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STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES. PROGRESS REPORT, AUGUST 1, 1983-JULY 31, 1984

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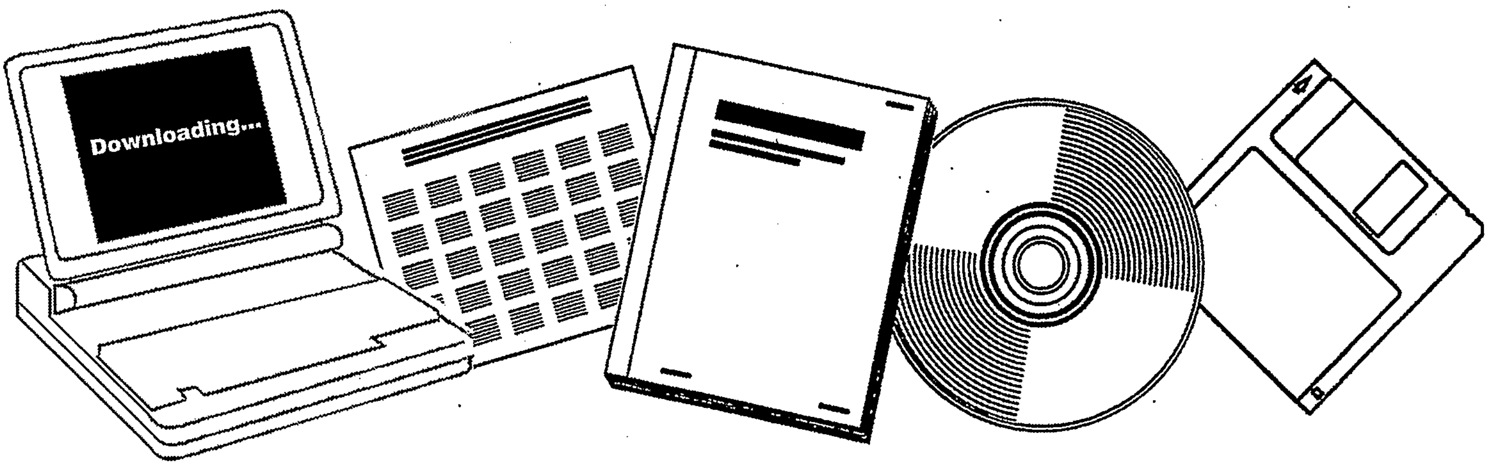

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STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES

Progress Report

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RESEARCH AND SCOPE AND OBJECTIVES

The primary objectives of the research are identification of the reaction intermediates present during CO hydrogenation reactions, determination of the reaction pathways whereby the intermediates are converted into products, identification of the active sites for the various steps in CO hydrogenation and the development of an understanding of the causes for catalytic activity and selectivity. Iron oxide and zirconium dioxide catalysts were used to study the Fischer-Tropsch and isosynthesis processes, respectively. Both involve CO hydrogenation but display very different selectivity and catalytic chemistry.

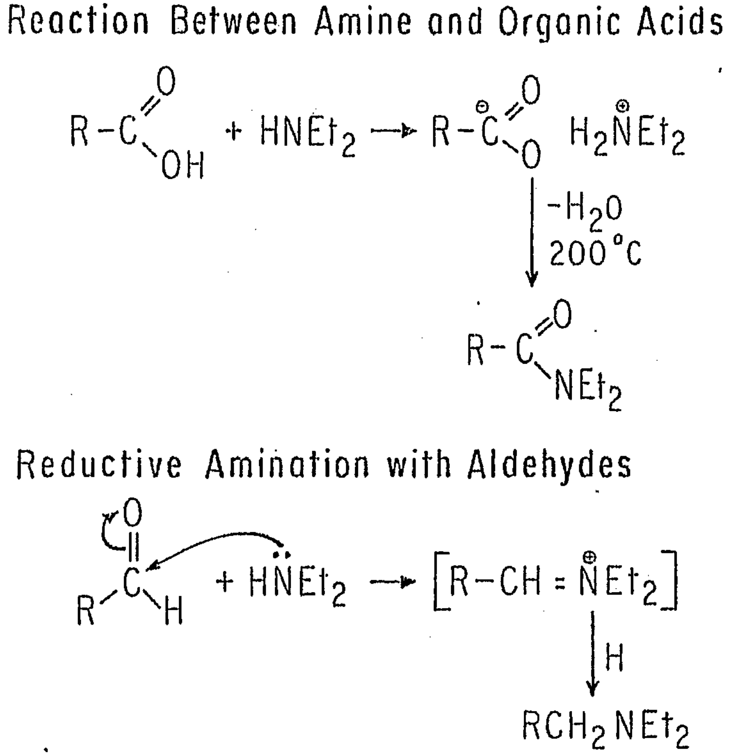
The iron oxide studies which were initiated during the preceding contract period (1980-1983) concentrated upon the propagation reaction. These studies (1,2) revealed that alkyl fragments were involved in the propagation reaction and were the immediate precursors to alkanes and olefins. However, the mechanism by which alkyl fragments propagate, methylene insertion versus carbon monoxide insertion, could not be established. The early studies suggested a possible way to establish the precedence for CO insertion over a heterogeneous catalyst and to determine if acyl species were involved in either propagation or termination. Investigation of acyl species was begun prior to the anniversary data of this contract and has recently been concluded. The results are discussed in the next section.

The zirconium dioxide studies have been concerned with all aspects of the isosynthesis reaction: interaction of the reagents with the oxide, the initiation reaction, the iso or branching reaction and the propagation reaction. The majority of our effort during the past year and all of our effort during the coming year will focus on the isosynthesis reaction. Our past and ongoing studies are discussed below and form the basis for the research we will perform next year.

DESCRIPTION OF THE RESEARCH EFFORT

The presence of acyl intermediates and their role if any in the Fischer-Tropsch process over iron-based catalysts was studied at one to ten atm total pressure and 225°C. The studies involved introducing a scavenger into the CO/H_2 feed mixture which would selectively react with acyl species and form a compound which was easily identified. Another criterion for the scavenger was that it marginally inhibits the CO/H_2 synthesis reactions. Diethyl amine was selected as the scavenger because of known reactions between the amine and carbonyl carbon (see Figure 1) and because the presence nitrogen containing molecules in a complex mixture of hydrocarbons is easily established with the appropriate gas capillary column and a nitrogen phosphorus detector. The anticipated surface reactions between an acyl and diethyl amine are represented in Figure 2.

Amides and trialkyl amines were formed when diethyl amine was added to the CO/H_2 feed. Iron is known to produce acids, aldehydes, alcohols and hydrocarbons (3). Control experiments were performed to establish that the scavenged products were formed between a primary species (one which forms directly from CO/H_2) and diethyl amine as opposed to forming CO/H_2 from reaction products as shown in Figure 1. Formic and acetic acid reacted in the reactor with diethyl amine and H_2 to form formamide and acetamide. These acids were not identified as CO/H_2 synthesis products at the conditions of the experiments, however, they could have been present and may have been responsible for the formamide and acetamide observed during CO/H_2 scavenging. Hydrocarbons, alcohols, and aldehydes are not responsible for the methyl-

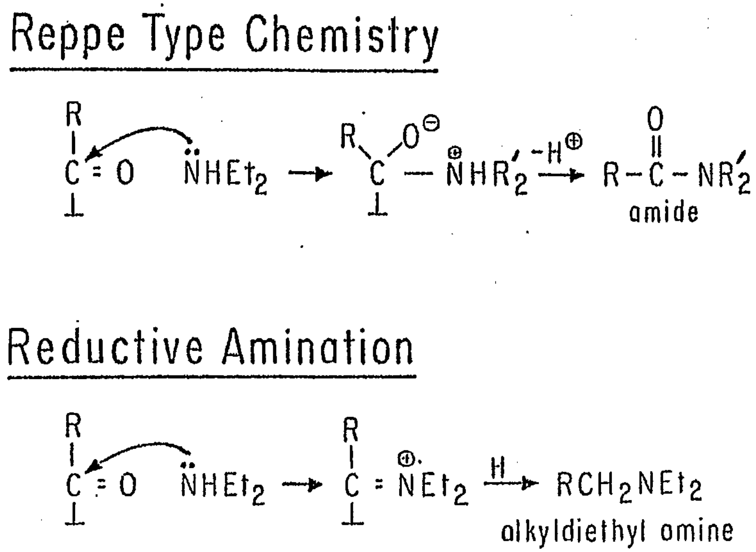


Reaction Between Amine and Organic Acids

Reductive Amination with Aldehydes

Figure 1

Possible Reactions Between Diethyl Amine and Formyl / Acyl Species



Reppe Type Chemistry

Reductive Amination

Figure 2

diethyl and triethyl amines formed when diethyl amine was added to the CO/H_2 feed. Amides were not hydrogenated to trialkyl amines over the iron catalyst or silica carrier. We have concluded that the trialkyl amines form between diethyl amine and formyl and acetyl surface species (4).

The significance of our experiments and their interpretation is difficult to assess at present. We were unable to correlate the concentration of hydrocarbon or oxygenated synthesis products, chiefly methanol and ethanol, with the concentrations of trialkyl amines. A correlation may have suggested if acyl species are formed during the propagation reaction or if they are formed as precursors to aldehyde and alcohol products. The diethyl amine studies do provide consistent evidence that CO insertion does occur over a heterogeneous surface during Fischer-Tropsch synthesis. This observation alone is highly significant because it suggests that CO insertion may be an important elementary reaction during Fischer-Tropsch synthesis.

The acyl species may be intermediates in one or more Fischer-Tropsch synthesis reactions. Additional experiments over a different catalyst are required to address this issue. The new catalyst system should catalyze a significant amount of C_1 to C_5 alcohols as well as hydrocarbons so that the likelihood of a correlation of trialkyl amines versus total activity or oxygenated activity is enhanced. One possibility may be thallium promoted iron (5). However, scavenging studies alone may not reveal the answer.

The isosynthesis studies have included work at 35 atm and at 1 atm. The high pressure work is examining the branching reaction and the C_2-C_4 isosynthesis products. The 1 atm studies are examining the C_1 surface species which may initiate the reaction as well as participate in the formation of C_2+ products and are examining the role of surface sites in CO/H_2 reactions over ZrO_2.

Previous work in our group (6) revealed that isobutene and 1-butene were primary C_4 products and that they formed in a stepwise fashion by the interaction of C_3 and C_1 surface intermediates and/or stable intermediate products. These studies were performed in a stainless steel tube (0.25 in-O.D.) which was filled with 3-4 grams of ZrO_2 (5.8 m^2/gram BET). The blank activity of the tube prevented us from examining C_1 to C_3 isosynthesis products. Therefore, it was decided to redesign the reactor to suppress the blank activity problem and to develop methods to synthesize higher area ZrO_2 than was available commercially.

Early work on isosynthesis was performed in copper-lined tubing (7). We fabricated a reactor from heavy-wall 3/8-O.D. stainless tubing into which 0.250 inch-O.D. copper tubing was forced. This displayed much lower blank activity than the stainless steel reactor. However, ZrO_2 deactivates at 35 atm over a period of 5-6 hours and its activity is restored by contacting with air or H_2. (The exact nature of this deactivation/reactivation phenomena is under investigation; coke formation is suspected.) Oxidation of fresh (as supplied) or used ZrO_2 is necessary to enhance and maintain activity. This oxidation, at temperatures as low as 250°C, adversely affected the blank activity of the Cu-lined reactor and increased it above the blank activity displayed by stainless steel.

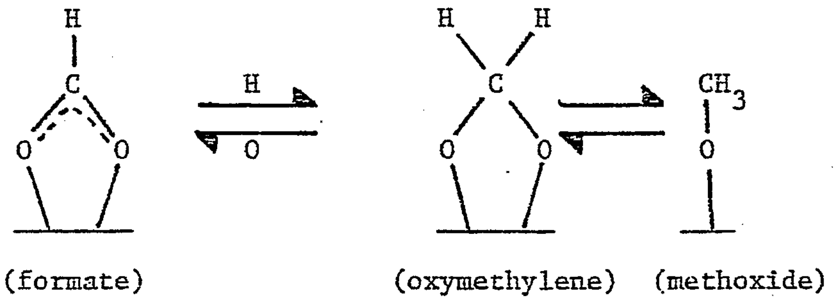
We are currently using a stainless steel reactor and intend to test the feasibility of using a glass-lined reactor. Glass-lined tubing for HPLC columns has been ordered which can operate within our requirements, 450°C and 40 atm, and is designed to be used with swagelok-type metal-to-metal fittings. This reactor should enable us to investigate the C_1-C_3 isosynthesis products. Because the glass-lined tubing is 0.250 in-O.D. no other system modifications are required.

Stainless steel does not interfere with the C_4 products which are produced over ZrO_2. We are reexamining selected experiments of Barker (6) and intend to investigate the C_4 branching reaction under conditions previously reported. It is reasonable to propose that C_4's form by an alkylation reaction between propylene and a C_1 species. This will be tested by cofeeding propylene into the CO/H_2 reaction mixture and measuring the resulting change in C_4 products. It may be necessary to use perdeuterated propylene or ^{13}C-labeled propylene in these studies. We expect to complete this set of experiments in the next few months.

We have established the proper techniques to synthesize high area, monoclinic ZrO_2. (Our early work was performed over 5.8 m^2/gram BET area, monoclinic ZrO_2.) Two methods were attempted. The first involved precipitating $Zr(OH)_4$ from a zirconyl nitrate solution (Nyacol Products) with ammonium hydroxide. The published methods of Davis and Ganesan (8) were followed but the best we could do was produce ZrO_2 which was 10% monoclinic and 90% tetragonal. (The inability to produce the monoclinic form from the zirconyl nitrate was probably due to this solution having been made from tetragonal crystals of zirconia with incomplete dissolution in the zirconia nitrate solution (9).) The second method employs $ZrCl_4$ as the starting reagent (9,10) and has given us 90+% monoclinic ZrO_2 with a BET area of 25 m^2/gram. We have begun to use this ZrO_2 in studies which are discussed later.

The preliminary studies at one atm which were described in the last progress report were continued. Briefly, temperature-programmed (11) and infrared (12) techniques were used investigate the C_1 surface species which form between CO, CO_2 and ZrO_2 in the presence and absence of added H_2. These studies and a later study (13) enabled us to establish that CO_2

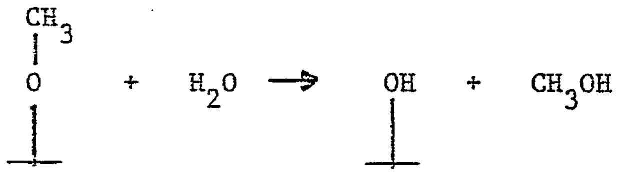
adsorbs as a bicarbonate which can be reduced to formate, whereas CO adsorbs as the formate. Once the formate has formed the reactions listed below can occur.



(1)

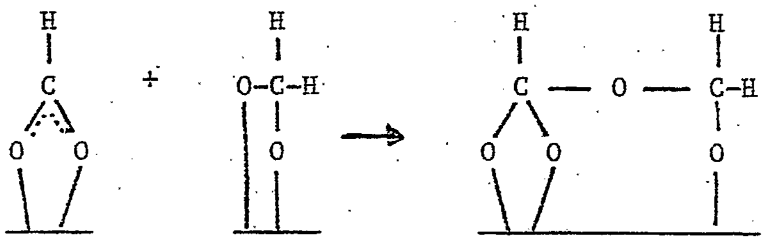
We have reported infrared and reaction data which substantiate the reactions above and the presence of these species on ZrO_2. At one atm and in the presence of gas phase H_2 the methoxide reacts to methane.

We have recently reported studies (13) directed toward the role the species listed in reaction 1 may have in methanol formation over ZrO_2 at isosynthesis pressures, 30-300 atm. Methanol may be directly or indirectly involved in the formation of C_4 products (7), therefore, an understanding of methanol formation is important over ZrO_2. Methanol forms via two routes during temperature-programmed reactions and appears as a product at low temperature (125-200°C) and at high temperature (580-620°C). The low temperature methanol is formed in a catalytic reaction. We proposed (13) that methoxide reacted with molecular water to methanol and a surface hydroxyl.



$$\overset{CH_3}{O} + H_2O \rightarrow OH + CH_3OH \qquad (2)$$

The high temperature methanol was formed in a stoichiometric reaction over fresh ZrO_2 which was heated in O_2 at 620°C. Exposure of ZrO_2 to H_2 at 620°C poisoned this reaction. The mechanism whereby high temperature methanol formed was investigated using dueterium-labelling techniques; however, evolution of O_2 with the methanol and MeOH-MeOD exchange in the quadrupole prevented us from establishing the mechanism. We proposed that a methyl formate-like species (one with a C-O-C skeleton) formed via nucleophilic attack by either oxymethylene or methoxide on the carbon of a formate. The oxymethylene reaction is shown below.



(I)

Intermediate I may rearrange further or undergo hydrogenolysis to CH_3OH.

While the high temperature methanol was stoichiometric it may reveal some interesting features about the role oxygen lattice sites may have in the catalytic properties of ZrO_2. The selective formation of branch alkanes over the isosynthesis catalysts, ThO_2 and ZrO_2, should, in some manner, be related to the acid-base sites. The oxygen treatment may have affected the surface concentration of O^{2-} and O^-. A high concentration may be required to facilitate the nucleophilic attack of CH_3O^- or $H_2CO_2^-$ on $HCOO^-$. The acid and base sites over ZrO_2 will be measured and their concentration and type (Bronsted versus Lewis) will be correlated against H_2-O_2 pretreatment. The relative concentration and/or reactive properties of the C_1 species shown in reaction 1 will then be correlated against acid-base sites to determine how to enhance ZrO_2 activity without adversely affecting isosynthesis selectivity. These studies may help us understand the effect of oxygen pretreatment and reactivation of ZrO_2 in the high pressure work mentioned earlier.

Published methods (14-20) will be used to measure acid and base sites. The dosing manifold and infrared cell have been fabricated. These studies will be initiated in the next few months and will continue into the next contract year.

At present we are continuing to examine the low temperature methanol reaction. We are beginning ^{18}O-^{16}O and D-H labelling experiments which should help to establish if the C-O or O-Zr bond is cleaved by water during the course of reaction 2. Methoxide may be the C_1 species which reacts with a C_3 species to form isobutene and 1-butene. A detailed investigation of reaction 2 will increase our understanding of methoxide reactions and reactivity. These studies will be conducted over high area ZrO_2.

FUTURE RESEARCH

The high pressure studies will examine the C_1 to C_3 isosynthesis products and the means by which they form. Attention will be paid to the role acid and base sites have in the formation of C_1 to C_4 isosynthesis products. The rate data will be used to formulate a mechanism for isosynthesis. Once a proposed mechanism is developed we will have a model upon which we can test the effects of alkali promotors and acid or base additives.

The low pressure studies will continue. These will examine the reactivity of the C_1 surface species with various hydrocarbons, such as propylene, and with each other. We intend to address the reaction whereby C_2 surface species form and provide evidence for a mechanism for isosynthesis. The causes for different selectivity and yields from CO and CO_2 will also be investigated.

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