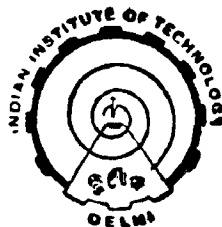


**PHYSICO-CHEMICAL CHARACTERISTICS  
AND CATALYTIC ACTIVITY OF SOME MIXED  
FIRST TRANSITION SERIES METAL OXIDES**

**A THESIS  
SUBMITTED IN FULFILMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY**

**BY  
S. K. MAZUMDAR**



**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY, DELHI  
1987**

*Dedicated*  
*to*  
*My Parents*

C E R T I F I C A T E

This is to certify that the thesis entitled, "Physico-Chemical Characteristics and Catalytic Activity of Some Mixed First Transition Series Metal Oxides", being submitted by S.K. Mazumdar to the Indian Institute of Technology, Delhi, for the award of Degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. S.K. Mazumdar has worked under my direct supervision and has fulfilled all the formalities as required under statutes before the submission of a Ph.D. thesis. This thesis has reached the requisite standard and is worthy of consideration for the award of Ph.D. degree.

The work embodied in this thesis has not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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*8/7/87*

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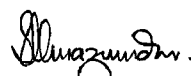
I am greatly indebted to my close friend R.K. Dhar, without whose help I would have been lost in the groves of acadme. It was usually his one or two offbeat suggestions that were most opportune at times of great need. To my brother Rajib, I owe a lot for his encouragement over the whole length of time. He has been a constant source of inspiration during hours of dispondency. My thanks are also due to Nand Kishore, who, in his ever friendly manners was also a great source of help.

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Care has been taken to give proper credit for work of other authors in the literature. I regret for any unintentional omissions which might have occurred by oversight.

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(S.K. MAZUMDAR)

## ABSTRACT

The work described in this thesis comprises of preparation, characterization, and determination of catalytic activity of three series of mixed oxides of manganese-iron, cobalt-iron and nickel-iron respectively. The catalytic activity of these oxides has been determined by static as well as dynamic methods.

The three series of mixed, first transition series, metal oxides having the two metals in different atomic ratios were prepared by calcination process. Pure oxides of the respective metals were also prepared under identical conditions for effective comparison. Calcination was carried out at temperatures as established from thermoanalytical studies of the starting materials.

In view of understanding the structural features of the catalysts, their physico-chemical characterization has been carried out by employing various spectroscopic, diffraction and microscopic techniques. Mössbauer, FTIR and diffuse reflectance spectroscopic techniques supplemented by X-ray diffraction study were extensively used to gain an insight into the nature of chemical composition of the principal components of the catalysts. Scanning electron microscopy was effectively used to study the morphology of catalyst samples and for calculation of particle size over a wide range of distribution. Atomic absorption spectroscopy was used for metal estimation in pure as well as mixed oxide catalysts. Investigations have also been made on a series of properties of solid catalysts viz., surface area, pore volume, pore size, surface acidity, surface basicity and electrical conductivity. The physical properties have been correlated with the chemical composition of the catalysts. The kinetics of catalytic decomposition of hydrogen peroxide at different temperatures, concentrations and pH was studied to determine the catalytic activity by static method. The activity pattern was established by comparing the rates of decomposition of  $H_2O_2$  over different catalyst surfaces. A probable

(v)

mechanism, consistent with the kinetic data, has been presented. Activation energy and related thermodynamic parameters like  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  have been computed and discussed. The compensation effect has also been investigated. Mixed oxides of manganese-iron was found to exhibit very high catalytic activity for decomposition reaction. Effect of  $\gamma$ -rays irradiation on the catalytic activity was also studied.

The catalytic activity of the mixed oxides for dehydrogenation reaction was determined by studying the reaction in dynamic state. Catalytic dehydrogenation of cyclohexane and cyclohexene were chosen as model reactions for determining the activity for aromatization while ethylbenzene was chosen as the substrate for studying the reaction of the type where an unsaturated system is extended. A fixed bed reactor was used for this purpose. The percentage conversion and gas phase kinetics were monitored with the help of gas chromatography. The structural changes occurring in the catalyst samples during the catalytic conversion have been investigated by XRD and FTIR.

The mixed oxides of nickel and iron were found to exhibit an appreciable catalytic activity for reactions leading to aromatization of cycloparaffins at only low temperatures. The cobalt oxide-iron oxide system suffered a rapid loss in its catalytic activity whereas the dehydrogenation reaction was sustained for considerable period of time in the presence of manganese oxide-iron oxide catalysts. These catalysts were also found to be highly active for selectively catalysing the dehydrogenation of ethylbenzene to styrene over an extended period of time. Activity scales have been constructed for these reactions in favour of kinetic evidence and product analysis, and probable mechanisms consistent with the experimental findings have been put forth.

## C O N T E N T S

	<u>Page No.</u>
CERTIFICATE	(i)
ACKNOWLEDGEMENT	(ii)
ABSTRACT	(iv)
CHAPTER ONE : GENERAL INTRODUCTION	1
CHAPTER TWO : EXPERIMENTAL DETAILS	14
CHAPTER THREE: PHYSICO-CHEMICAL CHARACTERISTICS OF THE CATALYSTS	30
CHAPTER FOUR : CATALYTIC ACTIVITY BY STATIC METHOD: CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE	99
CHAPTER FIVE : CATALYTIC ACTIVITY BY DYNAMIC METHOD:	146
SECTION ONE : CATALYTIC DEHYDROGENATION OF CYCLOHEXANE	148
SECTION TWO : CATALYTIC DEHYDROGENATION OF CYCLOHEXENE	169
CHAPTER SIX : CATALYTIC ACTIVITY BY DYNAMIC METHOD: CATALYTIC DEHYDROGENATION OF ETHYLBENZENE	187
SUMMARY AND CONCLUSION	222
REFERENCES	229
PUBLICATIONS	243