DISCLAIMER

K. Abstract

Results were repeatedly obtained that were consistent with a hypothesis proposed at the beginning of this program, i.e., due to Metal-Support Interactions (MSI), unique active sites can be created in the metal-support interfacial region to enhance activity and improve selectivity in certain types of reactions, especially those involving the hydrogenation of carbonyl and unsaturated C=C bonds. Higher turnover frequencies (TOF-molecule/s/site) and increased selectivity for C=O bond versus C=C bond hydrogenation was established in the hydrogenation reactions of: acetone, crotonaldehyde, acetophenone, phenylethanol, acetylcyclohexane, benzaldehyde, benzyl alcohol, phenylacetaldehyde and citral over Pt/TiO_2 MSI catalysts. Higher rates of hydrogenation of benzene, toluene and xylene could be obtained over certain supported Pt and Pd catalysts. Au/TiO_2 catalysts were developed that were active for CO hydrogenation at subambient temperatures. The influence of support and metal crystallite size were established for the adsorption of H_2, CO and O_2 on families of Pt and Pd catalysts.

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Since 1984 the research sponsored by this grant has focused on the influence of Metal-Support Interactions (MSI) on the adsorption properties of selected molecules (H_2, CO and O_2) and the activity and selectivity of catalyzed reactions, with an emphasis placed on the hydrogenation of molecules containing a carbonyl bond. This program resulted in the publication of 49 peer-reviewed manuscripts that contain the details and conclusions of these studies. These publications are listed in Appendix A. Additional papers are in preparation. This program was also responsible for the training of young scientists, who produced 6 Ph.D. and 4 M.S. theses, as well as 6 postdoctoral fellows.

Our studies were predicated on a hypothesis developed during the DOE grant prior to this one, i.e., that unique active sites involving oxygen vacancies are created at the metal-support interface and they can selectively activate C=O bonds for hydrogenation. This typically results in a much higher turnover frequency (TOF-molecule/s/site) and a significant enhancement in the selectivity for hydrogenation of C=O bonds relative to C=C double bonds. Compounds which have been studied to establish and verify this behavior include the hydrogenation of: acetone, crotonaldehyde, acetophenone, phenylethanol, acetylcyclohexane, benzaldehyde, benzyl alcohol, phenylacetaldehyde and citral, including some of its reaction intermediates, over Pt/TiO_2 and Pd/TiO_2 MSI catalysts in particular.

The influence of MSI behavior on the hydrogenation of aromatic compounds such as benzene, toluene, and o-, p- and m-xylene was also examined in detail. The kinetic analyses of these reactions indicated that higher TOFs could be obtained after certain pretreatments, and this was attributed to the creation of additional sites at or near the metal-support that could adsorb the aromatic molecule, which could then be hydrogenated via H spillover from the metal surface.

In addition, MSI effects were discovered to activate supported gold catalysts with regard to CO oxidation, and high activity at room temperature could be achieved with

Au/TiO_2 catalysts. This latter system was further examined and characterized using UHV techniques.

All of these investigations involved a large extent of catalyst characterization using chemisorption, XRD (X-ray Diffraction), TEM (Transmission Electron Microscopy), IR spectroscopy, DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) and DSC (Differential Scanning Calorimetry). Using the first and last techniques, the influences of the support and metal crystallite size were determined for H_2, CO and O_2 adsorption on Pd and Pt catalysts.

Finally, at the time this program ended, our studies have been directed to a determination of solvent effects on the kinetics and selectivity of liquid-phase hydrogenation of citral, a quantitative evaluation of the importance of H_2 solubility in the solvent, and a new, more quantitative method to determine effective liquid-phase reactant diffusivities so that the possibility of internal mass transfer effects can be accurately calculated. These studies are continuing with other funding.

Appendix A

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