CATALYTIC HYDROGENATION OF CO: CATALYSIS BY SUPPORTED METALS

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Research Scope and Objectives

The purpose of this program is to develop a fundamental understanding of the catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Attention is focused on defining reaction pathways, the structure of reaction intermediates, and the relationships between catalyst composition/ structure and catalyst performance.

Description of Research Effort

1. Characterization of Carbon Deposits Formed During CO Hydrogenation Over Ruthenium

Isotopic tracer experiments have been carried out to identify the nature of carbon-containing species present on the surface of a Ru/SiO_2 catalyst during CO hydrogenation. In addition to chemisorbed CO, two forms of elemental carbon were identified. These latter two species, designated as C_α and C_β, can be distinguished by their relative rates of hydrogenation. C_α is highly reactive and appears to be the principal form of carbon involved in the synthesis of CH_4 and C_2^+ hydrocarbons. The coverage by C_α rises rapidly to a steady-state level which depends on the ratio of H_2 to CO partial pressures. C_β is much less reactive than C_α and accumulates slowly with time. Since the total accumulation of C_β can exceed several tenths of a Ru monolayer without influencing the extent of CO chemisorption, it is believed that most of the C_β resides on the support, rather than on the surface of Ru. The coverage by C_β increases with increasing H_2 and CO partial pressures. The experimental results indicate the C_α is formed by the dissociation of adsorbed CO and that C_β is, in turn, formed from C_α but only in the presence of adsorbed hydrogen.

A collaborative project has been undertaken with Dr. Michael Duncan of Bell Laboratories to characterize the structure of C_α and C_β by means of solid-state ^{13}C NMR. The initial results have been very encouraging. The spectrum of C_α is similar to the spectrum of isolated carbon atoms in $Ru_{10}C_2(CO)_{24}^{2-}$. The spectrum of C_β resembles that of SiC, suggesting that C_β resides on the SiO_2 support. NMR spectroscopy has also revealed evidence for graphitic carbon. This species appears when C_α and C_β are annealed at 190°C and the reactive forms of carbon are then removed by hydrogenation.

2. Effects of Metal-Support Interactions on the Synthesis of Methanol Over Pd

Previous studies have shown that metal-support interactions strongly influence the activity and selectivity of Pd for methanol synthesis. Recent

efforts have focused on elucidating the ways in which support composition alters the physical, chemical, and catalytic properties of Pd. This work has involved close examination of Pd/SiO_2 and Pd/La_2O_3 catalysts. It has been established that Pd/La_2O_3 is roughly an order of magnitude more active than Pd/SiO_2. For both supports, Pd dispersion has no effect on the turnover frequency for methanol synthesis, but the turnover frequency for methanation increases monotonically with decreasing Pd dispersion. In situ infrared spectra of adsorbed CO suggest that the morphology of Pd microcrystallites supported on SiO_2 are unaffected by dispersion. For La_2O_3-supported Pd, though, the microcrystallite morphology changes with dispersion. Quite surprisingly, the turnover frequency for methanol synthesis is found to increase with an increasing predominance of Pd(100) over Pd(111) planes. The activation energy for methanol synthesis and the dependence of the methanol synthesis rate on the partial pressures of H_2 and CO are the same for both Pd/SiO_2 and Pd/La_2O_3. This suggests that the observed differences in specific activity arise from differences in the preexponential factor of the global rate coefficient and differences in the fraction of active sites.

Catalyst characterization by means of CO chemisorption, infrared spectroscopy of adsorbed CO, and XPS reveal that La_2O_3 affects the properties of Pd whereas SiO_2 does not. In general, the strength of CO and H_2 chemisorption appears to be weaker on Pd/La_2O_3 than on Pd/SiO_2. XPS spectra indicate that Pd supported on SiO_2 has the properties of bulk Pd, whereas Pd supported on La_2O_3 appears to have a higher electron density in the 3d state than metallic Pd.

Future Research

The studies of carbon deposition during CO hydrogenation will be extended to examine the influence of metal composition and metal-support interactions. Isotopic tracer experiments and ^{13}C NMR will be used to characterize the relative amounts C_α and C_β deposited under different reaction conditions. Particular attention will be devoted to defining what factors influence the conversion of C_α to C_β and C_β to graphite, since these processes may have relevance to understanding catalyst deactivation.

Studies of the properties of supported Rh will be initiated with the aim of understanding how support composition influences catalyst characteristics. This effort will parallel the work being completed on Pd and will help esetablish the extent to which one can generalize about the influence of supports on transition metals.

TPD studies will be conducted to determine the influence of metal dispersion and metal-support interactions on the interactions of H_2 and CO with supported Pd and Rh. The results from this effort will complement those obtained from studies of reaction kinetics, and infrared spectroscopy, and XPS.

A newly completed Raman spectroscopy facility will be used to characterize the structure and chemistry of mixed metal oxide catalysts. It is planned to initiate this project by examination of $LaRhO_3$, a material which is known to favor the synthesis of oxygenated products. It is anticipated that data from Raman spectroscopy may be able to explain how the catalyst composition changes under reaction conditions and the relation of these changes to changes in the selectivity of the catalyst.

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