CATALYTIC VAPOUR PHASE OXIDATION OF p-XYLENE

THESIS SUBMITTED BY

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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

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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 :

$$V\text{-}Fe\text{-}O > V\text{-}Ce\text{-}O > V_2O_5 > V\text{-}P\text{-}O > V\text{-}Mg\text{-}O > V\text{-}Co\text{-}O$$

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

The mixed oxide catalyst (V-Ce-O) has been characterized along with the individual starting materials -V_2O_5 and CeO_2 by thermal analysis, X-ray, electron microscopy and BET studies. The X-ray analysis has indicated the presence of V_2O_5 along with V_7O_{13} in minor quantity in the pure vanadium oxide sample. Cerium oxide is present in the form of CeO_2 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° to 637°C whereas CeO_2 does not exhibit any endothermic or exothermic peak in the temperature range (30°C - 900°C). BET study indicates the decrease in surface area from 9.0 m^2/gm to 7.1 m^2/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°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.

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