The methanation reaction on ruthenium thin films
A mechanistic investigation

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The kinetics of the methanation reaction were measured on ruthenium thin films in the temperature range 548-623K. The pressures of the reactant gases were varied over the ranges 1.5-1500 μm for CO and 300-75000 μm for H_2 to yield kinetic orders for each gas. The CO kinetic order varied from +1 at low pressures to -2 at high pressures. As the H_2 pressure was increased its kinetic order varied from +2 to -1. Both of these order plots had unusually sharp maxima. The reaction is zero order in both CH_4 and H_2O. The apparent activation energy was dependent upon temperature with a value of 21.9 kcal/mole at 573K.

Both the H_2/D_2 and the $^{13}C^{18}O/^{12}C^{16}O$ isotopic exchange reactions proceeded rapidly on the thin film at 573K. The rate of exchange of the CO was found to decrease with increasing amounts of hydrogen in the feedstream such that under the conditions of methanation the exchange rate was negligible. Auger spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) indicated that the surface was always covered with carbon. This carbon could be divided into two types based upon its reactivity toward hydrogen. Type-1 was very reactive to 3.5 torr hydrogen doses at 573K and was completely removed in less than 300 seconds. Type-2 was less reactive and required about 48 hours under the same conditions for removal. No oxygen was ever detected on the surface after methanation. Low energy electron diffraction (LEED) and XPS indicated respectively that neither graphite nor bulk carbide was associated with the used catalyst. The deposition of up to 0.75 monolayer of carbon enhanced the rate of methanation. More carbon caused a drop in the initial rate. Methanol could be hydrogenated to methane at about the same rate as carbon monoxide.

A mechanism was developed which quantitatively fits the kinetic data and qualitatively predicts all of the other observations. This mechanism involves adsorbed hydrogen interacting with non-dissociated carbon monoxide. The rate limiting step involves the interaction of Ru-H and Ru-CH_3 to form methane. A methylene carbonyl hydride is believed to act as a reversible poison at high H_2:CO ratios.