

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Over the past 30 years, Thailand has been rapidly transformed from an agricultural country into an industrial developing country following the increasing of growing population's demand and export business. The petrochemical industry is one of the most rapid thriving industry because it produces the essential products for daily life that was shown by increasing of product values of 423 million U.S. dollars in 1996, 737 million U.S. dollars in 1997, 990 million U.S. dollars in 1998, and 1225 million U.S. dollars in 1999.¹ In addition, Figure 1.1² presents the values of plastic, one of the petrochemical products, which also increases every year.

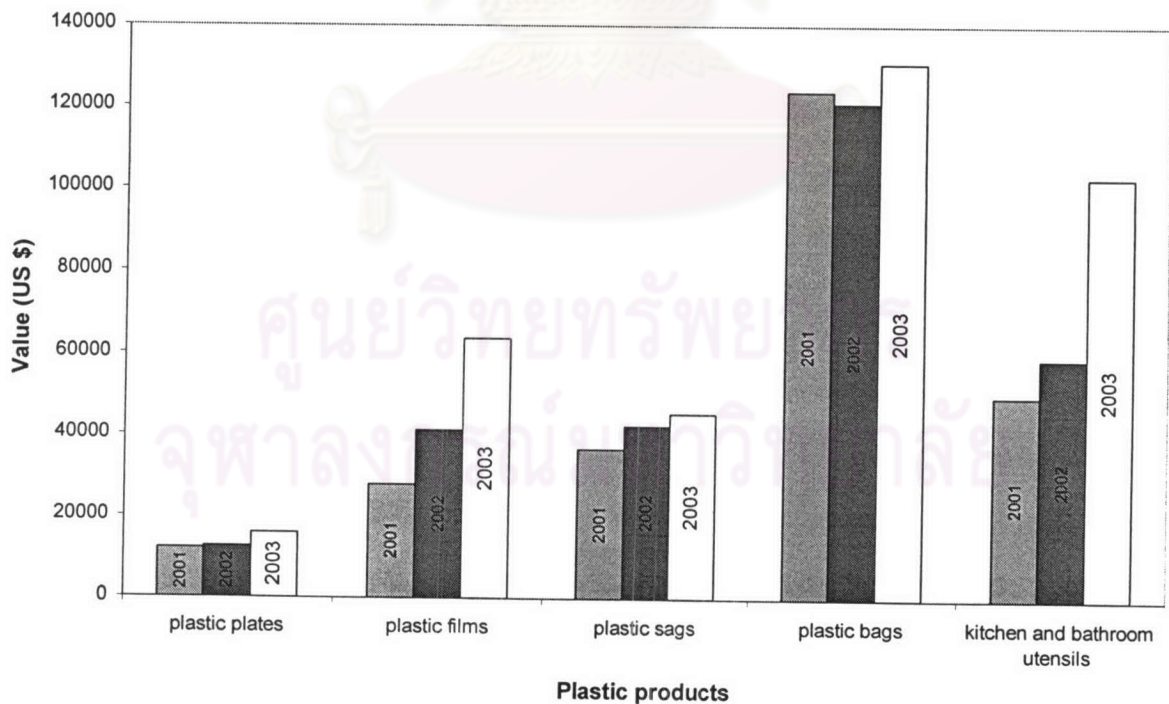


Figure 1.1 The value of plastic produced in 2001, 2002, and 2003 in Thailand.²

Nowadays the serious attention is the environmental problem such as pollution, as well as toxic and hazardous waste that is caused by expanding industry.³⁻⁶ Moreover people's awareness pressurizes industrial companies to use clean technologies and the government to enforce protective laws. The industries respond their solicitation by develop alternative manufacturing technologies that produce a minimum amount of waste and avoid the use of toxic or hazardous reagents.⁷ Furthermore, from the world oil crisis of the 1970s all countries realize that fossil fuel resources which are the main raw materials of many industries, especially transportation and petrochemical industries, are limited.⁶ The crude oil and its distilled products are high cost. To produce enough products and reduce the waste, the plants need to develop their process. One interesting topic in process improvement is the usage of catalyst. It was found that more than sixty percent of all commercial chemicals and ninety percent of industrial processes utilize catalysts.⁴

It was found that many chemical reactions could be catalyzed by iron compounds in both homogeneous and heterogeneous systems. Because it is cheap and less toxic, iron is one of transition metals that several researches have been interested to study its properties and apply it to use as catalysts. The use of heterogeneous catalyst is now interesting since the catalyst is easy to be separated and recovered. Iron can be introduced on the porous materials of high surface area by several methods such as ion exchange, impregnation, and so on. For insertion of irons in the framework of silicate materials, iron source solutions must be added into synthesized gel before crystallization. This method shows highly dispersed irons in materials with two forms, tetrahedrally coordinated irons at the framework positions and octahedrally coordinated irons at the extraframework positions of silicates. Extraframework iron can be use as catalysts in redox reaction, especially in reduction of NO_x compounds. The acid sites are generated when iron atoms are located at the tetrahedral positions. It was found that the acid properties of silicate materials incorporated with iron are different from those with other metals. For example, acid strength of Al-MFI is higher than that of Fe-MFI⁸⁻¹⁰.

The mesoporous material SBA-15, discovered recently in 1998^{11,12}, showed higher thermal, hydrothermal, and mechanical stabilities than other mesoporous materials. Metal incorporation in the silica framework of SBA-15 have been rarely studied.¹³⁻¹⁶ Moreover, the synthesis of iron incorporated silicate porous materials has been normally performed using ferric ions (Fe^{3+}) as iron source, but there are a few reports on the synthesis by using ferrous ions, Fe^{2+} as iron source. Furthermore, quite few researches concern about the synthesis of iron in the structure of mesoporous SBA-15.

This project aims to study the optimal condition for the synthesis of Fe-SBA-15 and its activities in the methanol conversion.

1.2 Objectives

- 1.2.1 To study the optimal condition for the direct synthesis of Fe-SBA-15 with various factors:
 - Iron sources in form of Fe^{2+} and Fe^{3+}
 - Si/Fe molar ratios in gel of 90 and 180
 - pH of gel between 1.0-2.5
- 1.2.2 To test the catalytic activity of Fe-SBA-15 in the methanol conversion

1.3 Related works

1.3.1 Related work on SBA-15 structure

From the success in the synthesis of hydrothermally stable mesoporous silica SBA-15 with nonionic template, (polyethylene oxide)₂₀-*block*-(polypropylene oxide)₇₀-*block*-(polyethylene oxide)₂₀, [(PEO)₂₀-(PPO)₇₀-(PEO)₂₀], under strong acidic condition in 1998^{11,12}, there have been many researches concerning properties, applications, and modifications. Several kinds of block copolymer were studied in their micellar behavior. Triblock copolymers of the PEO-PPO-PEO type, commercially known as Pluronics, are important non-ionic surface-active agents used in emulsifying, defoaming/antifoaming,

coating, cleaning, lubrication, and petrochemical industries.^{12,17} They display excellent interfacial stabilization properties and are low cost, nontoxic, and biodegradable.

In synthesis of porous material, nonionic block copolymers are an interesting structure-directing agent with self-assembly characters. Moreover, they are successful in modifying their ordering properties via adjusting solvent composition, molecular weight, or copolymer architecture, so the new morphologies and material properties can be produced. Bagshaw and co-workers¹⁸ used nonionic surfactants in aqueous solutions to synthesize wormlike disordered mesoporous silica and alumina in neutral media. Next the octaethylene glycol dodecyl ether, C₁₂EO₈, solutions were used as hydrophilic templates to prepare hexagonal mesoporous silica phases, and Attard *et al.*¹⁹ proposed the formation mechanism of mesoporous silica that occurs by a real liquid crystal template route. In 1997, Templin *et al.*²⁰ synthesized lamellar and hexagonal aluminosilicate that are highly ordered on length scales to 40 Å from diblock copolymer poly(isoprene-ethylene oxide) under acidic and nonaqueous solution. Voegtlin and co-worker²¹ found that fluoride anions promote the order of mesoporous silica using nonionic surfactant template under near-neutral conditions. The F⁻ ions are coordinated to silica species, which apparently provide sufficient electrostatic shielding and effective hydrogen bonding to form mesoporous silica structures.

After the discovery of SBA-15, its properties were studied by many research groups. Firstly the groups of Stucky^{11,12}, who first synthesized SBA-15 material, published in many papers. They studied the influence of 1,3,5-trimethylbenzene (TMB) and ethanol as cosurfactant to the formation of Pluronic template indicated that the increasing of micelle size could be controlled by the increasing of the TMB concentration and temperature, same as ethanol that enables swelling of the template micelles.^{12,22} Besides, from the report of Wang *et al.*²³, they found that the post-synthesis heat treatment after reaction at 35 °C is more effective for increasing the pore diameter and volume of SBA-15 than the addition of TMB before reaction.

Surprisingly, SBA-15 material is not only found in the mesopores but also found the micropores with size less than 20 Å in the wall connecting between mesopores

shown in Figure 1.2.^{24,25} Ryoo *et al*²⁶ found that the presence of micropores in the silica wall of SBA-15 exhibits a complicated relation between the pore size, pore volume, and specific surface area which is significantly different from that for normal hexagonal pores. When the SBA-15 was calcined at 1000 °C, its properties were found close to that of MCM-41 because the calcination at high temperature leads to the condensation of silanol groups at the micropore wall. Moreover, the amount of micropores decreases with the increasing of synthesis temperature, to end up with no micropores in matrixes for synthesis close to 130 °C showed in Figure 1.2.²⁴ Newalkar and Komarneni²⁷ proposed that the micropore volumes were found to decrease with an increase in added salt concentration, such as sodium chloride.

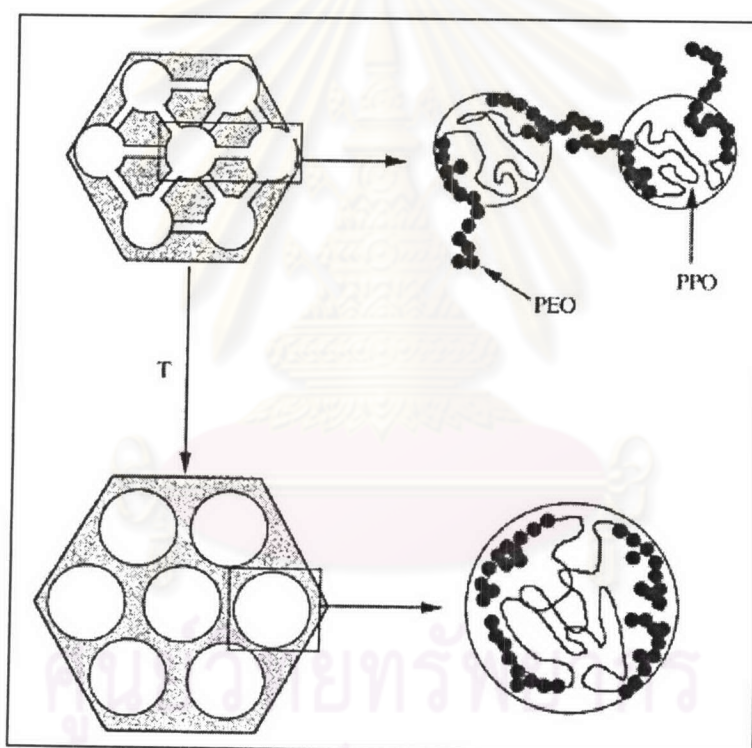


Figure 1.2 The micropores connecting the mesopores in the SBA-15 matrix (upper) and results from increasing the synthesis temperature (lower).²⁴

For using the SBA-15 as a catalyst, many applications were used the SBA-15 as the support for actual catalysts, particularly metal oxides because the high surface area allows the metal oxides to coat on the surface as monolayers. In addition their large pores also

permit access to bulky reagents. Many metal oxides were studied on the SBA-15 support for their catalytic application, for example, titanium oxide grafted on SBA-15 for oxidative catalysts, Cobalt oxide impregnated on SBA-15 was used as a catalyst for Fischer-Tropsch synthesis reaction, and rare earth oxides including La oxides were coated on the surface of SBA-15 with a high dispersion.^{23,28} Besides, SBA-15 immobilized with proteins including enzymes was used as a biocatalyst.²⁸ However, these techniques are limited by the tendency of many metal to agglomerate on the surface.

Many efforts have been devoted to incorporate the active metals into the framework of SBA-15. The first metal attempted was aluminium which was added into the gel during synthesis. It was found that very small amounts of aluminum was incorporated in silica framework.¹³ Afterwards Luan and co-worker¹⁴ investigated the three postsynthesis methods which were more effective to incorporate aluminum in the framework. SBA-15 was reacted with AlCl_3 in dry ethanol for route 1, with aluminum isopropoxide in dry hexane for route 2, and with aqueous solution of sodium aluminate for route 3. At the same amount of doped aluminum, the percentage of aluminum in framework was 100%, 76%, and 71% for route 1, 2, and 3, respectively. Another method, named microwave-hydrothermal synthesis^{15,16}, was successful in substitution of titanium and zirconium in SBA-15 framework. In addition, Zhang *et al.*²⁹ used fluoride ion to accelerate the hydrolysis rate of silica source (tetramethoxysilane) which reacted with Ti species to form titanosilicate, but the Ti content was quite low. Recently, the synthesis of metal incorporated SBA-15 started from the precursor of metalosilicate nanoclusters, for example the synthesis of Ti-SBA-15 was prepared from titanosilicate precursor.³⁰ However its catalytic properties were more like the metal incorporated in zeolite structure than that in mesoporous materials, such as MCM-41.

1.3.2 Related work on incorporation of the iron in silicate materials

The first report in 1972 showed that iron impurities in faujasite zeolites could occupy substitutional framework positions. From the electron spin resonance (ESR) study of local site of iron in silicate materials revealed that iron can be simultaneously present

in three forms; 1) iron ions in the framework, 2) iron ions acting as counterions, and 3) aggregating iron oxides on the surface of materials.³¹ Thus many researchers intentionally have attempted to synthesis of iron incorporated in zeolite framework. The iron in the framework position presents in the tetrahedral coordination surrounded by silica framework sharing oxygen atoms.

The insertion of iron in silica structure can be performed via the direct synthesis method. The basic synthesis of ferrisilicate in a zeolite structure starts from the mixing of iron and silica source solution at a low pH to form stable $\text{FeSiO}(\text{OH})_3^{2+}$ complexes. Then organic templates and bases are subsequently added to achieve the nucleation and crystallization of the zeolite structure. The formation of the complexes is prerequisite to incorporate iron in the tetrahedral framework. Mesoporous materials containing iron such as Fe-MCM-41, Fe-MCM-48, and Fe-HMS were also prepared with the formation of the ferrisilicate complexes and were tested for their catalytic activities, yet the framework iron easily escaped from their structures when they were calcined at high temperature. Recently, Han and co-worker³² synthesized the stable iron-incorporated SBA-15 structure, named MFS-9, via the two-step adapted direct synthesis method. They formed nanoclusters of Fe-MFI, which are like the ZSM-5 structure in the first procedure. In this step iron species would be fixed in the framework of nanoclusters, and then template and acid were added into the solution to form SBA-15 structure. It was successful in substitution of iron into framework of SBA-15, however, its catalytic activity in phenol hydroxylation reaction was closer to iron in microporous materials than that in mesoporous materials.

In case of iron source, there were a few studies in the use of Fe^{2+} , commonly Fe^{3+} . Inui *et al.*³³ synthesized Fe-silicates from both Fe^{2+} and Fe^{3+} , he found that the acid strength of acid sites on the Fe(II)-silicate is higher than that on the Fe(III)-silicate. Moreover, there was a study of difference in using Fe^{2+} and Fe^{3+} in $\text{AlPO}_4\text{-5}$ ³⁴, a kind of molecular sieve composed of alumina and phosphate as major structure. Although the synthesis started with Fe^{2+} source, it could easily be oxidized to Fe^{3+} during calcination to remove organic templates.