CATALYTIC REACTIONS ASSOCIATED WITH COAL LIQUEFACTION AND FUEL SYNTHESIS

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Research Scope and Objectives.

To develop models for fundamental reactions, especially those of carbon-carbon bond cleavage and hydrocarbon synthesis, involved in coal liquefaction and in the synthesis of fuels from coal gasification products. Models are also sought for fundamental reactions of interest in the cleanup of combustion reactions, for example, the catalytic decomposition of ammonia and the catalytic reduction of oxides of nitrogen. The research approach has emphasized ultrahigh vacuum techniques, clean surfaces (single crystal faces and evaporated films), and kinetic investigations covering thousand-fold variations in reactant partial pressures.

Description of Research Effort.

Kinetic studies of the hydrogenolysis of ethane, isobutane, and neopentane on evaporated iridium films have been completed. In all three cases methane was the only product observed, the reaction rate was independent of methane partial pressure over the range of methane partial pressures reached in the reaction, and in all cases the reaction showed Langmuir-Hinshelwood character, with positive kinetic order in each reactant when the reactant partial pressure was low, and negative kinetic order when it was high. In each case kinetic results could be represented by mechanisms involving dissociative chemisorption of the hydrocarbon, attack of the chemisorbed alkyl radical by a hydrogen atom, and surface site occupancy by hydrogen adatoms, alkyl radicals, and methyl radicals.

A kinetic study of the methanation reaction on evaporated ruthenium films was also completed; this reaction was also of Langmuir-Hinshelwood character with zero order dependence on water and methane partial pressures over the range of these pressures studied. In contrast to findings at high pressure there was no evidence for appreciable oxygen-containing species on the surface (e.g., molecularly adsorbed CO) over the range of CO and H_2 partial pressures studied. A kinetic mechanism consistent with rate data obtained was derived.

A kinetic study of the decomposition of methanol on zinc oxide powder was completed. The decomposition was found to proceed in steps; with formaldehyde and hydrogen forming first, and the formaldehyde predominantly desorbing (at low temperatures) and decomposing to hydrogen and carbon monoxide at higher temperatures. A kinetic mechanism consistent with rate data was derived.

Future Research.

A kinetic study of the reduction of NO by CO on a Rh(100) single crystal face is near completion. This reaction is also of Langmuir-Hinshelwood character with rate zero order in the N_2 and CO_2 products over the partial pressures encountered in the experiment. The kinetic data suggest N_2O and NO_2 surface intermediates in the reaction sequence.

Following a hypothesis that sulfur vacancies might be of major importance in hydrodesulfurization catalysts, a set of substoichiometric rare earth sulfides was surveyed for hydrodesulfurization catalytic activity, and the compoun $NdS_{1.45}$ was found to hve some activity. Kinetic data for hydrodesulfurization of $(CH_3)_2S$ on this catalyst are being obtained.

Industrial catalytic processes are generally conducted at pressures far in excess of those commonly used in "clean surface" catalytic studies, so it is quite possible that quite different surface compositions and reaction mechanisms exist. Yet the low pressures are essential to the use of electron diffraction and most electron spectroscopy techniques commonly used for surface characterization. One approach to this problem, pioneered by Somorjai, essentially uses a high pressure cell within an ultrahigh vacuum system, develops a steady state catalytic process within the high pressure cell, then vents the cell and employs surface analyses on the surface resulting. This then requires a demonstration that the venting has not changed the system in an unknown way. We are trying to develop an alternate attack, in which surface concentrations much higher than could be obtained normally at low pressures are attained by using excited species (e.g., atomic nitrogen) in hopes of duplicating high pressure surface compositions at very low pressures.