STUDIES ON THE PHYSICO-CHEMICAL PROPERTIES OF NICKEL OXIDE CATALYST

A Thesis

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STUDIES ON [illegible] PHYSICO-CHEMICAL
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CATALYST

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CHAPTER I

INTRODUCTION

For long-time, the phenomena of heterogeneous catalysis have been known to involve gas adsorption by solids (1). According to Taylor (2 & 3), the active fraction of the catalytic surface is due to certain sites or active centres. Since for high catalytic activity the chemisorption of reactants should be weak and rapid, the factors which affect the velocities of adsorption and desorption of reactants and the heat of adsorption determine the catalytic activity of the catalyst . The geometric factor which is connected with the lattice spacings of the catalyst (4) is known to affect mainly the velocities of adsorption and desorption of the reactants while the electronic factor which is related to the electronic structure of the catalyst affects mainly the heat of adsorption.

A- Catalysis by Semiconductors

A-1. Introductory Remarks :

Metal oxides are either semiconductors of various types or insulators. The experimental results obtained during the last twenty years indicate that the electronic structure of semiconductors controls their electrical ,

optical and magnetic properties. Sometimes the electronic structure determines also the catalytic activity of the semiconductor oxides (5 & 6). Wilson and Fowler (7 & 8) have proposed an energetic model for semiconductors. The different energetic levels which can be occupied by the electrons of the solid are gathered in two bands called the valency band and the conductivity band. These two bands are separated by an energetic gap called the forbidden band. Sometimes, an energetic level exists in the last band which is called the impurity level. Such level is due to the presence of a defect in the crystal structure of the solid. According to the position of the impurity level in the forbidden energy band, two types of semiconductivity can be distinguished. When this level is situated near the conductivity band, and the passage of electrons is possible from this level to the conduction band, an n-type semiconductor results. Such type of semiconductors is exemplified by ZnO and TiO_2 where the nonstoichiometry results from a deficiency in the oxygen content and these semiconductors are called normal or negative hole semiconductors. On the other hand, when the impurity level is situated near the valency band it can accept electrons from the valency band and we receive the abnormal p-type or positive hole semiconductors

(NiO and Cu_2O which have an excessive oxygen content). Besides the n- and p-types of semiconductors which are called the extrinsic types of semiconductors, we have a third intrinsic type (Germanium). In this third type, the thickness of the forbidden band is not great enough to prevent the passage of electrons from the valency band to the conductivity band and vice versa.

Thus, the electrical conductivity in n-type semiconductors is due to transfer of electrons in the conduction band while in p-type semicondutors, the conductivity is governed by the positive holes in the valency band. The concentration of the impurity centres defined by the number of electrons transferred to the conductivity band or taken from the valency band determines the semiconducting character of the solid. This character depends upon a certain parameter called the Fermi level which, from the thermodynamic point of view, has a value corresponding to the average free energy or chemical potential of the crystal. The position of the Fermi level depends on the number of ionized centres contained in the solid, i.e., on the number of electrons gained by the conduction band or lost from the valence band. Therefore any change in the number of these centres results in a shift of this level. The relation between the surface properties of semiconductors and the position of the Fermi level has been discussed

by Wolkenstein (9). According to this author, the position of the Fermi level affects the chemisorption capacity of the surface, the amount and sign of surface charge, the relative proportions of the different forms of adsorbed gas and finally the catalytic activity of the surface and its reactivity to a certain catalytic reaction. Shifts in the position of the Fermi level can be produced by the adsorption of a gas where electron transfer occurs, by increase of lattice defects which create levels that are acceptors or donors of electrons and finally by introduction in the solid of ions having a different valence from that of the lattice ions. The last process is called doping and results according to the principle of valence induction (10 & 11) in a shift of the Fermi level.

A-2 Chemisorption of Gases by Semiconductors :

i - Mechanisms of Adsorption :

The adsorption of a gas by a solid semiconductor may be accompanied by a variation of the electrical conductivity of the solid. In this case the adsorbent acts as a donor or acceptor of electrons depending on whether the gaseous molecule can give or receive one or

more closely now. The direction of electron transfer depends on the respective positions of Fermi level and of the acceptor and donor levels of the adsorbate, i.e., on the work function of the solid and on the electron affinity and ionization potential of the molecule. The chemisorbed gas brings about superficial imperfections which lead to the appearance of new energy levels in a manner that the electrical character of the surface is totally different from that of the bulk of the crystal. The existence of these energetic levels have been considered by Barden (12) in an attempt to explain certain electrical properties of germanium. This author declares that a double energy barrier is formed at the surface of the crystal during adsorption and that this barrier raises the energy level in comparison with that of the bulk of crystal. The effect of such a barrier has been discussed by several authors (13, 14 & 15).

According to Fensham (16) when O_2, an electron acceptor gas, is chemisorbed on an n-type semiconductor the electrons are transferred from donor sites towards the surface which leads to decrease of conductivity. When the quantity of adsorbed gas increases the crystal surface is charged negatively and consequently positive charges are formed beneath the surface. The electric

field so formed between the adsorbed layer and the surface weak energy levels increases the potential of the energy levels of electrons which makes the adsorption more and more difficult since the transfer of electrons necessary for the chemisorption takes place with an increasing difficulty. In case of a p-type semiconductor, the adsorption of oxygen is accompanied by removal of electrons from the filled valence band towards the impurity level and the remaining holes cause increased conductivity . The electrical field thus created is much more weak and the energy barrier to be crossed is therefore much more weak also. Hauffe (5) has called the adsorption in this case cumulative adsorption while in n-type semiconductors it is a depletive adsorption. The existence of a potential barrier which increases during adsorption leads to the expectation of an adsorption limit achieved when this barrier prevents the transfer of electrons. In case of depletive adsorption, this limit is achieved after a small coverage of the surface and the results of adsorption of H_2 on Cu_2O (17) and O_2 on ZnO (18) are concordant with this hypothesis. On the other hand, cumulative adsorption must lead to high surface coverages which was observed for O_2 adsorption on Cu_2O (19) and on NiO (20) and for H_2 and CO adsorption on ZnO (21).