

CHAPTER I INTRODUCTION

Zeolite is a crystalline, porous aluminosilicate. Some of relative materials having the virtual structure of zeolite, but containing other oxides of the element besides silicon and aluminum atoms are evolved in zeolite synthesis in recent years. Expansion of the zeolite definition includes all materials that have porous oxide structure, containing the pore or cavity with well regularity together with high degree of crystallinity. However, it might obscure many crystalline solids having high density of crystal. Thus, the better criterion to classify the zeolite from other dense crystal is the framework density, the number of tetrahedrally coordinated atom (T-atom) per 1000 Å. The boundary range is from 19 to 21 T-atom per 1000 Å. Differences of the density and pore or cavity are present in zeolite materials, and most of zeolite materials have pore or cavity size less than 20 Å which can be defined as microporous material as well.

Oxide of the 3-5 main group elements (i.e. B, Al, Si, P, Ga, etc) in the tetrahedral form is the basis structure of zeolite. T-atom of silicon is electrically neutral and the major component in many type of zeolite, which typically exists in a 4+ oxidation state. However, aluminum typically exists in the 3+ oxidation state so that aluminum T-atom forms center being one electron electrically deficient. Thus, zeolite frameworks are typically anionic, and charge-compensating cations populate the pores to maintain electrical neutrality. These cations are exchangeable and maintain the important property of the zeolite material.

The exchangeable counter ion in the pore or cavity can thus be used in the application of water treatment, as ion-exchange resin for making soft water. These ions are exchanged with acid, resulting in acid property of the zeolite, thus the zeolite is a kind of acid presenting in the solid form which is useful for petrochemical industry, such as acid catalyst in fluidized bed cracking process. The strength of the acid depends on the composition and structure, relating to the pore size. Variety of application is due to requirement of different acid strength. Moreover, by exchanging the counter-ion in the structure with large size of alkali ion, such as Cs, the basic property of this material is obtained. Due to the small size of pore or cavity, it is

applied to use as molecular sieve having capability in screening sizes of molecule, and thus widely used for separation process.

Different pore structure of zeolite that naturally cannot be found provides many specific purposes, thus creating tremendous utilities. Two reactions involved the zeolite synthesis in the early stage of formation are hydrolysis and condensation of precursor, such as silicic acid, fumed silica, tetraethoxysiloxane (TEOS), sodium aluminate, etc. The gel network comes from condensation of the precursor sol, and it is found that different rates of hydrolysis and condensation affect to the properties of the gel. If the hydrolysis rate is faster than the condensation rate, the gel structure is weakly branched, while with the opposite direction the gel is highly branched. This gel stage is an intermediate before nucleation takes place. Temperature and pressure are normally applied to drive the reaction forward similar to the occurrence of natural zeolite that is pressurized and heated beneath earth surface.

A new technique of microwave was considered as an alternative method to generate heat. It shows many advantages over the conventional heat method, for example, rising temperature at very high rate even in large amount of samples, giving homogeneous heat for short period of time. By applying the electromagnetic field in the range of microwave region, a mixture containing dipole in the molecule tries to re-orient the dipoles and displace the charge equivalent to an electric current. Thus, the feature of microwave is to promote the reaction go faster at required shorter reaction time. The MFI zeolite, our aimed zeolite, is the one that generally requires long period of heating for several days to weeks. However, with the microwave technique the MFI zeolite can be successfully synthesized within few hours.

The addition of other metal as catalyst into the zeolite structure has been studied for more than decades due to its high surface along with the molecular screening property. Many attempts were input to the study to force heteroatom into the structure of zeolite, for instance, TS-1 containing Ti atom in the framework of MFI for oxidative reaction. The vanadium, our interest metal, shows good performance on the oxidation reaction, however, gives less surface area, resulting in less active site to interact with the reactant. The combination of high surface area together with regularity of the channel in the structure might promote higher reactivity and give more selectivity of product.

Propane can be found in the natural gas and has been used as liquefied petroleum gas (LPG), which has low price in the market. However, propylene, counterpart molecule with double bond is more valuable many industrial uses, such as, used as the starting material for polypropylene production, used as a feedstock for other synthesis application, as propylene oxide monomer for making epichlorohydrin.

The straight way to convert propane to propylene is dehydrogenation (DH) reaction, Eq 1, which is endothermic with a ΔH° value of 117 kJ mol^{-1} . Thus, the reaction temperature for this reaction is relatively high at low pressure with short contact time to prevent coke formation on catalyst. Using high temperature and coke formation are disadvantages of this method.



An alternative way is oxidative dehydrogenation (ODH), an exothermic reaction, Eq 2. The advantage is that there is no equilibrium limitation and the reaction takes place at lower temperature generating less coke to be formed, however, the reaction is non-selective and gives other products, such as CO and CO₂.

This proposal, thus, involves the synthetic study of MFI zeolite catalyst support for ODH of propane using vanadium catalyst.