

Chapter 6

Conclusions

The use of the temperature programmed reaction method throughout this work allowed the successful preparation of niobium oxynitride and bimetallic Nb-Mo oxycarbide catalysts for use in hydroprocessing application.

The solid state transformation during the niobium oxynitride synthesis was investigated and identified to occur directly from Nb_2O_5 to NbN_xO_y without any suboxide intermediates. For this catalyst, HDS activity was found to be low and HDN activity was stable but still inferior to the ones obtained for commercial hydrotreating catalysts.

The subsequent introduction of a second metal forming the bimetallic alloys Nb-Mo oxycarbides was motivated by the relatively low HDN/HDS activities found for the monometallic niobium nitride and the likewise very low HDN/HDS activities reported in the literature[1] for the monometallic niobium carbide.

The following part of this work dealt with the preparation and characterization of a series of a new supported bimetallic Nb-Mo oxycarbides. The catalysts exhibited a remarkably high HDN activity and excellent HDS activity. The influence of the Mo/Nb ratio on the activity was analyzed and an optimum ratio equal to 1.5 was found for HDN reactions. NEXAFS was found to be extremely effective for the characterization of the supported carbides. The differences in the C K-edge spectra of the supported bimetallic and the bulk material indicated that the electronic environment of the carbon atom was significantly altered due to the interaction with the alumina support. The O K-edge of the

supported bimetallic carbide suggested that most of the oxygen atoms were associated with the niobium rather than the molybdenum component.

It can be seen clearly from the present investigation of the bimetallic carbide system and from previous studies with transition metal carbides [1,2,3] that the major advantage of the carbides over the commercial sulfide catalysts resides in the greater activity towards the HDN reaction. This fact, together with the absence of studies concerning the mechanism and nature of the active sites on transition metal carbides and nitrides was the motivation for the remainder of the work.

A study of the HDN reaction mechanism was carried out over bulk unsupported Mo_2C , NbC , $\text{NbMo}_2\text{-O-C}$, and compared with the mechanism over a sulfide, $\text{MoS}_2/\text{SiO}_2$. The results suggested that a β -elimination mechanism was the main reaction pathway for amine bond cleavage over both carbide and sulfide catalysts. The number of Brønsted acid sites was found to correlate with catalytic activities for C-N bond cleavage reactions. The similar results obtained for the carbide and sulfide catalysts suggest that a similar surface composition, a carbosulfide, was attained during reaction giving rise to the same mechanism on the catalysts for the deamination reaction. The mechanism is based on a push-pull process by basic sulfide centers and acidic-sulphydril groups of Brønsted acid character.

The previous studies were expanded to encompass the steps prior to the formation of the aliphatic amines, which are the hydrogenation of pyridine and hydrogenolysis of piperidine. Under the reaction conditions employed in this study, the hydrogenation of the heterocyclic amine, as well as the ring-opening step were both considerably slower than the deamination of the aliphatic amine. Therefore, the rate-determining step in the

denitrogenation of pyridine is either the hydrogenation of the aromatic ring or the rupture of this ring. The ratio of the rate constants of these two steps was obtained for each catalyst and was related to the selectivity for HDN products. The results indicate again that the reaction pathway is similar on carbides and sulfide catalysts and that comparison of catalytic activity has to be strictly related to the nature and structure of the probe molecules.

References

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- [1] S. Ramanathan, S.T. Oyama, *J. Phys. Chem.* 99:44 (1995) 16365.
 - [2] D.J. Sajkwoski, S.T. Oyama, *Appl. Catal. A* 134 (1996) 339.
 - [3] S. Ramanathan, C.C. Yu, S.T. Oyama, *J. Catal.* 173 (1998) 10.