

1. INTRODUCTION

1.1. General :

Results of pure research and experiences in industrial practice have shown beyond doubt that heterogeneous catalysis is a phenomenon associated with the surfaces of solids. Though in its applied aspects catalysis is largely centred in chemistry, chemical physics has helped in establishing firmer foundations through the development of new experimental methods and sound theories which conjoin catalysis to solid state science¹. In earlier years such a link was sought to be secured on the basis of semiconductor physics^{2,3}. Notwithstanding conflicting claims on the type of relationship between collective electrical properties and catalysis, a general correlation between catalytic activity and width of the forbidden zone of a semiconductor catalyst has been recognised⁴. Another property, the determination of which has been found frequently helpful in defining or solving a problem in catalysis is magnetic susceptibility⁵. Surface area and surface acidity are two other features of a catalyst surface which are of vital importance to catalysis since catalytic rates depend primarily on the availability and effectiveness of the active centres. As a consequence special emphasis has been laid on physico-chemical characterisation of catalysts prior to their use in various heterogeneous catalytic reactions.

1.1.1. Catalysts for Oxidation :

Most of the more important catalysts for heterogeneous reactions are metals or oxides. Metals are undoubtedly unsurpassable catalysts for hydrogenation. In oxidation reactions, however, only those metals which themselves do not get oxidised at the high temperatures prevailing in the reaction zone can be used as catalysts. At least surface oxidation is bound to occur on all metals except the noble ones like platinum, gold and silver, which pre-eminently resist getting oxidised. Cost considerations and risk of surface fouling preclude any large scale use of these noble metals. Moreover, in the few instances where a noble metal has been used as catalyst it turned out to be only a dehydrogenation catalyst⁶.

Oxides, on the other hand, can reversibly adsorb gaseous oxygen, or allow their lattice oxygen ions to participate in the reactions and have them replenished by gaseous oxygen, or bring into play the Lewis or Bronsted acid or basic sites present on their surfaces. Further, their insulating or semiconducting behaviour offers immense scope for modifying their catalytic properties either through formation of intrinsic defects (vacancies) or doping with impurities or both. Oxides of the p-type, for instance, activate oxygen by cumulative adsorption⁷ or convert lattice or adsorbed O^{2-} ions to the more reactive O^- ions through the agency of holes⁸.

Transition metal oxides are frequently used as oxidation catalysts because of the presence of partially filled d orbitals

in them, the consequent ease of remaining in more than one oxidation state and the ligand field produced by oxygen on these orbitals. Combination of a transition metal oxide with a second transition metal oxide or a non-transition metal oxide often gives rise to synergetic effects (as for instance in $V_2O_5-MoO_3$ and $V_2O_5-Al_2O_3$), or acts as a bifunctional catalyst ($Bi_2O_3-MoO_3$). Irrespective of whether it is a binary mixture or a chemical compound, the combination is more effective than the individual components. The chemical compounds so formed, usually known as ternary oxides, owe their catalytic activity primarily to their specific crystal structures. For instance, on ternary oxides of the perovskite type, each reacting gas molecule can adsorb only on a single site due to the large distance between adjacent metal ions specific to perovskite crystal structure⁹. More than anything else, the stabilisation of some labile oxidation states, achieved through oxy-anion formation, is considered significant for catalysis by these ternary oxides¹⁰. On the other hand, it is also possible to change the oxygen content in a given ternary oxide within definite, often wide, limits without any change in phase composition. The resulting non-stoichiometry adds a new dimension to the versatility of these catalysts. This flexibility within the structure helps in fashioning new heterogeneous catalysts. Perovskites are particularly suited for creating such non-stoichiometry.

1.1.2. Perovskites as Catalysts :

The first recorded use of a perovskite oxide as catalyst dates back to 1952 when Parravano¹¹ attempted a correlation between the ferroelectric and catalytic properties of KNbO_3 and LaFeO_3 . He also investigated¹² the catalytic properties of a ferromagnetic Sr-substituted LaMnO_3 and observed that the energy of activation for CO oxidation did not change on crossing the Curie point. Alkali metal tungsten bronzes having the perovskite structure were used as catalysts for the recombination of oxygen atoms by Dickens et al¹³.

Interest in the potential catalytic behaviour of oxide perovskites as a class was aroused by the discovery¹⁴ that a few cobaltites and manganites having perovskite structure could be used as fuel cell electrodes. Libby^{15,16} suggested cobaltite perovskites as good materials for catalysing autoexhaust conversions. In pursuance of this idea a Sr-substituted LaCoO_3 was studied as catalyst for the reduction of NO by CO and for the air oxidation of CO by Baurle et al¹⁷ who attributed the high activity of one of the solid solutions to the presence of lattice defects in the non-stoichiometric perovskites. Further detailed catalytic studies on perovskite cobaltites for exhaust conversion were undertaken with the object of developing a perovskite rival for platinum (usually used for this purpose) by different schools independently^{18,19,20}.

A study of the oxidation of CO and C_2H_4 over perovskite type cobaltites and manganites under conditions simulating that

in the exhaust gases was made by Yao²¹. When the poisoning of the perovskite catalysts by traces of SO₂ became known, attempts to develop them as competitors to platinum in auto-exhaust treatment were given up. Instead a new approach covered by a patent²² was pursued with considerable success. The oxides were mixed with small amounts of platinum and the effect of dispersed platinum on the activity assessed²³. ESCA revealed that the 100-fold enhancement in activity on working platinum into the perovskite was due to the presence of platinum as Pt⁴⁺.

Voorhoeve et al who reviewed the progress in the field of catalysis by perovskites²⁴ had systematically substituted Sr²⁺ for La³⁺ in LaCoO₃, LaCrO₃, LaMnO₃ and LaFeO₃²⁵ and found that the substitution reduced the activity of the first two oxides and enhanced the activity of the latter two for oxidation of CO. He classified reactions occurring over perovskite catalysts as belonging to intrafacial (catalyst actively involved) and suprafacial (catalyst providing only a surface of suitable energy and symmetry). Reduction of NO is said to belong to the intrafacial type, while the oxidation of CO is said to occur through suprafacial mechanism.

A comparative assessment of the performance of a number of perovskite oxides as electrocatalysts for oxygen reduction was made by a Japanese group of workers²⁶, and the results explained on the basis of a molecular orbital model. Coal liquefaction is another important field where perovskites