CATALYTIC WET AIR OXIDATION OF OXALIC ACID OVERCERIA PROMOTED Pt/Al_2O_3 CATALYST

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by

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Submitted in fulfillment of

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DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, **"CATALYTIC WET AIR OXIDATION OF OXALIC ACID OVER CERIA PROMOTED Pt/Al_2O_3 CATALYST"** being submitted by **Mr. Shyamal Roy** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology, Delhi.

The research report and results presented in this thesis have 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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ABSTRACT

Large volumes of industrial wastewaters containing refractory organic pollutants are produced from various industries such as pulp, dye, chemical, petrochemical etc. These pollutants are too difficult to be treated through conventional processes and alternate treatment methods need to be developed for the remediation of these effluents.Among these methods are adsorptions on activated carbon,advanced oxidation processes and wet air oxidation.These methods allow oxidation of refractory organic pollutants to carbon dioxide and intermediates which are more amenable to biodegradation.The use of heterogeneous catalysts in the wet air oxidation process facilitates the operation under milder conditions of temperature and pressure. Moreover, a catalyst improves the oxidation of the most refractory compounds,reducing the number of intermediates, which makes the later application of conventional processing, for example,aerobic or anaerobic biological treatment,possible.Oxidation catalysts can be broadly categorized into three groups: noble metals,metallic and metallic salts, and their complexes.One of the major limitations for commercial application of catalytic wet air oxidation processes is the search for an active, durable and environment friendly catalyst. Keeping this in mind, it was decided to study the catalytic wet air oxidation of oxalic acid since oxalic acid is most stable of the carboxylic acids.

Oxidation of oxalic acid was carried out in a four-neck glass reactor operated at atmospheric pressure. Most of the experiments were performed using Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 catalysts. The catalysts were prepared by excess solution impregnation (ESI) method. Catalysts supported on alumina with different Pt loadings

(0.2 to 0.7 wt %) and different ceria contents (2 to 15 wt %) were prepared. The surface morphology of the prepared catalysts was investigated using a scanning electron microscope (SEM) analyzer. Their phases were analyzed with powder X-ray diffraction. In addition to these the characterization was enriched by energy dispersive X-ray spectroscopy (EDX), nitrogen adsorption, chemisorptions and thermo-gravimetric (TGA) analysis.

Non-catalytic and catalytic wet air oxidation of oxalic acid using ZnO, CeO_2, Al_2O_3,Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 was carried out. The degradation of oxalic acid obtained by CWAO was found to be much higher as compared to non-catalytic oxidation.The effect of various parameters such as size of the catalyst particle, air flow rate and agitation speed, catalyst dosage and loading, initial concentration of oxalic acid and reaction temperature was investigated. The kinetic data for the catalytic oxidation was used to determine the activation energy which has a fairly good agreement with the data reported in the literature.A rate equation has been proposed for the oxidation of oxalic acid.

The usefulness of addition of cerium oxide as a promoter for the catalytic oxidation of oxalic acid was studied by performing experiments with different CeO_2 contents.The addition of transition metal oxides like ceria further enhanced the degradation of oxalic acid.The optimum amount of ceria to be added as a promoter was found to be 10 wt %.Catalyst deactivation studies were carried out and negligible deactivation effects were noticed for the ceria promoted Pt/Al_2O_3 catalyst over a time on stream of 10 h.

Therefore, addition of ceria was found to increase the activity of alumina-supported platinum catalyst and enhance the stability of the catalyst. Catalyst regeneration study was performed to restore the activity of the spent catalyst.

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