

**Study of the heterogeneous Catalytic
reactions of Conversion of
Cycloalkanes on metal Supported
Catalysts in flow system
under normal pressure**

Thesis

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STUDY OF THE HETEROGENEOUS CATALYTIC
REACTIONS OF CONVERSION OF CYCLOALKANES ON METAL
SUPPORTED CATALYSTS IN FLOW SYSTEM UNDER NORMAL
PRESSURE

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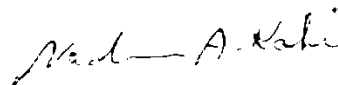
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" TO THE SPIRIT
OF MY FATHER "

C O N T E N T S

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LITERATURE

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CHAPTER I

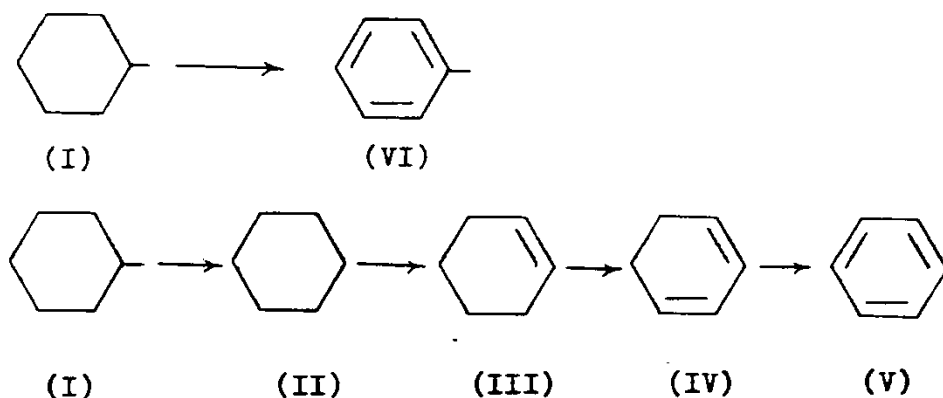
I N T R O D U C T I O N

I.A. The Mechanism of Catalytic Conversion of Methylcyclohexane:

The formation of aromatic hydrocarbons by the catalytic dehydrogenation of saturated six-membered ring is a well known reaction . The transition metals and their oxides are active catalysts for such dehydrogenation reactions .

The two⁽¹⁾ known basic modes of methylcyclohexane decomposition that can take place simultaneously over metal oxide catalyst are :

- a) dehydrogenation to form toluene .
- b) dehydrodemethylation to form benzene..



According to the multiplet theory of catalysis the dehydrogenation of hydrocarbons was treated as a free radical mechanism which is supported by Zelinskiy⁽²⁾.

The multiplet theory considered that the-CH₂ parts of the molecule get into the deepest valleys, this must lead to an activated adsorption which is often accompanied by the break of a bond .

In 1960 Hurwitz and others⁽³⁾ studied the kinetics of methylcyclohexane dehydrogenation over Pt/Al₂O₃ catalyst at 315 - 372 °C, and at methylcyclohexane partial pressure ranging from 0.07 to 2.2 atms., and hydrogen pressure ranging from 1.1 to 4.1 atms. The reaction was zero order with respect to methylcyclohexane and hydrogen. The activation energy for the reaction was 33 Kcal/mole . The near zero order behaviour of the reaction suggests that the active sites of the catalyst are almost completely covered with adsorbed hydrocarbon molecules or radicals formed from the methylcyclohexane . Since the adsorption of methylcyclohexane probably involves dissociation of hydrogen from the molecule, thus increasing hydrogen pressure, and reducing the concentration of the adsorbed species, which results a decrease in the rate of toluene formation .

It is suggested that the active sites of the catalyst are heavily covered with adsorbed toluene, which is then desorbed from the surface, and that the reaction rate corresponds to the rate of desorption of toluene . It is supposed that the rate determining step is the rate of toluene desorption .

In 1965, Balandin⁽⁴⁾ explained the dehydrogenation of methylcyclohexane using a flow system over a catalyst composed of 82 % Al_2O_3 , 3 % K_2O , and 15 % Cr_2O_3 at 470 - 520 °C , the activation energy was 17.3 Kcal/mole .

Accordinging to the multiplet theory; the extra-index parts of the molecule, do not change on catalysis and do not influence much the course of the reaction i.e. the substituted cyclohexanes as become evident from kinetic research⁽⁵⁻⁶⁾ are dehydrogenated, similarly to cyclohexane itself with very similar activation energies . This suggests an edgewise orientation of the ring, the index group pointing toward the catalyst. Thus on Cr_2O_3 for cyclohexane , methylcyclohexane, and 1,3-dimethylcyclohexane the activation energy is equal respectively to 25.9, 23.7 and 22.2 Kcal mol⁻¹ .

Reaction with added C^{14} , methylcyclohexane was shown to take place without any hydrogenation of methylcyclohexene or toluene ; no evidence for irreversible catalytic change of methylcyclohexane was found . The rate of dehydrogenation of methylcyclohexane and methylcyclohexene were very close to each other .

David, Burton ⁽⁷⁾ investigated the dehydrogenation of methylcyclohexane over $Pt-Al_2O_3$ catalyst by using C^{14} tracer . It was found that the C^{14} distribution in the products shows that methylcyclohexane is converted primarily to aromatic compound . Dehydrogenation to toluene and demethylation to benzene occurs by a metal catalyzed pathway . Conversion of the aromatics (or naphthalene) to paraffins occurs by a dual-functional metal-acid pathway.

The direct degradation dehydrogenation was also studied by many authors ^(8,9). It was suggested that the formation of C_6H_6 and CH_4 in the dehydrogenation of cyclohexane ring of methylcyclohexane were due to C - C bond rupture at $280 - 400^\circ C$. The main products were methylcyclohexene isomers and toluene . The rate determining step in dehydrogenation of methylcyclohexane was the formation of methylcyclohexene . Corma et al ⁽¹⁰⁾ in (1980) studied the kinetics for the dehydrogenation of methylcyclohexane to toluene over Pt on Na Y zeolite at $340^\circ C$ and

1 atm. Cumulative conversion data yielded rate constants for both dehydrogenation and catalyst decay . The reaction occurs via a series of consecutive partial dehydrogenations, the first dehydrogenation being the rate determining step .

The kinetics of the dehydrogenation of methylcyclohexane over Na Y zeolite containing 5 wt. % Pt as a catalyst was studied in the presence of hydrogen by Lopez (11) in a flow system at 350 - 390 C° and atm. pressure . The results were analyzed by the Hougen Watson method and indicate a rate determining surface reaction (two equal sizes) and a step-wise mechanism.

In 1981, Corma, A., Agudo (12) studied the isomerization, dehydrogenation and cracking of methylcyclohexane over HNA-Y zeolites . It was found that the fractions of acid sites which are active for the above reactions do not increase linearly with increasing degree of exchange. Isomerization and dehydrogenation involve a similar activated complex; cracking proceeds through a different activated complex and requires stronger acid sites . Activation energies are independent of exchange degree.

I.B. The Mechanism of Heterogeneous Catalytic Dehydrogenation of Cyclohexane :

One of the essential problems in heterogeneous catalysis is studied by means of the undisturbed analysis and through the description of the reaction intermediates . In the recent years, new techniques have lead to conceivable principles which permit a reaction to be described as a " radical mechanism " or a " carbonium ion mechanism " . These classifications are still insufficient for predicting catalytic systems . A more detailed explanation of surface reactions is still far from being complete, and the prediction of catalytic mechanisms in terms of molecular action faces numerous uncertainties . Evidently, reaction intermediates are described primarily as chemical entities with definite chemical composition . Moreover, the degree of intramolecular excitation and the behaviour of molecular energy exchange as an intermolecular property are decisive . Since these fundamental questions of excitation are generally unknown even for homogeneous reactions, investigations in heterogeneous catalysis have first to be restricted to simple structural problems of intermediate compositions .

The dehydrogenation of cyclohexane (II) is one of the catalytic reactions with numerous contradictory statements.
