STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES

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Research Scope and Objectives

The primary objectives of the research are identification of the reaction intermediates present during CO hydrogenation reactions and a determination of the reaction pathways whereby the intermediates are converted into products. Systems under investigation include the Fischer-Tropsch synthesis of hydrocarbons and alcohols over iron oxide and the isosynthesis of branched hydrocarbons over zirconium dioxide and promoted zirconium dioxide. An understanding of the elementary reactions is needed to design more selective catalysts for these synthesis gas conversion reactions.

The iron oxide studies have concentrated upon the propagation reaction. The objective was to determine whether propagation proceeds via methylene or CO insertion into alkyl surface intermediates. The studies utilized reactive scavenging under synthesis conditions; therefore, a secondary objective was to develop this experimental technique.

The zirconium dioxide studies have concentrated on all aspects of the isosynthesis reaction: interaction of the reagents with the oxide, the initiation reaction, the branching mechanism and the propagation reaction. This includes determining the role oxygen containing surface species, formate and methoxide, have in the propagation reaction versus methanol formation, and whether the intermediate diethylether product forms via methoxide dimerization. The isosynthesis products are suggestive of acid/base catalysis. Zirconia is weakly acidic and basic; however, these sites may have a central role in directing the selectivity of the isosynthesis reaction. The research will investigate means to enhance activity by promoting those sites which initiate the reaction and supply the C_1 intermediate while retaining high selectivity to isobutane and low gas yields.

Description of Research Effort

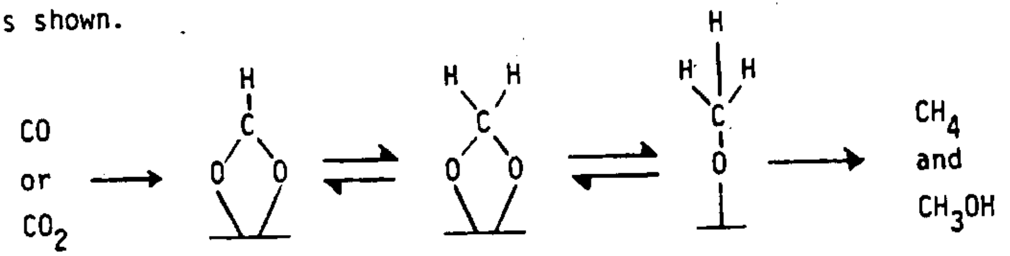
The Fischer-Tropsch propagation mechanism was investigated using a reactive scavenging technique in which a low partial pressure of a probe molecule is added to the CO/H_2 reactant feed. This probe has a unique identifying characteristic, such as the nitrogen heteroatom in pyridine and diethylamine, which enables it and any of its reaction products to be easily and unambiguously identified. The probe reacts with Fischer-Tropsch reaction intermediates enabling one to establish the presence of certain intermediates. Correlations between the distribution and/or concentrations of scavenged products and Fischer-Tropsch products can, in principle, be used to establish the means by which the scavenged intermediates form synthesis products.

Pyridine was used to scavenge C_1 to C_3 alkyl species from Fe/SiO_2 at 1.54 atm total pressure. The distribution of C_1- to C_3- substituted pyridines was dependent upon the synthesis conditions. The CO and H_2 partial pressure dependences of the distribution were used to demonstrate that alkyl fragments are involved in the propagation reaction and are the immediate precursors to alkanes and olefins. It was not possible to use Langmuir-Hinshelwood rate expressions to discriminate between the methylene or CO insertion propagation mechanisms.

Diethylamine is being used to scavenge acyl intermediates over Fe/SiO_2 at 4.4 atm total pressure. Formamide and acetamide are formed from the reaction between amine and a formyl group, HCO, and an acyl group, CH_3CO, respectively. Control experiments establish that these acyl groups are formed from CO/H_2 over the iron and are some type of Fischer-Tropsch reaction intermediates. Experiments are in progress to determine if the distribution of substituted amines are related to the Fischer-Tropsch activity, substantiating a CO insertion propagation mechanism, or alcohol yield, substantiating the methylene insertion mechanism. The latter possibility is based on the postulate that CO insertion into alkyl species is a termination reaction leading to alcohol products. The fact that acetamide is observed provides the first direct experimental evidence that CO insertion occurs over supported metals during Fischer-Tropsch synthesis.

The isosynthesis reaction was investigated at 37 atm and one atm. The high pressure studies were conducted in a differential fixed-bed reactor. Stainless steel blank activity prohibited a detailed investigation of C_1 to C_3 products. Examination of the C_4 products revealed that isobutene and 1-butene were the primary products and isobutene was the major product. Alkanes appear to form by hydrogenating the olefins. Isomerization studies revealed that 1-butene undergoes double bond migration over ZrO_2 but does not isomerize to isobutene. The ratio of iso/normal hydrocarbons was constant with temperature and residence time suggesting that isobutene and 1-butene formed from a common intermediate in a stepwise manner, presumably in a reaction involving C_3 and C_1 reactants.

The one atm studies investigated the interaction between the reactants, CO, CO_2 and H_2, and ZrO_2 using FT-IR and temperature programmed techniques. These studies have revealed that surface hydroxyl groups act as the hydrogen source during the reaction and that a common set of intermediates form from CO and CO_2. The process of forming the first key intermediate, the surface formate, is under investigation, a bicarbonate species is suspected to be involved. The one atm studies have established the following reactions and the presence of all the surface species and products shown.



Future Research

The scavenging studies with diethylamine will be concluded. These studies should establish the role that acyl intermediates have in alcohol formation or in the propagation reaction. Additional scavenging studies of Fischer-Tropsch intermediates are not planned.

The high pressure differential reactor has been redesigned to suppress the majority of the C_1 to C_3 blank activity. The studies will concentrate on the primary C_1 to C_3 isosynthesis products and the means by which they form. The possible reaction between propylene and methoxide as the mechanism to C_4 products will be investigated. These studies will also investigate the importance of acid and base sites on the activity and selectivity of the isosynthesis reaction.

Low pressure studies will continue. These will investigate the reactivity of methoxide with additives such as propylene. The effect of promotors on the C_1 intermediates mentioned earlier, specifically their surface concentration, will be investigated. Finally, causes for enhanced methanol yields from CO_2 versus CO will be investigated. The role of lattice oxygen as opposed to reactant oxygen will be determined.