DESIGN AND PREPARATION OF NEW, HIGHLY ACTIVE FISCHER-TROPSCH CATALYSTS

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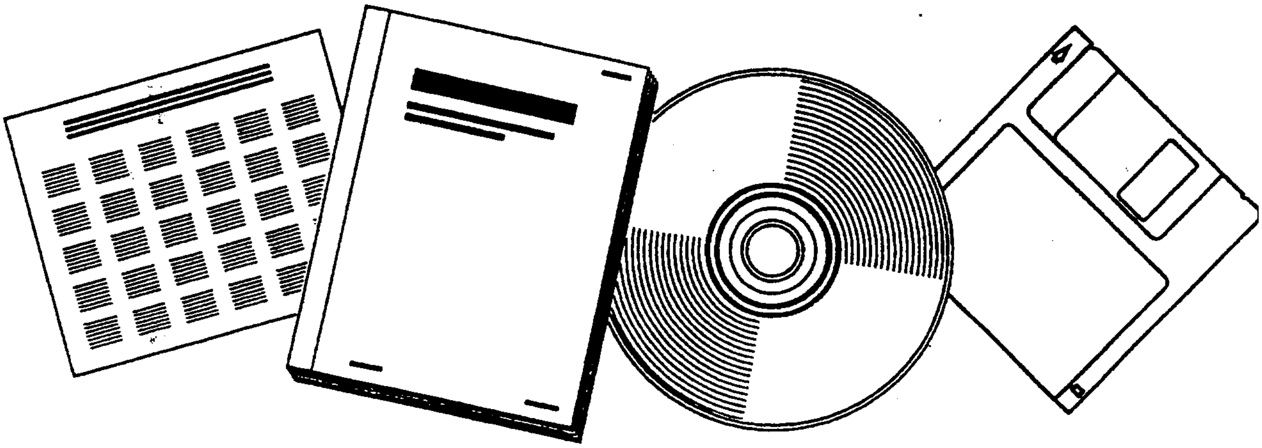

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THE DESIGN AND PREPARATION OF NEW, HIGHLY ACTIVE FISCHER-TROPSCH CATALYSTS

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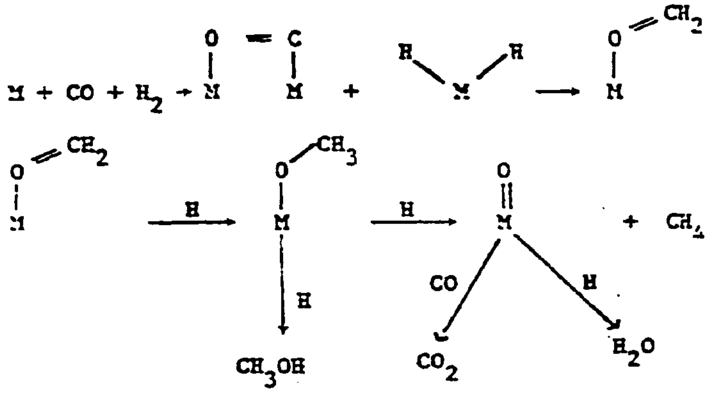
INTRODUCTION

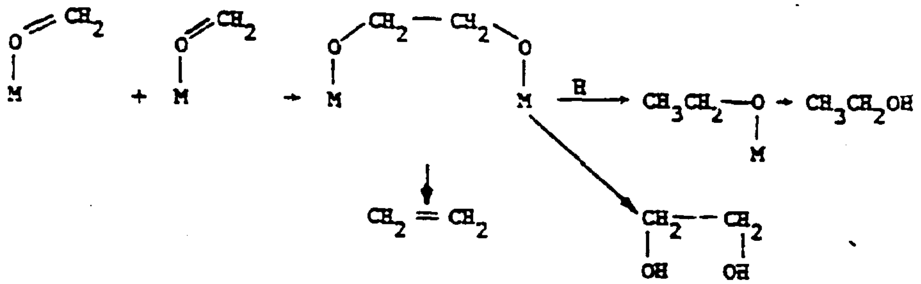
Great efforts have been made in the development of Fischer-Tropsch (F-T) chemistry, but the mechanism of the reaction and the behavorial patterns of Fischer-Tropsch catalysts have yet to be unequivocally defined. Numerous empirical attempts have been made to refine the synthesis in terms of improved effectiveness of the catalyst, but little improvement over the original German technology has been realized. Studies probing the metal surface and other sophisticated scientific investigations have not yielded satisfactory results and controversy over the key steps of the reaction mechanism continues as it did 30 years ago.

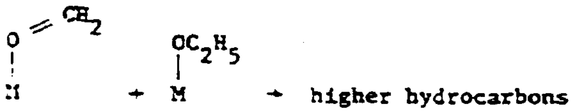
Although many of the reaction phenomena may be explained by previously proposed schemes for the F-T reaction, these have not or could not be used as diagnostic tools for the prediction of activity patterns or as guides to experimentation. We propose that the oxide mechanism, which encompasses the observations of these earlier theories, can explain and predict catalyst behavior in the reaction. The application of this simple approach to F-T chemistry has led us to the design of catalyst systems of enhanced activity. The successful results of such catalyst designs lend credence to the validity of the principles of this theory.

THE OXIDE MECHANISM

The oxide mechanism is a simple yet novel explanation of the experimental observations associated with synthesis gas reactions. Fundamental to this understanding is that chemisorbed carbon monoxide reacts with hydrogen over metal surfaces yielding an oxygen rather than a carbon coordinated species. The formed metal-oxygen bond thus will determine the reaction characteristics. The reaction scheme is outlined below.







The possibility of oxygen and carbon bonding in the chemisorption of carbon monoxide has been ignored, but this structural assignment may account for various spectroscopic observations.[1] The carbon monoxide may be first adsorbed as a carbonyl, but the oxygen interaction is necessary to form the active reacting species. This type of chemisorption of CO would explain the oxidation of iron[2] and cobalt[3] catalysts under what would be considered reducing synthesis conditions.

The energetics of carbon monoxide reduction via bonding to the metal surface through oxygen are more favorable than bond formation through carbon. If carbide formation is alternatively described as proceeding through CO disproportionation, the energetics still favor the surface metal oxide due to the extremely low carbide stability (see Table 1).

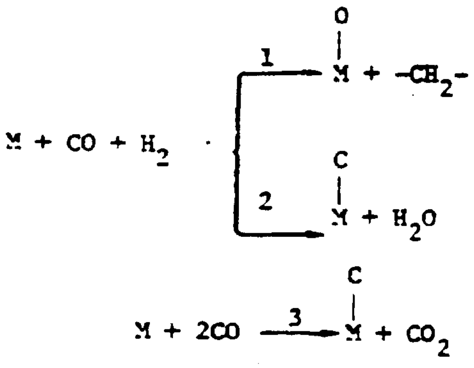
TABLE 1

Thermodynamics of Carbon Monoxide Reduction Paths

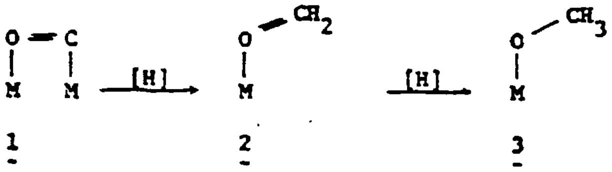
(in kcal/mole)

	Fe	Co	Ni
$-\Delta H_1$	42	36	37
$-\Delta H_2$	28	24	22
$-\Delta H_3$	37	33	31

with the respective reactions being,

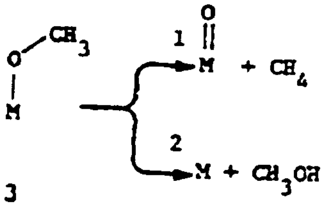


The hypothesis of CO reacting on a metal surface with oxygen and as well as carbon coordination suggests the existence of the following species



The highly reactive species 1 is rapidly converted to an oxymethylene 2 (oxygen-coordinated formaldehyde). This species corresponds in stoichiometry (1CO:$1H_2$) to the intermediate indicated by the Co adsorption of carbon monoxide and hydrogen on a F-T catalyst surface.[4] Small amounts of formaldehyde have been detected under conditions favorable for the recovery of intermediates,[5] and it has been found that small yields of methane may be obtained from formaldehyde adsorbed on metal surfaces under conditions which preclude carbon monoxide and hydrogen reacting.[6] These observations indicate that formaldehyde or some species derived from formaldehyde may well be an intermediate.

The oxymethylene further reacts with hydrogen to form the methoxy moiety **3**. Methanol is adsorbed on first-row transition metals in this manner,[7,8] and the participation of this type of intermediate in the Fischer-Tropsch reaction is supported by tracer experiments which indicate that methanol incorporation in the synthesis does not proceed via decomposition to CO and H_2.[9] This species may then react further with hydrogen to yield either methane or methanol.



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The heat of reaction for paths 1 and 2 are given by

$$\Delta H_1 = \Delta H_f(M\text{-}O) + \Delta H_f(CH_4) - \Delta H_f(M\text{-}O\text{-}CH_3),$$

$$\Delta H_2 = \Delta H_f(M) + \Delta H_f(CH_3OH) - \Delta H_f(M\text{-}O\text{-}CH_3).$$

Subtracting the above two equations and substituting the heats of formation of methane ($\Delta H_f = 17.78$), methanol ($\Delta H_f = 57.02$), and metal ($\Delta H_f = 0$) leads to the following expression:

$$\Delta H = \Delta H_1 - \Delta H_2 = \Delta H_f(M\text{-}O) + 39.13 \ .$$

If $\Delta H > 0$, then the energetics favor the formation of methanol. On the other hand, methane formation is favored by $\Delta H < 0$. Thus, metal oxides whose heats of formation are more negative than 39 kcal/g-atom exygen should form methane, while those whose heats are less negative will give methanol. The former group would include oxides or iron,[10] cobalt,[10] nickel,[10] zinc,[11] titanium,[12] etc., while the latter group would include copper,[13] palladium,[14] iridium,[14] rhodium,[15] etc. Indeed, corroborating experimental results are given in the references listed with each metal.

The consequences of this theory are many. The bond strengths of metal oxides should directly correspond to the specific activity of methanation, but should inversely correspond to methane selectivity because of the longer surface lifetime of the oxymethylene species. Using the data of Vannice,[16] this correspondence can be verified (see Table 2).

TABLE 2

Predicted vs. Observed Methanation Behavior

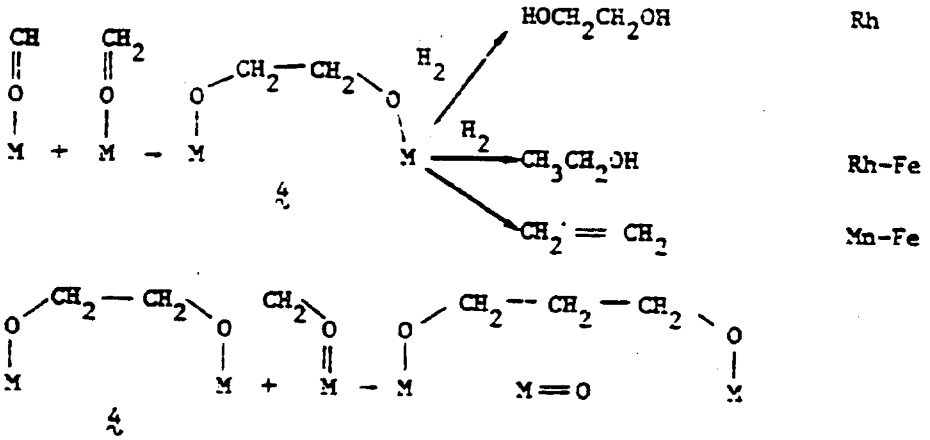
Specific Methanation Activity	Ru > Fe > Ni > Co > Rh > Pd
Selectivity	Pd > Ni > Rh > Co > Fe > Ru
Oxide Strengths	Ru > Fe > Ni > Co > Rh > Pd

Oxidation of the catalyst surface should decrease catalytic activity and selectivity. Although nickel is considered a selective methanation catalyst, the degree of surface reduction was found to correlate directly with its selectivity.[17] Also, low tungsten methanation activities found previously were due to inadequate surface reduction.[18] It should be noted that in industrial operations 100% reduction of the catalyst gives too great an initial activity to be feasible.

Metals which form nonreducible oxides should react with carbon monoxide and hydrogen giving methane and leaving a surface oxide coating. Indeed, the methanation of syngas over titanium yields surface titanium oxide.[12]

Attempted homogeneously catalyzed reductions of carbon monoxide have indicated that the formation of metal-oxygen bonds may be necessary for synthesis to occur.[19-21] The strong bond strengths of the oxides of the metals investigated may explain why these reactions could not be made catalytic.

The trivalent oxymethylene intermediate can undergo chain growth by reaction with similar species, thus generating straight chain products in an analogous manner to other proposed theories, but would account for the presence of oxygenated products. The initial dimerization would be similar to the formation of pinacols by the bimolecular reduction of carbonyl compounds. Further chain growth would occur via steps analogous to those proposed for metal oxide catalyzed olefin metathesis reactions. This polymerization with the oxymethylene intermediate as the monomer is consistent with the fact that the molecular weight distribution of the primary F-T products can be described by the Schulz-Flory equation.[22] Chain termination is a hydrogenolysis of the alcohol-like surface complex (4). The hydrocarbon chain length will be determined by competetion between polymerization of the oxymethylene and hydrogenation and desorption of the surface polymer in the termination step. The ability of the metal to hold the complex (metal-oxygen bond strength) is the determining factor.



The strengths of the metal oxide bond will also determine probable product characteristics. The dimerization of the oxymethylene over a weak oxide-forming metal such as rhodium should produce ethylene glycol,[15] while this same reaction over a strong oxide such as an iron-manganese bimetallic system would yield ethylene.[22] A mixed system such as rhodium-iron would give good yields of ethanol.[23]

The effect of product distribution caused by the use of a transition metal promoter on a specific catalyst can also be determined. Therefore, the addition of a weak oxide former should cause a decrease in methane and olefin production, whereas strong oxide producers should increase methane, CO_2, and olefin formation. Experimental findings match these predictions very well (e.g., 23).

THE DESIGN

In general, catalyst design is a trial and error process and not amenable to scientific analysis but the oxide mechanism, derived from empirical observations and thermodynamics calculations, suggests several possibilities for the basis of a new Fischer-Tropsch catalyst. Translating the mechanism in terms of adsorbed intermediates and surface reactions defines certain catalyst requirements. The metal system selected should have a high oxygen bond strength for a longer surface lifetime of the oxymethylene intermediate, but oxidation of the catalyst surface will decrease activity so the formed metal-oxygen bonds should be easily reduced under reaction conditions.

Although these fundamental properties only address chemical composition, this is certainly the beginning of scientific catalyst development. Further improvements may be achieved by delving deeper into the mechanism and considering desired chemisorbed complexes, but transcribing the reaction sequence to the catalyst surface would be difficult. Conceivably, catalysts surface properties may be very different from the bulk, but a simplistic approach based on correlating activity with bulk properties is easy to apply.

By example, the high activity of ruthenium catalyst can be explained by its unique physical properties. Ruthenium has a high oxygen bond strength, but the formed oxide is readily reduced. Therefore, ruthenium has the proper interacting requirements of an active Fischer-Tropsch catalyst. Our goal was to use this combination of properties to design a new, highly active system; a material which could be thought of as a ruthenium mimic. We constructed this new system around cobalt, since the most active non-noble metal catalysts known to this point were cobalt based. A cobalt Fischer-Tropsch catalyst had also been shown to give long chain hydrocarbons via a presumed formaldehyde intermediate.

Cobalt has a reasonably high metal oxygen bond strength, but unfortunately the formed metal-oxygen bond is very strong.

TABLE 3

Thermodynamic Data Used for Catalyst Selection

	D(M-O)	ΔH_f(M-O)
Ru-O	115 ± 15	28
Co-O	88 ± 5	57

Therefore, cobalt must be promoted with a material which will assist cobalt oxide reduction. The selection of this material to fine tune and improve the performance of cobalt is the critical feature of the new catalyst system. We chose palladium and platinum because these metals are well known hydrogenation catalysts and had been shown to promote various metal oxide reductions. But, platinum and palladium can form solid solutions with cobalt and the alloying of two active metals with each other does not impart the catalytic behavior expected from averaging the properties of the pure metals. So we knew which catalyst system should be prepared but how to prepare it became important.

We have found that cobalt carbonyl reacts under the proper conditions with certain materials used as heterogeneous catalyst supports, in particular alumina, resulting in a deposition of cobalt metal. The resulting Co/Al_2O_3 catalyst displays quite good activity for the Fischer-Tropsch reaction. This result is particularly intriguing considering earlier reports that suggested that alumina is a poor support for cobalt catalysts.[24]

The application of this catalyst preparation technique led to the development of a highly active series of Fischer-Tropsch catalysts. 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. Furthermore, this method of catalyst formulation appears to be unique in Fischer-Tropsch chemistry, yet is simple and reproducible. These catalysts are referred to by the generic term SOSS.

The Activity of the SOSS Catalysts

Table 4 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 Kolbel 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 5). These data again show the remarkable activity of the SOSS catalysts. Also notable is the observation that decreasing the cobalt loading (entries 1 and 2, Table 5) 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 Co/Al_2O_3 or Pd/Al_2O_3 approaches the high activity observed with the SOSS system. Furthermore, neither the $Co:ThO_2$: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 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.

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

Table 4
Comparison of Hydrocarbon Production Rates of Several Catalysts

Catalysts	Temp. °C	Activity g prod/(kg metal·hr)
SOSS-7A-2C-I-87[a] ($120Co:5Pt:100Al_2O_3$)	225°	3000
SOSS-2A-2B-I'-61[b] ($40Co:5Pd:100Al_2O_3$)	225°	1080
SOSS-7A-2B-I'-94[c] ($120Co:5Pd:100Al_2O_3$)	125°	40
Lurgi catalyst ($100Fe:10Cu:2K_2CO_3:9Al_2O_3:30SiO_2$)[d]	225°	24
Brabag catalyst ($100Fe:20Cu:20Zn:1K_2CO_3$)[d]	225°	10
Bureau of Mines 2A catalyst ($100Co:18ThO_2$:100 kieselguhr)[e]	195°	50
Pichler acid-promoted Ru/Al_2O_3 catalyst for polymethylene[f]	120°	120
Kölbel slurry catalyst ($100Fe:0.1Cu:0.05K_2O$)[g]	268°	450
Vannice (5% Fe on glassy carbon)[h]	235°	4

[a] 2.2 g catalyst, containing 1.2 g metal on high surface area Al_2O_3. 100 mL cyclohexane, 1200 psi 2:1 syngas, 300 mL AE reactor, catalyst prepared *in situ*.

[b] 1.4 g catalyst, containing 0.4 g metal on low surface area (80-100 mesh) Al_2O_3, 100 mL cyclohexane, 1200 psi charge 2:1 syngas, 300 mL AE reactor, catalyst prepared *in situ*.

[c] 2.2 g catalyst, containing 1.2 g metal on low surface area (80-100 mesh) Al_2O_3, 100 mL cyclohexane, 1200 psi charge 2:1 syngas, 300 mL AE reactor, catalyst prepared *in situ*.

[d] H.H. Storch, N. Golumbic, and R.B. Anderson, *The Fischer-Tropsch and Related Syntheses*, p. 308 (Table 86), Wiley, New York, 1951.

[e] Ibid., p. 132 (Table 5).

[f] H. Pichler and F. Bellstedt, *Erdol u. Kohle* *26*, 560 (1973).

[g] H. Kölbel, P. Ackermann, and F. Engelhardt, *Erdol u. Kohle* *9*, 153, 225, 303 (1956).

[h] M.A. Vannice, paper presented at 181st Am. Chem. Soc. Meet., Atlanta, GA, March 29-April 3, 1981.

Table 5

COMPARISON OF SEVERAL CATALYST SYSTEMS IN CYCLOHEXANE SLURRY[a]

Catalyst	Activity g prod/(kg metal*hr)	Rate of Syngas Consumption	Gaseous Products, mmol	Consumption Ratio	Products
SOSS-7A-2C-I-87 prepared from 1g 5% Pt/Al_2O_3 and 3.4g $Co_2(CO)_8$, <u>in situ</u> (2.2g of catalyst containing 1.2g metal)	3000	55%/20 min	8.3 CH_4 0.09 C_2H_4, 1.4 C_3H_6 0.1 C_4H_{10} 3.1 CO_2	2.2 2.0[b]	principally linear paraffins
SOSS-7A-2B-I'-59 prepared from 1g 5% Pd on 80-100 mesh Al_2O_3 and 3.4g $Co_2(CO)_8$, <u>in situ</u> (1.4g catalyst containing 1.2g metal)	860	50%/70 min	17 CH_4, 2.0 C_2H_6, 1.0 CO_2	2.0 1.9[b]	principally linear paraffins
SOSS-2A-2B-I'-61 prepared from 1g 5% Pd on 80-100 mesh Al_2O_3 and 1.13g $Co_2(CO)_8$, <u>in situ</u> (1.4g catalyst containing 0.4g metal)	1080	33%/80 min	13 CH_4, 1.4 C_2H_6 0.5 CO_2	3.2	principally hydrocarbons with small amounts of alcohols
Co on Al_2O_3, prepared from 1g 80-100 mesh Al_2O_3 and 3.4g $Co_2(CO)_8$ (2.2g catalyst containing 1.2g metal)	270	33%/120 min	18 CH_4, 0.9 C_2H_6, 2.3 CO_2	3.2	hydrocarbons and alcohols
5% Pd on 80-100 mesh Al_2O_3 (1g of catalyst containing 0.05g metal)	0	none	-	-	no hydrocarbons or alcohols detected
100Co:18ThO_2:100 Kieselguhr (7.5g of K_2CO_3 precipitated catalyst, reduced at 400° with H_2, containing 1.2g Co)	71	66%/350 min	3.4 CH_4, 0.2 C_2H_6, 0.5 CO_2	2.3	hydrocarbons, rich in lower molecular weight oxygenates
4Fe:1Cu (3g of precipitated catalyst, reduced at 400°C with H_2, containing 1.3g Fe)	180	40%/120 min	2.4 CH_4, 24 CO_2 1.2 C_2H_4, 0.8 C_2H_6	1.8	hydrocarbons rich in olefins
5% Ru/Al_2O_3 (2.2g catalyst, containing 0.11g metal)	21000	46%/25 min	27 CH_4, 0.02 C_2H_4 0.13 C_2H_6 0.14 C_3H_8, 1.6 CO_2	2.1	principally linear paraffins, rich in high molecular weight waxes

[a] General Conditions: 100 mL cyclohexane, 300 mL AE reactor charged with 800 psi H_2 and 400 psi CO with reaction carried out at 225°C (18 min to temperature).

[b] Consumption ratio, exclusive of methane formation.

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 <u>in situ</u>, under syngas pressure, from the $Co_2(CO)_8$ and either supported platinum or palladium components, in an appropriate solvent.

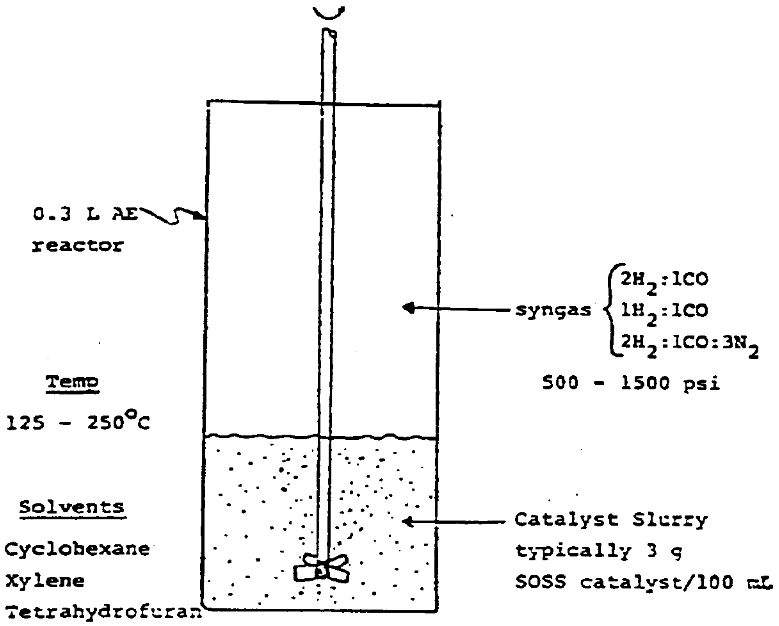


Figure 1. Schematic of Slurry Reactor

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 the soluble cobalt 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, decalin, 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 to carbonyl species under our reaction conditions. This should be compared to our results with Ru/Al_2O_3, in which a very significant portion of the metal was converted to homogeneous species.

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, containing Pt, 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 a 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 only slowly decrease in activity until the partial pressure of either the H_2 or CO component drops below about 70 psi. The consumption ratio is always near 2:1 H_2:CO, closely obeying the equation $CO + 2H_2 \rightarrow (-CH_2-)_n + H_2O$, 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 H_2 component. Even dilute feedstreams of syngas ($2H_2$:1CO:$3N_2$) are effective. Such versatility in syngas supplies is another attribute of the SOSS system. This system has not yet been found effective for the Kolbel-Engelhardt reaction, $3CO + 2H_2O \rightarrow (-CH_2-)_n + 2CO_2$, and this is reasonable considering that the normal consumption ratio is 2:1, little CO_2 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. However, more recent modification of the SOSS catalysts have allowed for a significant decrease in the consumption ratio.

The catalyst may be pre-formed, 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 require 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 air for 2 hours, after which solvent was added and the reactor was charged with synthesis gas; at 200°C the catalyst had the same activity as before atmospheric exposure. In other cases, the catalyst dried at 120°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. Kolbel 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 on whether or not the catalysts are prepared in situ, that is, a significant portion 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 oxiding 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 compositon of matter. Although a number of compositions have been tested, only cobalt with platinum and cobalt with palladium may be made by this method of preparation and 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 sites and the surface area of the metal are remarkably low (about 45 m^2/g) 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.

As mentioned above, cobalt carbonyl 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 palladium with cobalt had been left plated on the walls of the slurry reactor from previous reactions. In this case, cobalt carbonyl decomposed to cobalt metal 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-I). Perhaps the best explanation is that palladium or platinum serves as a nucleation site for a specifically structured form of cobalt; 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.

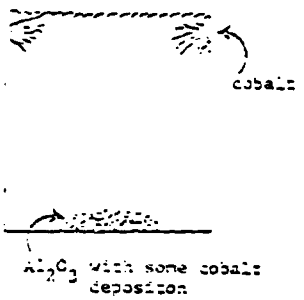


Figure 2. Initial Interaction of Cobalt Carbonyl with Alumina

After the first deposition experiment, the reactor was extensively cleaned, by both physical and chemical techniques. Cobalt 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.

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 5% Pd/Al_2O_3 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 alumina which will allow more conclusive analysis of the metallic layer. Of course, the effect of these variables on catalyst activity needs to be determined.

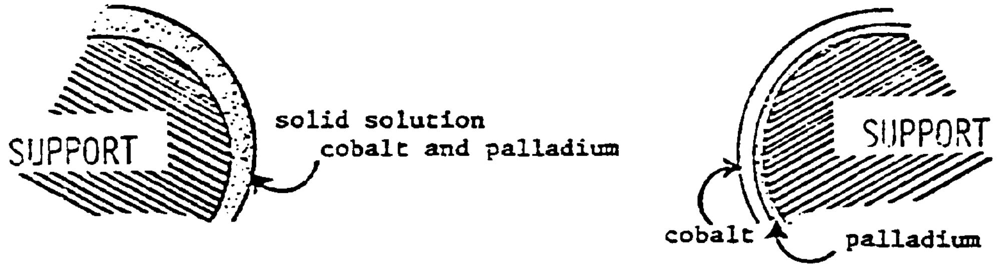
Our opinion, based on the method of preparation, is that a layer of cobalt was deposited on the thin layer of palladium. However, if the above x-ray scattering results are correct, a very significant interaction of the two metals must take place on the surface of the catalyst during its formation.

Powder x-ray diffraction analysis has been done on one formulation of SOSS, an alumina-supported catalyst prepared in situ as described above from $Co_2(CO)_8$ and 5% Pd/Al_2O_3 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 soluble component (cobalt) and a heterogeneous or insoluble component (palladium or platinum); the usual formulation consists of about 2% palladium or platinum and about 50% cobalt the remainder being support. The diffraction results now seem to suggest a preference for the layered structure, i.e., support, with a layer of palladium followed by a layer of cobalt. 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). With 5% Pd/Al_2O_3 lines due to both species are present. However, when SOSS-7A-2B-I is examined, a line (see below) for cobalt is the principal feature observed; lines for AlO(OH) and palladium are very weak. Another catalyst SOSS-2A-2B-I (similar to SOSS-7A-2B-I except that the loading of cobalt is lower by a factor of 2), gives more intense lines for AlO(OH) and palladium. These results seem to indicate that in SOSS-7A-2B-I the x-rays are being diffracted principally by cobalt at and near the surface and that little if any palladium is present here. These x-ray diffraction results appear to provide much more meaningful information about the surface and near-surface character of SOSS than the aforementioned electron microscopy work and seem to favor the layered structure shown in Figure 3.



ALLOY STRUCTURE

LAYERED STRUCTURE

Figure 3. Possible SOSS Structures.

3) The most remarkable feature of the diffraction pattern is the presence of only one line for cobalt in the SOSS formulations examined. As shown in Figure 4, face-centered cubic (fcc) cobalt is easily distinguished from hexagonal close packed (hcp). Unlike the precipitated cobalt catalyst which shows a broad assortment of peaks, the SOSS catalyst displays one sharp peak very similar in angle to that reported for fcc cobalt.[25] This anomaly may be due to any of three effects: (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 cobalt has some unusual structure. We lean toward the last possiblity, in view of the observation that cobalt deposited on alumina under SOSS reaction conditions has the strong line found in SOSS as well as weaker lines normally associated with cobalt. The predominant structure appears to be that of face-centered cubic (fcc) cobalt. An Al_2O_3-supported SOSS catalyst affords a similar diffraction pattern. Furthermore, a sample of SOSS previously heated to high temperatures has the diffraction pattern normally associated with cobalt, suggesting that the unique structural feature of SOSS has been lost. This sample has much lower activity for hydrocarbon synthesis, roughly comparable to that of a conventional Fischer-Tropsch catalyst.

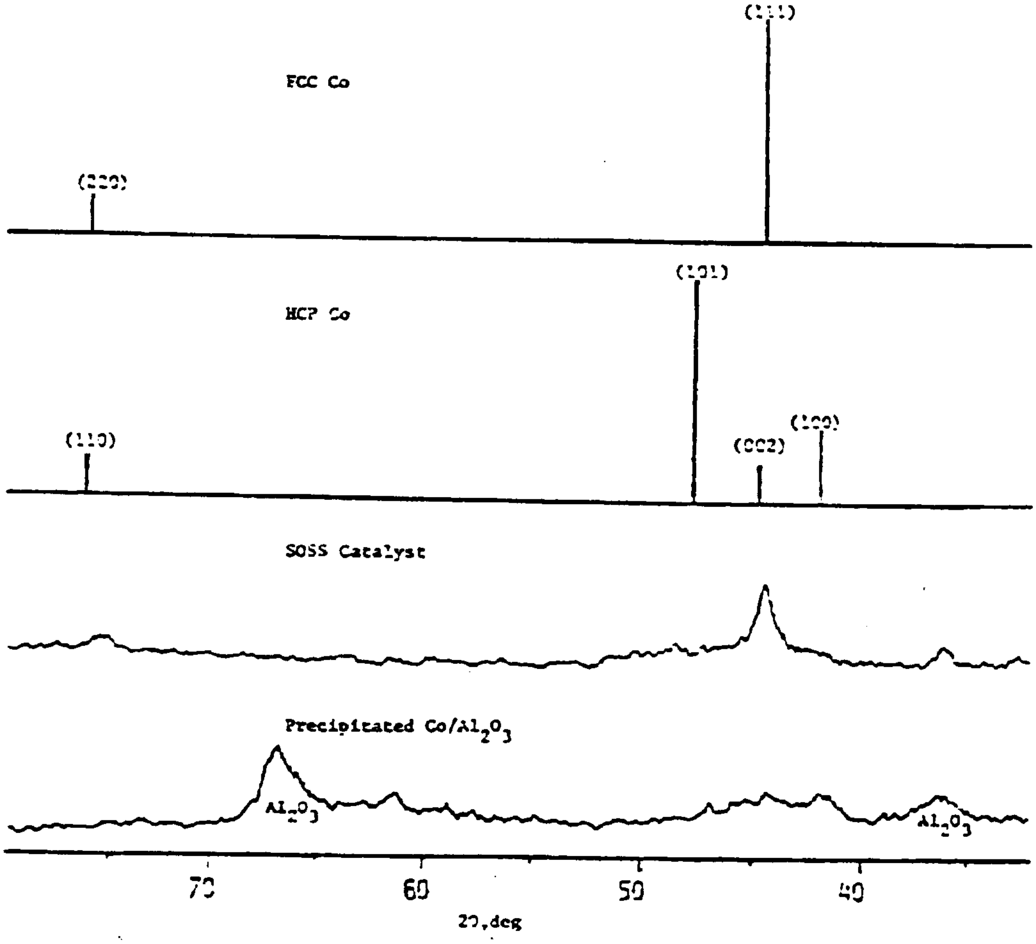


Figure 4. X-ray Diffraction Patterns of HCP and FCC, SOSS, and Precipated Co/Al_2O_3 Catalysts

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

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 (approximately fcc, as defined by x-ray diffraction) of cobalt by itself on a support is not a sufficient condition alone to impart the high activity observed with the SOSS catalysts; the presence of palladium alone is also not a sufficient condition. The results above suggest that palladium promotes the fcc 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.

SOSS Products

At the end of a run, the reactor is cooled and the gas phase is analyzed by thermal conductivity gas chromotography for H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{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; reused catalysts give relatively low CH_4 concentrations. Usually only small concentrations of other gases and hydrocarbons are detected, and they include only traces of unsaturates and little CO_2. The nature of the liquid products is determined by temperature-programmed gas chromatographic analysis. The principal products obtained with the SOSS catalysts are C_1 to $>C_{40}$ 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.

SUMMARY

In conclusion, the application of the fundamental principles of the oxide mechanism, which emphasizes the relation between metal-oxygen bond strengths and catalyst activity, has resulted in a new series of highly active Fischer-Tropsch catalysts. These systems may point the way to future syngas catalyst development. The unique structural features of these catalyst have demonstrated the importance of surface structure and its relationship to catalyst composition and activity.

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