

CHAPTER I INTRODUCTION

1.1 Motivation

Esterification of carboxylic acids with alcohols represents, producing water as by-product, a well-known category of liquid-phase reactions of industrial interest due to the importance of organic ester products in area of fuel, food, cosmetics and pharmaceuticals. The esterification is easily reversible by addition of water, so-called hydrolysis. Currently, the synthesis of esters via the esterification is achieved commercially the presence of liquid acid catalysts, such as sulfuric acid, hydrochloric acid, and *para*-toluene sulfonic acid (*p*-TsOH). These catalysts actively promote the complete conversion of carboxylic acids, giving a high yield of the esters since they possess high acidity and are soluble in the reaction mixture. However, at the end of the production process, a neutralization step is necessary to stop the catalytic reaction, and then a purification of the ester products can be attempted. Typically, the use of these homogeneous acid catalysts is associated with high toxicity, material corrosion, large amount of liquid waste and product contamination.

Recently, application of heterogeneous acid catalysts to the esterification has attracted considerable attention since the process would be simplified using of a designed-column reactor packed with the solid catalysts [1-3]. Consequently, need of the subsequent steps for the catalyst separation and the product purification can be reduced. More importantly, the most of heterogeneous catalysts themselves are recyclable, less toxic and non-corrosive. Various acidic materials have been investigated as heterogeneous catalysts for the esterification of simple carboxylic acids, such as sulfated zirconia [4], zeolites [5], heteropolyacids [6] and acidic ion-exchange resins (Amberlyst series) [7]. For example, Amberlyst-15, an acidic ion-exchange resin, can be used as a catalyst in the esterification. It has a high density of sulfonic acid group. Moreover, it possesses a high hydrophobicity that can reduce poisoning of acid sites due to water adsorption. So, the Amberlyst resin has been explored a powerful catalyst for various acid-catalyzed organic reactions. Nevertheless, its applicability to the esterification is limited by low thermal stability (less than <140 °C). Other solid acid candidate used in the esterification is SAC-13, a silica-supported Nafion[®] catalyst (SAC-13) [8]. It has higher acid strength than the conventional solid acids and higher thermodynamic stability than the acidic resins (Amberlyst series). Furthermore, SAC-13 exhibits highly accessible acid sites due to



the porous silica matrix with adjustable pore openings in nanometer scale that diminishes the likelihood of mass diffusion limitation, making it possible for the catalytic reaction of bulky reactants. Although it has great potential for the esterification, this commercial catalyst is expensive.

Hexagonal mesoporous silicas (HMSs) functionalized with organo-sulfonic acid groups are attractive catalysts in esterification due to their combination of an extremely high surface area and strength of sulfonic acid groups [9, 10]. The organo-functional groups on the mesoporous surface can be incorporated by either post grafting [11, 12] or by direct co-condensation [13]. The post-grafting method exhibit a relatively well-ordered meso-structure, but there are limited by the non-uniform distribution of the organic moieties due to organosilane precursors congregating on the pore mouth of the mesoporous channels and the external surface of mesoporous materials [14, 15]. Co-condensation can performed in one-step process in which the hydrolysis and the condensation of silica source as tetraethoxysilane (TEOS) and mercapto-organosilane simultaneously occur around the micellar organic template in the presence of hydrogen peroxide (H_2O_2) as the oxidizing agent to convert the thiol groups *in situ* to the corresponding sulfonic acid [16]. Although organo-functionalized mesoporous materials via co-condensation method provides a better control of the quantity and distribution of organo-functional groups, residual silanol groups ($\equiv Si-OH$) on their surface encourage hydrophilicity and promote the hydrolysis of esters via the adsorbed H_2O . The amount of surface silanol groups in functionalized mesoporous silica could be reduced by the successive grafting of trialkylorganosilane [17, 18]. However, the resulting materials have low textural properties.

Natural rubber is a polymer that has *cis* 1,4- isoprene as monomer and hydrophobic property. There are many attempts to modified properties of natural rubber through various techniques such as functionalization and adding nanofillers etc. Especially, preparation of natural rubber and silica as composite via sol-gel is able to increase the natural rubber properties, including mechanical properties, surface area and thermal stability. As report in the previous studies, silica itself can be modified with organosilanes via the reaction of surface silanol group. Sulfonic acid group-functionalized silica can be used as an acid catalyst in esterification. The purpose of this work is to prepare natural rubber and silica composites functionalized with sulfonic acid group that have appropriate properties for the esterification of simple carboxylic acids. It is expected that the silica matrix functionalized with



sulfonic acid group would provide high acidity and high surface area while the hydrophobic nature of natural rubber could reduce water adsorption and inhibit the reverse reaction of ester products.

1.2 Objectives

1.2.1 Preparation of natural rubber and silica composites functionalized with sulfonic acid group via a sol-gel method

1.2.2 Characterization of the prepared composites by several techniques

1.2.3 Study of catalytic performance of the prepared composites in an esterification

1.3 Scope of this work

This work was separated into 3 parts. The scope of this study is as follow and the experimental framework is shown in Figure 1.1.

1.3.1 Firstly (Part A), mesoporous composites based on natural rubber (NR) and hexagonal mesoporous silica (HMS): NR/HMS composites were prepared via *in situ* sol-gel method. The effects of molar composition of silica source (tetraethylorthosilicate:TEOS) : H₂O : organic template (dodecylamine:DDA) on the physicochemical properties of the NR/HMS composites obtained were investigated. In addition, the characterization of synthesis composites was analyzed by thermogravimetric/differential thermal analysis (TG/DTA), Fourier-transform infrared spectroscopy (FTIR), ²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), particle size distribution analysis, N₂ adsorption-desorption measurement and H₂O adsorption-desorption measurement.

1.3.2 Part B, propylsulfonic acid-functionalized mesoporous composites based on natural rubber (NR) and hexagonal mesoporous silica (HMS): NR/HMS-SO₃H composites were prepared via an *in situ* sol-gel process using tetrahydrofuran as the synthesis media. Tetraethylorthosilicate as the silica source, was simultaneously condensed with 3-mercaptop



propyltrimethoxysilane in a solution of NR followed by oxidation with hydrogen peroxide to achieve the mesoporous composites containing propylsulfonic acid groups. The effects of molar composition of organosilane (3-mercaptopropyltrimethoxysilane: MPTMS)/tetraethyl orthosilicate (TEOS) on the physicochemical properties of the NR/HMS-SO₃H composites obtained were investigated. The characterization of synthesis composites were analyzed as in section 1.3.1.

- 1.3.3 Finally (Part C), the catalytic activities of synthesis composites were studied in esterification of various carboxylic acids. The NR/HMS-SO₃H composites were compared their activities with the propylsulfonic acid-functionalized HMS (HMS-SO₃H) prepared under similar conditions and SAC-13. In addition, effects of type of carboxylic acids (acetic acid, octanoic acid and lauric acid) and alcohols (ethanol) and reaction conditions on conversion and selectivity were investigated.



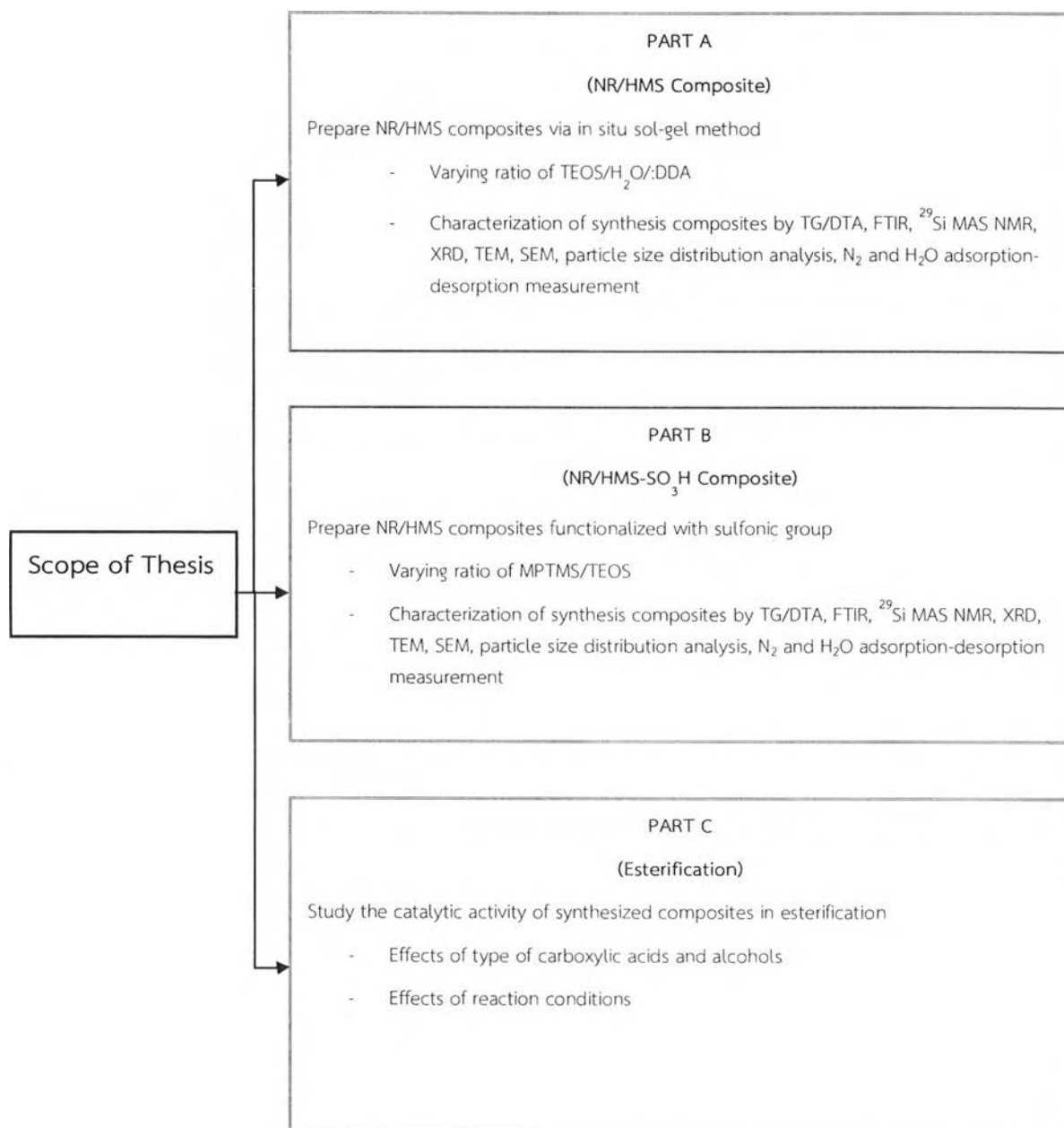


Figure 1.1 Experimental framework of this study.



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