

An Exploratory Program for Using Hydrous Metal Oxide Ion Exchangers as Fischer-Tropsch Catalysts*

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ABSTRACT

The purpose of this program is to investigate the potential of hydrous metal oxide (HMO) ion exchangers, invented at Sandia National Laboratories, as Fischer-Tropsch (F-T) catalysts. Metals known to be active in F-T synthesis (e.g. Fe, Co) were ion exchanged on hydrous metal oxide supports. Although HMO catalysts based on Zr, Nb and Ta have been investigated in direct coal liquefaction studies, this effort focused on formulations based on the hydrous titanium oxide (HTO) system. The program has the goals of developing a catalyst with (1) high activity, (2) selectivity to fuel range or other useful products, and (3) better properties for use in slurry reactors. The program has three main tasks: (1) catalyst synthesis, to develop methods for preparing catalysts having desirable F-T properties, (2) characterization, to investigate catalysts proving to have desirable properties by a variety of analytical techniques to determine correlations between activity and material properties and (3) testing to determine activity and selectivity of catalysts. This paper discusses results of activity testing of Ruhrchemie catalyst and some catalyst formulations prepared using ion exchange on hydrous titanium oxide and precipitation. For example, at 250°C the Ruhrchemie catalyst converts ~50% of the syngas feed to reaction products. In comparison, iron catalysts prepared by ion exchange and precipitation had conversions ranging from 20 to 50% over a temperature range of 250 to 275°C of the syngas feed. In addition, results from Auger surface analysis of Ruhrchemie catalyst are presented.

INTRODUCTION

The development of a slurry-phase Fischer-Tropsch process using an iron based catalyst is an important item in the agenda of DOE's indirect liquefaction program. Iron compounds have been the catalysts of choice by many investigators for the following reasons: (1) they are inexpensive; (2) they have high specific activity for Fischer-Tropsch synthesis; and (3) their high water gas shift activity can convert low H₂/CO ratio syngas without an external shift reaction. In spite of the large number of studies completed for iron catalysts there is still uncertainty regarding the following aspects of catalyst synthesis and testing: (1) the role of promoters (i.e. K) and additives (SiO₂, Cu); (2) optimum method

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of preparation; (3) reproducibility of large batches of catalyst; and (4) optimum pretreatment of iron catalysts (e.g. H_2 vs CO vs H_2+CO).

In recent years, Sandia has identified a group of hydrous metal oxide ion exchange compounds of Ti, Zr, Nb and Ta that are being developed as catalysts for direct coal liquefaction processes. The catalysts have been shown to have a variety of unique properties that suggest their use as Fisher-Tropsch synthesis catalysts [1]: (1) active metals or mixtures of metals can be atomically dispersed on the substrates over a wide range of concentration by an easily controlled process, (2) they have high surface area, (3) they are chemically stable, (4) the oxidation state of the active metal can be controlled, (5) the substrate can be acidic or basic, (6) the catalysts can be prepared on transition metal oxide supports known to provide strong metal-support interactions [2], (7) the ion-exchanger substrates are stable in oxidizing and reducing atmospheres, (8) the ion-exchangers can be prepared as thin films on a wide variety of supports. The latter property offers the potential for tailor-made catalysts for chosen chemical, physical, and mechanical characteristics.

Hydrous metal oxide ion exchangers are amorphous, inorganic ion-exchange compounds synthesized in the form of salts of weak acids represented by the empirical formula $C(M_xO_yH_z)_n$, where C is an exchangeable cation and M is Ti, Zr, Nb, or Ta. For example, hydrous titanium oxide catalyst can be prepared by a technique that consists of synthesis of sodium hydrous titanate ion exchange material followed by exchanging the sodium for active metal ions. The synthesis involves three steps where an empirical formula, $NaTi_2O_5H$, is used to represent the amorphous HTO support:

(1) Reaction of tetraisopropyl titanate with an alkali or alkaline earth metal hydroxide in alcohol solution to form a soluble intermediate:



(2) Hydrolysis of the soluble intermediate in an acetone/water mixture to form the hydrous metal oxide exchange material:



(3) Ion exchange of the alkali or alkaline earth metal for active metal ions in aqueous solution to form the catalyst:



Catalysts may also be prepared by coating inert supports with a thin film of hydrous metal oxide ion-exchangers. This method of preparation offers the potential of tailoring catalyst activity and selectivity by the appropriate choice of active metal combinations and substrate physical properties such as surface area and pore size. Additionally, better dispersion of active metal may be achieved by this technique.

Although hydrous metal oxide catalysts based on Zr, Nb and Ta have been investigated, this effort is focused on formulation of catalysts based on the hydrous titanium oxide (HTO) system. The potential of the HTO catalysts will be investigated by attempting to formulate and pretreat an active precipitated iron catalyst and then use that stoichiometry and pretreatment to formulate an active FeHTO catalyst. In addition to catalyst preparation and activity testing, a variety of analytical techniques will be used to characterize the catalysts.

The apparatus used for activity testing is a fixed bed reactor that contains one gram of 30-40 mesh catalyst. The catalyst is diluted with glass ground to the same size. Wax produced during reaction is trapped at reactor pressure at ~165°C. The gas then passes through a pressure letdown valve and into a trap maintained at 0°C. The remaining gas composition is determined by a Carle refinery gas analyzer. The light oils and wax are weighed and then analyzed by capillary gas chromatography.

RESULTS

Iron Catalysts

Screening experiments conducted in the fixed bed reactor system during FY '90 have focused on various iron containing catalysts. Ruhrchemie, an iron based catalyst, has been chosen as the baseline catalyst in programs associated with Pittsburgh Energy Technology Center. A sample of the Ruhrchemie catalyst was pretreated and tested according to the recommendations provided by D. Bakur of Texas A&M. A one gram sample of catalyst, sized to 30-40 mesh, was diluted with fused silica of the same size. The top third of bed was diluted 2/1 (silica/catalyst), the middle third was 1/1 and the bottom third was pure catalyst. A temperature of 250°C was maintained during the run. The space velocity during the run was 2Nl/g catalyst/hour (Nl = normal liter at 0°C and 1 atm) at a nominal H₂/CO ratio of 0.7. The experiments were run for 6 hour periods. Between runs the reactor was cooled to room temperature under flowing helium. From the results shown in Figure 1 a decrease in CO+H₂ conversion from ~60 to 50 % during the course of the experiment can be seen with carbon mass balances determined at the end of each 6 hour run. The average carbon recovery was ~89%. The deviation in mass balance from 100% recovery is believed to be a result of wax holdup between the reactor and trap and/or light hydrocarbons that are not captured in the cold trap. Table 1 shows the distribution of carbon compounds obtained during the 36 to 48 hour period where the mass balance averaged ~97 %. The experiment was terminated after 48 hours. These results will be used for comparison with the other catalyst formulations that will be tested.

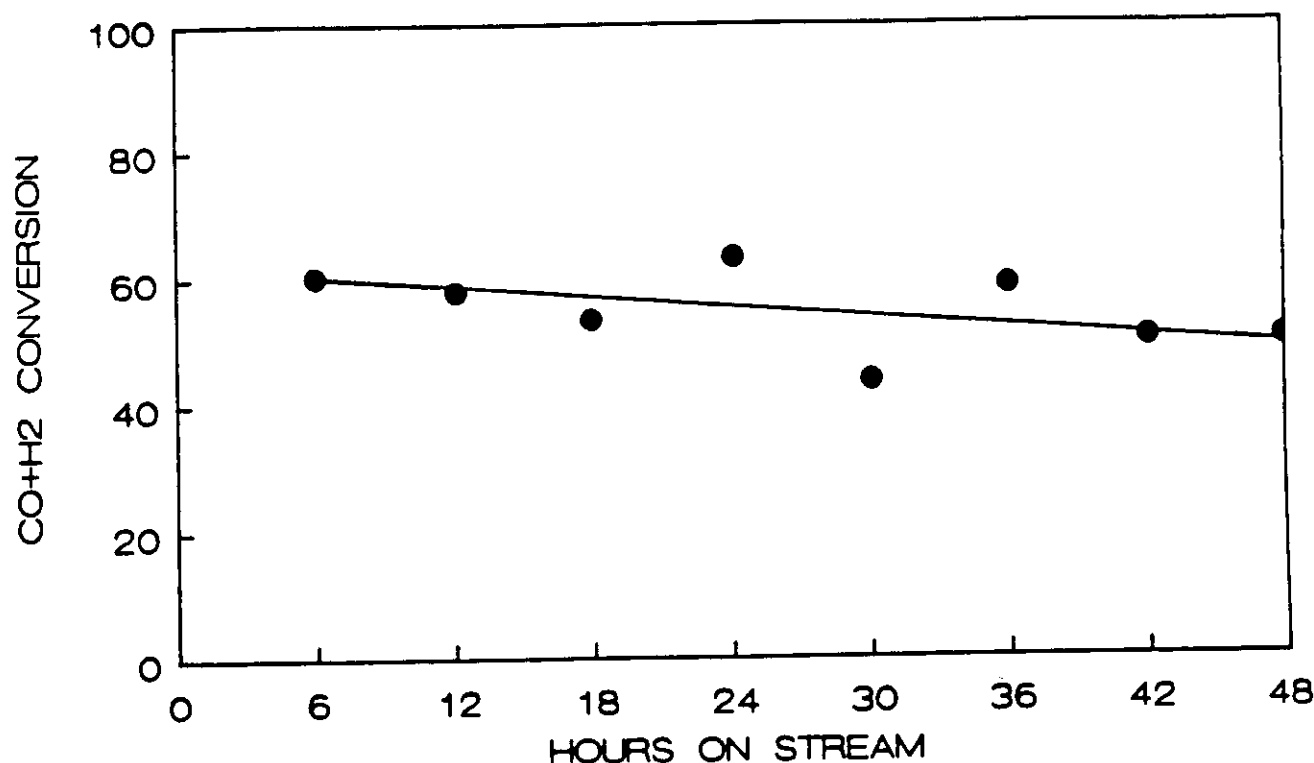


Figure 1. CO+H₂ Conversion of Ruhrchemie Catalyst

Table 1. Distribution of Carbon Products From Rhurchemie Catalyst

Compound	% of Carbon Converted
CO ₂	45
C ₁	4
C ₂	5
C ₃	7
C ₄	6
light oils	5
wax	20

A sample of iron catalyst that was prepared by a combination of ion exchange on hydrous titanium oxide and precipitation (Fe/Fe(Ti₂O₅H)₂) was run under the same conditions as the Ruhrchemie catalyst except for temperature. This catalyst contained 22% Fe and no additives or promoters. A CO+H₂ conversion of 20% was obtained after 18 hours at 250°C. Upon increasing the temperature to 275°C, the CO+H₂ conversion increased to 47%.

A sample of iron catalyst containing potassium promoter was prepared by coprecipitating the chlorides of iron and copper with potassium oxalate solution. After the precipitate was filtered, washed to remove K and calcined, potassium was added by the incipient wetness technique. The material was pelletized and again calcined (400°C) to produce a catalyst containing 60% Fe, 3.2% Cu and 5.8% K. The potassium was higher than anticipated apparently due to some potassium being co-precipitated with the iron and copper from the oxalate solution. The surface area was 73 m²/g. The material (30-40 mesh) was loaded into the fixed-bed reactor; then conditioned and reduced in a manner similar to that recommended for Ruhrchemie catalyst. A 20% H₂ + CO conversion was reached after 16 hours at 250°C, compared to a 50% conversion for the Ruhrchemie catalyst.

A precipitated iron catalyst (52.3% Fe) containing potassium (1.8%), copper (2.6%), and silicon (9.2%) was formulated by coprecipitating iron, copper and potassium and then doping with silicon. The silicon was added for the purpose of establishing and maintaining surface area. The resulting material had a surface area of 239 m²/g, a pore volume of 0.19 cc/g and an average pore diameter of 31 angstroms. The catalyst (30-40 mesh) was calcined, conditioned and activated, in a fixed bed reactor, using the same method used for the baseline Ruhrchemie catalyst obtained from Texas A&M. After 42 hours of reaction at 250 to 260°C, the catalyst produced a H₂+CO conversion of 30%. (See Table 2). The temperature was raised to 275°C and a 50% conversion was achieved. The experiment was terminated after 65 hours on stream.

Table 2. Comparison of Conversions of Ruhrchemie with Precipitated Iron

<u>Catalyst</u>	<u>Conversion</u>	<u>Temperature</u>
Ruhrchemie	50 %	250°C
Fe/FeHTO	20 %	250°C
Fe/Cu/K	20 %	250°C
Fe/Cu/K/Si	30 %	250 - 260°C
Fe/Cu/K/Si	50 %	275°C

Cobalt HTO

A hydrous metal oxide (HTO) catalyst containing ~14% cobalt was tested in the Fisher-Tropsch reactor. The material was pelletized, calcined (400°C) and crushed to 30-40 mesh. Because prior analysis by thermogravimetric and differential scanning calorimetry indicated phase changes associated with reduction occurring near 300°C, the catalyst was reduced at 300°C with CO and then hydrogen. The catalyst had little activity at 250°C and required 275 to 300°C to obtain low but measurable H_2+CO conversion. In addition, most of the carbon was converted to CO_2 and light hydrocarbon gases. References in the literature on cobalt catalysts indicate that reduction temperatures of >350°C are required to activate cobalt catalysts. Future experiments with CoHTO will utilize the higher reduction temperature as well as a potassium promoter.

Surface Analysis

A study of the effects of various activation treatments on the surface composition of a Ruhrchemie (R-C) Fischer-Tropsch catalyst (Fe/Cu/K/Si) and a Fe/Cu/K catalyst has been initiated. This study uses a combined ultra-high vacuum (UHV) analysis chamber and atmospheric pressure (1 atm) reactor system. With this system catalysts can be subjected to pretreatments in the reactor followed by surface analysis in UHV without exposure of the pretreated catalysts to air. This capability is crucial since activated F-T catalysts undergo rapid oxidation upon exposure to air.

The experiments are designed to elucidate differences in surface composition resulting from different activation procedures. Specifically, differences between surfaces reduced in hydrogen vs. CO are of interest because studies have shown that for Fe/Cu/K catalysts, activation by CO at 280°C yields higher initial activity than activation in hydrogen at the same temperature [3], while for the R-C catalyst initial activity is essentially independent of activation procedure [4].

Figure 2 shows the Auger electron spectra (AES) of the Ruhrchemie catalyst reduced under various conditions: a) H_2 , 500 Torr, 220°C, 1 hour; b) H_2 , 500 Torr, 280°C, 1 hour; c) CO, 630 Torr, 280°C, 8 hours. The spectra have been normalized to the oxygen(510 eV) peak. Prior to activation, the R-C catalysts were calcined for 5 hours at 300°C to remove adventitious carbon and fully oxidize the surface to Fe_2O_3 .

The only noticeable difference among the spectra is in the sulfur peak at 150 eV. Sulfur is believed to be a bulk contaminant that migrates to the surface during activation. Since AES is extremely sensitive to sulfur [5], the small sulfur peaks observed here represent minute quantities of sulfur. The close similarity among the surface compositions of the activated catalysts is consistent with the observation that F-T activity is insensitive to

activation procedure for the R-C catalyst [4]. Interestingly, the O/Fe ratios and the shapes of the Fe Auger peaks indicate that the iron is in a partially oxidized state [6]. No evidence for metallic iron on the surface is seen. Also note that there is no evidence for a peak due to either carbidic or graphitic carbon at 272 eV. The absence of carbon or metallic iron on the surface is surprising since it is well known that iron catalysts form bulk carbides as well as metallic iron during F-T synthesis. This result may therefore mean that the bulk and surface compositions of the R-C catalyst differ considerably.

SUMMARY

From the results thus far it can be concluded that the reactor facility is capable of screening catalysts by determining activity and selectivity of catalysts under a variety of conditions. The Auger surface analyses show promise as a tool for comparing the surfaces of catalyst after various pretreatments. Future surface analysis work will involve measuring the surface compositions of Fe/Cu/K catalysts (no silicon) following reduction in CO and hydrogen. For these catalysts, significant differences in initial activity are observed depending on the activation procedure used [3]. Reduction by CO appeared to generate higher activity than reduction by H₂ and these differences in activity should be reflected in the surface composition of the catalysts. Methods for preparing catalysts using alternative techniques and materials such as cobalt on a zirconate support will continue to be investigated.

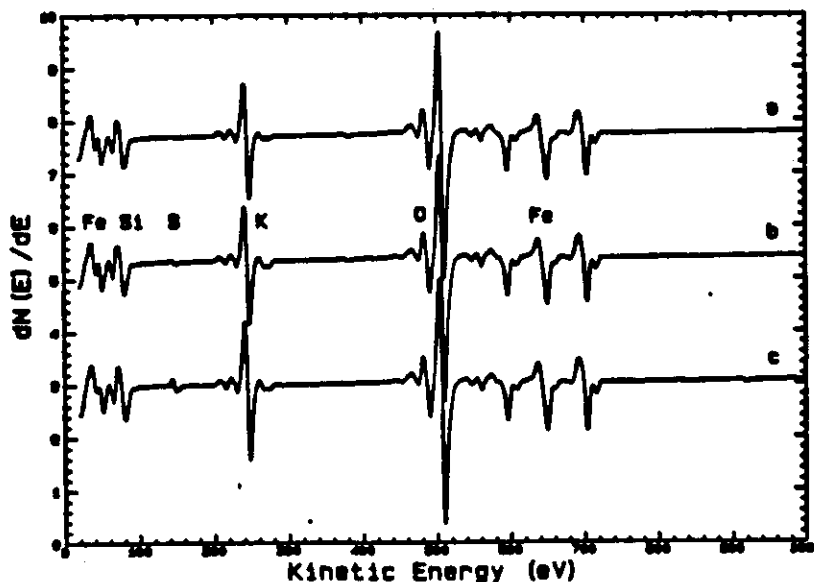


Figure 2. Auger spectra of Ruhrchemie catalysts.

REFERENCES

1. Dosch, R. G., Stephens, H. P., Stohl, F. V., Bunker, B. C., and Peden, C.H.F., "Hydrous Metal Oxide-Supported Catalysts: Part I. Preparation Chemistry and Physical and Chemical Properties," SAND89-2399, Albuquerque: Sandia National Laboratories, February 1990.
2. Dosch, R. G., Stephens, H. P., and Stohl, F. V., "Hydrous Metal Oxide-Supported Catalysts: Part II. Catalytic Properties and Applications," SAND89-2400, Albuquerque: Sandia National Laboratories, February 1990.
3. D. Bukur, X. Lang, J. Rossin, W. Zimmerman, M. Rosnyek, E. Yeh and C. Li, I&EC Research, 1989, 1130.
4. D. Bukur, Indirect Liquefaction Discussions, PETC, September 6, 1990.
5. L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach and R. E. Weber, "Handbook of Auger Electron Spectroscopy," 2nd ed., Perkin-Elmer, Eden Prairie, MN, 1978.
6. M. Seo, J. B. Lumsden and R. W. Staehle, Surface Sci, 50 (1975) 541.