STUDY ON THE CATALYTIC AND PHYSICAL CHARACTERISTICS OF THERMALLY TREATED SUPPORTED COBALT OXIDE CATALYSTS

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Study on the Catalytic and Physical Characteristics of Thermally Treated Supported Cobalt Oxide Catalysts

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بسم الله الرحمن الرحيم

TO MY PARENTS

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Salwa A. Sadek

NOTE

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

1. Advanced Surface Chemistry.
2. Advanced Electrochemistry.
3. Statistical Thermodynamics.
4. Quantum Chemistry.
5. Solvent Extraction.
6. Nuclear Chemistry.
7. Inorganic Reaction Mechanism.
8. Application on Group Theory.
9. Analytical Chemistry.

She has successfully passed a written examination in these courses.

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I. INTRODUCTION

I- INTRODUCTION

The catalysis and surface chemistry of solid catalysts is a subject which has developed very rapidly in the course of the last two or three decades. Its scope is extraordinarily wide, for it deals with all those chemical and physicochemical phenomena occuring mainly on the catalyst surface. Thus, the study of the catalytic and surface properties of solids, in particular, their specific activity, specific surface area and behaviour towards activation and sintering is of great importance in industry, as well as, in academic research.

Supported catalysts find widespread application in the oil, gas, and chemical industries. The purpose of the support in these catalysts is basically twofold: (i) to facilitate the preparation of a well-dispersed, high surface area catalytic phase (ii) to stabilize the active phase against loss of surface area. Until recently, the effects of support and dispersion on activity and selectivity of the active metal or metal oxide phase were generally assumed to be of secondary importance.

Recent investigations$^{(1-8)}$, however, have provided evidences that the support can significantly influence the morphology, adsorption, and activity/selectivity properties of the active phase, especially in well-dispersed systems.

1.1. Current Trends in the Assessment of Physical Characteristics of Titania Support:

Recently, interest in titanium oxide as a support in heterogeneous catalysis has grown appreciably. Although the support is frequently an inert material and is considered to have little effect on the catalytic properties of the metal in contact with its surface, a study by Tauster and co-workers(2), however, showed that metal-support interaction (SMSI) does exist for G VIII noble metals on TiO_2.

One of the more important areas in which the support has a positive role to play is in chemical interaction with the catalyst. In the first kind of interaction, the geometry of the catalyst is dependent upon the support, at least to some extent. Preparation methods are also important in determining catalyst crystallite size and the extent of such catalyst - support interaction(9). The second kind of support-catalyst interaction occurs in alloys or in solid solutions of two metals, where a catalytically inactive metal (i.e. support) could affect the structure of the active catalyst. The third kind of interaction usually involves deactivation of a catalyst as a result of chemical reaction between the catalyst and the support. Perhaps the most widely known example of the latter type of interaction is the formation of spinels(10), with subsequent loss of catalytic activity. The fourth kind of catlyst-support interaction rests on the ability of some adsorbed gas to move across the surface from the catalyst to the support. This phenomenon, known as spillover, can be very important in the context of hydrogenation reactions(11,12).

Regarding the specific properties of titania support as discussed in literature, it seems worthy to recall some of its main characteristics.

The deviation from stoichiometry, charactiristic for titania was interpreted in view of the proposed model, assuming a defect structure involving both divalent O vacancies, and tri - and tetravalent titanium ions(13).

In the studies of some specific aspects of O-deficient TiO_2, an attempt was made by Buessem and

Buttler(14) to distinguish between two mechanisms that could account for the loss of O from TiO_2 at elevated temperatures;

$$2Ti^{+4} + O^{--} \rightleftharpoons AV + \frac{1}{2}O_2 + 2Ti^{+++} \quad \text{and}$$

$$O^{--} \rightleftharpoons AV + \frac{1}{2}O_2 + 2e^{-} \quad (AV = \text{anion vacancy})$$

The comparison of velocity constants, based on statistical mechanics, favoured the first reaction.

An x-ray study by Magneli(15) in the Ti-O systems revealed that, the simple tetragonal structure of TiO_2 undergoes an increasing distortion by decreasing O-content. The excess of Ti atoms in the defect structure was found to occupy interstitial positions.

Certain properties of thermally treated hydrous titania have attracted the attention of some researchers. For example, the specific surface area was found to decline continuously with increasing the temperature of calcination, yet, the pore volume showed little change below 600°C. Between 600° (which is close to the Tamman's temperature) and 1000°C, the loss of specific surface area was accelerated and the pore volume diminished markedly(16).

During the sintering of TiO_2; anatase type; electron microscopic study(17) has shown that, 3-temperature regions could be recognized. Below 900°C, growth of