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BOOK REVIEW

Hydrotreating Catalysts. Preparation, Characterization, and Performance. Edited by M. L. OCCELLI AND R. G. ANTHONY. Elsevier Science, Amsterdam, 1989. $144.00.

This is a very interesting compilation of a series of papers from the proceedings of the Annual International Meeting of the American Institute of Chemical Engineering in Washington, D.C., November 1988. The opening paper is a detailed review of the structure and functional relationships for transitional metal sulfide catalysts by Chianelli and Daage. The paper sets the stage for a series of papers dealing with hydrodesulfurization and hydrodenitrogenation catalysis. The development of a precise structure for nickel or cobalt promotion of either MoS_2 or WS_2 is still controversial because of the uncertainty of the dispersion of the MoS_2 and the concentration of Co at the MoS_2 edges. The authors believe that the 4*d* and 5*d* electrons play an important part in the most active catalysts. More detailed evidence to resolve the dispersion question will be needed before a definite model is developed and universally acceptable. Chianelli and Daage have presented an excellent review on the status of the models proposed by a number of researchers.

Continuing on with the theme of the first paper, Ryan and co-workers indicate that the stacking of MoS layers is an important feature of Ni-containing hydrotreating catalysts and that phosphorus improves HDN activity by promoting the formation of stacks by occupying part of the alumina support surface area. The concept is supported by high-resolution TEM micrographs. Conversely, Co-promoted catalysts show less HDN activity because tetrahedrally coordinated Co does not occupy octahedral sites between MoS_2 layers but resides in the same plane as that of Mo. Thus, the Ni catalysts can better promote the aromatic hydrogenation necessary for HDN.

In the symposium section on preparation/structure, Diaz *et al.* found that coprecipitation of cobalt–molybdenum sulfides resulted in the formation of Co_9S_8 whereas impregnation leads to either dispersion or aggregation of Co on the surface of MoS_2 and a more active catalyst. Several papers deal with the use of pure compounds to study HDS and HDN. The Moreau *et al.* presentation was one of the more interesting ones, although it only reconfirms previous findings that in the HDN of quinoline, H_2S increases the C–N bond hydrogenolysis rate. In mixtures, for example, they found that when 2,6-diethylaniline was added to quinoline, competitive effects needed to be considered. This leads one to wonder how to extrapolate pure compound studies to complex industrial feedstocks. Competitive adsorption was also evident in using model compounds to simulate the inhibition effects by asphaltenes in the second paper on HDN by the same authors. A following paper by Bonnelle and coworkers points out that reduction of Ni/Mo may lead to a destabilization of the decorated positions and modification of the S/Mo. Destabilization affects reaction sensitivities, which suggests that variations in S/Mo require different site structures.

Five papers deal with instrumental techniques for studying HDS catalysts. One deals with a historical review of XRD and concludes that uncertainty still exists in the exact nature of the active site and that new models could lead to new more reactive catalysts. However, the columnar arrangement as expressed by Topsoe and others is still most generally accepted as presenting more reactive metals to the prospective reactant. XPS and especially *in situ* methods offer techniques which have the potential for giving us a clearer understanding of the active components. Thin film studies and the description of a new on-line XPS/reactor should be of interest to those working on new techniques. Although this study was limited to carbon-supported catalysts, Crage *et al.*, in a paper on Mössbauer emission spectroscopy of sulfided HDS catalysts, raise the question of concluding that only one well-defined CoMoS species governs the HDS activity. Two papers deal with industrial applications of hydrotreating catalysts—one on hydrotreating naptha from coprocessing vacuum bottoms and coal to reformer grade feedstock and the other on stacked beds of hydrotreating catalyst followed by zeolitic hydrocracking to optimize the production of middle distillate. The latter paper is probably of more immediate interest to industrial researchers because it deals with a currently practiced refining process. Gobolos *et al.* studied the use of Ru supported on zeolites of varying acidity for hydrotreating and concluded that, in a practical system, the acidity needs to be tailored to the reaction of interest, as the catalyst will react differently for HDS, HDN, and cracking as the acidic function is varied.

Microbial upgrading was studied for heavy oils and pure compounds were used to mimic actual feedstocks. When comparing microbial removal to industrially practiced catalytic processing, results were not too encouraging. However, the authors used novel hollow fiber and membrane reactors which could lead to new approaches for using microbial upgrading. A literature citation on microbial oil desulfurization should be helpful to those interested in the topic.

Two papers, one on EXAFS/NEXAFS of Pt/Sn bimetallic catalysts for reforming and the other on a reverse flow gas chromatographic technique for studying

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adsorption/desorption of reactants/products, were included in the symposium. The bimetallic structural study shows that Pt/Sn prepared from chloride precursors supported on either SiO_2 or Al_2O_3 are coordinated either to oxygen or chlorine. The authors found no evidence for bimetallic entities in their preparations. It would be interesting to see a similar study on Pt/Re.

This continuation of the "Studies in Surface Science and Catalysis" series should be of interest, particularly to those researchers interested in HDS and HDN catalysis. The price may be only a minor consideration. The editors and organizers are to be congratulated for arranging a well-structured symposium dealing with an important topic.

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