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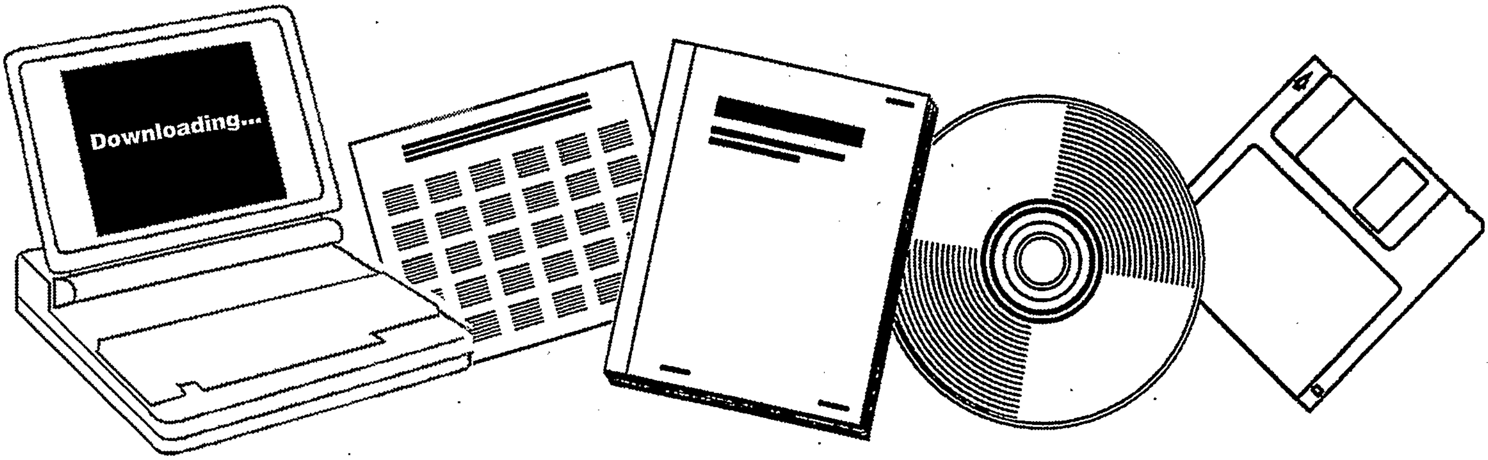

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STUDY OF FISCHER-TROPSCH SYNTHESIS THROUGH THE USE OF SURFACE INTERMEDIATE SCAVENGERS

Progress Report

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ABSTRACT

The primary objective of the research effort is to develop a more complete understanding of the reaction intermediates and the reaction pathways by which the intermediates convert CO into hydrocarbons. Fischer-Tropsch synthesis and Isosynthesis systems are being studied. The Fischer-Tropsch studies are directed toward the causes for synthesis selectivity over metals which are thought to exhibit a common reaction pathway and at the same time a different product distribution. The Fischer-Tropsch work has been limited to 20.44 wt % Fe_2O_3/SiO_2 at 1.54 atmospheres. Pyridine is used to chemically scavenge hydrocarbon fragments, probably alkyl fragments, from the surface during the synthesis reaction. Correlations between the alkylsubstituted pyridine and Fischer-Tropsch synthesis product distributions support a mechanistic scheme in which surface chain growth involves methylene insertion into alkyl fragments. The kinetic parameters which characterize alkyl fragment reactivity are being determined and will be related to Fischer-Tropsch product formation kinetic parameters as a means of understanding synthesis selectivity.

The Isosynthesis work is directed toward understanding the causes for the high selectivity to branched alkanes and aromatics exhibited by certain oxide catalysts. The work has centered upon the reaction products formed at very low conversion as a means of understanding primary product formation and possible rereaction to secondary products. Reactions are studied over unsupported ZrO_2 at 37 atmospheres and temperatures ranging from 300 to 600°C in a differential reactor.

Scavenging Studies

Over the past year studies have proceeded over an iron catalyst. The complete details and the interpretations of the successful portion of the effort are presented in Appendices I and II. The efforts, accomplishments and future directions will be summarized in this section of the report.

All of the experiments have been carried out over a 20.44 wt % Fe_2O_3/SiO_2 catalyst. Iron catalysts introduce a certain elements of uncertainty into the interpretations because the bulk composition and surface composition are dependent upon synthesis conditions and the composition can only be established with sophisticated electromagnetic probes. The catalyst used in this study was always conditioned for six days at 4/1 H_2/CO and 230°C prior to any scavenging. The catalyst was never exposed to temperatures in excess of 250°C, a temperature beyond which rapid deactivation was observed. Finally, the catalyst was always maintained under H_2 and CO between 200 and 250°C to minimize large composition changes.

Analysis of the catalyst at various stages of reduction or exposure to H_2/CO suggest that after the six day induction period the iron phase consists of a mixture of carbides and α-iron. The catalyst reaches a steady activity after induction and maintains this activity for approximately 100-1200 hours. Scavenging studies were conducted over the catalyst as long as it displayed an activity close to that observed after induction.

The composition of the catalyst during the steady activity period is inferred from the composition of a catalyst analyzed after 1340 hours of use. An experiment, currently in progress, will establish the composition immediately following induction. We expect to observe some Fe_3O_4 in addition to the α-iron and carbides.

It is not possible to know the state of the catalyst under synthesis conditions with the techniques available. The activity and the low molecular weight hydrocarbon selectivity remain essentially constant over the course of the scavenging experiments. This suggests that minor bulk changes are occurring but that the catalyst composition is nearly constant.

Additional studies of the iron catalyst have shown that once the activity begins to decline the activity can not be satisfactorily restored. Both surface and bulk carbon were removed as methane by exposing a deactivated catalyst to 2/1 H_2/He at 230°C for 24 hours. The catalyst was subsequently exposed to 4/1 H_2/CO at 230°C. Within 24 hours the methanation rate was less than that observed during the steady activity phase, hours 150 to 1200.

Fischer-Tropsch selectivity and activity dependences upon synthesis conditions were measured. Total activity increased with temperature and H_2/CO ratio. The selectivity to low molecular weight products increased with temperature and H_2/CO ratio. Olefins appear to be the major hydrocarbon product for the C_2's to C_5's. These dependencies are similar to other reported iron work and provide nothing new. The dependence over our particular iron is important because the relationships between Fischer-Tropsch selectivity and scavenged product selectivity indicate that the scavenged fragment is a product precursor.

Two of the objectives of this work are to gain insight into the reaction mechanism and causes for catalyst induced selectivity. To accomplish this a chemical scavenging technique is used. This involves injecting a scavenger into the reactant feed gas and alkylating it with hydrocarbon fragments present on the surface. Alkyl fragments are thought to be the chain growing surface species as well as product precursors. Olefins can be alkylated by alkyl and/or alkylidene fragments, therefore, they are the logical choice for the scavenger. In addition to reactivity toward the suspected fragments, the scavenger must have a structure that easily distinguishes it from the Fischer-Tropsch products and is not readily broken apart over the catalyst.

The scavenged work was initiated with cyclohexene. This was done because of the PI's experience with cyclohexene as a scavenger. Alkylcyclohexenes and alkylcyclohexanes were expected. The details of the attempts and the results with cyclohexene are presented in Appendix I. Briefly, cyclohexene is a poor scavenger over iron. Iron was found to synthesize methylcyclohexene, the major anticipated scavenged product. In addition, H_2 and CO are also converted into cyclohexene, toluene, benzene and alkylbenzenes. Attempts to observe a significantly larger signal for methylcyclohexene upon addition of cyclohexene to the feed were met with limited success.

Pyridine was chosen as the scavenger because it can not possibly be made from H_2 and CO alone and because alkylpyridines are easily distinguished from Fischer-Tropsch products by GC-MS analysis. Little precedence was found for the reaction between adsorbed pyridine and hydrocarbon fragments over a metal. Extrapolation of work reported over nickel suggested that alkyl fragments should form α-alkylpyridines over iron.

The results of the pyridine work are discussed briefly in Appendix I and in much greater detail in Appendix II. Pyridine interacts with fragments formed from H_2 and CO over iron to produce 2-methypyridine, 2-ethylpyridine, and 2-propylpyridine. The distribution of the alkylpyridines and the dependence of the distribution upon synthesis conditions suggests that alkyl fragments are being scavenged by pyridine.

Presently, only qualitative comparisons can be made between alkylpyridines and Fischer-Tropsch products. More experiments are planned for July and August which will allow the hydrogen and carbon monoxide partial pressure dependences and the temperature dependence of alkylpyridine formation to be determined. The rates of alkylpyridine formation will be fit to power-law expressions of the form

$$\text{rate} = k_0 \,[\exp - E/RT]\, P_{H_2}^{x}\, P_{CO}^{y}$$

for each alkylpyridine. These will be compared to E, x and y for the Fischer-Tropsch products to determine the quantitative relationship between alkyl fragments and gas phase products. The results of this work will be submitted to J. Catalysis and discussed at the Kansas City ACS meeting in September.

The concentrations of the alkylpyridines decreased by approximately an order of magnitude with an increase in alkyl size. This trend and the magnitude of the propylpyridine signal imply that if buylpyridine is formed it can not be detected with the FID of the gas chromatograph. A Varian Vista 64 gas chromatograph will be purchased in September. This will be equipped with a thermionic specific detector (TSD). This detector is highly specific to nitrogen, should be an order of magnitude more sensitive toward the alkylpyridines, and is almost insensitive toward hydrocarbons. These features will greatly simplify the identity of the eluted compounds and should enable C_4- and possibly C_5-pyridines to be observed.

Future work will be at higher pressures to investigate the effect of alcohol formation on alkyl fragment concentrations. Alcohols may form by CO insertion into an alkyl fragment, followed by hydrogenation to the alcohol. The work should show if alkyl concentrations can be associated with alcohol concentrations. Prenitrided and promoted iron will also be studied in the coming year. These future studies and the kinetic studies will be used to develop quantitative insight into some of the reaction steps involved in hydrocarbon synthesis over iron.

Isosynthesis Studies

Isosynthesis of branched alkanes and aromatics is a poorly understood system. Over the past 30 years few publications have specifically addressed the topic. Isosynthesis is a high pressure (20-100 atm) and high temperature (400-500°C) process resulting in a product which can be used as a motor fuel substitute or a chemical feedstock substitute. The exciting aspect of isosynthesis is the high selectivity to a narrow band of products.

Current studies are directed toward understanding initiation and propagation over ZrO_2. The products over ZrO_2 at high CO conversion are similar to the products observed upon passage of methanol over ZSM-class zeolites, branched alkanes and aromatics. A number of reactions have been proposed over the zeolite involving methanol dimerization, dimethylether dehydration, ethylene dimerization and alkylation, and acid catalyzed rearrangements of the C_4+ products. The proposed reactions involve a series of events which are kinetically and thermodynamically controlled as well as being constrained by the geometry of the catalyst. The presence of branched alkanes and aromatics over ZrO_2 implies sequential reactions. In an attempt to study the initial reactions rate studies have been limited to low CO conversion.

Initial efforts were directed toward the nature of CO adsorption on ZrO_2 (Alfa, 99+%, 1-3 micron powder). This included atmospheric IR studies and temperature programmed desorption studies. The transmission IR work was attempted in a stainless steel cell which could not be operated above 285°C.

Exposing a ZrO_2 disk to CO, H_2/CO, O_2 followed by CO, or hydrogen followed by CO at temperatures between 25 and 285°C failed to produce identifiable C-O absorption bands in the region of 2400 to 1500 cm^{-1}. Temperature programmed desorption of CO adsorbed on ZrO_2 also failed to detect measurable CO adsorption. In these studies ZrO_2 was either exposed to an oxidizing or reducing atmosphere at temperatures less than 400°C prior to admitting CO. It was at this point that the reaction studies were initiated.

Further infrared studies were carried out at our suggestion by a graduate student working under the direction of Professor J. M. White of the University of Texas Chemistry Department. They used an all quartz cell in which the ZrO_2 disk can be moved into a furnace zone for conditioning and an FT-IR with greater sensitivity. Carbon-oxygen bands were observed. The studies are incomplete and more are in progress, however several observations can be made. The studies indicate that ZrO_2 must be oxidized and subsequently reduced at temperatures in excess of 400°C before measurable C-O absorption bands are generated. In all cases the CO was adsorbed at 20 torr CO and at 25°C. The C-O absorption band frequency, 2159, indicates CO is linearly adsorbed and weakly held to the surface. Band intensity is weak and the band slowly disappears with time. Reappearance of the band is only achieved by reoxidation and reduction. Finally, the CO band is displaced by water and as it disappears a set of carbonate bands are observed. An interpretation awaits the results of further experimentation. The results do show that ZrO_2 is relatively inactive at temperatures less than 400°C and explain our negative results at temperatures closer to 300°C.

The reaction system is shown schematically in Figure 1. The reactor is a 2.5 inch section of 0.25 inch OD stainless steel. Approximately 2 grams of catalyst is charged to the reactor and CO conversions are less than 2%. The gases are metered with micrometering valves and the reactor effluent is directed through a gas chromatograph sampling valve prior to venting.

Reaction rates have been measured over a range of temperatures, 350 to 600°C, and H_2/CO ratios, 1/1 to 4/1. All the work was performed at 545 to 550 psig (38 atmospheres). Recent experiments have indicated that the stainless steel tube wall was approximately as active as the ZrO_2. Early blank experiments did not suggest such a high level of background conversion. The tube has since been deactivated by exposing it to H_2S at 500°C for eight hours. Blank activity runs have been made, however, only one ZrO_2 run has been made since passivating the reactor.

The results are presented in Table 1. The blank condition differs in residence time and temperature. Residence time should act to decrease the blank concentrations and temperature should act to increase the blank concentrations with respect to the ZrO_2 catalyzed results. Over ZrO_2 the CO conversion is about 2.1% based on the hydrocarbons listed. Methane represents the major hydrocarbon and olefins are favored over alkanes. An interesting feature is seen in the C_4's where nearly half are branched.

The low conversion studies are continuing over ZrO_2. The effect of temperature and reactant partial pressures upon C_1 to C_4 products will be determined. Examination of the C_4 product as a function of synthesis conditions may suggest if branching is a secondary reaction via isomerization or a primary reaction via propylene alkylation. This work will be directed toward characterizing the initial products.

The next step will involve studies at high CO conversion where aromatic products are expected. This will be done in a Berty reactor system which is currently being assembled. Familiarity with the isosynthesis products and a determination of the reaction kinetics is needed before mechanisms can be proposed. Our goal is to collect and analyze a sufficient amount of rate data to enable mechanism development.

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Table 1. Isosynthesis over ZrO_2

Conditions		
Temperature	482°C	500°C
Pressure	548 psig	550 psig
Flow rate	64 sccm	60 sccm
H_2/CO	1.0	1.0
Catalyst Charge	2 grams ZrO_2	None
CH_4	7,500[a]	671
C_2H_4	180	61
C_2H_6	142	3
C_3's[b]	114	17
i-C_4H_{10}	215	3
1-C_4H_8	241	1
n-C_4H_{10}	6	1
trans 2-C_4H_8	14	trace
cis 2-C_4H_8	23	trace

(a) Concentrations in ppm

(b) The OV-101 column does not separate C_3H_6 from C_3H_8 at the conditions used.

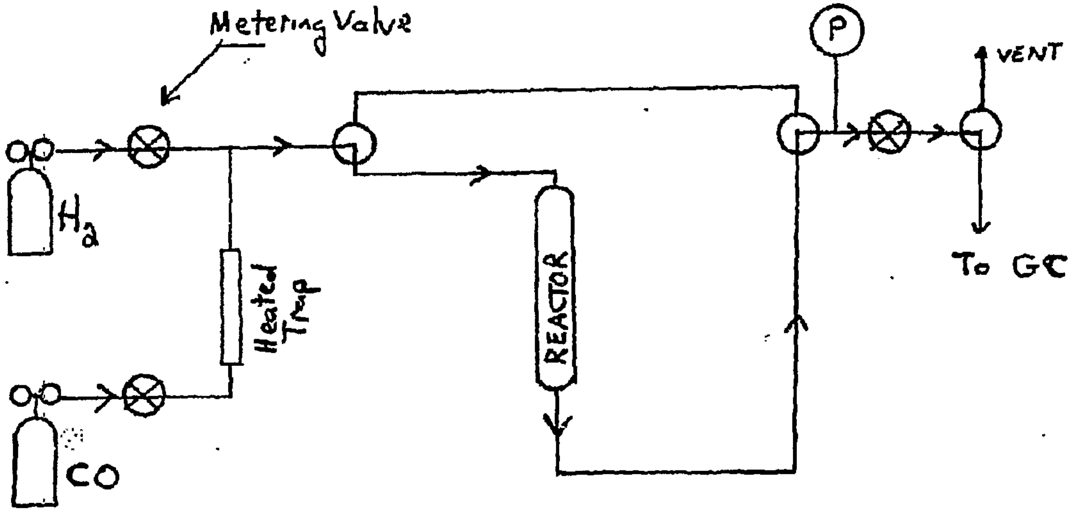

Figure 1. Isosynthesis system schematic.