SECTION III

STRONG ACIDS AS CATALYSTS FOR THE DIRECT LIQUEFACTON OF COAL

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Summary

This review is concerned with the conversion of coal to liquids using very strong acids known as superacids. Superacids are acids with extraordinary proton strengths which are strong or stronger than 100% sulfuric acid. They can react with very weak bases, even with methane, to furnish a CH_5^+ carbocation which decomposes to CH_3^+ and hydrogen gas. The srongest superacids contain fluorine but the presence of this element is to be avoided because of difficulty of handling and tendency to be corrosive.

Coal has been converted to liquids using fluorinated acids and the more stable, less corrosive solid superacids. The acidity of a number of solid oxides such as Fe_2O_3, ZrO_2 and TiO_2 is raised remarkably by addition of sulfate ion; thus Fe_2O_3-SO_4^{2-} is thousands of times stronger as an acid than is Fe_2O_3.

Strongly acidic catalysts were found to be active and selective for the liquefaction of a bituminous coal. Traditional hydrogenation catalysts appear more effective for lignite conversion to liquids. Evidently acidity properties of catalysts are important in carbon-carbon bond cleavage while hydrogenation ability of a catalyst is important for carbon-oxygen bond cleavage.

The study of the direct liquefaction of coal with superacids is in its infancy and promises to yield new approaches to both coal conversion and to elucidation of the constitution of coal.

Introduction

The objective of using strong acids, sometimes in the presence of a hydrogen donor solvent, is to depolymerize coal and stabilize the reactive fragments by hydrogen donated from the solvent. Several acids, including sulfuric acid, p-toluenesulfonic acid, and phosphoric acid have been used in endeavors to hydroliquefy and remove sulfur from coal (Ouchi et al., 1973). McLean and Vermeulen (1977) studied the use of 65-100% H_3PO_4 as homogeneous catalysts for the liquefaction of coal at 250°C and 600 psig; molten phosphate and sulfate systems were also studied with limited success. Sulfuric acid was not effective as a liquefaction catalyst, promoting carbonization and gasification at 175°C and 600 psig. Substantial improvements in yield were claimed by Kiovsky (1973,1974) who added small amounts of mineral acids to molten halide catalytic systems: adding H_3PO_4 and $SbBr_3$ to a bituminous coal increased the yield of oils boiling below 250°C from 5.3 to 31.5% at 325° and 1700 psig.

Tin and zinc halides, both weak Lewis acids, have been used in numerous attempts to liquefy coals under various conditions. The Conoco Coal Development Company with the Shell Development Company developed a zinc halide hydrocracking process (Alpert and Wolk, 1981). The objective of this process, using stoichiometric amounts of zinc halide in the presence of hydrogen, was to maximize the conversion of coal to clean light distillates by severe catalytic cracking. The coal was cracked to products in the gasoline range, yielding, after distillation, a clear 90 RON gasoline without further processing plus a small amount of very low sulfur and nitrogen fuel oil. Regeneration and recovery of the spent catalyst from the product oils was severely complicated by the corrosive nature of the acid formed during recovery. But this process, not successful, is different from almost all the

other direct liquefaction processes: its products needed little or no upgrading and were of high quality. In addition, solvent quality was not a concern and excellent removal of heteroatoms was achieved. It would seem that this area of research carries the seed for a novel route to coal liquefaction.

Work has been carried out at the University of Utah with the use of catalytic amounts of halide and other catalysts in the hydropyrolysis of coal (Hill, 1970). This and other work is summarized in an excellent review of coal hydrogenation catalysis by Gavin (1982).

Recently, Anderson and Miin (1986) studied the catalytic action of Lewis acids at or below 300°C and 13.5 MPa of H_2 for the liquefaction of a Utah (hvBb) coal. They tested more than 80 such catalysts, finding only one property that correlated directly with the coal liquefaction yields -- the electronic softness of the Lewis acids investigated. Catalysts which gave moderate to high conversion yields consisted of "borderline" cations and nonhard anions as defined by a qualitative classification of acidity and basicity of Lewis acids and bases. Pearson (1963) classified acids and bases as hard, soft, or borderline. Hard acids (electron pair acceptors) usually have small electron acceptor sites of high positive charge and do not have unshared electron pairs in their valence shells. Hard acids have low polarizability and high electronegativity. Soft acids generally consist of highly electronegative donor atoms of low polarizability. Soft acids prefer to bond to soft bases and hard acids prefer to combine with hard bases.

Anderson and Miin (1986) reasoned that the effectiveness of borderline catalysts seemed to be that most reactive functional groups in bituminous coal were borderline after protonation by an acid. This gave more stable ion pairs which reacted with hydrogen to yield hydrogenation or hydrogenolysis products. It is interesting that zinc and tin halides gave the highest

conversions, often exceeding 90 wt% of liquids in addition to small amounts of gases. Model compound studies supported this postulate.

The usual concepts of hydrogen ion concentration and pH are meaningful only for dilute aqueous solutions of acids. A widely used method of estimating acidity in other media and at high concentrations is the Hammett (1932) acidity function termed H_o. This is defined in terms of the behavior of an indicator base, usually consisting of various substituted anilines as proton acceptors, B. The protonation equilibrium is

$$H^+ + B = BH^+$$

and the acidity function is defined as

$$H_o = pK_{BH^+} = \log \frac{[BH^+]}{[B]}$$

In very dilute solutions

$$K_{BH^+} = \frac{[B]\,[H^+]}{[BH^+]}$$

In water, therefore, H_o is the same as pH.

The concentrations of BH^+ and B can be measured spectroscopically and the pKa's of BH^+ are known. For instance, the solvent system composed of 60 wt% H_2SO_4 in water has an H_o value of -4.32; 2, 4-dinitroaniline ($pK_a(BH^+)$ = -4.38) was used as the indicator base to obtain this value. Once an H_o value is known for a solvent system, that system may be the basis for an experimental determination of an unknown pK_a.

For many strong acids in aqueous solutions up to about 8M concentrations, H_o values are very similar, suggesting that the acidity is independent of the anion. Values of H_o for some pure liquid acids are given in Table III-1.

Table III-1

Hammett Acidity Functions, H_o, for Some Pure Liquid Acids

Acid	$-H_o$	Acid	$-H_o$
SbF_3 (2.5 mol %) + HSO_3F	21.5	HF	11
SbF_3 (0.6 mol %) + HF	21.1	NaF(IM) + HF	8.4
HSO_3F	15	H_3PO_4	5.0
H_2SO_4	12	H_2SO_4 (63% in H_2O)	2.2

The strongest acids are referred to as superacids because they have extraordinarily high proton strengths. It is to be noted that the acidity of HF can be greatly increased by addition of a Lewis acid or fluoride ion acceptor

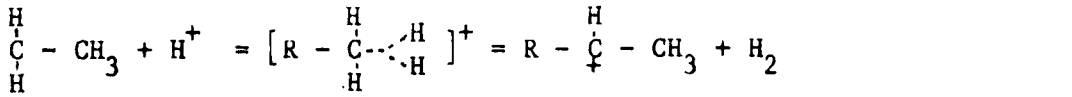
$$2HF + SbF_5 \rightleftarrows H_2F^+ + SbF_6^-$$

SbF_5 is often used as the Lewis acid; it is a liquid comparatively easy to handle and is available commercially. BF_3, NbF_5 and TaF_5 behave similarly.

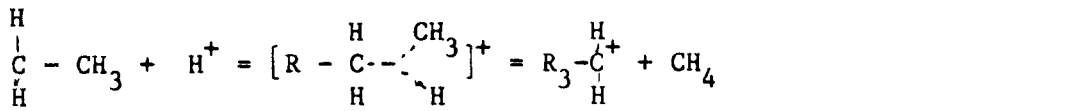
Superacids such as HSO_3F and SbF_5 are so strongly acidic that they can even protonate methane as well as other paraffins (Olah 1973).

$$CH_4 + H^+ \rightleftarrows [CH_5]^+ \equiv [H_3C\text{---}\begin{smallmatrix}H\\H\end{smallmatrix}]^+ \rightarrow CH_3^+ + H_2$$

and hydrocarbons. The CH_5^+ species can react further to give the unstable methyl carbenium ion, CH_3^+, and H_2. A similar reaction occurs with higher paraffins



or the protonated paraffin can undergo cleavage of a carbon-carbon bond



Superacids have been variously defined. A common definition is that as an acidic medium that has a proton donating ability greater than 100% H_2SO_4 is a superacid (Gillespie and Peel, 1971, 1973). Another definition is that acid media with $-H_o$ values greater than six are superacids since they are more than a million times stronger than a one molar aqueous solution of strong acid. Addition of SbF_3 to HSO_3F raises the $-H_o$ value from 15 to 21.5 at 25 mol % SbF_5.

There are several notable publications on superacids. An outstanding book on superacids is a recent one by Olah et al. (1985). Tanabe (1970) has also written an excellent book and a more recent review (Tanabe, 1981).

Olah et al. (1985) have outlined a practical if somewhat arbitrary classification of superacids as follows:

a. <u>Lewis Superacids</u> such as SbF_5, AsF_5 TaF_5, NbF_5, etc.

b. <u>Bronsted and Conjugate Bronsted-Lewis Superacids (4 classes)</u>

- Perchloric acid, halosulfuric and perfluoroalkanesulfonic acids such as $HClO_4$, HSO_3F, CF_3SO_3H, R_FSO_3H, etc.

- Oxygenated Bronsted acids such as H_2SO_4, HSO_3F, CF_3SO_3H, R_FSO_3H combined with Lewis acids such as SbF_5, SO_3, AsF_5, etc.
- Hydrogen fluoride combined with fluorinated Lewis acids such as SbF_5, BF_3, TaF_5, NbF_5.
- Friedel-Crafts acids such as $HCl-AlCl_3$, $HBr-AlBr_3$, etc.

c. Solid Superacids

- Solid acids whose acidity can be enhanced, such as acid-treated metal oxides, mixed oxides and zeolites. Included under solid acids are perfluorinated resins and sulfonated cation exchange resins complexed with Lewis acids. Supported Lewis or Bronsted acids are also found in this category.

Strong Acids as Liquefaction Catalysts

The acid catalyzed depolymerization of coal has been studied for converting coal into soluble products at low temperatures for structural investigations. Heredy and Neuworth (1962) depolymerized coal at about 100°C using phenol as a solvent and BF_3 as the catalyst. They achieved an aromatic interchange reaction with phenol. These workers were able to show the existence of methylene and ethylene linkages (Heredy et al (1964, 1985) as well as the presence of free isopropyl groups in coal (Heredy et al (1963).

The alkylation and depolymerization of coals with isobutylene, catalyzed by H_2SO_4, was investigated by Larson and Kuemmerle (1976). Denson and Burkhouse (1976) alkylated coal with ethylene, propylene and isobutylene using anhydrous HF at 135°C and moderate pressure. Ouchi et al (1973) depolymerized a number of coals using phenol and p-toluenesulfonic acid. Numerous other depolymerization reactions of coal with acid catalysts have been reported (Kroger and deVries, 1962); Hodek and Kolling (1973). Several studies on the

acid catalyzed hydrogasification of coal were carried out by Butler and Snelson (1980) and by Low and Ross (1977).

The Conoco-Shell process for the conversion of coal to a C_5-200°C distillate with stoichiometric amounts of $ZnCl_2$ at 370-425 under H_2 pressure has already been referred to (Alpert and Wolk, 1981). Olah found that coal, when treated with HF-SbF_3 gave an intractable rock-like material in contrast with a patent claim by Amendola (1980) that coal liquefies at about 400°C with superacid systems consisting of Group V halides, chiefly SbF_5 and FSO_3H.

Olah and coworkers (1984), in an extensive screening of superacid systems, found HF:BF_3 (H_o-16) to be an effective catalyst for direct coal liquefaction. Although both HF and BF_3 are readily available and are used commercially, they are highly corrosive, especially at high temperatures, thus requiring that reactors be built from special alloys (Monel metal). The reaction temperatures, only 110 - 180°C, are influenced by the fluoride donating ability of HF systems at lower temperatures to carbocations formed from the products of coal liquefaction (the critical temperature of HF is 188°C).

Any direct coal liquefaction process involves pyrolysis of the organic matter and cleavage of certain bonds (in a way, a depolymerization) followed by addition of hydrogen to the fragments. It is generally assumed that these cleavages involve the formation of free radicals that are either capped by hydrogen atoms or undergo retrogressive reactions. The mechanisms involved in liquefaction in the presence of superacids, however, involve, to a large extent, acid catalyzed reactions.

The authors recognized that pyridine, a highly polar solvent, yields extracts that appear to contain very fine particles. Although the extractability in pyridine does show that the coal has depolymerized to some

extent, it is not a good solvent for evaluation of coal liquefaction effectiveness. They therefore turned to a nonpolar solvent, cyclohexane, which yielded clear solutions. After remaining essentially constant at a coal liquefaction temperature of about 90°C, the cyclohexane extractability rose rapidly as the temperature was increased. At 130°, 22% was extracted by cyclohexane, suggesting that reduction and cleavage of the coal to more aliphatic-type products takes place at higher temperatures.

Importantly, the role of isopentane, $CH_3CH_2CH(CH_3)CH_3$, as a hydrogen donor solvent, stands out. Cyclohexane extractability is better in isopentane than with H_2 at comparable temperatures. The rate of primary degradation of coal to pyridine solubles is much more rapid than cleavage and reduction to secondary degradation which leads to cyclohexane solubility (see Table III-2). The distillation results support the interpretation that coal is depolymerized and hydrogenated by the superacid reducing system.

The products, prior to distillation, contained 4-10% of fluorine. Adsorbed or carbon-bound fluorine is released as HF during distillation of the liquefaction products. The distillate and cyclohexane extracts have low fluorine contents, 0.2 and 0.6 wt% respectively.

As noted earlier, hydrocarbons, in the presence of superacids, yield carbenium ions plus H_2. It would be of great interest to use superacids as catalysts in coprocessing of coal in heavy oils (hydrogenation of coal in heavy oils which contain aliphatic and naphthenic structures). In the presence of superacids, these may furnish H_2 for donation to coal.

Table III-2

Liquefaction of Illinois No. 6 Coal with $HF:BF_3:H_2$[a] (Olah, 1984)

Coal (g)	Temp. (°C)	HF (ml)	Isopentane (ml)	Yield (%)	Extractability With Pyridine (%)	Extractability With Cyclohexane (%)	Distillation[b] Yield (%)
5[c]	60	50	25	86	71	7	-
5[c]	75	50	25	86	88	7	16
1	70	5	-	-	56	-	-
5[c]	90	50	25	68	90	8	24
5[c]	105	50	25	84	92	6	28
5[c]	105	50	25	81	95	16	25
1	112	5	-	96	79	5	-
5	130	25	-	90	87	18	-
5	130	25	25	82	95	22	-
1	153	5	-	96	97	14	26

a. BF_3 pressure 900-980 psig at 25°C; H_2 pressure at 500-600 psig at 25°C.

b. Distillation at 300-400°C and 5×10^{-3} Torr.

c. Reaction carried out for 2 hrs; all others for 4 hrs.

In a second paper by Olah and Husain (1984), a number of model compounds supposedly representing structural entities in coal were treated with $HF:BF_3:H_2$ under mild coal liquefaction conditions. Diphenylmethane and bibenzyl gave almost quantitative conversion at ambient temperatures in the absence of H_2. Diphenyl gave only a 30% conversion at 150°C with H_2 pressure. Benzyl phenyl ether and dibenzyl ether were quantitatively converted at room temperature without added H_2; products included benzene, toluene, p-xylene, anthracene and 2-methylanthracene. In contrast, about 5 MPa hydrogen pressure at 155°C was required to convert diphenyl ether in 70% yield to traces of benzene, phenol (33.6 mol %) and C_1-C_4 gases.

Model compounds containing sulfur and nitrogen were also studied. Dibenzyl sulfide and benzyl phenyl sulfide were easily converted (95%) in the absence of H_2; products included benzene, toluene, p-xylene and anthracene. But both diphenyl sulfide and diphenyl disulfide required about 5 MPa of H_2 pressure at 150°C to attain similar conversions (~ 95%). Quinoline gave a 20% conversion with the $HF:BF_3:H_2$ system at 150°C and 5.5 MPa of H_2 to benzene and C_1-C_4 hydrocarbons. Thiophene-type compounds, probably the principal way in which sulfur exists in bituminous and other coals, were not investigated in this superacid system.

It was concluded that the high pyridine extractability at the low temperatures achieved by liquefying coal in the presence of superacids results from the cleavage of bridges such as are present in dibenzyl ether, diphenylmethane and bibenzyl type structures. The increased cyclohexane extractability obtained at higher tmperatures under H_2 pressure may be due to the hydrogenation and cleavage of the aromatic backbone in the coal structure.

The results obtained by Olah and his coworkers (1984) with the superacid system, $HF:BF_3:H_2$, for the liquefaction of coal is enlightening and

provocative. It leads to the possibility of a coal liquefaction system that is carried out at low temperatures, perhaps below 150°C, and low H_2 pressure (< 10 MPa). But any superacid system containing HF or fluorinated components would very likely only be feasible on a small laboratory scale with special materials of construction and fairly elaborate safety precautions, even though HF is used industrially on a rather large scale.

As shown by cryoscopic, conductometric and other acidity measurements, it appears that antimony pentafluoride (SbF_5) is by far the strongest Lewis acid known (Olah, 1985). SbF_5 is a colorless, very viscous liquid (mp 7.0°C) at room temperature. It is hygroscopic, fuming in moist air. When pure, the liquid can be handled and distilled in glass in the absence of moisture; it is shipped in steel cylinders or perfluoroethylene bottles. It is a powerful oxidizing agent and a fairly good fluorinating agent forming adducts with almost all nonbonded electron pair donors. It is a very widely used Lewis halide in the study of ionic intermediates. Another superacid, termed "Magic acid," a mixture of fluorsulfonic acid (HSO_3F) and SbF_5 is also widely used as a superacid in many reactions.

Solid Strong Acids and Superacids

A more promising highly acidic class of catalysts for the liquefaction of coal is the solid strong acids and superacids. Solid acids such as mixed oxides have been used extensively as catalysts in the petroleum industry. Although they generally are somewhat weaker strong acids than the liquid superacids, they have several advantages over these liquid acids:

- little or no corrosion, since they contain no halogen atom;
- little or no environmental problem when used as catalysts;

- ease of separation from the reaction mixture allowing continuous operation;
- possibility for regeneration and reuse;
- higher selectivity in certain reactions.

Tanabe (1984) has reviewed the chemistry and use of some of these acids. Among these acids, the most unusual of the solid superacid catalysts seem to be Fe_2O_3, ZrO_2 and TiO_2 activated with sulfate ions.

The Fe_2O_3-SO_4^{2-}, ZrO_2-SO_4^{2-} and TiO_2-SO_4^{2-} catalysts show several hundreds or thousands times activity as compared with the simple oxides without sulfate ions. Pronounced enhanced acidity effects have also been found for SnO_2 and SnO_2-ZrO_2. These catalysts show high activities for the reactions known to be catalyzed by acids, i.e., isomerization, dehydration, esterification, acylation and even the liquefaction of coal (Tanabe and coworkers, 1982).

TiO_2 has moderate acid strength (H_o = +1.5) and weak basic strength (Tanabe et al., 1982). ZrO_2 acts as both a very weak acid and very weak base (Nakano and coworkers, 1979); while Fe_2O_3 is an almost neutral oxide (Kayo et al., 1983). However, these oxides begin to act as superacids when they contain a small amount (0.5 - 2 wt%) of SO_4^{2-} or if a small amount of $(NH_4)_2SO_4$ or H_2SO_4 is added. The acid strength of ZrO_2-SO_4^{2-} (H_o = -16) (Hino et al., 1979) is about 20 times stronger on the H_o scale than is ZrO_2. ZrO_2-SO_4^{2-} may therefore be classified as a solid superacid since its acid strength is higher than that of 100% H_2SO_4 (H_o = -11.9).

What is the origin of this effect? The increase in acidity caused by SO_4^{2-} may be due to the formation of a complex shown in Figure III-1; the SO_4^{2-} is not removed and does not decompose when the catalysts are calcined at 500°C for three hours. In the infrared, the double bond character (1380 cm^{-1})

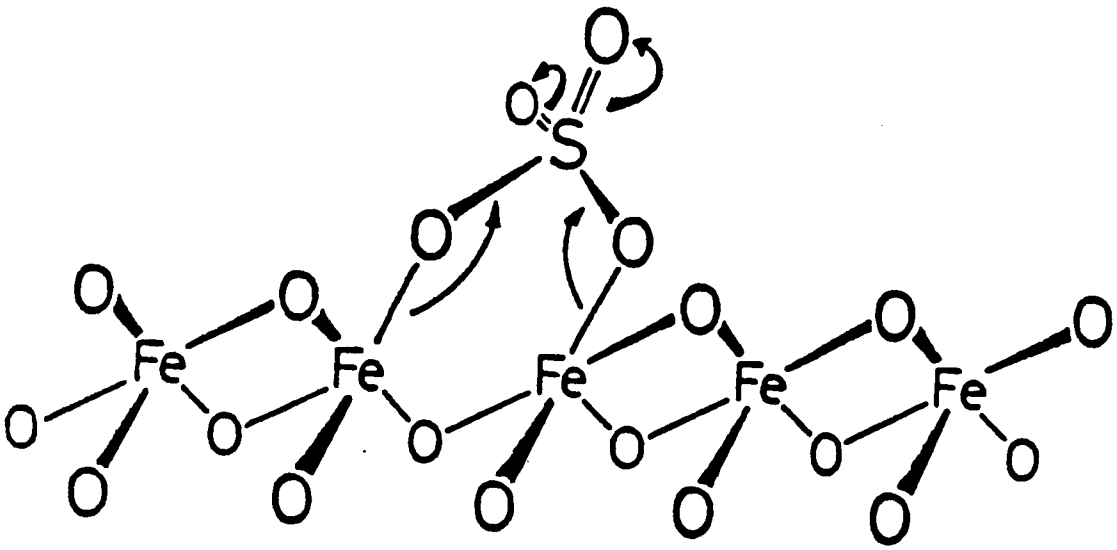


Figure III-1: Model of Super Acidity Generation on Fe_2O_3-SO_4^{2-}
↷ shows electron shift.

of the postulated complex is much stronger than that of a simple iron sulfate (1100 - 1235 cm^{-1}) which is only moderately acidic. The remarkable increase in the Lewis acid strength of Fe^{3+}, Zr^{4+} and Ti^{4+} may be due to the inductive effect of S = O in the complex shown in Figure III-1. In the presence of water, these Lewis acid sites become Bronsted acid sites.

The addition of SO_3 to these metal cations is the same as that achieved by adding SO_4^{2-}. The acidity seems to be dependent on the oxidation state of the sulfur on interaction with metal oxides. Importantly, it has been reported that Fe_2O_3 activated with either SO_4^{2-} or SO_3 loses its acidic property when reduced with H_2 but this needs further investigation. We shall examine the effect of Fe_2O_3-SO_4^{2-} on coal reactions involving the presence of H_2.

The coal liquefaction results obtained by Tanabe et al (1986) are shown in Table III-3.

Tanabe et al. (1982) determined the effect of SO_4^{2-} on the catalytic activity of Fe_2O_3 for the hydrocracking (liquefaction) of a bituminous coal (C, 83.0; H, 6.1; N, 2.0; O, 8.4; S, 0.5 wt% (daf) at 400°C, 1.01×10^4kPa for one hour. The benzene-soluble material, essentially the percentage of total conversion to liquid products, increased upon addition of Fe_2O_3 as a catalyst. Addition of SO_4^{2-} to the Fe_2O_3 catalyst increased the conversion from 51.2 to 69.4%. The asphaltenes (hexane-insoluble) and oil (hexane-soluble) products were also increased by the addition of the sulfate ion. Both Fe_2O_3 and Fe_2O_3-SO_4^{2-} yielded about 2 wt% of gases while the $FeSO_4$-SO_4^{2-} catalyst gave larger amounts of resins and stronger polar compounds. These results were attributed to the increase of surface acidity by addition of SO_4^{2-} (Tanabe et al., 1981).

Table III-3

Catalytic Liquefaction of Akabira Bituminous Coal at 400°C with Several Metal Oxides and 100 kg/cm^2 H_2 Pressure for One Hour.[a] (Tanabe, 1986)

Catalyst	Conversion, %[b]
None	23.6
MoO_3-CoO-Al_2O_3	79.6
Fe_2O_3-SO_4^{2-}	75.0
MoO_3-TiO_2	71.7
MoO_3-Fe_2O_3-SnO_2 (1:1:8)	68.4
SnO_2	64.0
iron ore	63.4
red mud + S	61.8
Fe_2O_3-SiO_2 (9:1)	61.2
MoO_3-Fe_2O_3-SnO_2 (0.1:0.1:9.8)	60.4
Fe_2O_3	60.2
MoO_3-SiO_2	54.8
Fe_2O_3-Al_2O_3 (9:1)	48.9
Fe_2O_3-ZnO (1:1)	43.5
MoO_3-SnO_2 (1:1)	40.7
Fe_2O_3-ZrO_2 (1:1)	35.1
Fe_2O_3-TiO_2-Al_2O_3	32.5
Fe_2O_3-MgO (9:1)	31.0
Fe_2O_3-SiO_2 (1:9)	26.2
Fe_2O_3-MgO (1:1)	23.3
Fe_2O_3-TiO_2 (1:1)	22.1

[a] 5 g. of coal, 0.5 g of catalyst
[b] (1-benzene insoluble part) x 100.

In later work (Hattori et al., 1984) investigated the activities and selectivities of ten complex metal oxides for hydrocracking the same bituminous coal at 400°C and 200 kg/cm^2 of H_2 pressure. The highest percentage conversions were obtained with the following catalysts: $FeSO_4$-SO_4^{2-} (75.0%), MoO_3-TiO_2 (71.7%), and MoO_3-Fe_2O_3-SnO_2 (68.4%). For highest selectivities for formation of oil, the ranking of these catalysts was MoO_3-Fe_2O_3-SnO_2 (33%), Fe_2O_3-SO_4^{2-} (31.0%) and MoO_3-TiO_2 (28.6%).

The conversion and product distribution from liquefaction of the Akabira bituminous coal are shown in Table III-3. Again, the addition of SO_4^{2-} resulted in an increase in activity of the Fe_2O_3 catalyst (from 60.2 to 75.0% in this case). The surface area (13 m^2/g) of Fe_2O_3 was increased to 53.5 m^2/g by addition of 2 wt% of sulfate ion; the commercially available MoO_3-CoO-Al_2O_3 catalyst, however, has a much higher surface area (230 - 250 m^2/g). The average particle size of Fe_2O_3-SO_4^{2-} was 5 μm, a value smaller than that of the MoO_3-CoO-Al_2O_3 catalyst (10 - 20 μm). The crystalline form of Fe_2O_3 was α-Fe_2O_3; Fe_2O_3-SO_4^{2-} was amorphous by x-ray diffraction. The Fe_2O_3-SO_4^{2-} may be calcined in air at 500°C.

Tanabe et al. (1986) have recently reviewed the function of metal oxide catalysts for the liquefaction of bituminous coal and of lignite. Although hydrogenation, dehydrogenation or acid strengths of catalysts seem to play important roles in the hydroliquefaction (and hydrocracking) of any particular coal under chosen reaction conditions, no definite conclusions concerning chemical properties of catalysts for these roles can be drawn. But it does appear reasonable that an efficient coal liquefaction catalyst must have at least two fundamental chemical properties: hydrogenation ability and cracking ability (acidic property). The acidic property is likely effective in the cracking of the coal polymer to smaller units, probably via cation

intermediates. Almost all catalysts (except molten metals) have some acidic properties. Since the coal fragments must be stabilized to avoid retrogressive reactions, hydrogenation ability is an extremely important function of the catalysts. The experiments of Tanabe et al. (1986) led to the reasonable conclusion that the importance of the two chemical properties change with the particular kind of coal and with reaction conditions.

There is an important balance between the hydrogenation ability and cracking ability and this optimum balance depends on the reaction conditions and kind of coal. The best catalysts, MoO_3-Fe_2O_3-SnO_2 and MoO_3-TiO_2 for subbituminous coal (Yamaguchi and coworkers, 1981) and the newer Fe_2O_3-SO_4^{2-} were also good catalysts for bituminous (Akabira) coal in terms of conversion and selctivity to oil product. For Big Brown lignite at 450°C, $FeSO_4$-SO_4^{2-} and MoO_3-Fe_2O_3-SnO_2 were very active, with MoO_3-TiO_2 most selective for oil production.

Activity appears to depend chiefly on the cracking ability (acidity) of the catalyst while selectivity is mainly controlled by the hydrogenation ability of the catalyst.

The reactivity of several model compounds, diphenyl ether, diphenylmethane and benzyl phenyl ether were compared with that for the hydrogenation of naphthalene using Fe_2O_3, Fe_2O_3-SO_4^{2-}, Fe_2O_3-ZnO (1:1), Fe_2O_3-Al_2O_3(1:1), Fe_2O_3-ZnO_2(1:1), SiO_2-Al_2O_3, MoO_3-CoO-Al_2O_3 and MoO_3-NiO-Al_2O_3 and other oxide catalysts. The study was aimed at correlating acidic hydrocracking ability with hydrogenation ability. It was determined that the carbon-oxygen bond is cleaved more easily than the carbon-carbon bond, results that agree with those obtained by Takemura et al. (1981).

The results of these studies may be summarized as follows:

- Strongly acidic catalysts such as Fe_2O_3-SO_4^{2-}, MoO_3-TiO_2, MoO_3-CoO-Al_2O_3 and MoO_3-Fe_2O_3-SnO_2 were highly active and selective for the liquefaction of a bituminous coal.
- For liquefaction of a lignite, which contains large amounts of oxygen, MoO_3-TiO_2 and MoO_3-CoO-Al_2O_3 had high hydrogenation ability and fairly high selectivity although the activity was low.
- The acidity properties of the catalysts are important in carbon-carbon bond cleavage; the hydrogenation ability of the catalyst is important for carbon-oxygen bond cleavage.
- Higher hydrogenation ability is needed for a catalyst selective for the liquefaction of lignite but stronger cracking ability is needed with a catalyst that is active and selective for the liquefaction of a bituminous coal.
- The balance between cracking ability (acidic property) and hydrogenation activity appears to be most important for design of optimum catalysts for various kinds of coal.

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