

## CHAPTER VI

### ESTERIFICATION OF CARBOXYLIC ACID WITH ALCOHOL OVER ACIDIC MESOPOROUS SILICAS AND NATURAL RUBBER/MESOPOROUS SILICA COMPOSITES

In this Chapter, the sulfonic acid-functionalized mesoporous composites based on natural rubber (NR) and hexagonal mesoporous silica (HMS): (NR/HMS-SO<sub>3</sub>H composite) were tested in the esterification of carboxylic acid with alcohol. To investigate the advantage of hydrophobicity of NR/HMS-SO<sub>3</sub>H composites on the catalytic esterification, they were evaluated with various carboxylic acids (acetic acid, octanoic acid and lauric acid) and using alcohol as ethanol. Their catalytic activities were compared with sulfonic acid-functionalized hexagonal mesoporous silicas (HMS-SO<sub>3</sub>Hs) and silica-supported Nafion<sup>®</sup> catalyst (SAC-13). Moreover, the effect of H<sub>2</sub>O addition on the catalytic performance of acidic mesoporous catalysts was investigated. The amount of acidic mesoporous catalyst was also studied in order to obtain high ester yield in the catalytic esterification. In addition, NR/HMS-SO<sub>3</sub>H was investigated for the reusability in the esterification of octanoic acid with ethanol.

#### 6.1 Study on esterification of various carboxylic acids with ethanol over acidic catalysts

##### 6.1.1 Esterification of acetic acid with ethanol

Esterification of acetic acid with ethanol was examined over acidic mesoporous catalysts (SAC-13, HMS-SO<sub>3</sub>Hs and NR/HMS-SO<sub>3</sub>Hs). The reaction was carried out in a three-neck round bottom flask by using amount of catalyst, 1 wt.%; reaction temperature, 80 °C; molar ratio (acetic acid to ethanol), 1:2; reaction time, 8 h. Figure 6.1 shows the profiles of acetic acid conversion from esterification in the absence and the presence of various acidic mesoporous catalysts. The data reported were obtained from 2 experimental replicates. In addition, the results from evaluating the catalytic activity, acidity and surface area of these acidic catalysts are summarized in Table 6.1.



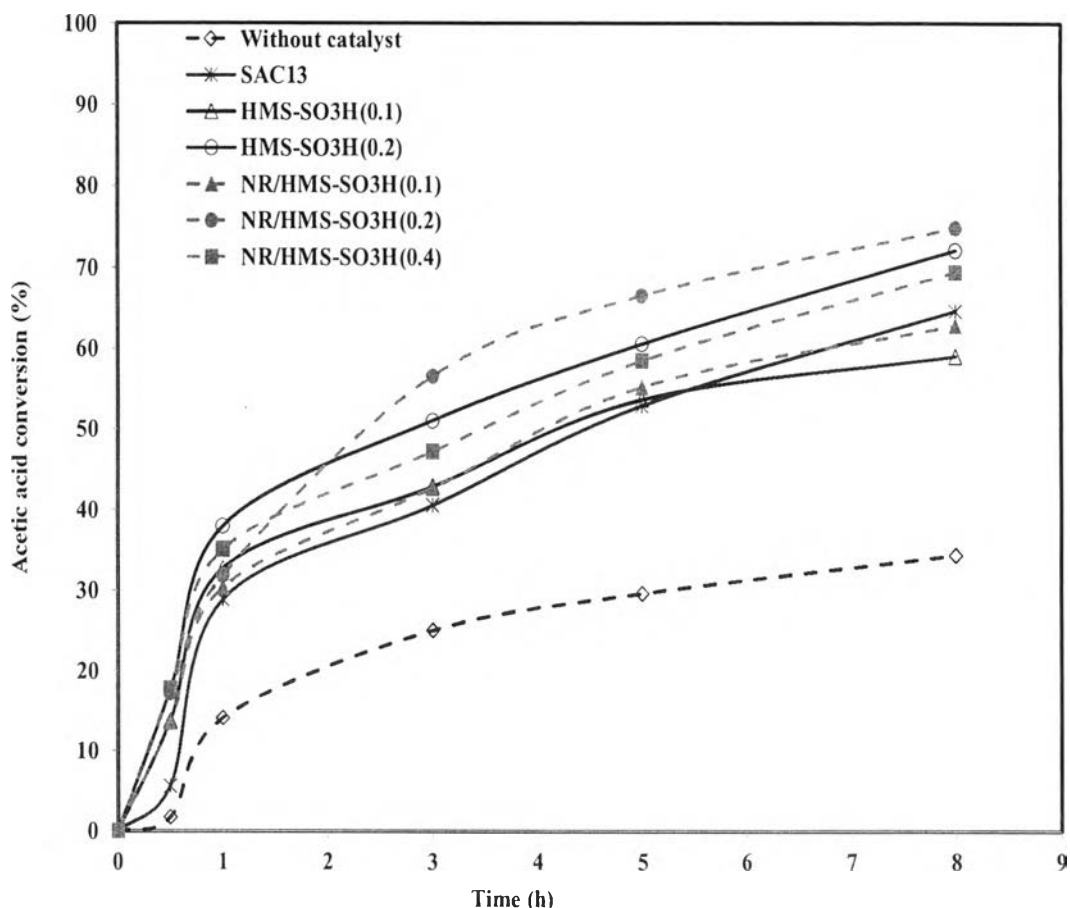


Figure 6.1 Esterification of acetic acid with ethanol over acidic mesoporous catalysts. Reaction conditions: amount of catalyst, 1 wt.%; reaction temperature, 80 °C; molar ratio (acetic acid to ethanol), 1:2; reaction time, 8 h.

From Figure 6.1, the esterification itself is an auto-catalyzed reaction. Without the addition of any catalyst, it was found that the esterification spontaneously occurred at 80 °C, giving the acetic acid conversion of 34.4% (Table 6.1). When the acidic solid catalysts were applied to the reaction, the acid conversion was enhanced as depicted in Figure 6.1. The ethyl acetate produced from the esterification of acetic acid with ethanol could not be determined by GC due to a similar boiling point of ethanol (78 °C), ethyl acetate (77 °C) and THF (66 °C) (as diluent) that resulted in overlapped peaks in chromatogram (Appendix A). With increasing the acidity of HMS-SO<sub>3</sub>H and NR/HMS-SO<sub>3</sub>H catalysts, the degree of acetic acid conversion was enhanced within the first hour. Moreover, the HMS-SO<sub>3</sub>H (0.2) catalyst gave the highest acetic acid conversion due to its high acidity and high surface area. After 3 h, the NR/HMS-SO<sub>3</sub>H (0.2) catalyst exhibited the highest acetic acid conversion despite it

possessed lower acidity and lower surface area than HMS-SO<sub>3</sub>H (0.2). It should be due to hydrophobicity of NR/HMS-SO<sub>3</sub>H that retarded the hydrolysis of ester.

**Table 6.1** Esterification of acetic acid with ethanol over acidic mesoporous catalysts.

| Catalysts                      | $S_{BET}^a$<br>(m <sup>2</sup> g <sup>-1</sup> ) | Acidity<br>(mmol g <sup>-1</sup> ) <sup>b</sup> | Initial rate<br>(mmol min <sup>-1</sup> ) <sup>c</sup> | Acetic acid<br>conversion (%) | TON (h <sup>-1</sup> ) <sup>d</sup> |
|--------------------------------|--|---|--|-------------------------------|-------------------------------------|
| Without catalyst               | -  | -   | 0.07   | 34.4                          | -                                   |
| SAC-13                         | 214  | 0.19  | 0.24   | 64.6                          | 978                                 |
| HMS-SO <sub>3</sub> H (0.1)    | 759  | 1.05  | 0.60   | 59.0                          | 436                                 |
| HMS-SO <sub>3</sub> H (0.2)    | 673  | 1.35  | 0.78   | 72.1                          | 432                                 |
| NR/HMS-SO <sub>3</sub> H (0.1) | 560  | 0.83  | 0.59   | 62.8                          | 546                                 |
| NR/HMS-SO <sub>3</sub> H (0.2) | 543  | 1.18  | 0.76   | 74.9                          | 483                                 |
| NR/HMS-SO <sub>3</sub> H (0.4) | 524  | 1.61  | 0.78   | 69.4                          | 369                                 |

Reaction conditions : stirring rate, 300 rpm; amount of catalyst, 1 wt.%; reaction temperature, 80 °C; molar ratio (acetic acid to ethanol), 1:2; reaction time, 8 h..

<sup>a</sup>BET surface area.

<sup>b</sup> Determined by acid-base titration with NaOH aq. (0.02 M).

<sup>c</sup> Acetic acid conversion rate (mmol.min<sup>-1</sup>) determined over 30 min.

<sup>d</sup> Turnover number, determined as the mmol of acetic acid conversion/(acid density × weight of catalyst loading × time (0.5 h)).

From the catalyst activity reported in Table 6.1, both of the functionalized mesoporous silicas and NR/HMS composites exhibited an increase in the initial rate of reaction with the acidity due to an increase in the amount of active site. Although the acidity of NR/HMS-SO<sub>3</sub>H composites was significantly lower than that of the HMS-SO<sub>3</sub>H prepared with the similar loading of MPTMS, the initial rates observed for both catalysts were different by a few percent. The negative effect of acidity loss on the reaction rate over NR/HMS-SO<sub>3</sub>H might be compensated by the reactants diffusion enhanced by the hydrophobic layer of NR. Therefore, the NR/HMS-SO<sub>3</sub>H catalysts exhibited higher conversion of acetic acid and turnover number (TON) than HMS-SO<sub>3</sub>H catalysts. However, the acid conversion was dropped to 69.4% when the esterification was catalyzed by NR/HMS-SO<sub>3</sub>H (0.4). It should be due to an increase in its affinity for H<sub>2</sub>O as revealed by the measurement of H<sub>2</sub>O adsorption-desorption



(Figure 5.10(b)). In addition, SAC-13 with the lowest amount of acid sites and surface area exhibited higher acetic acid conversion than HMS-SO<sub>3</sub>H (0.1) due to a higher acid strength of SAC-13. SAC-13 as Nafion/silica composite has the nature of the molecular environment of the SO<sub>3</sub>H sites different from the propylsulfonic acid groups that was functionalized in the mesoporous silica (HMS-SO<sub>3</sub>H). More electron withdrawing environments of the SO<sub>3</sub>H sites in Nafion molecule provide higher acid strength, leading to higher catalytic activity in esterification [107,108].

### 6.1.2 Esterification of octanoic acid with ethanol

To investigate an advantage of hydrophobic property of NR/HMS-SO<sub>3</sub>H in the catalytic esterification, the functionalized pure silica HMS and functionalized NR/HMS composites were comparatively tested in the esterification of carboxylic acid with longer hydrocarbon chain. The conversion of octanoic acid and the profiles of ethyl octanoate in the absence and the presence of various acidic mesoporous catalysts (SAC-13, HMS-SO<sub>3</sub>Hs and NR/HMS-SO<sub>3</sub>Hs) are shown in Figure 6.2 (a) and (b), respectively. The reaction was operated under the conditions those were similar to the esterification of acetic acid with ethanol except for the reaction temperature that was 100 °C.

As can be seen in Figure 6.2, the profiles of octanoic acid conversion are similar to the profiles of ethyl octanoate yield those correspond to the stoichiometry of esterification. This esterification is spontaneous reaction at 100 °C. Without the addition of any catalysts, the yield of ethyl octanoate is lowest (24.3%) as shown in Table 6.2. Both of the octanoic acid conversion and ethyl octanoate yield were enhanced when the acidic mesoporous catalysts were added to the reaction. Within the first 1 hour, NR/HMS-SO<sub>3</sub>H catalysts exhibited higher octanoic acid conversion and ethyl octanoate yield than the HMS-SO<sub>3</sub>H catalysts although they possessed lower acidity and surface area. These results were different from the esterification of acetic acid with ethanol. It should be due to the hydrophobicity of NR/HMS-SO<sub>3</sub>H catalysts that enhanced the diffusion of octanoic acid to the acid sites. After the first hour, NR/HMS-SO<sub>3</sub>H catalysts also exhibited higher acid conversion and ester yield than HMS-SO<sub>3</sub>H catalysts until 8 h of reaction time. Moreover, NR/HMS-SO<sub>3</sub>H (0.2) gave the highest acid conversion and ester yield. These results indicated that the hydrophobic property of NR/HMS-SO<sub>3</sub>H catalysts benefited the esterification by preventing the readsorption of H<sub>2</sub>O onto the acid sites and retarding the hydrolysis of esters.



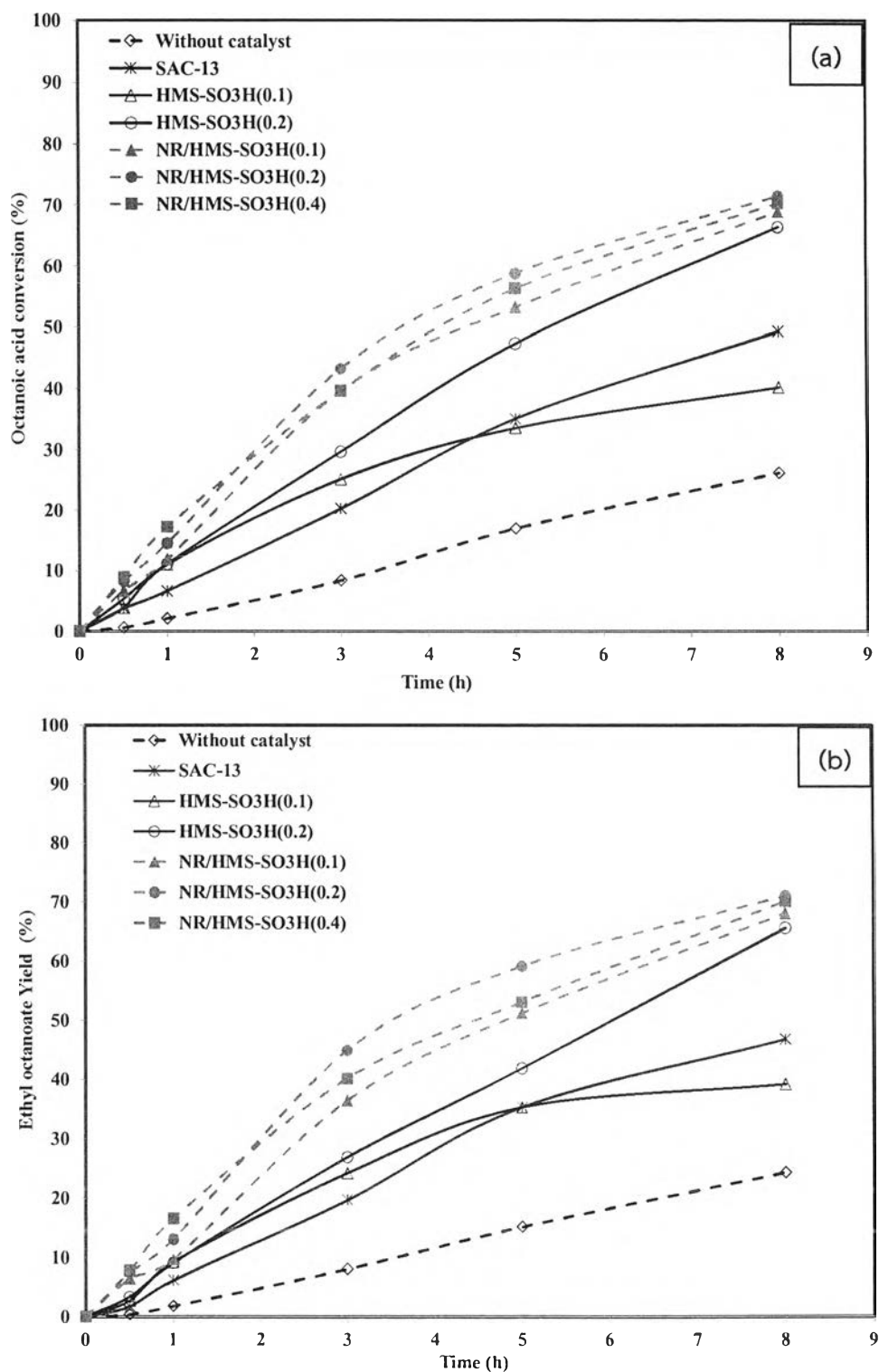


Figure 6.2 Esterification of octanoic acid with ethanol over acidic mesoporous catalysts: (a) octanoic acid conversion and (b) ethyl octanoate yield. Reaction conditions: amount of catalyst, 1 wt.%; reaction temperature, 100 °C; molar ratio (octanoic acid to ethanol), 1:2; reaction time, 8 h.

**Table 6.2** Esterification of octanoic acid with ethanol over acidic mesoporous catalysts.

| Catalysts                      | $S_{BET}^a$<br>( $m^2 g^{-1}$ ) | Acidity<br>( $mmol g^{-1}$ ) <sup>b</sup> | Initial rate<br>( $mmol min^{-1}$ ) <sup>c</sup> | Ethyl octanoate<br>yield (%) | TON ( $h^{-1}$ ) <sup>d</sup> |
|--------------------------------|---------------------------------|---|--|------------------------------|-------------------------------|
| Without catalyst               | -                               | -   | 0.01   | 24.3                         | -                             |
| SAC-13                         | 214                             | 0.19                                      | 0.05   | 46.8                         | 126                           |
| HMS-SO <sub>3</sub> H (0.1)    | 759                             | 1.05                                      | 0.08   | 39.1                         | 36                            |
| HMS-SO <sub>3</sub> H (0.2)    | 673                             | 1.35                                      | 0.10   | 65.6                         | 35                            |
| NR/HMS-SO <sub>3</sub> H (0.1) | 560                             | 0.83                                      | 0.18   | 70.1                         | 109                           |
| NR/HMS-SO <sub>3</sub> H (0.2) | 543                             | 1.18                                      | 0.21   | 71.0                         | 87                            |
| NR/HMS-SO <sub>3</sub> H (0.4) | 524                             | 1.61                                      | 0.22   | 68.1                         | 67                            |

Reaction conditions : stirring rate, 300 rpm; amount of catalyst, 1 wt.%; reaction temperature, 100 °C; molar ratio (octanoic acid to ethanol), 1:2; reaction time, 8 h.

<sup>a</sup>BET surface area.

<sup>b</sup> Determined by acid-base titration with NaOH aq. (0.02 M).

<sup>c</sup> Octanoic acid conversion rate ( $mmol.min^{-1}$ ) determined over 30 min.

<sup>d</sup> Turnover number, determined as the mmol of ethyl octanoate yield/(acid density × weight of catalyst loading × time (0.5 h)).

Table 6.2 summarizes the catalytic performance of SAC-13 and the synthesized acidic catalysts in the esterification of octanoic acid with ethanol. When the acid amount of HMS-SO<sub>3</sub>H catalysts and NR/HMS-SO<sub>3</sub>H catalysts was increased, the initial rate of reaction was enhanced similarly to the case of the esterification of acetic acid with ethanol (section 6.1.1). Moreover, these synthesized catalysts revealed higher the initial rate than the commercial mesoporous composite (SAC-13) because of their high acidity. Although the amount of acid site and surface area of NR/HMS-SO<sub>3</sub>H catalysts was significantly lower than those of the HMS-SO<sub>3</sub>H prepared with a similar MPTMS loading level, the initial rate, yield and turnover number (TON) of NR/HMS-SO<sub>3</sub>H catalysts were higher than those of HMS-SO<sub>3</sub>H catalysts. These results were related to hydrophobicity of NR/HMS-SO<sub>3</sub>H as mentioned in Figure 6.2. However, NR/HMS-SO<sub>3</sub>H (0.4) with the highest acid amount showed a decrease in the octanoate yield to 68.1 % because of higher amount of acid sites that resulted in an increase in the H<sub>2</sub>O affinity of NR/HMS-SO<sub>3</sub>H catalysts as mentioned in section 6.1.1.



### 6.1.3 Esterification of lauric acid with ethanol

Lauric acid with long hydrocarbon chain was also used as a reactant in the esterification with ethanol to evaluate the advantage of hydrophobic property of NR/HMS-SO<sub>3</sub>H catalysts on catalytic esterification.

Figure 6.3 (a) and (b) show the profiles of lauric acid conversion and the ethyl laurate yield, respectively, in the absence and the presence of various acidic mesoporous catalysts (SAC-13, HMS-SO<sub>3</sub>Hs and NR/HMS-SO<sub>3</sub>Hs). The reaction was operated at 120 °C, while the other conditions were similar to the esterification of acetic acid with ethanol (section 6.1.1). Both profiles of the lauric acid conversion and the ethyl laurate yield are similar corresponding to the stoichiometry of esterification as shown in Figure 6.3. The esterification of lauric acid with ethanol occurred spontaneous at 120 °C resulted in the ethyl laurate yield of 29.2% (Table 6.3). The increase of the lauric acid conversion and the ethyl laurate yield was observed when the acidic mesoporous catalysts were added in to the esterification as shown in Figure 6.3. NR/HMS-SO<sub>3</sub>H catalysts revealed higher degree of the lauric acid conversion and the ethyl laurate yield than that of the HMS-SO<sub>3</sub>H catalysts throughout 8 h of reaction time. Those were similar to the esterification of octanoic acid with ethanol. Furthermore, NR/HMS-SO<sub>3</sub>H (0.2) exhibited the highest ester yield among the synthesized acidic catalysts. These results suggested that the advantage of hydrophobicity of the NR/HMS-SO<sub>3</sub>H in catalytic esterification as mentioned in section 6.1.2.

The catalytic performance in the esterification of lauric acid with ethanol over these acidic mesoporous catalysts is summarized in Table 6.3. NR/HMS-SO<sub>3</sub>H catalysts exhibited higher catalytic activity than the HMS-SO<sub>3</sub>H catalysts similarly to the case of the esterification of octanoic acid with ethanol. Moreover, NR/HMS-SO<sub>3</sub>H (0.2) gave the highest ethyl laurate yield of 73.8%. These result indicated that the hydrophobicity of NR/HMS-SO<sub>3</sub>H catalysts benefited in the catalytic esterification of lauric acid with ethanol as mentioned in Figure 6.3.



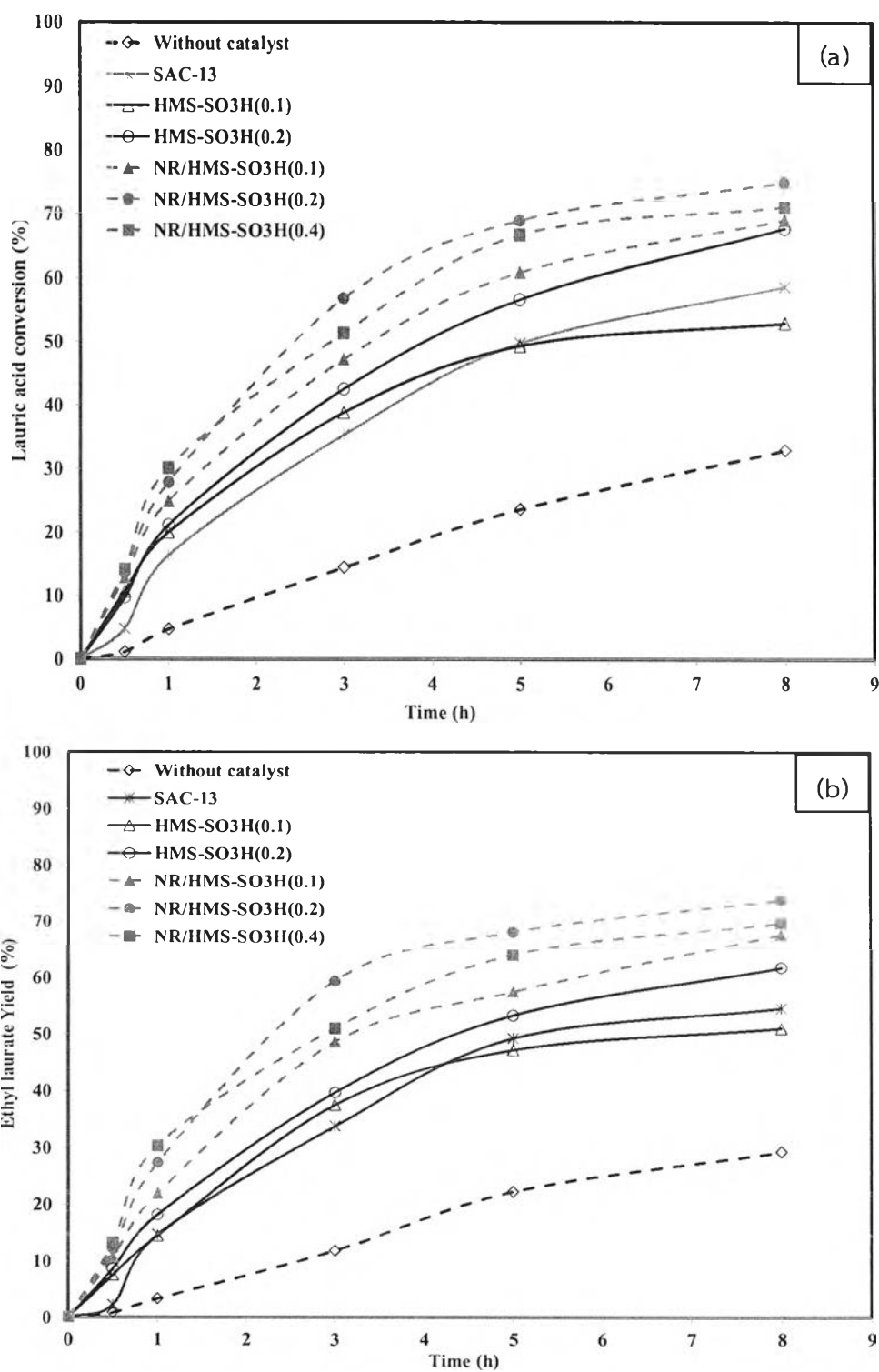


Figure 6.3 Esterification of lauric acid with ethanol over acidic mesoporous catalysts: (a) lauric acid conversion (b) ethyl laurate yield. Reaction conditions: amount of catalyst, 1 wt.%; reaction temperature, 120 °C; molar ratio (lauric acid to ethanol), 1:2; reaction time, 8 h.



**Table 6.3** Esterification of lauric acid with ethanol over acidic mesoporous catalysts.

| Catalysts                      | $S_{BET}^a$<br>( $m^2 g^{-1}$ ) | Acidity<br>( $mmol g^{-1}$ ) <sup>b</sup> | Initial rate<br>( $mmol min^{-1}$ ) <sup>c</sup> | Ethyl laurate<br>yield (%) | TON ( $h^{-1}$ ) <sup>d</sup> |
|--------------------------------|---------------------------------|---|--|----------------------------|-------------------------------|
| Without catalyst               | -                               | -   | 0.02   | 29.2                       | -                             |
| SAC-13                         | 214                             | 0.19                                      | 0.05   | 54.5                       | 118                           |
| HMS-SO <sub>3</sub> H (0.1)    | 759                             | 1.05                                      | 0.17   | 51.0                       | 71                            |
| HMS-SO <sub>3</sub> H (0.2)    | 673                             | 1.35                                      | 0.20   | 61.8                       | 64                            |
| NR/HMS-SO <sub>3</sub> H (0.1) | 560                             | 0.83                                      | 0.24   | 67.7                       | 129                           |
| NR/HMS-SO <sub>3</sub> H (0.2) | 543                             | 1.18                                      | 0.28   | 73.8                       | 102                           |
| NR/HMS-SO <sub>3</sub> H (0.4) | 524                             | 1.61                                      | 0.30   | 69.7                       | 83                            |

Reaction conditions : stirring rate, 300 rpm; amount of catalyst, 1 wt.%; reaction temperature, 120 °C; molar ratio (lauric acid to ethanol), 1:2; reaction time, 8 h.

<sup>a</sup> BET surface area.

<sup>b</sup> Determined by acid-base titration with NaOH aq. (0.02 M).

<sup>c</sup> Lauric acid conversion rate ( $mmol.min^{-1}$ ) determined over 30 min.

<sup>d</sup> Turnover number, determined as the mmol of ethyl laurate yield/(acid density × weight of catalyst loading × time (0.5 h)).

## 6.2 Effect of catalyst amount on esterification

The effects of catalyst loading on the esterification were studied by using different amount of the acidic mesoporous catalysts (SAC-13, HMS-SO<sub>3</sub>H (0.2) and NR/HMS-SO<sub>3</sub>H (0.2)). The catalyst loading is an important parameter that needs to be optimized to increase the ester yield. The catalytic activity of these catalysts in the esterification of octanoic acid with ethanol is summarized in Table 6.4. In addition, the degree of ethyl octanoate yield in various reaction times is exhibited in Figure 6.4.



As shown in Figure 6.4, the increasing amount of the acidic mesoporous catalysts from 1 to 3 wt.% resulted in higher degree of the ethyl octanoate yield. The maximum yield of ethyl octanoate was achieved in the presence of 3 wt.% of the acidic mesoporous catalysts. The increase of ethyl octanoate yield was expected as the higher amount of catalysts because the amount of acid sites was enhanced. The acidic mesoporous catalysts with similar amount exhibited the ethyl octanoate yield as following order: NR/HMS-SO<sub>3</sub>H (0.2) > HMS-SO<sub>3</sub>H (0.2) > SAC-13. It should be due to both advantages of hydrophobicity and high acidity of NR/HMS-SO<sub>3</sub>H (0.2), leading to higher ester yield in esterification.

From Table 6.4, the increasing amount of the acidic mesoporous catalysts also resulted in higher the initial rate and ester yield because of high amount of acid sites. In addition, the highest initial rate was observed in NR/HMS-SO<sub>3</sub>H (0.2) catalyst due to its hydrophobicity and acidity as mention in Figure 6.4. Furthermore, NR/HMS-SO<sub>3</sub>H (0.2) catalyst exhibited the highest ethyl octanoate yield (88.1%) among the others, when used 3 wt.% catalyst loading in esterification of octanoic acid with ethanol.

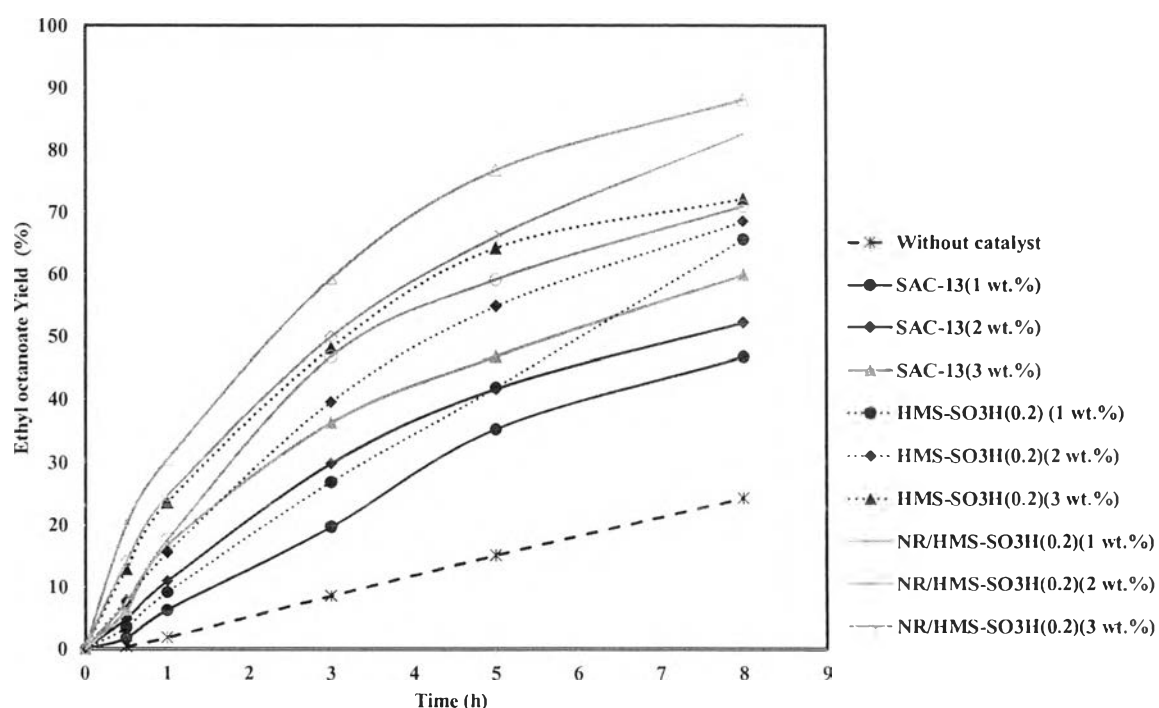


Figure 6.4 Effect of catalyst loading in esterification of octanoic acid with ethanol. Reaction conditions: amount of catalyst, 1, 2, 3 wt.%; reaction temperature, 100 °C; mole ratio (carboxylic acid to ethanol), 1:2; reaction time, 8 h.

**Table 6.4** Effect of catalyst loading in catalytic esterification of octanoic acid with ethanol over SAC-13, HMS-SO<sub>3</sub>H catalysts and NR/HMS-SO<sub>3</sub>H composites.

| Catalysts                     | Acidity <sup>a</sup><br>(mmol g <sup>-1</sup> ) | % Catalysts<br>loading | Initial rate<br>(mmol min <sup>-1</sup> ) <sup>b</sup> | Yield of<br>ethyl octanoate (%) |
|-------------------------------|---|------------------------|--|---------------------------------|
| SAC-13                        | 0.19  | 1                      | 0.05   | 46.8                            |
|                               |   | 2                      | 0.14   | 52.2                            |
|                               |   | 3                      | 0.18   | 59.9                            |
| HMS-SO <sub>3</sub> H(0.2)    | 1.35  | 1                      | 0.10   | 65.6                            |
|                               |   | 2                      | 0.22   | 68.5                            |
|                               |   | 3                      | 0.37   | 72.2                            |
| NR/HMS-SO <sub>3</sub> H(0.2) | 1.18  | 1                      | 0.21   | 71.0                            |
|                               |   | 2                      | 0.40   | 82.6                            |
|                               |   | 3                      | 0.57   | 88.1                            |

Reaction conditions : stirring rate, 300 rpm; reaction temperature, 100 °C; mole ratio (octanoic acid to ethanol), 1:2; reaction time, 8 h.

<sup>a</sup> Determined by acid-base titration with NaOH aq. (0.02M).

<sup>b</sup> Octanoic acid conversion rate (mmol.min<sup>-1</sup>) determined over 30 min.

### 6.3 Effect of H<sub>2</sub>O on catalytic activity

In order to evaluate the effect of H<sub>2</sub>O addition on the catalytic activity of acidic mesoporous catalysts (SAC-13, HMS-SO<sub>3</sub>Hs and NR/HMS-SO<sub>3</sub>Hs), these catalysts were tested in the esterification of octanoic acid with ethanol. The amount of H<sub>2</sub>O addition was 5 wt.% based on the amount of octanoic acid. H<sub>2</sub>O was mixed with ethanol prior esterification.

The profile of the ethyl octanoate yield produced from the esterification over SAC-13, HMS-SO<sub>3</sub>H (0.2) and NR/HMS-SO<sub>3</sub>H (0.2) catalyst with and without H<sub>2</sub>O addition are shown in Figure 6.5 (a) and (b), respectively. Without the addition of H<sub>2</sub>O, it was found that the acidic mesoporous catalysts exhibited the ethyl octanoate yield as following order: NR/HMS-SO<sub>3</sub>H (0.2) > HMS-SO<sub>3</sub>H (0.2) > SAC-13 as shown in Figure 6.5 (a). These acidic catalysts showed lower the ethyl octanoate yield in the case of H<sub>2</sub>O addition. Especially, the ester yield of the HMS-SO<sub>3</sub>H (0.2) was drastically dropped, while observed a few deference of the ester yield over the acidic



mesoporous composites (SAC-13 and NR/HMS-SO<sub>3</sub>H (0.2)) as shown in Figure 6.5 (b). Moreover, NR/HMS-SO<sub>3</sub>H (0.2) still exhibited the highest yield of the ethyl octanoate. These results suggested that the hydrophobicity of NR/HMS-SO<sub>3</sub>H could prevent H<sub>2</sub>O adsorption onto acid sites.

Table 6.5 summarizes the catalytic results of SAC-13, HMS-SO<sub>3</sub>H (0.2) and NR/HMS-SO<sub>3</sub>H (0.2) catalyst in the esterification of octanoic acid with ethanol in the case with and without H<sub>2</sub>O addition. These acidic catalysts showed lower catalytic activity in the esterification in the case of H<sub>2</sub>O addition. Especially, the lower of initial rates of HMS-SO<sub>3</sub>H (0.2) catalyst was significant difference in the case of H<sub>2</sub>O addition. It should be due to high acidity of HMS-SO<sub>3</sub>H (0.2) catalyst that resulted in affinity for H<sub>2</sub>O adsorption onto acid sites, leading to lower ester yield in esterification. Whereas, SAC-13 exhibited a few difference the initial rate due to its low acidity. However, NR/HMS-SO<sub>3</sub>H (0.2) still exhibited the highest initial rate and yield of ethyl octanoate. These results suggested that the hydrophobicity of NR/HMS-SO<sub>3</sub>H could prevent H<sub>2</sub>O adsorption onto acid sites. This result implied that the NR/HMS-SO<sub>3</sub>H (0.2) catalyst has high amount of acid site remaining, leading to higher catalytic activity in the esterification.

**Table 6.5** Effect of H<sub>2</sub>O addition in catalytic esterification of octanoic acid with ethanol over SAC-13, HMS-SO<sub>3</sub>H (0.2) catalyst and NR/HMS-SO<sub>3</sub>H (0.2) catalyst.

| Catalysts                     | acidity <sup>a</sup><br>(mmol g <sup>-1</sup> ) | No H <sub>2</sub> O addition                           |                                 | H <sub>2</sub> O addition 5 wt.% (0.61 g)              |                                 |
|-------------------------------|---|--|---------------------------------|--|---------------------------------|
|                               |   | Initial rate<br>(mmol min <sup>-1</sup> ) <sup>b</sup> | Yield of ethyl<br>octanoate (%) | Initial rate<br>(mmol min <sup>-1</sup> ) <sup>b</sup> | Yield of ethyl<br>octanoate (%) |
| SAC-13                        | 0.19  | 0.05   | 46.8                            | 0.05   | 45.2                            |
| HMS-SO <sub>3</sub> H(0.2)    | 1.35  | 0.1  | 65.6                            | 0.08   | 27.4                            |
| NR/HMS-SO <sub>3</sub> H(0.2) | 1.18  | 0.21   | 71                              | 0.12   | 65.8                            |

Reaction conditions : stirring rate, 300 rpm; amount of catalyst, 1 wt.%; reaction temperature, 100 °C; molar ratio (octanoic acid to ethanol), 1:2; reaction time, 8 h.

<sup>a</sup> Determined by acid-base titration with NaOH aq. (0.02M).

<sup>b</sup> Octanoic acid conversion rate (mmol.min<sup>-1</sup>) determined over 30 min.

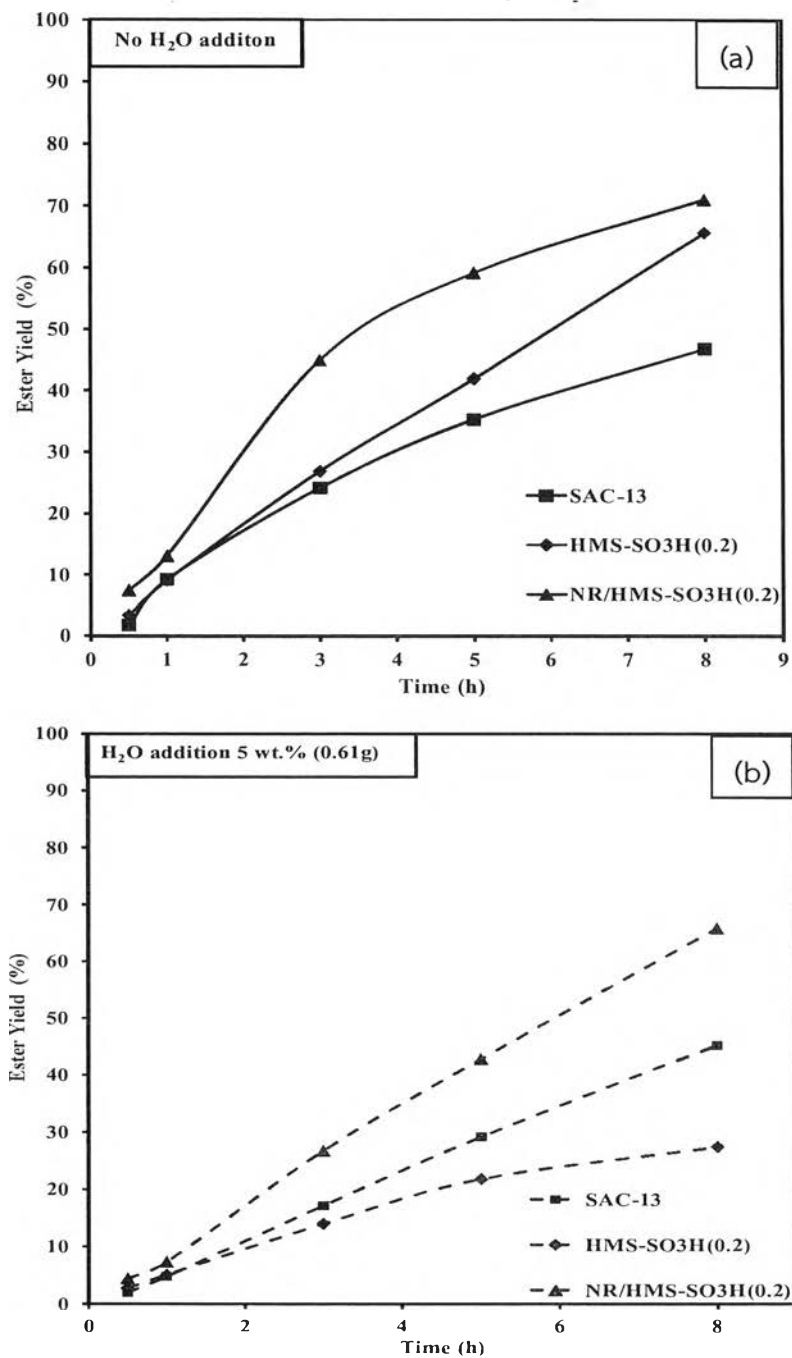
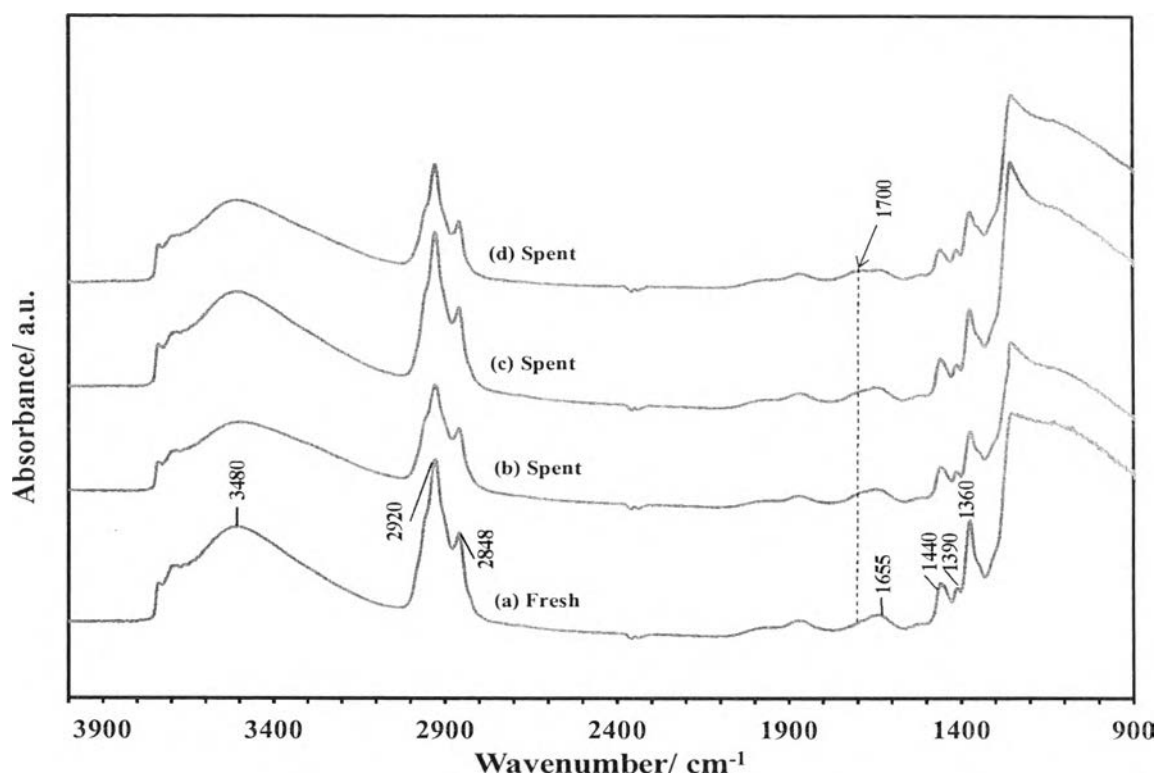


Figure 6.5 Effect of H<sub>2</sub>O on catalytic esterification of octanoic acid with ethanol over acidic mesoporous catalysts: (a) ethyl octanoate yield in case of without H<sub>2</sub>O addition and (b) H<sub>2</sub>O addition. Reaction conditions: amount of catalyst, 1 wt.%; reaction temperature, 100 °C; molar ratio (octanoic acid to ethanol), 1:2; reaction time, 8 h.

## 6.4 Reusability of NR/HMS-SO<sub>3</sub>H composite

### 6.4.1 Effect of organic solvent for washing spent NR/HMS-SO<sub>3</sub>H composite

The reusability NR/HMS-SO<sub>3</sub>H composite was evaluated in esterification of various carboxylic acids with ethanol. After completed the esterification, the spent NR/HMS-SO<sub>3</sub>H catalyst was filtered and washed with acetone to remove substances, products and by-products that attached on its surface and acid site, and then dried at 100 °C overnight. The spent NR/HMS-SO<sub>3</sub>H catalysts was analyzed by FTIR spectroscopy in order to investigate the effect of the solvent washing and the stability of organic species (NR and organo-functional group) on their structures as shown in Figure 6.6(b-d).



**Figure 6.6** FTIR spectra of (a) fresh NR/HMS-SO<sub>3</sub>H (b-d) spent NR/HMS-SO<sub>3</sub>H after 1<sup>st</sup> cycle in esterification of (b) acetic acid, (c) octanoic acid and (d) lauric acid with ethanol. Spent NR/HMS-SO<sub>3</sub>H was washed with acetone and dried at 100 °C overnight prior analysis.



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Figure 6.6(a) shows FTIR spectrum of fresh NR/HMS-SO<sub>3</sub>H catalyst. The bands of the fresh catalyst was observed between 1000 and 1300 cm<sup>-1</sup> which represented the Si–O–Si stretching of the silica framework, and observed around 3480 cm<sup>-1</sup> that related to hydrogen-bonded silanol groups. In addition, FTIR spectrum of the fresh NR/HMS-SO<sub>3</sub>H exhibited various characteristic bands of the NR structure at 2920, 2848, 1655, 1440 and 1390 cm<sup>-1</sup>, and showed the band of propylsulfonic acid at 1360 cm<sup>-1</sup>. From Figure 6.5(b-d), all FTIR spectra of the spent catalysts after acetone washing exhibited the bands similar to the fresh one. This result revealed the benefit of washing with acetone for removal organic substances and the stability of the NR and organo-functional group in composite structure. However, the spectra of spent catalysts exhibited additional band at 1700 cm<sup>-1</sup> that corresponded to the C=O group comparing to the fresh one. This result suggested that a part of carboxylic acid or ester products still remained and adhered on the surface of catalysts.

In addition, elemental composition as C, H, N and S content of the spent catalysts after acetone washing exhibited higher the C and H contents than that of the fresh one as shown in Table 6.6. This result suggested that there were some organic substances cumulative on the surface of catalyst. However, the amount of sulfur in the spent catalysts was not observed the significant difference comparing to the fresh one. This result could confirm the stability of propylsulfonic acid group on the composite structure after the esterification.

**Table 6.6** Elemental composition (C,H,N,S contents) of fresh NR/HMS-SO<sub>3</sub>H and spent NR/HMS-SO<sub>3</sub>H after used at 1<sup>st</sup> cycle in esterification.

| Sample   | CHNS analysis <sup>b</sup> |     |     |     |
|--|----------------------------|-----|-----|-----|
|  | wt. %                      |     |     |     |
|  | C                          | H   | N   | S   |
| Fresh NR/HMS-SO <sub>3</sub> H (0.2)                       | 12.5                       | 3.0 | 0.5 | 2.5 |
| Spent NR/HMS-SO <sub>3</sub> H (0.2) (rxn.-a) <sup>a</sup> | 14.5                       | 3.0 | 0.5 | 2.5 |
| Spent NR/HMS-SO <sub>3</sub> H (0.2) (rxn.-b) <sup>a</sup> | 15.5                       | 3.5 | 0.5 | 2.5 |
| Spent NR/HMS-SO <sub>3</sub> H (0.2) (rxn.-c) <sup>a</sup> | 15.5                       | 4.0 | 0.5 | 2.5 |

<sup>a</sup>Spent NR/HMS-SO<sub>3</sub>H was washed with acetone and dried at 100 °C overnight.

<sup>b</sup>Determined by CHNS analyzer.

rxn.-a = esterification of acetic acid with ethanol.

rxn.-b = esterification of octanoic acid with ethanol.

rxn.-c = esterification of lauric acid with ethanol.



#### 6.4.2 Reusability of NR/HMS-SO<sub>3</sub>H in the esterification of octanoic acid with ethanol

The reusability of NR/HMS-SO<sub>3</sub>H (0.2) catalyst was evaluated in the esterification of octanoic acid with ethanol as presented in Figure 6.6. The ethyl octanoate yield was not significant difference within 4 cycles. This result confirmed its reusability in the esterification. However the ester yield was dropped at the 5<sup>th</sup> cycle. Therefore, the spent NR/HMS-SO<sub>3</sub>H after the 5<sup>th</sup> cycle was investigated lower efficiency. This was caused by using CHNS analyzer as shown in Table 6.7. The spent catalyst exhibited higher C and H contents compared to the fresh one due to the organic substances remaining. This result suggested that the acid sites of the spent NR/HMS-SO<sub>3</sub>H were covered with the organic substances resulted in lower amount of active sites, leading to lower ethyl octanoate yield in the esterification. In addition, the spent catalyst was found the lower of S content than that of the fresh one. It should be due to the acetone washing for several times resulted in leaching of the acid sites.

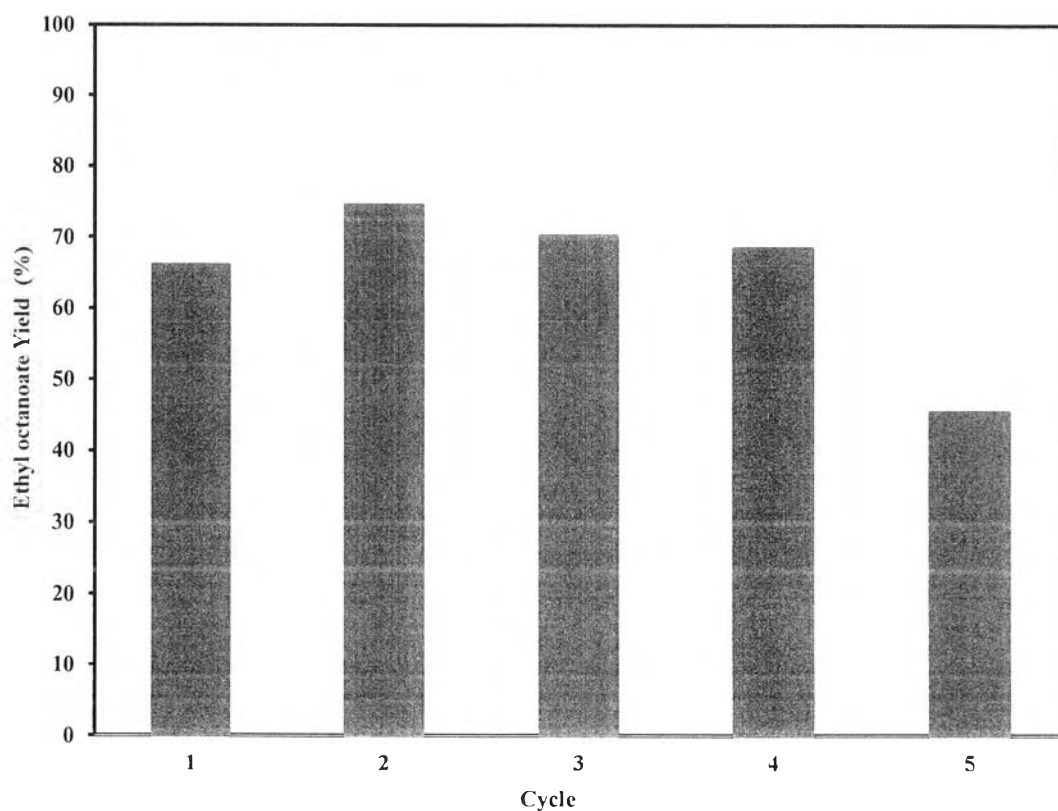


Figure 6.7 Reusability of NR/HMS-SO<sub>3</sub>H (0.2) in esterification of octanoic acid with ethanol.





**Table 6.7** Elemental composition (C,H,N,S contents) of fresh NR/HMS-SO<sub>3</sub>H and spent NR/HMS-SO<sub>3</sub>H after the 5<sup>th</sup> cycle in the esterification of octanoic acid with ethanol.

| Sample  | CHNS analysis <sup>b</sup> |     |     |     |
|---|----------------------------|-----|-----|-----|
|   | wt. %                      |     |     |     |
|   | C                          | H   | N   | S   |
| Fresh NR/HMS-SO <sub>3</sub> H (0.2)  | 14.0                       | 3.0 | 0.5 | 2.5 |
| Spent NR/HMS-SO <sub>3</sub> H (0.2) (5 <sup>th</sup> cycle -rxn.-b) <sup>a</sup> | 16.6                       | 5.0 | 0.2 | 1.5 |

<sup>a</sup> Spent NR/HMS-SO<sub>3</sub>H was washed with acetone and dried at 100<sup>o</sup>C overnight.

