

CHAPTER I

INTRODUCTION

1.1 Background

Linear alkylbenzene sulfonate (LABS) is one of the most important biodegradable surfactant[1]. For industrial applications, the number of carbon atoms in the alkyl sidechain has played an important role, for example, C₁₁-C₁₂ are used in formulations of light-duty detergents, C₁₂-C₁₄ are for heavy-duty detergents, C₁₆-C₂₄ are for lubricants and C₁₆ is for surfactant flooding in tertiary oil recovery. LABS represents more than 40% of all surfactants used worldwide[2]. The total productions of surfactants in USA, Japan and Western Europe are shown in Figure 1.

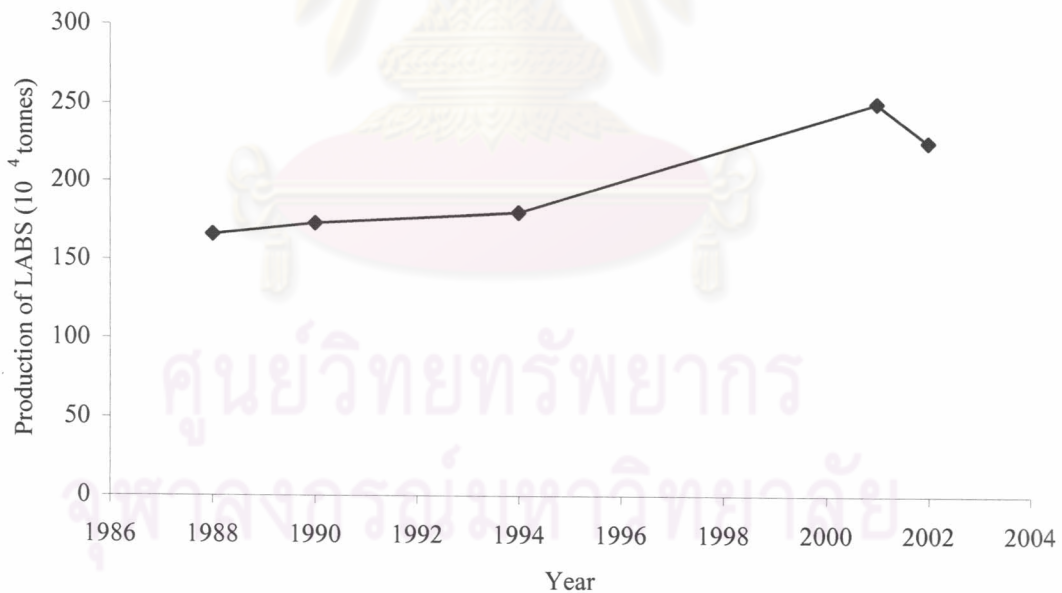


Figure 1 The worldwide production of LABS.

Generally, LABS is manufactured by sulfonation of linear alkylbenzene (LAB) with oleam. LAB is synthesized by Friedel-Crafts alkylation of benzene with α -olefins or

chloroalkanes in acidic condition[3]. Because of requirements for biodegradable detergents in many countries, there was a rapid changeover of using unbranched C₁₀-C₁₄ olefins as feedstocks for benzene alkylation to produce LAB. Many plants worldwide produce LAB using acidic catalyst, *i.e.* HF, HBF₄ and AlCl₃, in liquid phase at 40 to 70°C. Both HF and AlCl₃ being homogeneous acidic catalysts lead to formation of five isomers from 2-phenyl to 6-phenyldodecanes with variety in isomer distribution. 2-phenyldodecane is the most required isomer for industrial process because it is the best biodegradable one in environment. However, these catalysts are sources of pollution and corrosion of reactors and pose disposal problems. Further it is being hazardous and highly corrosive, HF requires special handling and equipment design. Thus, there is a tremendous scope to develop ecofriendly, reusable, noncorrosive and cheap catalysts for the alkylation of benzene with α -olefins.

In 1995s, the Detal process, a solid catalyst system, was introduced by UOP company[4]. This process can eliminate the problem of catalyst neutralization and disposal of HF. Since then, most of the new LAB plants have changed to solid catalyst-based process. In the case of environmentally safe, the heterogeneous catalyst is more advantageous.

It has been reported that clays have been used in alkylation reactions for over thirty years[5]. Montmorillonite was used to catalyze the alkylation of phenol with various alkyl halides as early as 1967. Clays loaded with mineral acids were proved to be successful catalysts for alkylation of phenol with alkenes producing mostly the ortho-structure. The development for cross-link of clays using polycations compounds, provided a new class of molecular sieves which are structurally different from zeolites. Cross-linked clays prepared are called pillared interlayer clays (PILC) and they have high thermal stability and surface area. As pillared property opens the clay layers, the accessibility of reactant molecules to the interlamellar catalytic site increases, resulting in high catalytic activity. Simultaneously, the pillar can exert a shape-selective effect which controls diffusion rates of reactants and products or formation of reaction intermediates. More recently, pillared clays especially Al-PILC materials[6], have been used in alkylation of aromatics with low carbon number of alkenes although acid-treated clay can

be more active. A simple bentonite earth has been used to catalyze the reaction of toluene with benzyl bromides.

Pillared clays also used in alkylation of aromatic with alcohols[7]. A pillared synthetic saponite is an efficient alkylation catalyst in the reaction of toluene with methanol. These pillared clays have high surface areas and interlayer spacing of 8.4 to 9.4 Å. They are stable at temperatures higher than 600 K.

The aim of this research is to synthesize iron and gallium doped iron oxides pillared clays. The clays, found in Thailand, are compared between hectorite and bentonite. This pillared clays were also tested for the catalytic activity in alkylation of benzene with 1-dodecene.

1.2 Objectives

1. To synthesize iron oxide and gallium-doped iron oxide pillared clays catalysts.
2. To compared catalytic activity of catalysts in alkylation of benzene with 1-dodecene.
3. To compare efficiency of reused catalyst with fresh catalyst.

1.3 Literature Reviews

In the 1940s, the first alkylbenzene sulfonate was produced by Friedel-Crafts alkylation of benzene with olefins followed by sulfonation with oleam[8]. Tetrapropene ($i\text{-C}_{12}\text{H}_{24}$) was the most important olefin feedstock for the manufacture of alkylbenzenes. This olefin could be manufactured along with other oligomers from propene-containing refinery gases using H_3PO_4 /support catalysts at 200 to 240°C and 15 to 25 bars. The result performed isododecylbenzenesulfonate with highly branched. This new synthetic surfactants had detergency characteristic and replaced natural soaps in the household laundry, dishwashing and several industrial applications. Although the branched alkylbenzene sulfonate was an effective detergent, it has slow rates of biodegradation in the environment. Until the early 1960s, the branched alkylbenzene sulfonate was largely

replaced by linear alkylbenzene sulfonate (LABS) in the United States, Japan and many European countries because of its superior biodegradability.

Many acidic liquids and solids including HF, H₂SO₄, clays[8], zeolites and metal oxides have been found to be a catalyst for the alkylation of benzene with various olefins.

Olson[9] studied the synthesis of phenyldodecane from alkylation of benzene with 1-dodecene using HF, H₂SO₄ and AlCl₃ as a homogeneous catalyst. All catalysts exhibited high conversion of 1-dodecene up to 70% and produced mainly 5 isomer products *i.e.* 2-, 3-, 4-, 5-, 6-phenyldodecanes. However, H₂SO₄ showed the highest selectivity (41%) to 2-phenyldodecane, the best biodegradable isomer, followed by AlCl₃ and HF.

Sivasanker and Thangaraj[10] investigated the 5 isomer product distributions from alkylation of benzene with 1-dodecene at 135°C over 6 different catalysts *i.e.* SiO₂-Al₂O₃, montmorillonite, amberlyst-15, zeolite, HF and AlCl₃. Homogeneous catalysts exhibited higher activity than heterogeneous catalysts. All catalysts mainly produced 2-phenyldodecane isomer more than 25%.

González et. al.[11] prepared mixed Al³⁺ and Ga³⁺ pillared montmorillonite. The basal spacing of samples decreased from 20 to 18 Å after thermal treatment at 500°C. The resulting materials had a high thermal stability, maintaining 71% of its specific surface area after being heated at 700°C for 2h. Moreover, the surface of sample showed a large number of acid sites.

Bradley and Kydd[12] prepared the Ga₁₃, Al₁₃, GaAl₁₂-polyoxocations pillared montmorillonite. The acidic characters of the samples were studied through infrared spectroscopic investigations of the sorption of the probe molecule pyridine. The results showed that all samples showed high acidic site. The Lewis acid sites were in the order of Ga₁₃ > Al₁₃ > GaAl₁₂, whereas the Brønsted acid site were followed by GaAl₁₂ > Al₁₃ > Ga₁₃-pillared montmorillonite. The obtained samples were tested for catalytic activity in cumene conversion. All samples showed high conversion of cumene up to 20% but it produced two main products from two reactions *i.e.* cracking and dehydrogenation. The Ga₁₃-pillared montmorillonite exhibited almost exclusively dehydrogenation activity, whereas the Al₁₃ and GaAl₁₂-pillared montmorillonite exhibited both of cracking and dehydrogenation.

Storaro et. al.[13] prepared aluminum and aluminum/iron pillared bentonite. Water and acetone were investigated as solvents for suspension clays in the pillaring process. The result showed that both solvents exhibited the same result. The prepared pillared bentonite gave highly ordered clay sheet with d-spacing in the range of 18 to 20 Å. They showed high specific surface area more than 300 m²/g.

Zurita et al.[14] prepared the Fe-pillared montmorillonite using [Fe₃(CH₃COO)₇OH·2H₂O]⁺NO₃⁻ as iron precursor. The basal spacing of obtained products depends on drying temperatures. The basal spacing was decreased from 21 to 17 Å when drying temperature rised up to 700°C. However, the Fe-pillared montmorillonite obtained from 500°C still showed high surface area up to 270m²/g. The catalytic activity of the samples was tested by the CO hydrogenation reaction, comparing with montmorillonite. The Fe-pillared montmorillonite exhibited higher conversion and better selectivity towards CH₄ and C₂-C₄ olefins.

Mishra and Parida[15] prepared the transition metals (Fe(III), Cr(III) and Mn(III)) pillared montmorillonite by ion exchange method. The samples were used as catalysts for nitration of chlorobenzene. All catalysts showed the catalytic activity in the order of Fe > Cr > Mn oxide pillared montmorillonites, whereas the selectivity to para-chlorobenzene was in the order of Cr > Mn > Fe-pillared montmorillonite. However, all catalysts exhibited high para selectivity more than 92%.

Govea and Steinfink[16] prepared the Fe-polyoxocation montmorillonite by ion exchange method. The Fe-polyoxocation precursor was prepared by hydrolyzing FeCl₃ solution with Na₂CO₃. The obtained sample showed the expansion of clay layer up to 15 Å. Moreover, this material was stable when heated to 500°C for 60 h.

Meriaudeau et. al.[17] reported the catalytic activity of H-form zeolites in alkylation of benzene with 1-dodecene. The reaction was performed at 100°C in batch mode. The results indicated that H-ZSM-5 and H-ZSM-12 performed low catalytic activity for production of linear phenyldodecane.

Price et. al.[18] prepared Al supported hexagonal mesoporous silica (Al-HMS). Al-HMS and homogeneous AlCl₃ were compared for their catalytic activity in production of linear alkylbenzenes. The obtained catalysts showed higher activity than AlCl₃.

In addition, the catalyst exhibited significant improvement in selectivity towards both the monoalkylated product and the preferred 2-phenyl isomer.

Cao et. al.[19] tested the catalytic activity of FAU, BEA and EMT zeolites in alkylation of benzene with 1-dodecene. Decane was used as solvent in this reaction. The reaction temperatures were performed in the range of 100 to 140°C. All zeolites achieved no greater than 25% conversion of 1-dodecene. The selectivities toward 2-phenyldodecane were very high up to 50%.

Lenarda et. al.[20] prepared montmorillonite pillared with aluminum or aluminum-gallium polyoxycations. The materials showed d-spacing and surface area up to 18 Å and 300m²/g, respectively. The catalytic activity for alkylation of benzene with ethylene to produce ethyl benzene was determined. The Al-Ga mixed pillar species resulted to be the more active catalysts than the pure Al pillar one.

Okumura et. al.[21] synthesized Ga-containing MCM-41 by two methods, direct synthesis (Ga-MCM-41) and impregnation (Ga/MCM-41). The obtained products were tested for the catalytic activity in benzene and benzyl chloride alkylation. The resulting showed that Ga/MCM-41 exhibited a higher conversion and yielded the diphenylmethane (DPM) than Ga-MCM-41. However, the formation of DPM was not found using MCM-41 as a catalyst.

Choudhary and Jana[22] tested the catalytic benzylation of benzene and substituted benzene by benzyl chloride over metal chloride supported on clays and Si-MCM-41. The catalysts were synthesized by impregnation method. The metal chloride supported catalysts showed the activity in the order of FeCl₃ > InCl₃ > GaCl₃ > ZnCl₃ supported clays and Si-MCM-41, respectively. Moreover, all catalysts exhibited high selectivity for diphenylmethane up to 80%.

Balci and Gökçay[23] studied the effect of drying methods *i.e.* air drying, spray drying and vacuum drying on the physical properties of iron intercalated clays. Bentonite clay and FeCl₃ were used as starting materials for synthesized iron intercalated clays. The Fe pillared species were prepared by hydrolyzing with Na₂CO₃. XRD patterns of samples from different drying methods showed clay-layered structure with d-spacing about 13 Å. Moreover all samples showed the specific surface area about 60m²/g at 200°C.

Yadav and Doshi[1] synthesized linear phenyldodecane from alkylation of benzene with 1-dodecene by 13 different catalysts such as montmorillonite K-10, Al-pillared K-10 and $\text{AlCl}_3/\text{FeCl}_3$ -exchanged K-10 etc. It was found that, Al-pillared K-10 showed higher conversion of 1-dodecene than montmorillonite K-10 and Al-exchanged montmorillonite K-10. These catalysts selected to 3-phenyldodecane more than 2-phenyldodecane isomer. Although $\text{AlCl}_3/\text{FeCl}_3$ -exchanged K-10 performed lower conversion, but the selectivity to 2-phenyldodecane was higher than 3-phenyldodecane.

Huerta et. al.[24] synthesized iron pillared clay. An oxocentered trinuclear iron (III) acetate aquo complex, $[\text{Fe}_3\text{O}(\text{OCOCH}_3)_6 \cdot 3\text{H}_2\text{O}]^+$ was used as an iron precursor. The obtained pillared clays showed the basal spacing of 18 Å and specific surface area about $200\text{m}^2/\text{g}$ at 450°C . A catalytic activity was performed in ethylbenzene dehydrogenation reaction. The results showed that iron pillared clay exhibited higher conversion of ethylbenzene and higher selectivity to styrene than pure clay in the same reaction period.

Zhang et. al.[25] investigated the kinetics of benzene alkylation with 1-dodecene over a SiO_2 supported tungstophosphoric acid catalyst. The activation energies suggested that low reaction temperature would be beneficial for increasing the selectivity of the reaction towards 2-phenyldodecane isomer.

Su et. al.[26-27] prepared Ga-modified HZSM-5 zeolites by ion exchange method. The catalytic activity was tested in alkylation of benzene with propane. The alkylated benzene with propane led to toluene and ethylbenzene with the conversion up to 30% at 550°C . Other alkylated products such as xylene, cumene and n-propylbenzene were also produced in lower quantities. The coke deposition probably occurred in the zeolite channel resulting from condensed polyaromatics.

Belver et. al.[28] prepared Fe-saponite catalyst by intercalation of mixed Al-Fe solution and impregnation of Al-pillared saponite with Fe. Both Fe-saponites showed the same d-spacing in the range of 14 to 18 Å at 500°C . XRD patterns of all samples still showed the clay-layered structure indicating that the samples had a high thermal stability. The resulting materials showed high specific surface area up to $200\text{m}^2/\text{g}$.

Belaroui et. al.[29] intercalated the iron into the layers of the lalithe which is a bentonite Algerian clay. Although Algerian clay is mainly composed of bentonite,

it contains impurities *e.g.* quartz, calcite. The iron intercalated clay was expanded to 16 Å and showed high specific surface area up to 260 m²/g.



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