



CHAPTER I

INTRODUCTION

Over the last quarter of the twentieth century, many chemical industries have mainly depend on petroleum as the raw material for organic synthesis. But nowadays, natural gas and associated gas are alternative resources to a petrochemical industry. Because of the oil crisis, petroleum has been replaced by coal in the steel industries, the electric power and other large scale energy generation systems. Accordingly, the excessive supply of petroleum has become a serious problem, and the development of new routes for effective utilization of petroleum has become of great significance. "C₁ chemistry" is one of the new routes which rised to replace petroleum chemistry. This new route is the catalyst-chemistry which uses syngas as starting materials. C₁ chemistry is a general term for synthesis technology starting from compounds contained one carbon atom such as CO, methanol (CH₃OH), CO₂, and methane (CH₄) from natural gas. This contrasted with "petrochemistry" which can be regarded as C₂ chemistry because ethylene (C₂H₄) is a primary material in this industry as mentioned above. C₁ chemistry is not particularly a new technological concept. The methanol synthesis from syngas has the oldest history. In 1913, BASF of Germany developed the technology for methanol synthesis from water gas, and industrialized it. After this development, France, Italy, and Japan successively started to prooduce methanol. The Fischer-Tropsch (F-T)synthesis (hydrocarbon synthesis from syngas) an epoch-making result in the history of catalytic synthesis, was industrialized in Germany and Japan over 40 years ago.

The synthesis of lower olefins from methanol is one of the major subjects in C_1 -chemistry. In early stage of the investigation, some kinds of narrow pore zeolites such as chabazite[1,2] and ZSM-34 of Mobil Oil [3,4] were found effective for this purpose. However, the short life caused by the coke deposition was the serious obstacle with these catalysts.

On the other hand, ZSM-5 catalyst exhibits longer life in the methanol-to-hydrocarbon conversions [5] because of its three-dimensional pore structure which reduces the pore blockage with coke [6]. Nevertheless, the typical ZSM-5 catalyst is not elective for the formation of light olefins because they are further converted to aromatics and paraffins on the strong acid sites. Since moderate acidity is necessary for highly selective synthesis of light olefins, some modifications for ZSM-5 to reduce the acid strength are conducted. Typical examples were the modification of ZSM-5 with the basic compounds such as P, Mg, Zn, Ca, Sr, and B [7-9]. Although the olefin selectivity was markedly increased by these modifications, the catalytic activity was greatly decreased because of the reduction of acid strength. Therefore, the catalysts were operated at higher temperatures such as above 550 °C for the reaction.

Recently, silicoaluminophosphate of 34 type (SAPO-34) has been found to exhibit a good catalytic performance for methanol conversion to light olefins. However, SAPO-5 and SAPO-11 may be concurrently formed with SAPO-34 causing the decrease of selectivity to light olefins.

In this work the major attempt will be made on studying various factors affecting the monophasic formation of SAPO-34. The optimum formula of the catalyst as well as the proper reaction conditions for methanol conversion to light olefins will be investigated.

The Objective of This Study

1. To study the preparation method of type-34 Silico-aluminophosphate catalyst.
2. To study the characterization of the prepared catalyst.
3. To study the ability of the prepared catalyst on methanol conversion to light olefins.
4. To study the stability of catalyst.

The Scope of This Study

1. Studying the effect of the several factors on the preparation of Silicoaluminophosphate-34. The factors were the mole ratio of component materials, and time for crystallization of catalyst .
2. Studying the characterization of prepared catalyst by the following methods :
 - Analyzing shape and size of the crystallites by Scanning Electron Microscope, SEM.
 - Analyzing surface areas of the catalysts by BET Surface Areas Measurement.
 - Analyzing the acidity of the catalysts by NH_3 -Temperature Programmed Desorption, NH_3 -TPD.
3. Studying the performance of the prepared catalysts on methanol conversion to light olefins under the following conditions :
 - Space velocity 2,000-10,000 h^{-1} .
 - Reaction temperature 250-600 $^{\circ}\text{C}$.
 - Time on stream
 - Methanol composition in feed gas, N_2 as diluent, 15-30%

The reaction products were analysed by Gas Chromatography.