

CHAPTER I

INTRODUCTION

Cresol is a compound which both has a wide variety of usage including the manufacture of synthesis resins, insecticides and herbicides [1]. Cresol is produced from methyl alkylation of phenol process which has products as meta-cresol (m-cresol), para-cresol (p-cresol), ortho-cresol (o-cresol) and anisole. It has the problem about high cost to separate the isomer of m-cresol and p-cresol [2]. This reaction consists of two steps: (1) The main method used to manufacture phenol for using in the next step can produce from cumene process or hydroxylation of benzene that is the directly insertion of a hydroxyl group to the benzene ring by hydrogen peroxide (H_2O_2) and (2) methanol alkylation of phenol to cresol. Therefore, a new route to produce cresol in one step is demanded and the concept of the hydroxylation of benzene to phenol is a guide line. For the overall diagram of cresol production by using phenol methylation path and a new route are illustrated in Figure 1.1. Since in industrial, benzene and toluene are always co-produced (from the catalytic reformer), to produce cresol with the direct hydroxylation of toluene by H_2O_2 as oxidant is considered in this research.

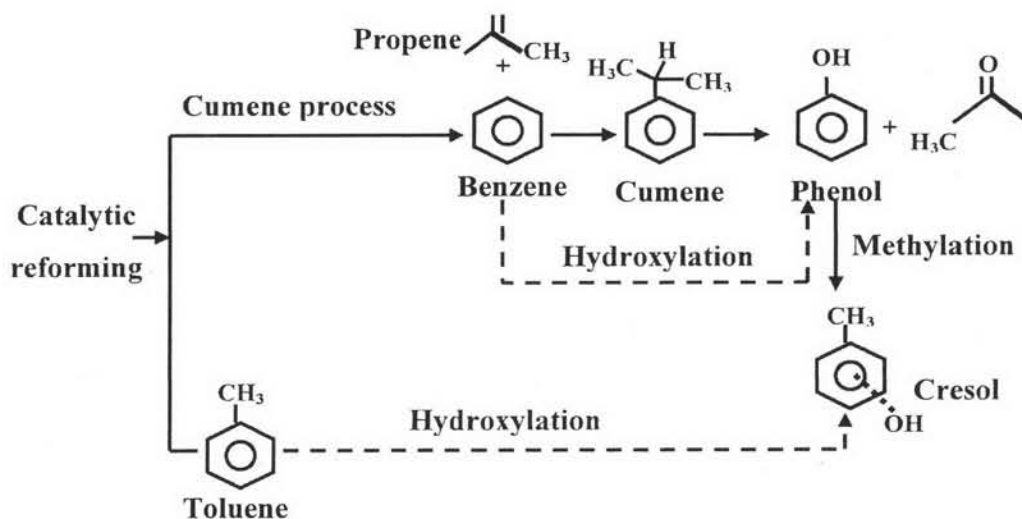


Figure 1.1 The routes of cresol production from phenol and toluene

Many researches have studied the hydroxylation benzene to phenol extensively and found that titanium silicalite-1 (commonly known in the name TS-1) is a potential catalyst since using TS-1 in the reaction can occur at a relative low temperature (i.e. 70-80°C), using H₂O₂ offers low cost per oxygen atom and the absence of by-products [3]. Despite the fact that TS-1 exhibits an excellent selectivity (near 100% to phenol) because the characteristic pores of TS-1 allowed the product molecules having sizes in range of the pore diameter can move out of pores. Therefore, it suffers a major drawback i.e. its activity is quite low. Therefore, an improvement of its activity is needed. The present work introduces a method to enhance the catalytic activity of the TS-1 by adding a second metal to the TS-1. The selected metals are Fe, Al, Co and V.

Alkylbenzene is organic compound that has an alkyl group bound to a benzene ring. Theoretically, the alkyl group activates the ring and makes the ring of the alkylbenzene become more active than benzene ring. For the hydroxylation of alkylbenzene, fundamental theory suggests that a hydroxyl group should substitute a hydrogen atom at the ortho- or para- position [4]. For example, the hydroxylation of toluene by using H₂O₂ and TS-1 as catalyst can give o-cresol and/or p-cresol as products without m-cresol that are easily separated products and the oxidation of ethylbenzene has been carried out over TS-1, VS-1 and Sn-silicalite-1 (MFI structure) using H₂O₂ as oxidant at 60-80°C and had different products which took place in two ways. One is the aromatic ring hydroxylation at para-position which is more preferable than ortho-position. This led to the formation of ortho- and para-hydroxy ethyl benzene as a minor side reaction. The other was the side chain oxidation at secondary carbon predominates over the primary carbon atom. In case of TS-1, the oxidation only occurs at the secondary carbon atom therefore the major products were 1-phenyl ethanol and acetophenone [5]. Despite the importance of this reaction, the hydroxylation of alkyl benzenes gains little interest.

In a previous work investigated the hydroxylation of aromatic hydrocarbons (such as benzene, toluene and anisole) over TS-1/H₂O₂ under triphase (catalyst-benzene-H₂O₂) and biphasic (catalyst-liquid (benzene-H₂O₂-solvent)) conditions. The results obtained in the hydroxylation of toluene and anisole found the enhancement of reaction and para-hydroxy products were predominantly obtained under the triphase

condition. For the biphasic condition, the ortho-hydroxy product was preferred further, this condition was observed that the solvent used for combined organic substrates and H_2O_2 , it is the competitive diffusion of the organic reactants and diffused into channel of TS-1 due to its smaller size [6].

The purpose of this work is to study the insertion of a hydroxyl group directly on the ring of benzene and alkyl benzene over various metal modified TS-1 catalysts (Co-TS-1, V-TS-1, Fe-TS-1 and Al-TS-1) using H_2O_2 a stirred slurry reactor under triphase condition. The aim of this research is to explore a new route for organic synthesis that can make the reactants more valuable. The research has scope following as:

- 1) Preparation of M-TS-1 (M = Co, V, Fe or Al) catalysts which have 50 Si to Ti and 150 Si to M ratio by using the incorporation method.
- 2) Pretreatment of these catalysts with 5M HNO_3 solution
- 3) Characterization of the synthesized TS-1 catalysts by using the following techniques.
 - Determination of bulk composition of Si, Ti and M by X-ray fluorescence (XRF).
 - Determination the surface area and pore volume by N_2 Adsorption based on BET method (BET).
 - Determination of structure and crystallinity of catalysts by X-ray diffractometer (XRD).
 - Determination of incorporation of Ti atoms as a framework element by IR Spectroscopy (IR).
 - Determination of acid sites of the synthesized catalysts by NH_3 -TPD technique.
- 4) Study the catalytic reactions in a stirred slurry reactor at 70 and 95°C to determine catalytic activity

This present work is organized as follows:

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

Chapter II fundamental theory concerning aromatic substitution and catalyst as TS-1 including reviews research works on the catalytic activity of metal modified TS-1 catalysts in the hydroxylation and comments on previous works.

Chapter III consists of catalyst preparation, catalyst characterization and catalytic reaction study in hydroxylation of alkyl benzene.

Chapter IV presents the experimental results of the characterization of catalysts, and the hydroxylation of alkyl benzene reactions over these catalysts, including an expanded discussion.

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

Finally, the sample of calculation of catalyst preparation and calibration curves from area to mole of reactants and products obtained from hydroxylation and data of the experiments which had emerged from this study research are included in appendices at the end of this thesis.