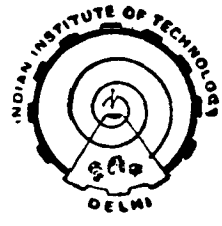
# PHYSICO-CHEMICAL CHARACTERISTICS OF MANGANESE CHALCOGENIDES AND THEIR ACTIVITY FOR SOME MODEL CATALYTIC REACTIONS

by

**D. RAJESHWER**

Thesis submitted in fulfilment of the requirements
for the award of the degree of

**DOCTOR OF PHILOSOPHY**




Department of Chemistry

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

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For Anu,

FOR A NUMBER OF REASONS

OF WHICH SHE KNOWS ONLY FEW.

# CERTIFICATE

This is to certify that the thesis entitled "PHYSICO-CHEMICAL CHARACTERISTICS OF MANGANESE CHALCOGENIDES AND THEIR ACTIVITY FOR SOME MODEL CATALYTIC REACTIONS" being submitted by Mr.D. Rajeshwer to The Indian Institute of Technology, Delhi, for the award of Doctor of Philosophy, is his own bonafide work. Mr. D. Rajeshwer has worked under my guidance and has fulfilled the requirments for the submission of the thesis which, to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any Degree or Diploma.

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## ABSTRACT

In this thesis attempt has been made to study the relationships between physico- chemical properties of manganese chalcogenides and their catalyic activity. These chalcogenides are prepared by different methods. Oxides have been prepared by the decomposition of manganese salts at varoius temperatures; sulphides have been prepared by precip itation methods; both in the non-aqueous and aqeous media; selenides and tellurides have been prepared by the interaction of their vapours with manganese in enclosed capsules .

Textural studies are based on measurement of surface areas,pore size distribution, X-ray line broadening and scanning electron microscopy,determination of acidities by n-butylamine titration,surface excess oxygen ,etc., Structural analysis is based on X-ray powder diffraction, Infrared spectroscopy, Diffuse reflectance spectroscopy. Chemical analysis is based on determination of total manganese, manganese(III)ions, manganese(II)ions, O/Mn ratio and S/Mn ratio.

The catalytic activity has been studied with the help of the following three model reactions.

1) Decomposition of $H_2O_2$.
2) Dehydrogenation of cyclohexane.
3) Dehydrogenation of isopropanol.

Various correlations have been made between physico-chemical properties and catalytic activities. In the case of Oxides, $Mn^{3+}$ ions have been found to be the seat of catalytic activity. In Sulphides, the catalytic reaction occurs on $Mn^{2+}$ sites. MnSe and MnTe are found to be inactive.

The linear correlation between the energy of activation for electrical conductivity and that for all the model catalytic reactions have been found. Energy of activation for the reaction is also linearly related to the logarithm of frequency factors, thereby suggesting an enthalpy-entropy compensation.

Catalyst samples attain increasing degree of crystallinity with agglomeration of particles with increase in temperature of decomposition and/ or pretreatment.

Both oxides and sulphides have been found to be p-type semiconductors and these catlytic reactions occur over them by a donor- type of mechanism.

In the case of $H_2O_2$ decomposition, ions and radicals takepart in the reaction. Inthedehydrogenation of cyclohexane in the partial pressure range (10mm - 40mm) and temperature range (50 - 500°C), Benzene and Hydrogen have been found to be main products with traces of cyclohexene. In the dehydrogenation of Iso- propanol, [partial pressaure range (10 - 30 mm) and temperature range (220 - 300°C)] Acetone and Hydrogen are the main products with Acetone getting adsorbed strongly thereby poisoning the surface. Acetone desorption is the rate determining step in isopropanol dehydrogenation.

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