

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

All of the results from Chapter IV to VI can be separately concluded in each part as shown belows;

Chapter IV: NR/HMS composites with a high structural order and mesoporosity were successfully prepared via *in situ* sol-gel process. THF was used for the first time as the media for the synthesis of HMS. The HMS-T exhibited superior structural and textural properties compared to the conventional HMS-E synthesized in ethanol. The incorporation of NR molecules into the mesoporous structure expanded the hexagonal unit cell and channel wall thickness. The FTIR and ^{29}Si MAS NMR results suggested that the amount of silanol groups on the surface of HMS were reduced by coverage of NR molecules. The NR/HMS composites exhibited the high BET surface area, large pore volume and narrow pore size distribution. Moreover, the formation of the NR/HMS composites induced the agglomeration of HMS nanoparticles, resulting in an enhanced textural porosity and hydrophobicity.

NR/HMS composites with good structural and textural properties could be achieved by carefully adjusting the synthesis composition. Increasing the amount of H_2O resulted in improving hexagonal arrays of the mesoporous structure and increasing total surface area, total pore volume and BJH pore diameter. The structural and textural properties of the NR/HMS composites could be enhanced by increasing DDA concentrations, but the excess of DDA or DDA: TEOS ratios were detrimental to the formation of hexagonal mesophase. In addition, increasing of the NR loading level blocked the primary mesoporous channels of the HMS.

Chapter V: A series of NR/HMS- SO_3H composites with hexagonal meso structure was successfully prepared as acidic composites using the *in situ* sol-gel process simultaneously with a one-pot functionalization of the HMS surface with a propylsulfonic acid group. The incorporation of NR and/or the organo-functional group into the HMS structure reduced the amount of free silanol groups and enhanced the hydrophobicity of the materials. Increasing the amount of MPTMS increased the acidity of the obtained materials, but decreased the structural ordering and the textural properties. The detrimental effect of the increased MPTMS/TEOS molar ratio on the S_{ext} was more pronounced in the NR/HMS- SO_3H composite than



the HMS-SO₃H one, suggesting that the functionalization occurred on the external surface of HMS to a certain degree in the presence of NR. In addition, NR/HMS-SO₃H composites possessed high acidity, high mesoporosity of HMS and the hydrophobicity of the NR.

Chapter VI: NR/HMS-SO₃H catalysts with hydrophobicity and high acidity exhibited better catalytic activity than those of HMS-SO₃H catalysts and SAC-13 in the esterification of simple carboxylic acids with ethanol. When increasing hydrocarbon chain of carboxylic acid as a reactant in the esterification with ethanol, NR/HMS-SO₃H catalysts enhanced the catalyst activity due to the advantage of their hydrophobicity. The NR/HMS-SO₃H with MPTMS:TEOS molar ratio of 0.2 provided the highest catalytic performance. The maximum yield of ethyl octanoate in the esterification of octanoic acid with ethanol was achieved by using NR/HMS-SO₃H (0.2) with 3% wt. of catalyst loading. Furthermore, NR/HMS-SO₃H catalyst still exhibited high catalytic activity in case of H₂O addition in the reaction mixture. In addition, NR/HMS-SO₃H catalyst exhibited reusability in the esterification of octanoic acid with ethanol at least 4 cycles.

7.2 Recommendation and future works

Although the NR/HMS-SO₃H catalysts gave the high catalytic performance carboxylic acid with ethanol, there are some limitations when using with severe condition (high temperature or pressure) because of low stability of NR polymer. Therefore, the polymer with high thermal stability proposed to prepared acidic mesoporous composites for further studies. In addition, the esterification of carboxylic acid with alcohol over acidic mesoporous silica and acidic mesoporous composite should be comparatively studied to obtain the kinetic data and revealed the reaction mechanism. Finally, these catalysts should be studied in continuous process.

