

The Synthesis and Applications of Sol-Gel Catalysts

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The synthesis of catalysts using sol-gel methods is now a mature science. This talk will center on several novel applications of catalysts prepared by sol-gel methods. In particular, the following applications will be discussed: (1) the synthesis of thermally resistant supported metal catalysts, (2) improved selectivity through the use ceramic membrane reactors, and (3) catalysis by solid acid catalysts.

Several years ago Ruckenstein and coworkers (1) proposed that if supported metal particles could be matched to average pore diameters, metal sintering could be significantly reduced. Their reasoning was based on both theory and TEM experimentation. In a series of studies performed in our laboratory (2-3) we were able to obtain a good match between particle size and average pore diameter by carefully controlling the water to alcoxide ratio used in the synthesis. In particular, it was shown that by increasing the water/alcoxide ratio (3) a narrowing in the average pore diameter was observed to occur. In the case of Pt supported on silica prepared using tetraethoxysilane (TEOS) as the silica precursor, a templating effect of the silica on the metal particle diameter occurred resulting in a very good match between particle diameter and the pore diameter (2). Catalysts prepared by this method were found to sinter at temperatures, which were at least 150°C higher than supported metal catalysts, prepared by conventional impregnation and ion exchange methods. Studies performed on other noble metals supported on both silica and alumina will also be mentioned.

In recent years, ceramic membranes have attracted considerable attention. The most common application of ceramic membranes is to trick thermodynamics by selectively decreasing the concentration of a reaction product by diffusing it through a membrane. A second application is to use the membrane as a membrane reactor. In this application the reactants are passed through the membrane reactor in a radial configuration. By coating the internal surface of a tubular by a thin layer of catalyst prepared by the sol gel method, the reactor residence time can be decreased. This application will be discussed with emphasis on reactions of the type $A \rightarrow B \rightarrow C$ type in which selectivity to be B can be increased by varying the thickness of the catalyst layer. In particular, the selectivity to ethylene was studied in the selective hydrogenation of acetylene (4) and in the hydrodechlorination of dichloroethane (5). In this study both theory and experiments were used to optimize selectivity to ethylene. A solution to the corresponding coupled non-linear differential equations resulted in a Peclet number 64.5 and a contact time of 9.5×10^{-3} sec through the

reactor at 100°C. A critical thickness can be predicted to exist for a maximum in ethylene concentration.

Because of a pressing need to replace corrosive liquid acids such as sulfuric and hydrofluoric acids the search for solid acids capable of comparable activities to these liquid acids has received increasing attention. In particular, sulfated and tungstated zirconia have been shown to be active catalysts in both alkylation and isomerization reactions. The synthesis and characterization of sulfated zirconia by sol-gel methods has occupied our attention for over a six-year period (6). Unfortunately, sulfated zirconia deactivates rather rapidly. This rate of deactivation can be decreased by reducing olefin concentrations, which contaminate the feed, or by the addition of a metal such as Pt. The formation of carbonaceous residues on active sites has been a major focus of our studies. Variables such as surface areas, sulfuric acid concentration, catalyst activation procedures and reaction temperatures will be discussed (6). In particular, sulfate site location has recently caught our attention. By using quantitative XPS studies it was found that virtually the entire inventory of sulfur was located at or near the surface (7).

References

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