1. INTRODUCTION

1.1. General

The art of catalysis has made great strides in recent years; theory still lags behind, but there have been promising developments. These developments, especially in the field of contact catalysis, has depended to a considerable extent on the evolution of our knowledge of the structure of solid state. The discovery of new experimental techniques has been equally important. But although we are nearer to an understanding of those factors which determine whether a solid shall or shall not be a good catalyst for a particular reaction, the prediction of catalytic activity underlying the selection of catalysts for a given reaction still remains one of the most important and complicated problem of the theory of catalysis. One can only hope to unravel the complicated problems by penetrating deeply into the heart of quite a number of major portions of the broad realm of catalysis. The presentation in this thesis is limited to a study of the electrical conductivities of some solid oxides and their catalytic activities. The discussions in the introduction will

therefore be mainly on the developments in our knowledge of the structure and properties of the solid state and on the background to the fields of chemisorption and catalysis.

The interplay of structure and properties of solids can be expressed in essentially two ways. One is to relate the structural features to the observed properties in a phenomenological way. The other is to make use of mathematical theories developed mainly with the aid of statistical mechanics and quantum mechanics to describe the behaviour of materials under the influence of various forces. So far as inorganic crystals are concerned, we may note the realisation that coulombic rather than resonance or exchange forces play the predominant role in the cohesion of solids. In the case of catalytic activity, however, where interaction between molecules and surface forces of solids need to be understood, the problem becomes more complex.

The physical properties of solids are determined to a large extent by the electron distribution; it is thus possible on an empirical basis, to divide solids into different groups corresponding to different types of electron distributions. Seitz(1) has classified crystalline solids into the following five empirical

types: (i) metals,(ii) ionic crystals, (iii) valence crystals,(iv) semiconductors and (v) molecular crystals. Of these, metals and semiconductors appear most frequently as active agents in heterogeneous catalysis, although ionic crystals (alumina) and valence crystals (silicon carbide) are common as catalyst supports.