

CATALYTIC VAPOUR PHASE OXIDATION  
OF p-XYLENE

THESIS SUBMITTED BY  
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IN FULFILLMENT OF REQUIREMENTS OF THE

DEGREE OF DOCTOR OF PHILOSOPHY

TO THE

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

SEPTEMBER, 1985

CERTIFICATE

This is to certify that the thesis entitled, "CATALYTIC VAPOUR PHASE OXIDATION OF p-XYLENE' being submitted by Mr. Vinay Kumar to the INDIAN INSTITUTE OF TECHNOLOGY, DELHI for the award of the degree of 'Doctor of Philosophy', is a record of bonafide research work carried out by him. Mr. Vinay Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

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

September 1985

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Supervisor

ACKNOWLEDGEMENTS

The author wishes to express his deep sense of gratitude and sincere thanks to Professor P.D. Grover, Department of Chemical Engineering, I.I.T. Delhi, for his enthusiasm guidance and keen interest during the course of this investigation.

Thanks are also due to all who have extended their assistance at hours of need, particular mention should be made of Dr. S.S. Sambhi, Dr. B.D. Pandey, Mr. S.K. Garg Mr. M.S. Lyal, Mr. K.K. Sahu.

Thanks are also extended to Dr. S.K. Goel, Indian Institute of Petroleum, Dehradun for surface area measurements of the catalysts.

Finally, thanks are also due to Mr. V.P. Gulati for his excellent typing.

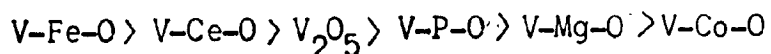
September 1985

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### ABSTRACT

Catalytic vapour phase oxidation of p-xylene is studied in an isothermal plug flow reactor using mixed oxides catalysts (vanadium pentoxide modified with different metal oxides) in the temperature range 325-450°C. The effect of various process parameters viz. reaction temperature and concentration of p-xylene has been studied on the conversion of p-xylene and yields of different products over pumice supported mixed oxides catalysts viz. V-Ce-O, V-Fe-O, V-Mg-O, V-Co-O and V-P-O. Among the catalysts investigated, only V-Fe-O and V-Ce-O exhibit sufficiently high activity with respect to products of oxidation.

The activity of the various catalysts is in the following order :



The catalyst (V-Ce-O) is found to be more selective for p-tolu-aldehyde than that of the most active catalyst V-Fe-O in the temperature range 325-425°C, therefore, it is used for the detailed studies.

The mixed oxide catalyst (V-Ce-O) has been characterized along with the individual starting materials -V<sub>2</sub>O<sub>5</sub> and CeO<sub>2</sub> by thermal analysis, X-ray, electron microscopy and BET studies. The X-ray analysis has indicated the presence of V<sub>2</sub>O<sub>5</sub> along with V<sub>7</sub>O<sub>13</sub> in minor quantity in the pure vanadium oxide sample. Cerium oxide is present in the form of CeO<sub>2</sub> and the mixed oxides catalyst

is found to contain  $CeVO_4$  and  $V_2O_5$ . The differential thermal analysis indicates the shifting of the endothermic peak by addition of 20%  $CeO_2$  to  $V_2O_5$  from  $690^\circ$  to  $637^\circ C$  whereas  $CeO_2$  does not exhibit any endothermic or exothermic peak in the temperature range ( $30^\circ C - 900^\circ C$ ). BET study indicates the decrease in surface area from  $9.0 \text{ m}^2/\text{gm}$  to  $7.1 \text{ m}^2/\text{gm}$  when 20%  $CeO_2$  is added to  $V_2O_5$ . Electron microscopy studies by SEM and TEM indicate the presence of needle-type structures for  $V_2O_5$  and V-Ce-O, and an irregular structure for  $CeO_2$ .

The kinetic data have been obtained in the differential plug flow reactor in the temperature range  $380-440^\circ C$  after the eliminating the mass transfer effects. The rate data are analysed on the basis of the Langmuir-Hinshelwood, Redox, Empirical, and Rideal mechanisms, and the two-stage redox model represents the data satisfactorily and the equation is given below:

$$r = \frac{k_1 k_o C_1 C_o}{k_o C_o + N k_1 C_1}$$

Further, the analysis of the reaction network reveals the formation of all the products from p-xylene under the condition of the investigation.

CONTENTS

|  | <u>Pa</u> |
|--|-----------|
| CERTIFICATE ..                                       |           |
| ACKNOWLEDGEMENTS ..                                  | i         |
| CONTENTS ..  |           |
| LIST OF TABLES ..                                    | vi        |
| LIST OF FIGURES ..                                   | vii       |
| ABSTRACT ..  | viii      |
| CHAPTER-1 INTRODUCTION ..                            |           |
| CHAPTER-2 LITERATURE SURVEY ..                       |           |
| 2.1 Non-catalytic oxidation of p-xylene ..           |           |
| 2.2 Catalytic vapour phase oxidation of xylenes ..   |           |
| 2.3 Literature survey-catalysts ..                   | 1         |
| CHAPTER-3 EXPERIMENTAL ..                            | 1         |
| 3.1 Experimental apparatus ..                        | 1         |
| 3.1.1 Feed preparation ..                            | 1         |
| 3.1.2 Reaction unit ..                               | 2         |
| 3.1.3 Product collection section ..                  | 3         |
| 3.2 Experimental procedure for p-xylene oxidation .. | 3         |
| 3.3 Reactants and chemicals used ..                  | 3         |
| 3.4 Identification of reaction products ..           | 3         |
| 3.5 Analytical procedure ..                          | 3         |
| 3.6 Material balance ..                              | 4         |
| 3.7 Catalyst preparation ..                          | 4         |

|           |   | <u>CONTENTS (Cont.)</u> | <u>Pa</u> |
|-----------|---|-------------------------|-----------|
| CHAPTER-4 | SELECTION OF CATALYST   | ..                      | 47        |
|           | 4.1 Thermodynamic considerations  | ..                      | 48        |
|           | 4.2 Rate expression for steady state flow reactor                             | ..                      | 53        |
|           | 4.3 Analysis of experimental data   | ..                      | 54        |
|           | 4.4 Selection of the catalyst   | ..                      | 57        |
|           | 4.4.1 Activity of the catalysts   | ..                      | 57        |
|           | 4.4.2 Effect of temperature   | ..                      | 60        |
|           | 4.5 Studies with V-Ce-O as catalyst   | ..                      | 71        |
| CHAPTER-5 | CHARACTERIZATION OF VANADIUM-CERIUM MIXED OXIDES CATALYST SUPPORTED ON PUMICE | ..                      | 75        |
|           | 5.1 Thermal characteristics   | ..                      | 75        |
|           | 5.2 Surface area measurement  | ..                      | 79        |
|           | 5.3 X-ray diffraction studies   | ..                      | 81        |
|           | 5.4 Electron microscopy studies   | ..                      | 88        |
|           | 5.4.1 Scanning electron microscopic studies                                   | ..                      | 88        |
|           | 5.4.2 Transmission electron microscopy  | ..                      | 90        |
| CHAPTER-6 | KINETIC ANALYSIS  | ..                      | 95        |
|           | 6.1 Mass transfer effects   | ..                      | 97        |
|           | 6.1.1 External heat and mass transfer effects                                 | ..                      | 97        |
|           | 6.1.2 Internal diffusion  | ..                      | 100       |
|           | 6.2 Kinetic experiments   | ..                      | 101       |
|           | 6.3 Analysis of kinetic data  | ..                      | 106       |

CONTENTS (Contd.)

|  | <u>P</u>   |
|--|--|
| 6.4  | Comparison of various models .. 1                                  |
| 6.5  | Evaluation of rate parameters .. 1                                 |
| 6.5.1  | Linear regression method .. 1                                      |
| 6.5.2  | Non-linear regression .. 1   |
| 6.6  | Evaluation of Arrhenius constants .. 1                             |
| CHAPTER-7  | REACTION SCHEME .. 1   |
| 7.1  | Experimental studies .. 1  |
| 7.2  | Probable reaction network .. 1                                     |
| 7.2.1  | Series scheme .. 1   |
| 7.2.2  | Parallel scheme .. 1   |
| 7.2.3  | Parallel-consecutive scheme .. 1                                   |
| 7.2.4  | Complex scheme .. 1  |
| 7.3  | Formulation of rate expression .. 1                                |
| 7.4  | Determination of rate constant .. 1                                |
| CHAPTER-8  | SUMMARY AND CONCLUSIONS .. 1                                       |
| APPENDICES   |  |
| I-IV   | Experimental and calculated data of different chapters .. 1        |
| V  | Derivation of stoichiometric coefficient and systematic error .. 1 |
| VI   | Effect of diffusion on heat and mass transfer .. 1                 |
| VII  | Sample calculations .. 1   |
| NOMENCLATURE .. 1  |  |
| REFERENCES .. 1  |  |
| COMPUTER PROGRAMME USED FOR NON-LINEAR LEAST SQUARES PARAMETER ESTIMATION .. 1 |  |