

CATALYSTS AND MECHANISMS IN SYNTHESIS REACTIONS

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Research Scope and Objectives

This research program may be broadly divided into two categories: alcohol synthesis over supported metals and the generation of gas phase radicals at surfaces of catalytic interest. The immediate objective of the research on alcohol synthesis is to understand the origin of the large differences in activity of palladium which have been observed when the support is varied or when certain alkali metal ions are added to the catalyst. The research on radical formation on surfaces has aided in the identification of surface sites and reaction conditions which are favorable for the production of specific gas phase radicals. A goal of this study is to determine the importance of these radicals in catalytic processes.

Description of Research

Methanol Synthesis: Research on alcohol synthesis has focused on the formation of methanol from carbon monoxide and hydrogen over supported palladium. Previously it has been shown that there are remarkable variations in activity and related selectivity for methanol synthesis depending upon the type of support employed, even to the extent of the grade of silica which might be used. Moreover, the presence of certain alkali or alkaline earth ions on the surface may greatly enhance the activity of supported palladium for this reaction. Acid sites on the support may promote the formation of methane or the secondary reaction of methanol to dimethyl ether, but they do not inhibit the formation of methanol.

In an effort to understand the influence of silica as a support we have obtained a large amount of rate data on catalysts prepared from different materials, both with and without promoters. From these results the following two generalizations can be made:

- (a) The addition of alkali and alkaline earth ions at any of several stages in the catalyst preparation greatly enhances the activity for methanol synthesis, with Li^+ being the most effective ion. Addition of Li^+ to an inactive catalyst makes it an active catalyst.
- (b) Regardless of the palladium precursor or the presence of a promoter the dispersions of the palladium on Davison grade 01 silica are about the same, but the turnover frequencies (TOF) vary by a factor of 25. By contrast the dispersion of palladium on $\text{SiO}_2(57)$ is enhanced by the promoter, and TOF values are about the same, with and without a promoter. These results suggest that dispersion itself is not a factor in the TOF for methanol synthesis. In a recent experiment carried out on $\text{Pd/SiO}_2(01)$ and $\text{Pd/SiO}_2(57)$ catalysts having approximately the same dispersion, the TOF's were found to differ by almost an order of magnitude. This result confirms that differences in activity cannot be attributed simply to differences in dispersion.

Although a number of phenomenological deductions can now be made, we still do not understand at a molecular level how the type of silica and/or the promoter influences the activity so significantly. Preliminary experiments using CO and NO as probe molecules are underway to explore whether the presence of preferred surface palladium planes can be found on the active catalysts. In addition, these experiments may provide evidence concerning unreduced palladium, which has been suggested as essential for the desired reaction.

Gas-Phase Radicals Formed on Surfaces: Radicals which are formed on a surface may enter the gas phase where they are subsequently trapped, using matrix isolation techniques, and analyzed by EPR spectroscopy. The first example of radical formation was the formation of allyl radicals from propylene over bismuth oxide. This is a known catalyst for the oxidative conversion of propylene to 1,5-hexadiene, and our results suggest that a significant fraction of the product molecules are formed by the gas phase coupling of allyl radicals.

As an extension of this study the kinetic isotope effect (KIE) has been determined for the formation of the allyl radicals. By determining these radical intermediates one can ascribe the effect to the breaking of a particular bond with more certainty. This is believed to be the first case in which a KIE has been determined for a radical intermediate in contrast to the KIE for stable product formation.

More recently the formation of methyl radicals from methane has been studied. Surprisingly lithium-promoted magnesium oxide in a highly oxidized state is the most effective catalyst that we have examined for this reaction. Apparently the active site for hydrogen atom abstraction involves an O^- ion which is associated with a lithium center.

Future Research

The work on alcohol synthesis will continue along two lines: (1) the application of more physical techniques such as IR, XPS and STEM to identify the active phase of palladium on the surface and (2) the incorporation of chain building components such as iron in order to synthesize higher alcohols. In the radical formation study we will focus on the production of benzyl radicals from toluene. Benzyl radicals may be an intermediate in the catalytic conversion of toluene to styrene.