CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

m-Al_2O_3 and M-Al_2O_3 impregnated with Cu^+ and Ni^{2+} were characterized by various methods. The adsorbents were prepared by incipient wetness impregnation method by using metal containing solution of $CuCl_2$ (very soluble in water) and $NiCl_2$, then followed by a reduction step of Cu^{2+} to Cu^+ by means of H_2.

In order to study the appropriate condition to reduce Cu^{2+} to Cu^+, TPR characterization was carried out. These adsorbents were reduced in two steps, from Cu^{2+} to Cu^+ at 316 °C and were further reduced from Cu^+ to Cu^0 at 529 °C.

The SEM, XPS, XRD and TPD characterization results were used to study the metal dispersion. It can be concluded that the heat treatment (H_2 reduction) was the major modification that affects the metal dispersion. It was also shown that the better the metal dispersion, the better the adsorption capacity. Furthermore, there was a slight effect of a dispersing agent (citric acid) on metal dispersion.

Inverse gas chromatography (IGC) has been used to study the adsorption of *n*-alkanes and other polar probes (toluene and thiophene) on the adsorbents. Moreover, properties such as enthalpy of adsorption, free energy of adsorption, surface free energy as well as the dispersive and specific component are also reported. The following conclusions were reached:

1. The adsorption characteristics of those adsorbents (m-Al_2O_3, M-Al_2O_3, reduced Cu/m-Al_2O_3, reduced Cu/m-Al_2O_3 modified with dispersing agent, Ni/m-Al_2O_3 and reduced Cu/M-Al_2O_3), are influenced by alumina, rather than by metal impregnation (Cu and Ni), since properties such as enthalpies of adsorption, free energy of adsorption and the dispersive component are similar for those materials.

2. Concerning the specific interaction component, it was observed that there are significant differences between those adsorbents for the adsorption of aromatic compounds and organosulfur compounds. The specific interaction of thiophene was higher than those of toluene around 1.7–2.1 fold positive effect. All these values are referred to selective adsorption.

3. Macroporous alumina was better to be used as support for the adsorptive desulfurization adsorbents than mesoporous alumina.

4. The effect of type of metal impregnation was insignificant for selective removal of organosulfur molecules, as there is no significant difference in specific interaction between polar probe molecules and the adsorbents.

5. Modification by dispersing agent gave a positive effect on the adsorptive desulfurization which exhanced around 1.2 times compared to those of unmodified adsorbents. It was in a good agreement with SEM characterization, XPS results and TPD by TGA-MS experiments.

5.2 Recommendations

Several recommendations for future work can be offered. As the IGC experiments were done with simulated feeds, it is recommended that these results must be confirmed by breakthrough tests with the real feeds.

To avoid diffusion limitation occurring in liquid phase during impregnation step, it will be necessary to increase the contact time or to use the wet impregnation method.

The heat treatment step seems to be important on the metal dispersion, and could be done after impregnation and removal of water before reduction. It must be carried out at slow heating rate to avoid the destruction of the alumina structure.

Checking the stability of Cu^{2+} and Cu^{+} after impregnation and reduction, respectively, is recommended, as $CuCl_2$ is unstable when exposed to the open environment. Thus, working in a closed system is interesting to carry out.

Impregnation of alumina with different granulometries should also be studied by IGC, the smaller particles being perhaps better impregnated tahn the bigger ones..

The characterization of Lewis acid sites of aluminas after impregnation and reduction must be studied in order to clarify the arguments of reduced adsorbent with high amount of metal loading impregnation.