

DIESEL AND JET FUELS FROM COAL

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Diesel and jet fuels are strategic fuels critical to our transportation industry and national defense. These fuels require aliphatic hydrocarbon components, substantially of a straight-chain nature. Such fuels are not readily available from coal by direct liquefaction processes. The Fischer-Tropsch (F-T) synthesis, an indirect process, normally produces principally linear paraffins and is particularly suitable for the preparation of these fuels.

Petroleum supplies are expected to become increasingly less available and more expensive. The economic strength and security of the nation would be well served by having available a clean, multipurpose alternate feedstock for use as a source of future raw materials and fuels. Carbon monoxide and synthesis gas qualify as such key materials. These are easily produced on a commercial scale from many different sources of carbon including coal, natural gas, biomass, shale oil, and tar sands. The resulting synthesis gas is already an important feedstock for the production of major chemical intermediates such as ammonia and methanol. It also finds use in the synthesis of esters, formaldehyde, higher aldehydes and alcohols, MTBE, acetic and other carboxylic acids. Future processes for the production of light olefins, glycols, vinyl acetate, chloromethanes and polymers represent exciting new uses for synthesis gas. The Mobil methanol-to-gasoline process and related reactions demonstrate more specifically the enormous potential of this intermediate(1).

We believe that because of the versatility of synthesis gas, with regard to both its downstream utility and the variety of materials from which it may be prepared, it would be the ideal feedstock for fuels production. Therefore, another attribute of the F-T synthesis is its ability to fit into an integrated chemical and fuels scenario, centered around synthesis gas.

Although a number of variations have been examined over the last half-century, the F-T process exhibits several problems related to activity, selectivity, and heat transfer, which are interrelated. For example, in fixed bed reactors, the removal of process heat (corresponding to roughly 20% of the combustion value of the synthesis gas) is a major problem. Catalyst activity could be increased by raising the temperature, but this only exacerbates and is ultimately limited by the heat removal problem. Pressures may be increased to increase activity, but normally a substantial decrease in selectivity results(2). Improved methods of heat removal are crucial to process improvement.

F-T Slurry Reactors

As a means of improving the operation of F-T processes, particularly with regard to heat control slurry reactor systems have been gaining increased interest. Such systems were examined during World War II in Germany, but have only gained worldwide acceptance through the work of Kolbel(3). The concept of the slurry F-T reactor has been examined by a number of workers(4-8). General agreement appears to exist among the investigators on certain advantages of the slurry system. These include:

1. Superior temperature control.
2. Simple reactor design.

3. Catalyst (usually between 1 and 40 microns in size) is easily added to or removed from the reactor without shutdown.
4. Product flexibility and selectivity is superior to other reactor systems.
5. There are no erosion problems.

Kolbel's work includes the following additional claims:

1. Feed gas ratios as low as 0.7 can be used without significant free carbon formation.
2. Single pass syngas conversions as high as 95% are attainable.
3. Gasoline yields in excess of those predicted by a Schulz-Flory distribution are attainable.
4. Methane yields are lower.

The slurry reactor system has captured the interest of some large corporations. UOP, with support from the U.S. Department of Energy, carried out an engineering evaluation of four F-T reactor systems and found the slurry system a clear leader with regard to both capital and operating costs(9). However, it is important to note that the data used in modeling these reactor systems has largely been those of Kolbel, employing iron catalysts. In fact, for the slurry F-T reactor system, virtually no data on non-iron catalysts are available.

The Design of the Catalyst

In general, catalyst design is a trial and error process and not amenable to scientific analysis but the oxide mechanism(10), derived from empirical observations and thermodynamics calculations, suggests several possibilities for the design of a new F-T 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 key reaction 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 translating the reaction sequence to the catalyst surface would be difficult. Conceivably, catalyst surface properties may be very different from the bulk, but a simplistic approach based on correlating activity with bulk properties is easy to apply.

For example, the high activity of a 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 F-T 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. This new system was constructed around cobalt, since the most active non-noble metal catalysts known to this point were cobalt-based.

As shown in Table 1, cobalt has a reasonably high metal oxygen bond strength, but unfortunately the formed metal-oxygen bond is very strong. 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 in our laboratories and by others 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.

TABLE I
Thermodynamic Data Used for Catalyst Selection

	D(M-O)	H _f (M-O)
Ru-O	115 ± 15	28
Co-O	88 • 5	57

The Nature of the Catalysts

We have found that cobalt carbonyl reacts, under the proper conditions, with certain materials (particularly alumina) used as heterogeneous catalyst supports, resulting in the deposition of cobalt metal. The resulting Co/Al₂O₃ catalyst displays quite good activity for the F-T reaction. This result is particularly intriguing considering earlier reports that suggested that alumina is a poor support for cobalt catalysts(11).

The application of this catalyst preparation technique led to the development of a highly active series of F-T 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 F-T chemistry, yet is simple and reproducible. These catalysts are referred to by the generic term SOSS.

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; catalysts with alumina, silica, or kieselguhr supports lead to comparable results. The surface area of the support plays a relatively minor role in the activity of these systems. 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 m²/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; this property has been used in cleaning our reactors after runs, and may be commercially useful in catalysts 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. Early experiments have shown 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.

Elucidation of the unusual metallurgical features of the SOSS catalysts has been undertaken. Examination of a SOSS catalyst by electron microscopy indicates that the particles are larger and less friable than those of the 5% Pd/Al₂O₃ used in their preparation. EDS data indicates that both metals are present in the catalyst, confirming our belief that the heterogeneous component (Pd/Al₂O₃) interacts with the homogeneous component (Co₂(CO)₈), converting the latter to the corresponding metal.

Powder x-ray diffraction data suggests that the catalyst consists of a thin layer of palladium or platinum deposited on the support, followed by a much thicker layer of cobalt. The usual formulation of the catalyst is 2% palladium or platinum and about 50% cobalt, with the remainder being support. This analysis appears to be consistent with the method of preparation and seems to indicate that the metals are not present as a solid solution. Furthermore, the cobalt is present in the face-centered-cubic orientation, as relatively large crystallites. This feature appears to be important to the activity of this catalyst. Additional characterization is underway.

Reactor Configuration and Operating Conditions

Most experiments with the SOSS series catalysts have been conducted in a batch slurry reactor. 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 proportioning temperature controller employing a 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 charging. The SOSS catalyst, once formed, is air stable.

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 or hydrogen pressure, from Co₂(CO)₈ and either supported platinum or palladium components, in an appropriate solvent. This leads to the formation of the heterogeneous SOSS catalyst conveniently in the slurried state. All 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 while the reactor is warming and is known to occur below 120°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.

A wide variety of reaction conditions may be used. The catalysts have been used in the temperature range of 150°C to 250°C, although one formulation 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 temperatures leads to significant improvement in catalyst activity. Slurry loadings have been examined in a relatively limited range (1 to 7 g 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 charges of 500 to 1500 psi, although they are effective at much lower pressures; normally, reactions decrease in activity only slowly 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 $\text{CO} + 2\text{H}_2 \rightarrow (\text{CH}_2)_n + \text{H}_2\text{O}$, and most reactions have been carried out with syngas of this ratio. The use of 1:1 syngas leads to comparable results (with 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. 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 buildup of water does not appear to promote catalyst deactivation. 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 F-T catalysts, which normally require a tedious, time-consuming reduction step, the precision of which has a pronounced bearing on the catalytic properties. In a particular case, a sample of the damp SOSS catalyst was exposed to air for 2 hours, after which time 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. However, in contrast to claims sometimes attributed to the slurry reactor, the SOSS system displays nearly constant consumption ratios and appears to afford only minor variations in product nature and distribution with hydrogen partial pressure.

The Activity of SOSS Catalysts

Several standard F-T systems have been compared with the SOSS systems under our reaction conditions (Table 2). These data show the remarkable activity of the SOSS catalysts. Also notable is the observation that decreasing the cobalt loading (entries 2 and 3, 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 Co/Al₂O₃ or Pd/Al₂O₃ 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.

The 5% Ru/Al₂O₃ catalyst affords very good activity in part due to its high metal dispersion. However, on a catalyst weight basis using 2.2g of catalyst, SOSS7A-2C-I-87 afforded 55% syngas consumption over 20 min, while the Ru/Al₂O₃ catalyst afforded 48% over 25 min. The SOSS catalysts prepared to date have poor surface areas and metal dispersions; if activity and selectivity can be maintained while decreasing metal loading, some startling improvements may be made. Furthermore, we have found that very significant amounts (about 20%) of the metal in the 5% Ru/Al₂O₃ catalyst go into solution in the form of homogeneous ruthenium carbonyls, whereas no solubility loss of the SOSS catalysts is observed.

TABLE 2

COMPARISON OF SEVERAL CATALYST SYSTEMS IN CYCLOHEXANE SLURRY^a

Catalyst	Activity g prod/(kg metal*hr)	Consumption Ratio	Products
SOSS-7a-2C-I-87 prepared from 1g 5% Pt/Al ₂ O ₃ and 3.4g Co ₂ (CO) ₈ , <u>in situ</u> (2.2g of catalyst containing 1.2 g metal)	3000	2.2 2.0 ^b	principally linear paraffins
SOSS-7A-2B-I'-59 prepared from 1g 5% Pd on 80-100 mesh Al ₂ O ₃ and 3.4g Co ₂ (CO) ₈ , <u>in</u> <u>situ</u> (2.2g catalyst containing 1.2g metal)	860	2.0 1.9 ^b	principally linear paraffins
SOSS-2A-2B-I'61 prepared from 1g 5% Pd on 80-100 mesh Al ₂ O ₃ and 1.13g Co ₂ (CO) ₈ , <u>in</u> <u>situ</u> (1.4g catalyst containing 0.4g metal)	1080	3.2	principally hydro- carbons with small small amounts of alcohols
Co on Al ₂ O ₃ , prepared from 1g 80-100 mesh Al ₂ O ₃ and 3.4g Co ₂ (CO) ₈ (2.2g catalyst containing 1.2g metal)	270	3.2	hydrocarbons and alcohols
5% Pd on 80-100 mesh Al ₂ O ₃ (1g of catalyst containing 0.05g metal)	0	-	no hydrocarbons or alcohols detected
100Co:18ThO ₂ :100 Kieselguhr (7.5g of K ₂ CO ₃ precipitated catalyst, reduced at 400°C with H ₂ , containing 1.3g Co)	71	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	1.8	hydrocarbons rich in olefins
5% Ru/Al ₂ O ₃ (2.2g catalyst, containing 0.11g metal) ^c	21000	2.1	principally linear paraffins, rich in high molecular weight waxes

^aGeneral Conditions: 100 mL cyclohexane, 300 mL AE reactor charged with 800 psi H₂ and 400 psi CO with reaction carried out at 225°C (18 min to temperature).

^bConsumption ratio, exclusive of methane formation.

^cForms homogeneous metal carbonyls under reaction conditions.

SOSS 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_{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. Methane is the predominant gas-phase product. 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. Although complete product characterization has not been carried out, it appears that the liquid products contain little or no aromatics, unsaturates, oxygenates or branched products and have an average chain length of about 18. It thus appears that the products could find use as diesel or jet fuels.

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