



## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

In this study, the adsorbents used for desulfurization were prepared by ion-exchanging NaX and NaY zeolites with  $\text{Ni}^{2+}$  and  $\text{Cu}^+$  cations using two different techniques: liquid phase ion exchange (LPIE) and solid state ion exchange (STIE). Our results have shown that up to 73.52% of total  $\text{Na}^+$  in NaX and 68.23% of total  $\text{Na}^+$  in NaY zeolite can be replaced by  $\text{Ni}^{2+}$  by LPIE technique. The amount of metal loading was varied by changing the solution:adsorbent ratio (S:A), which was found to go up with increasing the S:A ratio in the ion-exchange process. The optimum temperature for achieving sufficient amount of metal loading by this technique on NaX and NaY was found to be 45°C and 135°C, respectively. As compared with LPIE, STIE technique achieved markedly higher metal loadings corresponding with 100% ion-exchanged degree.

Adsorption experiments were subsequently performed both by a batch reactor and fixed-bed reactor at ambient conditions. The exchanged adsorbents, including the original zeolite, were evaluated for their efficiency in removing refractory sulfur compounds - 3-methylthiophene (3MT) and benzothiophene (BT) - in both binary and ternary systems of isooctane and benzene (or toluene) as simulated transportation fuels. From the static adsorptions of these two sulfur compounds, all the isotherms were found to be well-fitted with Langmuir isotherm model. Thus, the Langmuir parameters ( $Q_{max}$  and  $b$ ) could be determined. The sulfur adsorption capacity increased in the order NiY (LPIE at 135°C) < Ni-13X (LPIE at 45°C) < NiY (STIE) for both organic sulfur compounds. Moreover, in comparison with original zeolite, the metal ion-exchanged zeolites showed better sulfur adsorption capacity. This clearly illustrated the forming of  $\pi$ -complexation between sulfur compounds and  $\text{Ni}^{2+}$ , since  $\text{Na}^+$  ions could not create  $\pi$ -complexation bonds. Between the two types of sulfur compounds, BT showed higher strength of adsorption for all types of zeolites. The comparison between the adsorption capacity of sulfur compounds in isooctane and benzene revealed that the removal rate and the overall sulfur uptake

capacity of the adsorbent were significantly reduced when benzene was used, which can be attributed to the competitive  $\pi$ -complexation forming with the adsorbent between aromatic (benzene) and sulfur compounds. With respect to ternary systems, the results also registered a drastic reduction in the adsorption capacity (approximately 73.4% of 3MT and 58.2% of BT) with increasing aromatic content (up to 3% and 6% of benzene). Finally, The equilibrium capacity under dynamic conditions for 3-MT adsorption increased in the order of NaY < NiY < NiX < NaX < Cu<sup>(I)</sup>Y; while the selectivity factor for 3-MT over toluene exhibited the trend NaY < NiY < NaX < NiX < Cu<sup>(I)</sup>Y. In addition, the pre-adsorbed water was found to be detrimental to the  $\pi$ -complexation bonding between adsorbent and sulfur compounds by adsorption with zeolite.

## 5.2 Recommendations

On the basis of primary results, studies of the influence of olefin, also the influence of desorption and particle size (the pellet and crystal) should be investigated. In addition, for applying to industry purpose with the objective of significantly reducing the operation cost, the tests with real transportation fuels and the regeneration combined a continuous testing of adsorbent recovery are also recommended.

In order to improve the selectivity of sulfur compounds and reduce the hindrance of aromatic hydrocarbon on the desulfurization process, the effect of promoted  $\pi$ -complexation adsorbent (Ce<sup>3+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>) should be studied. Besides, developed kinetic model of sulfur removal from the liquid phase may be pursued.