

CHAPTER 1

INTRODUCTION

Zeolites have been an object of scientific research and a material beneficial to mankind for more than two centuries since its discovery in 1756. However, it was not until 10-15 years ago that zeolites attracted the keen interest of photochemists who wanted to use them in their research. Photochemists are most interested in controlling chemical reactions with the aid of supramolecular assemblies, aimed at constructing artificial photosynthetic systems, controlling chirality and inventing nanoscale advanced materials. Zeolites are found to be particularly useful for such purpose since they can host various organic molecules in their cavities and channels; such inclusions have often been shown to modify the photophysicals and photochemistry of a given species. Besides, photochemical reactions pursued in zeolites also provide product distributions considerably different from those in solution [1].

Zeolite nanospace could be considered as “hard” because of the frameworks of zeolite are rigid, and “active” because of the non-bonding interaction between the walls of the supercage and the included molecules. On top of these, the most desirable property of zeolite is that it is transparent to light in the near-UV and visible regions. Thus it eliminates the possibility of competitive absorption between the medium and the guest molecule presents [2].

The synthetic utility of intermolecular photodimerization of cyclic enones and the cycloaddition to unsymmetrical alkenes can be limited by the formation of the mixtures of the head-to-head (HH) and head-to-tail (HT) regioisomers [3, 4]. HT

regioisomers are always formed in much larger amount compared to HH isomer in solution reaction [5, 6]. In this research, cation-exchanged Y zeolites were applied to control the regioselectivity of photoproducts in photoreactions of 2-cyclohexenone.

1.1 Objectives of the Research

The objective of this research is to evaluate the feasibility of using zeolite as reaction medium to carry out intermolecular organic photoreactions, i. e. photocycloaddition and photodimerization. This could be further divided to two:

- (i) To compare the products selectivity of between the conventional homogenous photoreactions with solid state and/or slurry photoreactions in zeolite supercage
- (ii) To utilize the cation-exchanged property of zeolite to control the regioselectivity of desired photoproducts.

Faujasite-Y zeolite was used as host because it possesses large supercages volume which enable us to study a variety of photochemical reactions.

1.2 Scope of the Studies

At the first part of this research, locations of the paramagnetic probe in different adsorption sites of NaY zeolite were studied using Electron Spin Resonance Spectroscopy (ESR). Most of the research in the supramolecular photochemistry within zeolites deal with the intramolecular reaction. In order to study the different approaches used in the intermolecular photoreaction, we have studied the triplet sensitization technique and “spectator” method. The triplet sensitization technique had been applied in the dimerization of triethylamine (TEA) within Y zeolite, while

the “spectator” method was used in gaining selective asymmetric coupling products in the hydrogen abstraction of toluene by acetophenone (AcP).

After gaining experiences from the first part, we turned to the next part, the utilization of the size constriction effect and cation-guest interactions of the cation-exchanged zeolites to modify the selectivity of the regioisomers in photodimerization of 2-cyclohexenone (CH) and photocycloaddition of CH to vinyl acetate (VA).