CONVERSION OF METHANOL OVER PALLADIUM SUPPORTED ON ALUMINA

A THESIS

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بسم الله الرحمن الرحيم

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SUPPORTED ON ALUMINA.

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TO MY FAMILY

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NOTE

The canadidate has attended postgraduate courses for one year in inorganic and physical chemistry covering the following topics:

1. Surface chemistry.
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3. Symmetry and Molecular spectroscopy.
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INTRODUCTION

1. Conversion of alcohols over alumina:

The dehydration of alcohols to ether and/or olefins has been investigated by many workers[1-4]. In the dehydration over solid catalysts, ether formation takes place at lower temperatures, while at higher temperatures it proceeds to olefin formation except in methanol. The reaction takes place also in the liquid phase in the presence of an acid such as sulphuric acid or phosphoric acid. The analogy between the reaction over solid catalysts and that in the liquid phase suggests that the decomposition proceeds, via a protonized compound[5]. Alkoxide groups can be observed by IR-spectroscopy [6] and the decomposition proceeds via the alkoxide groups on the surface[3,4].

The heterogeneous alumina catalyzed dehydration of methanol has been known since the end of the 18 th century. Neverthless, it is only recently that efforts have been made to explain the elementary processes in heterogeneously catalyzed eliminations[15].

Ethanol decomposes over alimina above 120°C to form dimethyl ether and water but at higher temperatures ethylene is also formed in addition to ether[7].

YUKOS and ONISHI[7] found that above 180°C, ethylene and water the only decomposition products. When the decomposition of ethanol was followed with time in the circulating system, the evolution of dimethyl ether showed the same behavior, but ethylene formation was very slow at lower temperatures. In the initial stage, the water produced was absorbed on the surface. As ethanol in the vapor phase was consumed, the maximum point of ether formation appeared, while ethylene continued to increase. The chemisorbed species of ethanol were ethoxide group and hydrogen in the reaction temperature range 120-180°C, above 180°C the acetate form was also form was also formed on the surface [8]. Ethylene was also produced from the decomposition of diethyl ether.

$$ETOH \dashrightarrow Et\,O_{(ads)} + H_{(ads.)} \begin{cases} \rightleftharpoons EtOEt + H_2O \\ \rightarrow C_2H_4 + H_2O \end{cases} \quad ....(1)$$

Isopropanol decomposes over γ-alumina above 120°C to form propylene and water[7]. The rate of propylene formation was independent of the pressure of propanol, and proceeded continuously when propanol was trapped out of the circulating gas, first at a similar rate, then slowing down as the alcohol adsorbed on alumina surface decreased, thereby indicating that the rate of propylene formation is determined by the decomposition of the adsorbate on the surface.

By use of infrared spectriscopy, it was confirmed that the spectrum of chemisorbed isopropanol was the same as that of aluminium isopropoxide, thus isopropanol chemisorbs on alumina with dissociation to an isopropoxide group and hydrogen [7]. The decomposition rate of propoxide group was the same as that of evolution of propylene. The propoxide group on the surface behaved homogenously, and the decomposition proceeded down to zero coverage according to first order decay. The kinetic measurements indicated that water absorbed behaves as an inhibitor for the decomposition[7]

$$\text{i-prOH} \dashrightarrow \text{i-prO}_{(ads.)} + H_{(ads)} \dashrightarrow C_3H_6 + H_2O \quad \ldots\ldots(2)$$

Generally, two competing mechanisms were suggested for ether formation, namely:

(i) The Langmiur-Hinsheldwood mechanism:[9,10]

The ether is formed from surface alkoxide groups and molecular adsorbed alcohol