CHAPTER I

INTRODUCTION

Selective oxidation reactions using heterogeneous catalysts are of growing importance for modern chemical industry. The oxidation products of cyclohexane, viz., cyclohexanol and cyclohexanone, are important intermediates in the production of adipic acid and caprolactam, which are used in the manufacture of nylon-6 and nylon-6,6 polymers. In addition, they are also used as solvents for lacquers, shellacs, and varnishes as well as stabilizers and homogenizers for soaps and synthetic detergent emulsions. Other uses of cyclohexanone are as starting material in the synthesis of insecticides, herbicides, and pharmaceuticals. In general, both cyclohexanol and cyclohexanone are produced on an industrial scale by the oxidation of cyclohexane. In the early 1940s, Du Pont developed a process in which cyclohexane was oxidized in the presence of air to cyclohexanol and cyclohexanone using cobalt napthenate or cobalt acetate as catalyst. In this process, several by-products, viz., mono- and dicarboxylic acids, esters, aldehydes, ketones, and other oxygenated materials, were generated. Later, in the 1950s, Scientific Design (now Halcon International) developed a new process where anhydrous meta-boric acid was added as a slurry in the oxidation vessel. This led to the formation of cyclohexyl ester is subsequently hydrolyzed to cyclohexanol. In comparison to the former, the latter process showed good yield of cyclohexanol, which, however, requires high investment and a high operating cost to recover and recycle the boric acid.

On the other hand for the laboratory-scale reaction extensive literatures are available on the selective oxidation of cyclohexane using a variety of transition metal compounds in stoichiometric amounts or as homogeneous catalysts. In the cases of the latter, the use of initiators, e.g., cyclohexanone, cyclohexyl peroxide, methyl ethyl ketone, and acetaldehyde reduced the induction period as well as enhances the catalytic activity. However, owing to the limitations of these soluble (homogeneous) catalysts, viz., catalyst separation from the product and the disposal of solid/liquid wastes, which pose serious problems to the environment, in recent years attention has been focused on the development of transition metal-based heterogeneous catalysts

with oxygen or peroxides as nonpolluting oxidants. However in most cases, extreme reaction conditions such as high pressure (2 MPa) and high temperature (450 K) in conjunction with low activity make the process less attractive. In addition, leaching of active metal ions has often been observed under the reaction conditions. Hence, the oxidation of cyclohexane over heterogeneous catalysts under mild/moderate conditions is a topic of great interest.

Transition-metal-substituted polyoxometalates (M-POM for short) have attracted much attention as oxidation catalysts because of their unique ensemble of properties, including metal oxide-like structure, thermal and hydrolytic stability, tunable acidities and redox potentials, and alterable solubilities in various media, etc. It has been established that cobalt compounds, including Co-POM, are among the best catalysts for homogeneous aerobic aldehyde oxidation and cooxidation of alkenes with aldehydes [1]. Tetraalkylammonium salts have been prepared to ensure the solubility in the organic solvents. M-POM have small surface area (1–5 m^2g^{-1}) Dispersion M-POM on support, such as silica, alumina, resin, active carbon, clays and microporous zeolites, to enlarge the surface area, which increases the number of acidic sites on the surface and enhances catalytic activity was performed [2]. MCM-41s materials have very large surface area (typically 1000 m^2/g) and a uniform large pore size (20 Å), the MCM-41s materials can act as an excellent supports. This is because such mesoporous materials, which have relatively small diffusion hindrance, can aid the easy diffusion of bulky organic molecules in and out of their mesopores [3].

1.1 Objectives of the thesis

To synthesize supported polyoxometalates catalysts containing transition metal Co, Fe and Cu.

To study catalytic activities of the synthesized catalysts in the oxidation reaction of cyclohexane.