



CHAPTER I INTRODUCTION

Recently, epoxidation is one of the most important reactions in organic synthesis for the chemical industry. The epoxidation of olefins, namely ethylene, propylene, cyclohexene, etc., results in oxygenated molecules, so-called epoxides, by oxygen transfer reaction. Epoxides are valuable and versatile commercial intermediates to many chemical industries. Ethylene oxide and propylene oxide are the intermediates used in the production of polyurethane, polyester resins, polyether polyols, flame retardants, surfactant, etc. In addition, cyclohexene oxide, which has been steadily increased in the market demand over recent years, is one of the most important organic intermediates in the production of pharmaceutical, plant-protection agents, pesticides, rubber promoter, epoxy paints, and stabilizers for chlorinated hydrocarbons (Lu *et al.*, 2007, Jinka *et al.*, 2007).

In the epoxidation of cyclohexene, many oxidizing agents, e.g. hydrogen peroxide (H_2O_2), *tert*-butyl hydroperoxide (TBHP), peracid, etc. have been used. In many cases, hydrogen peroxide (H_2O_2) was selected because it is easy to handle and possesses high content of active oxygen. In addition, the use of H_2O_2 is inexpensive, economic, selective, safe, clean, and also environmentally friendly since the starting material produces only water as a by-product (Mandeli *et al.*, 2000).

Although several kinds of catalysts are able to promote epoxidation with hydrogen peroxide, the utilization of RuO_2 heterogeneous catalysts is probably the most studied catalysis aspect for a plenty of epoxidation reactions by being loaded on various kinds of support, such as $\text{RuO}_2/\text{TiO}_2$ (Sreethawong *et al.*, 2002), and $\text{RuO}_2/\text{CeO}_2$ (Hosokawa *et al.*, 2003).

The main problem of cyclohexene epoxidation to the cyclohexene oxide is undesired side reactions, which can take place owing to the two main reactions, namely allylic oxidation, resulting in the formation of 2-cyclohexen-1-ol and 2-cyclohexen-1-one, and ring-opening of the epoxide, resulting in the formation of *trans*-1,2-cyclohexanediol. Therefore, much effort has been devoted to the development of new active and selective catalysts for cyclohexene epoxidation to

circumvent the side reactions and the formation of large amounts of by-products (Mandelli *et al.*, 2001).

The main objective of this work is to investigate the cyclohexene epoxidation using different oxide catalysts, i.e. commercial TiO₂ (TiO₂(P-25)), sol-gel-synthesized mesoporous-assembled TiO₂ (TiO₂(SG)), SiO₂, Al₂O₃, and Fe₃O₄. Moreover, RuO₂ is loaded onto selected catalysts by incipient wetness impregnation (IWI) method and onto TiO₂(SG) by single-step sol-gel (SSSG) method. The catalysts are characterized by several techniques, including X-ray diffraction (XRD), surface area analysis (SAA), transmission electron microscopy (TEM), thermogravimetric-differential thermal analysis (TG-DTA), X-ray fluorescence analysis (XRF). The influences of calcination temperature, calcination time, RuO₂ content, and reaction parameters—reaction temperature, catalyst content, and H₂O₂-to-cyclohexene ratio—on the catalytic performance are investigated. Moreover, recyclability of selected spent catalysts is also studied.