CHAPTER I

INTRODUCTION

In the early stage of plastic industry, phenol played an important role as a major raw material. At present, although many new polymers (especially those products from addition polymerization) have been emerged, phenol is still a main product in the organic industry.

Despite the fact that, the production of phenol via cumene is widely accepted by the industry, a better production method is still being seeked. A potential route is the hydroxylation of benzene by hydrogen peroxide. This reaction has gained attention due to several advantages. For example, the hydroxylation reaction is an one-step reaction, the reaction can occur at a relatively low temperature (i.e. 70-80°C), low toxic and/or unwanted by-products are formed. The reaction, however, still has some drawbacks to be overcome. The major drawbacks of the hydroxylation technique are the phase separation between the two reactant and the very low yield of the phenol product.

Many researches have been focused on the hydroxylation of benzene with hydrogenperoxide using various type of catalyst. The titanium silicalite-1 (TS-1) is one of the famous catalysts used in this reaction because of its high phenol yield and selectivity. Many researchers studied the effect of operating condition. The most common way, the reaction was study in a stirred slurry reactor without the present of any solvent. Some researches have tried to improve the yield of phenol by adding some solvents, such as acetonitrile, acetone and methanol, to produce a single phase system. For example, Bhaumik et al. (1998) reported that the addition of any solvent that made H_2O_2 and benzene existed in the same phase, the solvent phase, could increase the yield of phenols. This technique, however, possessed a major draw-back, the difficult to separate the phenol product and the unreacted reactants from the solvent phase.

TS-1 has the morphology and average pore size nearly same as ZSM-5. Thus the external mass transfer is slow. Therefore, most of the reaction occurs at the external surface of the catalyst. The limiting step of this reaction should be the external mass transfer or the surface reaction. Consequently, the changing of the feeding system would affect the yield or selectivity of the reaction. In a previous work, Pimporn Chaijarat (2003) a periodic system was designed to overcome the above mentioned problem. The system wanted of a bed of TS-1. The feeds were liquid H_2O_2 and gaseous benzene. The advantages of this system are the yield of phenol was be increased and the phenol product exists only in the H_2O_2 phase. This work has demonstrated the potential of the periodic operation, but many factors influencing the performance of the proposal periodic system have yet to be explored.

The present study is the extension of the work of Pimporn Chaijarat (2003). This research aims to improve the conversion and selective by changing ratio of Si and Ti in the framework structure of TS-1 and investigates the appropiate pretreatment condition on the hydroxylation of benzene with H_2O_2 on TS-1 by periodic operation

In this study, the main objectives of this research are to investigate the oxidation properties of Titanium Silicalite-1 (TS-1) catalyst in the hydroxylation of benzene by hydrogen peroxide in a periodically operated three phase, co-current downflow packed bed reactor. The research has been scoped as follows:

1) Preparation of TS-1 catalysts which have 22, 32, 40 and 60 Si to Ti ratio by using the hydrothermal method.

2) Pretreatment of these catalysts with solution of 3M and 5M HNO_3

3) Characterization of the synthesized TS-1 catalysts by using the following techniques.

- Determination of bulk composition of Si/Ti by X-ray fluorescence (XRF).

- Determination of specific area by N_2 Adsorption based on BET method (BET).

- Determination of structure and crystallinity of catalysts by X-ray diffractrometer (XRD).

- Determination of incorporation of Ti atoms as a framework element by IR Spectroscopy (IR).

- Determination of acid sites of the synthesize catalysts by NH_3-TPD technique.

- Determination the structure of Ti coordination in the framework of TS-1 by UV-vis spectroscopy.

4) Catalytic reactions in three phase hydroxylation of benzene at 70°C to the determine catalytic activity

This present work is organized as follows:

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

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

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

Chapter IV consists of catalyst preparation, catalyst characterization and catalytic 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, and calibration curves from area to mole of benzene, phenol and data of the experiments which had emerged from this study research are included in appendices at the end of this thesis.