PHYSICAL STUDIES OF BIMETAL CATALYSTS IN THE HETEROGENEOUS REACTIONS

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PHYSICAL STUDIES OF BIMETAL CATALYSTS IN THE HETEROGENEOUS REACTIONS.

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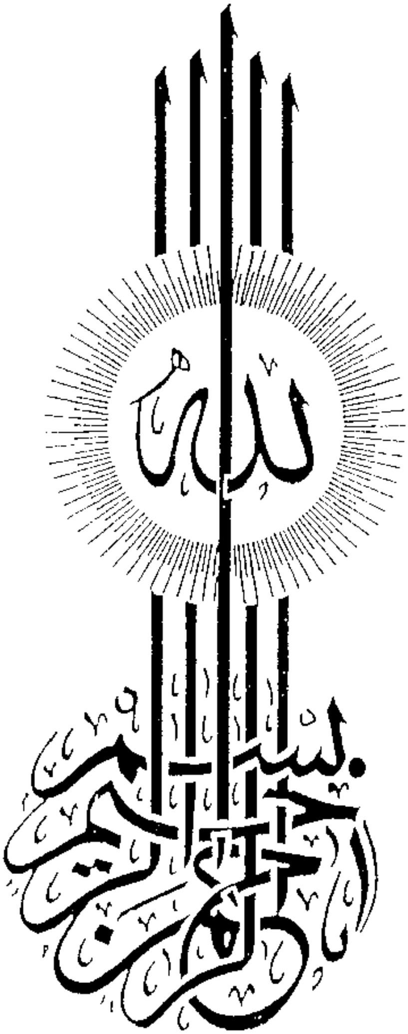
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Note

Besides 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. *Mechanism Electro Chemistry.*
2. *Spectroscopy.*
3. *Instrumental Analysis.*
4. *Surface Chemistry.*
5. *Polymer.*
6. *Photochemistry*
7. *Quantum Chemistry*
8. *Thermodynamics.*
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10. *Advanced reaction mechanism.*
11. *German Language*

She had successfully passed a written examination in these courses.

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CONTENTS

OBJECT OF THE WORK

The heterogeneous catalysis using transition metals on supports as catalysts is frequently applied at present. The object of the design of a complex catalyst for a new process is to prescribe a set of solid phases suitable in their specificity, their manner of association, their physical form and their methods of preparation and use.

In a previous study three bimetal nickel-silver supported on alumina were prepared with different degrees of dispersivity of metals and were studied in model reaction of dehydrogenation of cyclohexane by flow technique under normal pressure. A set of relations were found depending on metal, metal support interaction.

In the present investigation two bimetal nickel-molybdenum supported on alumina were prepared in an attempt to improve the catalytic activity of nickel alumina. The catalytic activity of the prepared solids was studied in the vapour phase conversion of cyclohexane and disproportionation of cyclohexene by flow system under normal pressure.

The textural proporties, thermal gravimetric analysis and X-ray diffraction were studied for the solid samples and the mechanism was proposed.

INTRODUCTION

CHAPTER I

INTRODUCTION

I.A. Bimetallic Catalysts:

The subject of the two or more components in catalysts as can affect their activity and selectivity has been well known for a long time [1]. Bimetallic catalysts, however, have been of interest to workers in heterogeneous catalysis. Since bifunctional catalysts play an important part in basic petroleum refining processes such as catalytic reforming and C_8 aromatic isomerization.

Many of the early works in this area were conducted with conventional metal alloys prepared in a suitable form for catalytic studies. A major theme of the works was the investigation of the relationship between catalytic activity and the electronic structure of metals [2]. The studies were conducted on unsupported metal alloys and involved only few selected reactions.

The synthesis or preperation of bimetallic catalysts, as with catalysts in general, is a highly important aspect of research and technology in the field. Since techniques for catalyst preparative variables have been useful in understanding the effects for catalyst characterization (stability, selectivity and activity). The preparation of bimetallic catalysts is divided into two parts, one on unsupported bimetallic systems and the other on supported systems.

Many commercial catalysts, however, supported on high surface are carriers [3-7]. These catalysts are characterized by having higher surface areas than unsupported metals, and are more resistant to surface area loss by sintering. The preparation of such highly dispersed bimetallic catalysts can be carried out by impregnating a high surface area carrier with an aqueous solution containing the appropriate concentrations of salts of the two metals. If the two metals do not interact in the highly dispersed state, one would expect to see an additive catalytic behavior of the individual metallic entities. However, if the metals do interact, one might expect to find a different behavior, especially if the individual metals have very different catalytic activities for a given reaction [4,5]. The term bimetallic cluster was chosen rather than alloys in referring to highly dispersed supported bimetallic systems in which significant interaction between the metallic components is indicated [Sinfelt et al.].

Indeed, for supported metals in particular, the support was initially perceived only to disperse the active metal, increasing and preserving its effective surface area. More recently [8], it has been accepted that the support can influence the activity of the metal by strong metal support interaction (SMSI) [2].

It was found that the catalytic properties of bimetallic system of a group VIII metal of the periodic table (iron-cobalt-nickel) with a group IB metal (copper-silver-gold) is of interest for hydrogenation and many conversion reactions. Owing to that the electronic structure of the group VIII metal in such that the band is only partially filled, whereas the d band of the group IB is completely filled. According to the early hypothesis, the addition of group IB metal gave an alloy with a more completely filled d band [2]. Besides, the group VIII-Group IB metal systems are still highly interesting in catalysis, since they exhibit a high degree of specificity with regard to the type of reaction being catalyzed.

Many of the researches which have been done with bimetallic catalysts have involved combinations of two metals of group VIII (Fe-Ni and Co-Ni), or of group IB (Ag-Au and Cu-Ag), these are of special interest for the partial oxidation of olefines, and of combination of a group VIII metal with a metal of group IB (Cu-Ni) [3-6].

The states of the two components in bimetallic catalysts are often poorly characterized and it is therefore difficult to settle how one of the components affects the catalytic properties of the other. Progress can be achieved by studying precisely built bi-metallic systems with smaller particle sizes than those obtained by reducing mixtures of metal oxides or salts [4].

The composition of an alloy surface, as well as its structure, plays an important role in its catalytic activity. Gibbs [9] showed a century ago that the composition of an alloy surface is not necessarily identical to its bulk composition; rather one element may segregate to the surface. This has been accepted recently by many authors (6,8).

Bimetallic systems have been the subject of growing interest in catalysis [6,10,11]. In particular with bimetallic catalysts composed by alloying two group VIII metals, recent accounts describe a wide-ranging set of experiments concerning their preparation, characterization and stability [11-13]. The reactivity of these alloy catalysts has also been tested in isomerization [14], hydrogenolysis [15], deuterium exchange [16] and hydrogenation reactions [17,18].

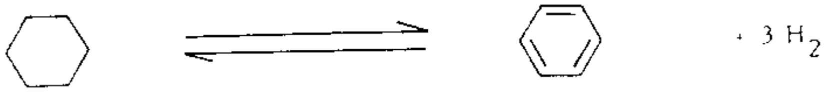
One of the factors which has renewed interest in catalysis by alloys was the finding that for various hydrocarbon conversion processes, the conventional platinum catalysts could be substantially improved by the addition of certain metals, such as Re, Ge, Sn [19], Pd[15,20], Mo [21] and Tc [22].

Bimetallic systems Ni-Mo/Al_2O_3 have been studied for various hydrocarbon decompositions [23-28].

I.B. The Mechanism of the Heterogeneous Catalytic Dehydrogenation

The conversion of cyclohexane (I) is one of the catalytic reactions with numerous contradictory statements [29].

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 [30] 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)

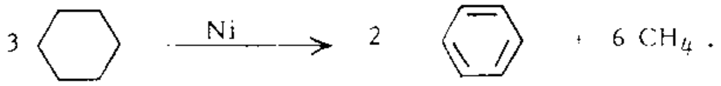
Since dehydrogenation reactions are endothermic reactions, then according to Le Chatelier principle the decrease of pressure and increase of temperature should accelerate the rate of dehydrogenation reactions.

The first study of catalytic dehydrogenation was discussed by Berthelot (31) in (1866) and by Sabatier et al. (32) 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 (33,34). On studying the dehydrogenation of cyclohexane over nickel catalyst, Zelinskii proposed the dissociation of C-C bond besides the dehydrogenation reactions:-



I IV

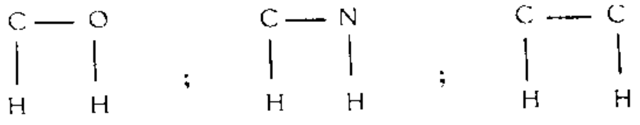
However, the conversion of cyclohexane was studied on nickel/glinsa catalyst at 330-350°C by Zelinskii (34,35) and Shuiken (35,36). The products were benzene, methane, toluene, xylene, methylcyclohexane and dimethylcyclohexane. Zelinskii and Shuiken proposed the formation of methyl radicals among the intermediate compounds, and gave the following reaction scheme:

1. $$\begin{tikzcd} & C_6H_6 + 3H_2 \\ C_6H_{12} \arrow[ur] \arrow[dr] & \\ & 6\ CH_2; \end{tikzcd}$$

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. (37-39).

According to the multiplet theory of heterogeneous catalysis proposed by Balandin (40-49), 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:



$$\begin{array}{cc} C - & O \\ | & | \\ H & H \end{array} ; \quad \begin{array}{cc} C - & N \\ | & | \\ H & H \end{array} ; \quad \begin{array}{cc} C - & C \\ | & | \\ H & H \end{array}$$