

SYNTHESIS, STATIC, AND REACTIVE CHARACTERIZATION OF SUPPORTED ORGANOMETALLICS

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Research Scope and Objectives

The research program is concerned with the development and evaluation of new heterogeneous catalysts prepared by thermal and photolytic activation of organometallic complexes directly deposited on high surface area refractory supports. Special emphasis is placed on the use of carbonyl complexes decomposed on alumina and in comparing the activity of the product catalysts to that of "traditional" catalysts prepared by the reduction of a supported salt.

Description of Research Effort

Previous research by this group has used temperature programmed decomposition (TPDE) to elucidate the surface species formed during catalyst activation and the activity of the catalysts supported on alumina has been determined for the model reactions of ethylene hydrogenation, ethane hydrogenolysis, and methanation. This work is now being expanded in several areas. (1) Much effort has been focused on replacing the glass synthesis-reaction systems with state of the art metal systems. These new systems maintain high purity and leak free conditions and afford an operating range of 10^{-10} to 100 atm. Extensive use is also made of automated reaction equipment and microcomputers. (2) The TPDE studies are being expanded to include other organometallics and supports. Particular attention is being focused on supports likely to show strong metal-support interactions such as titania, magnesia, and zeolites. Results to date indicate that the TPDE chromatogram is strongly dependent on the type of zeolite used as a support. (3) The model reactions are being expanded to include benzene hydrogenation and Fischer-Tropsch synthesis (FTS) at elevated pressures. Catalysts derived from $\text{Mo}(\text{CO})_6$ supported on dehydroxylated alumina have much higher activity for benzene hydrogenation than traditional catalysts of Mo. $\text{W}(\text{CO})_6$ on dehydroxylated alumina is much more active for FTS than traditional catalysts of W, but as is usually the case is still less active than catalysts derived from $\text{Mo}(\text{CO})_6$. (4) Special techniques of "reactive characterization" are being used to better understand the nature of the active sites and the influence of synthesis conditions on their formation. These techniques include studying H_2 - D_2 exchange, isotopic patterns of ethylene deuteration, and H_2/CO chemisorption ratios. H_2 - D_2 exchange over both partially hydroxylated and dehydroxylated aluminas as well as $\text{Mo}(\text{CO})_6$ deposited on these materials has been studied. Contrary to published data, we have found that surface OH groups are necessary for the exchange reaction over alumina, but only about 0.1% of the OH are involved. $\text{Mo}(\text{CO})_3(\text{ads})$ is of low activity for exchange, but catalysts which are further decarbonylated are of very high activity. (5) Photolytic activation of supported carbonyls at 295 K is being pursued as an alternative to thermal decomposition. The primary objective is to achieve complete decarbonylation without sintering. This goal is difficult due to the use of optically opaque supports. Medium pressure Hg lamps illuminating catalyst inside a fluidized bed reactor constructed of fused quartz initially provide rapid photolysis. However, the rate drops to a negligible value before photolysis is complete. The extent of photolysis depends on the support, complex, and sweep gas used. An interesting result in the case of $\text{Mo}(\text{CO})_6/\text{alumina}$ is that photolysis results in the facile formation of $\text{Mo}(\text{CO})_3$ (the same product formed by thermal activation at 373 K) but this material is resistant to further photolysis. Optimal conditions allow about 90% photolysis of most supported carbonyls.

Future Research

Each of the topics covered in the previous section is being vigorously worked on.