

Report 4

Development of Catalytic Systems for the Conversion
of Syngas to Jet Fuel and Diesel
Fuel and Higher Alcohols

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SUMMARY OF ACCOMPLISHMENTS

Development of Catalytic Systems for the Conversion of Syngas to Jet Fuel and Diesel Fuel and Higher Alcohols

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A highly active series of catalysts for the preparation of diesel and jet fuel-type hydrocarbons, affording rates in a three-phase slurry system more than an order of magnitude greater than conventional systems, has been developed. The method of catalyst formulation appears to be unique in catalytic chemistry, and these catalysts offer the promise of being superior to ordinary Fischer-Tropsch catalysts with regard to rate, operating conditions, handling techniques, and quite possibly, product selectivity and longevity. The catalysts are effective under a range of temperatures, pressures, feed gas ratios, catalyst loadings and reactor configurations. An exploratory program has led to a better understanding of support effects, oxide interactions, the roles of promoters, the mechanism of CO/H₂O and low ratio syngas reactions as well as the synergistic behavior of bimetallic catalyst systems.

SUMMARY

A highly active series of Fischer-Tropsch catalysts, yielding hydrocarbons suitable for use as diesel and jet fuels, were developed during FY 1980. The method of catalyst formulation appears to be unique in catalytic chemistry, and these catalysts offer the promise of being superior to ordinary Fischer-Tropsch catalysts with regard to rate, operating conditions, handling techniques, and, quite possibly, product selectivity and longevity. These catalysts, at present consisting of two different metal combinations, are referred to by the generic term SOSS.

Recent results with these catalysts in a slurry phase at 225°C and 1200 psi cold pressure indicate an activity nearly two orders of magnitude greater than those reported by the Bureau of Mines using conventional Fischer-Tropsch catalysts in fixed bed reactors. When conventional catalysts are compared with SOSS catalysts under our reaction conditions, the advantage drops to about a factor of 25; this reflects the desirability of the slurry phase for hydrocarbon synthesis but by no means diminishes the significance of the SOSS invention.

In addition to high rates, the SOSS catalysts offer several other advantages. High activity is observed over a range of temperatures and pressures, with maintenance of good selectivity for linear aliphatic hydrocarbons. Although 2:1 H₂:CO is normally used, the catalysts are effective with 1:1 H₂:CO (but maintain a consumption ratio near 2:1) and with dilute syngas (i.e., 50% N₂). The catalyst system remains active even when exposed to air. The catalyst is effective in a variety of slurry solvents, and is conveniently prepared *in situ*. Catalyst removal is easily accomplished magnetically. Since these catalysts are employed in a slurry, they should present little problem with heat transfer. These catalysts have not been found to be effective for the K lbel-Engelhardt reaction (CO + H₂O hydrocarbons).

Significant effort has been expended recently toward elucidating the unique structural features of the SOSS catalysts. It appears that these catalysts are layered, i.e., the support is coated with a layer of metal B, followed by a layer of A. Furthermore, the x-ray diffraction pattern of an active SOSS catalyst indicates of relatively low dispersion but high orientation. Our results indicate that metal B and high orientation of metal A are both necessary for high activity. In our opinion, a better understanding of the structure of SOSS will facilitate the patenting process, will afford a stronger patent position, and may offer information necessary for preparing even more active Fischer-Tropsch catalysts.

Much effort has been directed toward the SOSS catalysts, and an exploratory program has led to a better understanding of support effects, oxide interactions, the role of promoters, and the synergetic behavior of bimetallic catalyst systems. Such work may serve as a foundation for the development of improved catalysts for alcohol and hydrocarbon syntheses, as well as new catalyst systems for the K lbel-Engelhardt and low ratio synthesis gas reactions.

INTRODUCTION

A highly active series of Fischer-Tropsch catalysts were developed during FY 1980, on the basis of insights provided by the "oxide theory." The method of catalyst formulation is unique in Fischer-Tropsch chemistry, yet is simple and reproducible. These catalysts offer the promise of being superior to ordinary catalysts for hydrocarbon synthesis with regard to rate, operating conditions, and, quite possibly, product selectivity and longevity. The products of these catalysts appear to be ideally suited for use as diesel and jet fuels. Once formed, the catalysts display remarkable stability toward air. Specific descriptions of catalyst preparations and composition of matter must be withheld pending patent protection to secure the interests of the United States Government, Brookhaven National Laboratory, and the inventors. In this report these catalysts are referred to by the generic term SOSS.

Also during FY 1980, an exploratory program was directed toward achieving a better understanding of support effects, oxide interactions, the role of promoters, and the synergistic behavior of bimetallic catalyst systems. Some results dealing with bimetallic systems for hydrocarbon and alcohol synthesis will be discussed.

THE ACTIVITY OF THE SOSS CATALYSTS

Table 1 allows comparison of the rates of a number of conventional Fischer-Tropsch (F-T) catalysts reported in the literature with the rates of several SOSS catalysts. The data show that the activities of the SOSS catalysts, expressed in terms of conversions per catalyst volume per unit time or in terms of conversions per mole metal atoms per unit time, are considerably higher than the activities of conventional systems.

Like the data for the SOSS systems, the Kölbel and Pichler data are for slurry systems, but the remainder of the entries in Table 1 are for fixed bed systems. To provide an equitable comparison, several standard F-T systems have been compared with the SOSS systems under our reaction conditions (Table 2). These data again show the remarkable activity of the SOSS catalysts. Also notable is the observation that decreasing the metal A loading (entries 1 and 2, Table 2) leads to a lower overall activity for the SOSS catalyst, but normalization to metal loading gives a somewhat better activity, with reasonably comparable selectivity. Neither metal A nor metal B approaches the high activity observed with the SOSS system. Furthermore, neither the Co:ThO₂: kieselguhr nor the Fe:Cu catalysts approach either the high activity or the selectivity for linear aliphatic hydrocarbons found with the SOSS catalysts.

REACTOR CONFIGURATION AND OPERATING CONDITIONS

Most experiments with the SOSS series catalysts have been conducted in a batch slurry reactor (schematically illustrated in see Figure 1). The reactor system consists of a 300-ml Autoclave Engineers Magne-Drive reactor equipped with liquid and gas sampling valves. The heater is controlled by a Love Controls proportioning temperature controller employing an iron-constantan thermocouple. Fine control of the temperature is achieved by means of alternating heating and cooling cycles in the vicinity of the set point.

Table 1
Comparison of Hydrocarbon Production Rates of Several Catalysts

Catalysts	Temp. °C	Activity g prod/(kg metal·hr)
SOSS-7A-2C-I-87 ^a	225°	3000
SOSS-2A-2B-I'-61 ^b	225°	1080
SOSS-7A-2B-I'-94 ^c	125°	40
Lurgi catalyst (100Fe:10Cu: 2K ₂ CO ₃ :9Al ₂ O ₃ :30SiO ₂) ^d	225°	24
Brabag catalyst (100Fe:20Cu: 20Zn:1K ₂ CO ₃) ^d	225°	10
Bureau of Mines 2A catalyst (100Co:18ThO ₂ :100 kieselguhr) ^e	195°	50
Pichler acid-promoted Ru/Al ₂ O ₃ catalyst for polymethylene ^f	120°	120
Kölbel slurry catalyst (100Fe:0.1Cu:0.05K ₂ O) ^g	268°	450
Vannice (5% Fe on glassy carbon) ^h	235°	4

^a2.2 g catalyst, containing 1.2 g metal on high surface area Al₂O₃. 100 mL cyclohexane, 1200 psi 2:1 syngas, 300 mL AE reactor, catalyst prepared in situ.

^b1.4 g catalyst, containing 0.4 g metal on low surface area (80-100 mesh) Al₂O₃, 100 mL cyclohexane, 1200 psi charge 2:1 syngas, 300 mL AE reactor, catalyst prepared in situ.

^c2.2 g catalyst, containing 1.2 g metal on low surface area (80-100 mesh) Al₂O₃, 100 mL cyclohexane, 1200 psi charge 2:1 syngas, 300 mL AE reactor, catalyst prepared in situ.

^dH.H. Storch, N. Columbic, and R.B. Anderson, The Fischer-Tropsch and Related Syntheses, p. 308 (Table 86), Wiley, New York, 1951.

^eIbid., p. 132 (Table 5).

^fH. Pichler and F. Bellstedt, Erdöl u. Kohle 26, 560 (1973).

^gH. Kölbel, P. Ackermann, and F. Engelhardt, Erdöl u. Kohle 9, 153, 225, 303 (1956).

^hM.A. Vannice, paper presented at 181st Am. Chem. Soc. Meet., Atlanta, GA, March 29-April 3, 1981.

Table 2
Comparison of Several Catalyst Systems in Cyclohexane Slurry

Catalyst	Activity g prod(kg metal·hr)	Products
SOSS-7A-2B-I'-59	860	Principally linear paraffins; 0.3% CO ₂ , 5% CH ₄ , 0.6% C ₂ H ₆ , ~ 0.1g wax
SOSS-2A-2B-I'-61	1080	Principally hydrocarbons with small amounts of alcohols; 0.1% CO ₂ , 2.8% CH ₄ , 0.3% C ₂ H ₆ , ~ 0.1g wax
SOSS-7A-2C-I-87	3000	Principally linear paraffins; 1.0% CO ₂ , 9.3% CH ₄ , 0.03% C ₂ H ₄ , 0.45% C ₂ H ₆ , 0.03% C ₃ H ₆ , 0.3% C ₃ H ₈ , 0.4% C ₄ H ₁₀
Metal A deposited on Al ₂ O ₃ (by SOSS procedure, without metal B)	270	Alcohols & hydrocarbons; 0.5% CO ₂ , 4% CH ₄ , 0.2% C ₂ H ₆ , ~ 0.4 g wax
Metal B deposited on Al ₂ O ₃	0	No hydrocarbons or alcohols detected
100 Co:18ThO ₂ :100 kieselguhr	71	Hydrocarbons, rich in lower MW oxygenates; 0.2% CO ₂ , 1.5% CH ₄ , 0.08% C ₂ H ₆
4Fe:1Cu	180	Olefinic hydrocarbons; 6% CO ₂ , 0.06% CH ₄ , 0.03% C ₂ H ₄ , 0.2% C ₂ H ₆

Conditions: SOSS catalysts prepared in situ from Fisher chromatographic grade A-540 Al₂O₃, sieved to 80/100 mesh, (except SOSS-7A-2C-I-87, which is made from high surface area Al₂O₃); all reactions carried out as follows: 100 mL cyclohexane (Fischer certified), 300 mL reactor charged with 800 psi H₂, 400 psi CO, 225°C (18 min to reach temp).

Cooling is controlled by the flow of compressed air through a solenoid-actuated, internal, spiral cooling coil. Temperature can be readily controlled to within 2°C. Ordinarily, 100 mL of slurry solvent is used, allowing 200 mL of gas space. The system is normally purged with synthesis gas before final charging. Although the SOSS catalyst, once formed, is air stable, the soluble and insoluble components have been found to undergo reaction in air leading to ignition; a very slow interaction occurs between these components in the solid state under an inert atmosphere.

Although very simple, this reactor system allows for convenient screening of catalyst formulations, with activity being correlated with the observed pressure drop under isothermal and isochoric conditions. Normally the catalyst is prepared in situ, under syngas pressure, from the appropriate

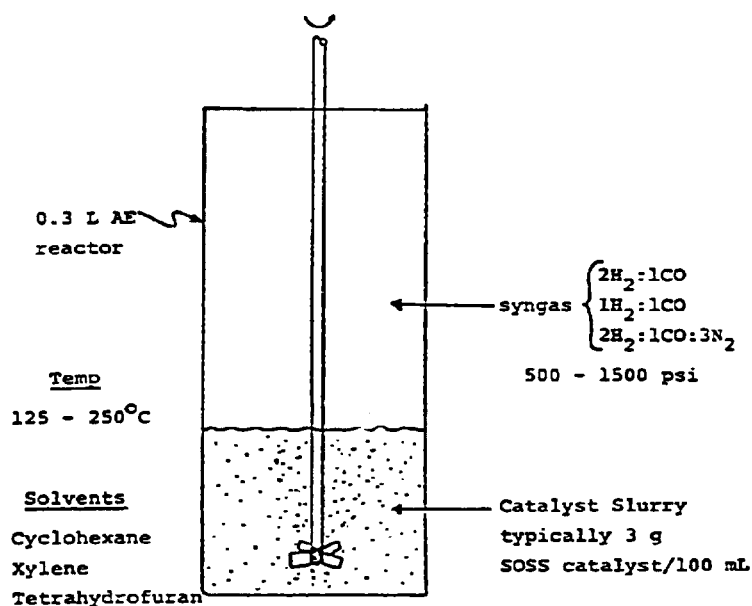


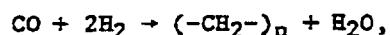
Figure 1. Schematic of slurry reactor.

soluble and insoluble components, in an appropriate solvent. Alternatively, hydrogen pressure alone can be used to prepare the catalyst. This leads to the formation of a new heterogeneous catalyst (the SOSS catalyst) conveniently in the slurried state. All types of evidence, including infrared spectrophotometric data, colorimetric data, chemical degradation, and magnetic susceptibility of the sampled liquid phase, indicate that virtually all of metal A (the initially soluble component) is lost from solution. The interaction of the soluble and insoluble components occurs in the temperature range 80° to 200°C.

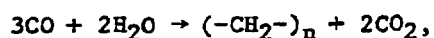
The type of solvent plays only a minor role in catalyst formation, activity, and selectivity; cyclohexane, tetrahydrofuran, and xylene have been found to lead to almost identical results. Once formed, the catalyst has good integrity, showing little if any tendency for dissociation under our reaction conditions.

A wide variety of reaction conditions may be used. The catalysts have been used in the temperature range 150° to 250°C, although one formulation SOSS-7A-2C-I, differing in the insoluble component, displays good activities at temperatures as low as 70°C. The wide range of usable temperatures and the ability to achieve reasonable activity at such low temperatures are notable features of the SOSS catalysts. Of course increasing temperature leads to significant improvement in catalyst activity. Slurry loadings have been examined in relatively limited range (1 to 7g of SOSS catalyst in 100 mL of solvent) with approximate correspondence in the rate of syngas consumption.

The catalysts are also effective with a range of syngas ratios and pressures. The systems display good and reasonably uniform activity with initial chargings of 500 to 1500 psi, although they are effective under much lower pressures; normally reactions approximate linear response until the partial pressure of either the H₂ or CO component drops below about 70 psi. The consumption ratio is always near 2:1 H₂:CO, closely obeying the equation



and most reactions have been carried out with syngas of this ratio. The use of 1:1 syngas leads to comparable results (with only a slight increase in lower olefins) but retardation in activity occurs sooner due to depletion of the H₂ component. Even dilute feedstreams of syngas (2H₂:1CO:3N₂) are effective. Such versatility in syngas supplies is another attribute of the SOSS system. This system has not yet been found effective for the K6lbel-Engelhardt reaction,



and this is reasonable considering that the consumption ratio is 2:1, little CO₂ is found in the final gas, and copious amounts of water are found in the slurry phase when xylene and cyclohexane are used as solvents (the water being partially soluble in the THF plus product hydrocarbon slurry solvent). The buildup of water does not appear to promote catalyst deactivation.

The catalyst may be preformed, stored in air, and later added to solvent and used directly in hydrocarbon synthesis without the need for a discrete activation step. This is in marked contrast to conventional Fischer-Tropsch catalysts, which normally requires a tedious, time-consuming activation (reduction) step, the exactness of which has a pronounced bearing on the catalytic properties. In a particular case, a sample of the damp catalyst was exposed to the atmosphere for 2 hr, after which solvent was added and the reactor was charged with synthesis gas; at 200°C the catalyst had the same activity as before air exposure. In other cases, catalyst dried at 100°C in air and stored in stoppered vials for weeks exhibited virtually identical activity for hydrocarbon synthesis. The stability of the SOSS catalysts in air is a distinctly favorable attribute.

The SOSS catalysts are normally used in a dilute slurry. No problem with heat transfer has arisen; this could be anticipated because of the large mass of heat-dissipating solvent present. K6lbel has done extensive work with slurry Fischer-Tropsch catalysts, normally under much more concentrated conditions, and has attributed a number of advantages to them, including (1) the activity observed in the reactor is determined by the inherent catalyst activity, i.e., no mass transfer limitations; (2) good temperature control, easily within 1°F; (3) because of better heat control, less methanation; (4) lower syngas consumption ratios; and (5) the ability to effect variations in product nature and distribution by variations in hydrogen pressure and operating temperature, with lesser effects due to other operating parameters and virtually no dependence on reactor configuration. However, some of these observations do not appear to hold in the SOSS system. As mentioned above, the SOSS systems display nearly constant consumption ratios and appear to

afford only minor variations in product nature and distribution with hydrogen partial pressure. Lower temperature seems to disfavor methanation to some extent.

The yields of methane appear to depend largely on whether or not the catalysts is prepared in situ, that is, the bulk of the methane appears to be produced during the catalyst formation period. Temperature control in the system has been good. Although the catalyst system leads to quite rapid conversion rates (40 psi synthesis gas consumption/min at temperature), mass transfer does not appear to be limiting, perhaps because of the large solvent/catalyst ratio and the rapidity of stirring due to the low apparent viscosity of the slurry system. Up to temperatures of 250°C, neither oxidizing or carbiding is significant, nor is catalyst sintering due to localized heating.

NATURE OF THE CATALYST

The SOSS series catalysts are unique in Fischer-Tropsch chemistry with regard to the method of preparation and the composition of matter. Although a number of compositions have been tested, to date only two different combinations of metals made by this method of preparation have been found to be effective for hydrocarbon synthesis. These catalysts are supported, and alumina, silica, and kieselguhr lead to comparable results. The surface area of the support plays a relatively minor role in the activity of these systems, and this seems reasonable in light of their high loadings. In fact, preliminary results suggest that the number of active series and the surface area of the metal are remarkably low for active catalysts; optimization of activity with respect to surface area is expected to lead to significant improvements in catalyst activity.

The SOSS catalysts are heterogeneous, and all results indicate that they remain so during the course of the reaction. The nature of the homogeneous and heterogeneous components is thought to affect the formation of the composite heterogeneous SOSS catalysts. The SOSS catalysts are magnetic; and this property has been used in cleaning our reactors after runs, and may be commercially useful in catalyst entrainment and recovery.

The soluble component has been found to interact with alumina under reaction conditions, but some intriguing results have been obtained in this area. In the earliest experiments, the reactor had been "dirty," that is, a small deposit of metal B with metal A had been left plated on the walls of the slurry reactor, and during the reaction. Metal A was deposited mainly as platelets in these areas of earlier deposition (see Figure 2). In this run, some activity was observed (about 1/7 that of SOSS-7A-2B-1). Perhaps the best explanation for the x-ray diffraction data (see below) and this deposition experiment is that metal B serves as a nucleation site for a specifically structured form of metal B; once formed this crystal structure may be retained, except perhaps at very high temperatures at which this particular structure is destroyed and catalyst activity is lost.

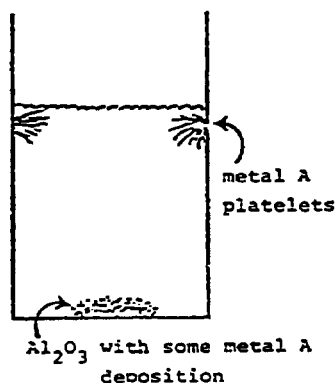


Figure 2. Interaction of the homogeneous component with alumina.

After the first deposition experiment, the reactor was extensively cleaned, by both physical and chemical techniques. The soluble component (metal A) was now deposited on the support. Once formed, this catalyst displayed good activities (about half that of SOSS-7A-2B-I) for syngas consumption although both hydrocarbons and oxygenates were formed. This is particularly important since this catalyst has been reported to have very low activity for the Fischer-Tropsch reaction.

Elucidation of the unusual features of SOSS has been undertaken by the BNL Metallurgy Department. Electron microscopy has not demonstrated anything unusual about SOSS-7A-2B-I, compared with the heterogeneous component from which SOSS is made, although the SOSS particles appear to be larger than those of the heterogeneous component and less friable. X-ray mapping (EDS) data indicate that both metals are present in the catalyst particles. These results are consistent with our opinion that the heterogeneous component interacts with the homogeneous component, essentially converting it to the corresponding metal. Further work, involving polishing a catalyst particle and scanning the resulting surface with an electron beam, indicates that the catalyst surface consists of a reasonably uniform mixture of the two metals, apparently a solid solution. However, these results are not conclusive, because of depth penetration effects of the electrons and the rough surface of the catalyst particles. Efforts are under way to prepare a SOSS-type catalyst with a more geometrically ideal shape and a smoother surface, and/or with a greater degree of metal deposition and perhaps on larger particles of oxide, which will allow more conclusive analysis of the metallic layer. Of course, the effect of these variables on catalyst activity needs to be determined.

Our opinion, based on the method of preparation, is that a layer of the metal of the homogeneous component was deposited on the metal of the heterogeneous component. However, if the above x-ray scattering results are correct, a very significant interaction of the two metals must take place on

the surface of the catalyst during its formation. An experiment is planned to prepare a similar alloy on the surface of an oxide by conventional catalyst preparation methods.

Powder x-ray diffraction analysis has been done on one formulation of SOSS, an alumina-supported catalyst prepared in situ as described above and used successfully for hydrocarbon synthesis. The results were as follows:

(1) The alumina used in the catalysts prepared for these studies (Fischer absorption alumina, for chromatographic analysis, A-540, unactivated, sieved to 80/100 mesh = 150 to 180 μ) appears to be $AlO(OH)$. This seems to us to indicate that the surface may have adsorbed water, and to have little bearing on the nature of SOSS, since other samples of alumina as well as silica gel and kieselguhr lead to equally effective catalysts.

(2) The SOSS catalysts are prepared from an originally homogeneous or coluble component (metal A) and a heterogeneous or insoluble component (metal B); the usual formulation consists of about 2% metal B and about 50% metal A, the remainder being support. The diffraction results now seem to suggest a preference for the layered structure, i.e., support, with a layer of metal B followed by a layer of metal A. Although the depth of penetration of the x-rays in these samples has not been established definitively, the following results seem to corroborate this. The support alone gives lines for $AlO(OH)$. When metal B is deposited on alumina, lines due to both species are present. However, when SOSS-7A-2B-I is examined, a line (see below) for metal A is the principal feature observed; lines for $AlO(OH)$ and metal B are very weak. Another catalyst, SOSS-2A-2B-I (similar to SOSS-7A-2B-I except that the loading of metal A is lower by a factor of 3 and the rate of syngas consumption is lower by about a factor of 2), gives more intense lines for $AlO(OH)$ and metal B. These results seem to indicate that in SOSS-7A-2B-I the x-rays are being diffracted principally by metal A at and near the surface and that little if any metal B is present here. The results from electron microscopy seem to indicate a solid solution for another, somewhat less effective batch of SOSS-7A-2B-I. These x-ray diffraction results appear to provide much more meaningful information about the surface and near-surface character of SOSS, and seem to favor the layered structure shown in Figure 3.

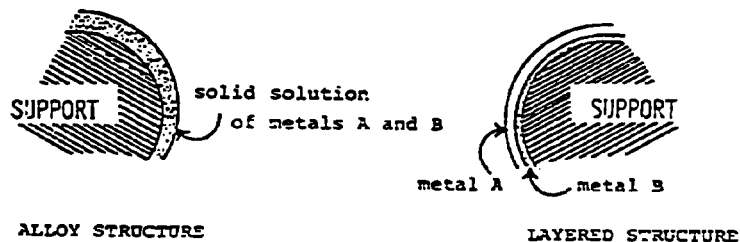


Figure 3. Possible SOSS Structures.

(3) The most remarkable feature of the diffraction pattern is the presence of only one line for metal A in the two SOSS formulations examined. This is most unusual since metal A normally yields several lines. This anomaly may be due to any of three affects: (a) the thin film effect, if there are not enough metal atoms to offer a "structure," (b) a strain effect, if the normal lattice is deformed, and (c) an orientation effect, if metal A has some unusual structure. We lean toward the last possibility, in view of the observation that metal A deposited on alumina under SOSS reaction conditions has the strong line found in SOSS as well as weaker lines normally associated with metal A. A kieselguhr-supported SOSS catalyst affords a similar diffraction pattern, whereas a standard metal A:kieselguhr catalyst shows only a very broad assortment of bands. Furthermore, a sample of SOSS previously heated to high temperatures has a diffraction pattern including the bands normally associated with metal A, suggesting that the unique structural feature of SOSS has been lost, and has much lower activity for hydrocarbon synthesis (roughly comparable to that of a conventional Fischer-Tropsch catalyst).

(4) The platelets of metal A (described above) were also examined by x-ray diffraction. The results suggest that the platelets are indeed highly structured and afford a pattern similar to that of SOSS-7A-2B-I, confirming the hypothesis that metal B serves as a "seed" for a highly structured form of metal A.

These x-ray diffraction data support the contention that the SOSS catalysts are highly oriented and therefore have relatively little metallic surface area. We have found that the structured state (as defined by x-ray diffraction) of metal A by itself on a support is not a sufficient condition alone to impart the high activity observed with the SOSS catalysts; the presence of metal B alone is also not a sufficient condition. The results above suggest that metal B favors this structure and also imparts some intriguing chemical properties to the SOSS catalysts. We hope to define this synergism better through continued cooperation with the Metallurgy Division and with some interested BNL physicists.

In understanding the activity of SOSS, its structure may be more important than its composition. Catalytic and surface chemists have long felt that certain crystal structures and faces may offer better activity than others but have been unable to incorporate, in a predictive fashion, these features in "real" catalysts. Possibly, clarification of SOSS activity will drastically alter the status of catalyst preparation and the understanding of those "black art" techniques used to improve catalyst effectiveness. A wide range of possibilities in this area have been considered and it is hoped that these will be tested in the near future.

PRODUCTS

At the end of a run, the reactor is cooled and the gas phase is analyzed by thermal conductivity gas chromatography for H_2 , CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , C_4H_8 , C_4H_{10} , C_5H_{10} , and C_5H_{12} . By noting the pressure drop during the reaction, the above results allow calculation of consumption ratio, fraction of liquid phase products, etc. Ordinarily, the consumption ratio

approaches 2:1. The yield of methane depends on whether the catalyst is prepared in the reactor; used catalysts give low CH₄ concentrations. Usually only small concentrations of other gases and hydrocarbons are detected, and they include only traces of unsaturates and little CO₂. The nature of the liquid products is determined by temperature-programmed gas chromatographic analysis. The principal products obtained with the SOSS catalysts are C₁ to >C₄₀ paraffins; only small amounts of lower alcohols have been detected. A typical reaction employing 3 g of catalyst in 100 mL xylene, carried out under three synthesis gas charges, yielded a pale yellow solution plus water. The xylene was distilled off under a vacuum, and a yellow oil remained. Infrared analysis of the reaction solution and the oil indicated little in the way of oxygenates or olefins and no metal carbonyls. Integrated nuclear magnetic resonance spectra of the yellow oil indicated highly linear paraffinic products with an average chain length of 18, with little or no aromatics, unsaturates, oxygenates, or branched products.

SOSS PATENTABILITY STATUS

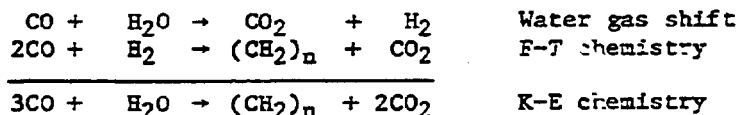
The SOSS system was described in three Records of Invention, one relating to the method of preparation, another to the composition of matter, and the third to the use of this catalyst in the synthesis of hydrocarbons from carbon monoxide and hydrogen. Four potentially interfering patents have been uncovered pertaining to the SOSS composition of matter. To secure optimal protection, the Records of Invention attempted to cover the interaction of one triad of elements with another triad of the periodic table, as this appears to be common practice in patenting catalyst formulations. However, on advice from counsel, the application will be restricted to only two metallic combinations, unless subsequent experiments warrant otherwise.

The interfering patents are broad in coverage and are relatively recent. None of the described catalysts has been used for the Fischer-Tropsch synthesis, although one has been described as a catalyst for methanation. Counsel has indicated that these patents impede composition of matter patent coverage for SOSS, even though their claims involve substantially different molar ratios of the two metallic elements.

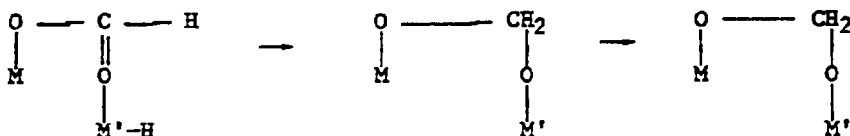
The prime impetus at this time for structurally characterizing the SOSS catalysts is the need to define the "uniqueness" of the system as an aid in obtaining the strongest patent coverage. Adequate characterization is now at hand, the disclosure is in preparation, and the patent application is expected to be filed in early to mid 1981.

CARBON MONOXIDE/WATER SYSTEMS

The development of hydrocarbon synthesis utilizing water in place of hydrogen (Kölbel-Engelhardt chemistry) will compensate for the low hydrogen content of the synthesis gas produced from second generation gasifiers. The standard approach to this work has been the addition of a water gas shift catalyst component to the hydrocarbon synthesis component in an attempt to run the two reactions sequentially:

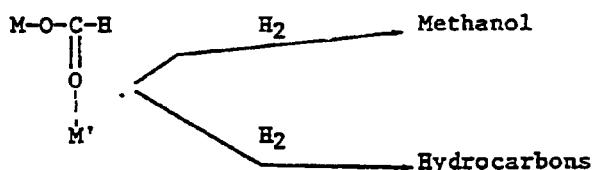


Recent mechanistic studies at BNL have implicated the water-gas shift formate intermediate as the important transfer agent in K-E chemistry. This work suggests that the shift reaction occurs on one component of the catalyst and the hydrocarbon synthesis follows a different path than the F-T synthesis. The shift component, often the support, is an integral part of the hydrocarbon synthesis system, generating the surface formaldehyde intermediate:



where M represents the shift component and M' represents F-T metal component.

Product character and distribution are determined by the metal component in a manner similar to that described by the oxide interpretation of the F-T synthesis. Thus, the metal formate may be hydrogenated to either hydrocarbons or alcohols,



and the results of a number of experiments with zinc formate using various promoters (M') are shown in Table 3. This description of K-E chemistry has allowed us to develop catalysts which use cobalt and nickel in these synthesis although these metals have little inherent shift activity. In fact, the activity of iron in this chemistry is probably due to integrated reaction of oxidized iron (Fe₃O₄) (water/gas shift component) and reduced iron.

Some experiments with supported cobalt catalysts (Table 4) afford interesting results. At the conditions chosen, zinc oxide and alumina yield surface formates, but magnesium oxide, a higher temperature water-gas shift catalyst, does not. Silica has been shown to inhibit the water-gas shift reaction, and, although cobalt on this support is the most active F-T catalyst, almost no K-E activity was found. Similar results have also been found with nickel.

Of further interest is the observation that the activity of Co/ZnO for K-E activity displays a pronounced dependence on temperature (5% conversion at 190°C, 30% at 230° and 80% at 250°). These series of experiments demonstrate

Table 3
The Use of Various Promoters for the Hydrogenation of Zinc Formate

<u>M'</u>	<u>t_{CH₃OH}</u>	<u>t_{C_xH_y}</u>
Cu/ZnO	1.7	--
Pt/Al ₂ O ₃	11.5	—
Pd/Al ₂ O ₃	22.6	0.1
Ni/SiO ₂	—	8.9
Co/SiO ₂	0.1	14.8
Fe/Al ₂ O ₃	—	2.4

water as solvent, 500 psi H₂, 245°C, τ = mole prod/mol M'

Table 4
The Use of Various Supported Cobalt Catalysts
for the Kölbel-Engelhardt Reaction

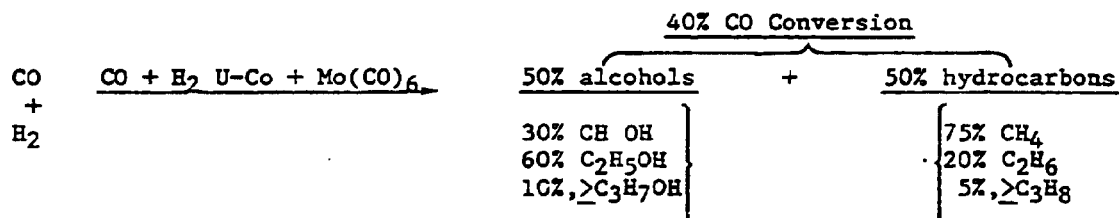
<u>Catalyst</u>	<u>Δmmole CO</u>	<u>ROH</u>	Products (mmole)	
			<u>CH₄</u>	<u>C₅⁺</u>
CoZnO	340	0.2	23	85
Co/Zn/ZnO	245	0.1	19	56
Repeat above	240	0.1	23	51
Co/Al ₂ O ₃	260	2	11	61
Co/Mg	15		Trace	
Co/SiO ₂	10		Trace	

Conditions: 1.0g catalyst, 150 mmol H₂O, 450 mmol CO, 245°C, 16 hr.

the importance of the shift component, usually the support, in this chemistry. Only those supports which yield a surface formate under the reaction conditions are useful in the catalyst system. With this approach, theoretically any F-T catalyst can be converted to use carbon monoxide/water mixtures.

OTHER BIMETALLIC SYSTEMS

By encouraging the intermediate formation of "isocarbonyl" species, neutral metal carbonyls can become active centers for F-T activity, and new catalyst systems can be developed. We have observed that cobalt will interact with the oxygen of molybdenum hexacarbonyl, providing synergistic effect, and F-T activity could be modified by this reagent. At 160°C under 300 psi 2:1 H₂:CO the molybdenum carbonyl-Urushibara cobalt system in tetrahydrofuran gave hydrocarbon and alcohol products:



The cobalt catalyst alone generated only hydrocarbon products in a lower total conversion. Further investigation in this area is continuing with emphasis on improving the higher-alcohol yield of the reaction.

These results fit the carbon monoxide termination step described by R. Pettit of the University of Texas and offer an interesting method for preparing higher alcohols by using hydrocarbon-forming F-T catalysts with homogeneous metal carbonyls.

PROGRAM DIRECTION

The results obtained with the SOSS series catalysts have necessitated a minor departure from the originally proposed work plan. Further work will be directed toward determining the scope and limitations of the SOSS catalysts, especially in comparison with other catalysts systems having high activity in hydrocarbon synthesis. Particular effort will be directed toward securing adequate patent protection.

Of major importance will be longevity studies using an isobaric gas-flow system. The effects of pressure and temperature on catalyst lifetime and activity need to be examined. The effects of potential "poisons" will also be studied.

The effect of metal loadings requires greater study. The study of surface area, number of active sites, porosity, and their relationship to activity and product distribution will be facilitated by a chemisorption apparatus anticipated to be available in mid-1981. An optimized dispersion will minimize catalyst cost while providing greater insight into the reasons

for the high activity. The effect of slurry loadings is under examination. The use of SOSS catalysts in other types of reactors, such as fixed bed, will be examined. The importance of support interactions will be further studied.

The recent acquisition of a metal vapor reactor is expected to allow facile preparation of SOSS-type catalysts by alternative means. A recently constructed high pressure infrared cell will allow monitoring of the catalyst preparation and reactions under conditions closely approximating those in our slurry reactor.

A better understanding of the underlying reasons for the high activity of the SOSS catalysts will probably lead to the development of a number of improved catalyst systems and is sure to capture the interest of surface scientists. Collaboration with scientists of other disciplines should provide important insights in this area.