KINETICS AND MECHANISM OF SULFATION REACTIONS(*)

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Roasting of metallic sulfides have been studied by a large number of investigators in recent years. Wadsworth, McCabe in U.S.A. and Smirnov and his group have contributed to our understanding of the roasting mechanism to a very considerable extent. On the basis of these works, two kinds of mechanisms have been proposed for the formation of metallic sulfate from metallic sulfide and oxygen. One of the theory suggests a direct formation of metallic sulfate, whereas the other theory assumes prior formation of metallic oxide and subsequent formation of sulfate by catalytic oxidation of SO_2 to SO_3, which combines with metallic oxide to give sulfate. Present investigation is aimed at further clearing up the mechanism of sulfate formation and establishing the role of individuality of the system on a more generalised basis.

Following are the observations made on the basis of experimental results obtained from these studies:

1) Weight change vs time curve for oxidation of zinc sulfide in a SO_2 and O_2 gas mixture beyond diffusion controlled range of flow rate, at temperature below the decomposition temp. of $ZnSO_4(720^oC)$, shows an initial fall in weight followed by a rise in the weight.

2) Formation of $ZnSO_4$ out of ZnO and SO_2 and O_2 mixture in similar temperature range shows a linear weight change with time.

3) Addition of vanadium pentoxide to the system leads to a much faster rate.

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4) Aluminium oxide did not show any weight change when subjected to conditions as in systems

5) Nickel oxide subjected to conditions as showed an elovich type of equation where as when subjected to conditions as in system (3) did not show any effect.

6) Lithiated zinc oxide or nickel oxide when subjected to sulfation with SO_2 and O_2 mixture showed higher activation energy.

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From the first observation it is clear/prior formation of ZnO is essential for formation of sulfate and this observation when combined with observations in (2) & (3) indicates that zinc oxide acts as a catalyst for the formation of SO_3 e.g. V_2O_5 which is a known catalyst for SO_3 formation enhances the process.

Aluminium oxide neither can catalyse the formation of SO_3 or even if SO_3 is supplied by incorporation of V_2O_5, does not react to form aluminium sulfate. This indicates that the property of the oxide is very important in sulfation reactions.

Lack of enhancement in case of nickel oxide sulfation indicates that behaviour of this system differs from the earlier two systems.

Zinc oxide, aluminium oxide and nickel oxide are well known examples of n-type, insulator and p-type oxides. In the case of zinc oxide, interstitial ions and electrons are present where as in case of nickel oxide vacant cation sites and holes are predominant. Zinc oxide can donate electron and oxygen can adsorb easily (adsorption of oxygen on zinc oxide reduces conductivity and decreases electron concentration), forming anionic adsorbed species, where as nickel oxide shows less tendency to donate electron for low concentrations of electron available in the conduction band. Aluminium oxide having no such capacity does not react to give aluminium sulfate.

To explain the observed enhancement of the rate of sulfation of zinc oxide in the presence of V_2O_5 compared to nickel oxide, one has to understand that SO_3 can adsorb only by accepting electrons from conduction band which is very much available in zinc oxide but poorly available in nickel oxide. The observed rise of activation energy in case (6) can be explained in the following way:

In the case of zinc oxide when lithium ions is introduced it substitutes Zn^{++} from the lattice and so one electron falls short in the conduction band. Similarly for nickel oxide it introduces more holes thereby decreases electron concentration (it is known that the product of $e^- \times e^+ = $ constant). In both theses cases, energy of electron transfer from the absorbate to the solid results in a higher energy difference because deeper energy levels are involved, resulting in a higher activation energy.

The kinetics rate law difference can also be explained on this basis, assuming an electron transfer from adsorbate to solid as the rate controlling process.

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