposed by **Balandin**(13-22), the dehydrogenation reactions of aliphatic hydrocarbons contain in their indeces two hydrogen atoms. Besides, the index contains one more horizontal bond (which passes into a double bond during the reaction). The reaction is monomolecular and therefore more convenient for kinetic measurements. In the doublet mechanism of the dehydrogenation of alcohols, amines and hydrocarbons, the indeces are accordingly:



The multiplet theory(13-22) first gave the sextet model of the dehydrogenation of cyclohexane and its derivatives. The reaction took place nearly at 300°C on metal catalysts. The transitions of hydrogen atoms are shown by arrows in the following figure.



There is a geometrical correspondence between elements of symmetry of the molecule and the catalyst. A six membered ring was superimposed flatly on the (III) face. The atoms of the latter were arranged in the manner of equilateral triangles. The common basis of these discussions was the absence of intermediates like cyclohexene (II) and cyclohexadiene (III). The reacting molecule (I) was postulated to split the six hydrogen atoms after just one adsorption step. Benzene and hydrogen remain, then, as the only desorbed reaction products.

The carbonium ion mechanism was proposed to explain the isomerization products for the dehydrogenation of naphthenes(23). In 1968 **Block**(24) proposed the following general scheme of dehydrogenation of cyclohexane.

$$\begin{tikzcd}
I_{gas} \arrow[dd, shift right] & II_{gas} \arrow[dd, shift right] & & H_2 \text{ gas} \arrow[dd, shift right] & III_{gas} \arrow[dd, shift right] & & 2H_2gas \arrow[dd, shift right] & IV_{gas} \arrow[dd, shift right] & & 3H_2 \text{ gas} \arrow[dd, shift right] \\
& & + & & & + & & & + & \\
I_{ads}. \arrow[r, shift left] \arrow[uu, shift right] & III_{ads}. \arrow[l, shift left] \arrow[uu, shift right] & & H_2 \arrow[r, shift left] \arrow[uu, shift right] & III_{ads} \arrow[l, shift left] \arrow[uu, shift right] & & 2H_2 \arrow[r, shift left] \arrow[uu, shift right] & IV_{ads} \arrow[l, shift left] \arrow[uu, shift right] & & 3H_2 \arrow[uu, shift right]
\end{tikzcd}$$

According to Block the dehydrogenation of cyclohexane (I) proceeded by forming the intermediates; cyclohexene (II) and cyclohexadiene (III). Moreover, ionic radicals which are explained by the half-hydrogenated state of adsorbed hydrocarbons were found.

In 1969 **Richardson et al.**(25) studied the dehydrogenation of cyclohexane in a flow reactor on different oxide catalysts. The rate constants and the apparent activation energies were determined in the temperature range 400-465°C. It was shown that the reaction is essentially first order with respect to cyclohexane pressure. Comparison of the rate constants at 450°C for the studied oxides indicated that the catalytic activity is determined by the 3d electrons of the metal ion configuration. The results supported the application of crystal field theory to the formation of surface complexes. This point of view was previously given by **Jermen**(26) and **Krilov**(27).

In 1970 **Horescu and Rudenko**(28) studied the kinetics of dehydrogenation of cyclonexane and methylcyclohexane on Pt/C catalyst using a flow technique under low pressure from 700 mmHg to 70 mmHg. They found that the speed of dehydrogenation of methylcyclohexane was decreased 9 times, while that of cyclonexane was not affected by lowering the total pressure. They proposed the polymolecular mechanism for the dehydrogenation via the formation of polymolecular catalytic complex. This complex is formed owing to the condensation products on the catalyst surface. The rate determining step is the formation of this polymolecular catalytic complex.

The role of Pt/alumina and Pd/alumina catalysts in the dehydrogenation of cyclohexane were studied by **Maatman et al.**(29,30). It was shown that the reaction