CHAPTER I
INTRODUCTION

Phenol was discovered in coal tar as early as 1834. In quantity produced, phenol ranks near the top of the list of synthetic aromatic compounds. Its principal use is in the manufacture of the phenol-formaldehyde polymers.

A certain amount of phenol, as well as the cresols, is obtained from coal tar, but nearly all of it is synthesized. One of the synthetic processes had ever been used is the fusion of sodium benzenesulfonate with alkali; another is the Dow process, in which chlorobenzene is allowed to react with aqueous sodium hydroxide at a temperature of about 360 ^{o}C. Like the synthesis of aniline from chlorobenzene, this second reaction involves nucleophilic substitution under conditions that are not generally employed in the laboratory. Nearly all phenol is made today, however, by a newer process that starts with cumene, isopropylbenzene. Cumene is converted by air oxidation into cumene hydroperoxide, which is converted by aqueous acid into phenol and acetone (Morrison *et al.*, 1992).

The hydroxylation of benzene by hydrogen peroxide (H_2O_2) to phenol in the presence of oxidizable metal ions, and super acids is well known. A direct catalytic method using heterogeneous, solid catalysts which can efficiently hydroxylate benzene, will have significant advantages and the titanium silicalite-1 (TS-1) catalyst have much more advantage than others. The synthesis of TS-1 was first reported by Taramasso *et al.* in 1983. TS-1 has received considerable interest in recent years because of its unique catalytic properties in oxidation reaction involving H_2O_2 as the oxidant. It is possible to perform the selective oxidation of olefins and diolefins to epoxides (Clerici *et al.*, 1991b), the hydroxylation of aromatic compounds (Kraushaar-Czarnetzki and van Hooff, 1991; Reddy *et al.*, 1990; Thangaraj *et al.*, 1990, 1991a; Tuel and Ben Taârit, 1993; Martens *et al.*, 1993; Astorino *et al.*, 1995), the selective oxidation of primary and secondary alcohols (Maspero and Romano, 1994), the oxidation of saturated hydrocarbons (Clerici, 1991a) and the ammoximation of ketones (Thangaraj *et al.*, 1991b; Tvaruzková and Zilková, 1993) with high selectivity.

The use of H_2O_2 offers some advantages, such as low cost per oxygen atom and the absence of by-products. These reactions, because of the absence of by-products, are considered as ''clean reactions''. A heterogeneous catalytic system has advantages over homogeneous systems since it allows simple separation and recovery of the catalyst from the reaction mixture and its subsequent regeneration, once it is deactivated.

The direct catalytic hydroxylation of benzene with H_2O_2 to phenol was chosen as a test reaction in the present work, owing to its simplicity (it yields only two products) and the fact that this reaction has not been studied extensively in the past. Moreover, this reaction presents several contacting alternatives and deals that the co-current up flow and stirred slurry poses mixing problems of the phenol-rich and H_2O_2-rich phases and will be complicated by mass transfer from the liquid phase to the solid surface (Thangaraj *et al.*, 1990; Tendulkar *et al.*, 1998; Bhaumik *et al.*, 1998; Bengoa *et al.*, 1998; Kumar *et al.*, 1999)

The contacting alternative explored in this investigation employs periodic switching of benzene in vapor phase and concentrated H_2O_2 solution in downflow through the packed bed of catalyst. Since the TS-1 has a structure and pore size similar to ZSM-5, the internal diffusion is very slow and the hydroxylation reaction must occur primarily on the external surface of catalyst particle. Rate controlling step then will be either film type mass transfer from the liquid phase to TS-1 or a surface reaction step. If it is the former step that controls, periodic switching of flows should increase the rate of reaction and yield.

In this study, the effect of cycle period time and concentration of benzene were the main focus. The study has been scoped as follows:

1) Preparation of the TS-1 samples using the hydrothermal procedure.
2) Charcterzation of TS-1 samples by the following methods.
    - Determination of bulk composition of Si / Ti by atomic absorption spectroscopy (AAS).
    - Specific surface area by N_2 adsorption based on BET method (BET).

- Structure and crystallinity of samples by X-ray diffractrometer (XRD).
- Incorporation of Ti atoms as a framework element by IR spectra (IR).
- Morphology of sample by Scanning Electron Microscopy (SEM).

3) Reaction study of the catalyst samples in hydroxylation of benzene at 70 °C and 1 atm in order to measure catalytic activity.

The main objectives of this research were to study and compare the periodic operation and the co-current downflow operation and to develop a better understanding of the effect of cycle period time and concentration of benzene on the conversion of benzene.

This present work is organized as follows:

The background and scopes of the study are described in chapter I.

Chapter II reviews research works on the hydroxylation of benzene reactions, TS-1 catalysts and periodic operation on various reactions in the past and comments on previous works.

The theory of this research, studies about the hydroxylation of benzene reaction and its possible mechanisms, and the properties of TS-1 catalysts are presented in chapter III.

Chapter IV consists of catalyst preparation, catalyst characterisation and reaction study in hydroxylation of benzene.

The experimental results, including an expanded discussion, are described in chapter V.

Chapter VI contains the overall conclusion emerging from this work and some recommendations for future work.

Finally, the sample of calculation of catalyst preparation, external and internal diffusion limitations, calibration curves from area to mole of benzene, and phenol, and data of the experiments which had emerged from this study are included in appendices at the end of this thesis.