SECTION II

COAL LIQUEFACTION USING TRANSITION METAL CARBONYL CATALYSTS

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Summary

Metal carbonyl complexes have been used as catalysts or catalyst precursors for the liquefaction of coal. There are two ways in which these complexes have been employed.

As catalytic agents, transition metal carbonyl complexes are usually effective at temperatures below 250°C, depending on the CO pressure needed to prevent the complex from decomposing to yield the zerovalent metal. In some cases, temperatures above 250°C can be used but the CO pressure then must be very high to prevent decomposition of the complex. This is one method of using these catalysts in hydrogenation of coal constituents or coal-derived liquid products. It is important to note that organic covalent bonds are not split, to any extent, by metal carbonyl complexes at the low temperatures used.

The second major method of using these transition metal complexes is as catalyst precursors. Here, the temperature is above 250°C, often reaching 450°C and the complex decomposes to finely divided, well-dispersed zerovalent metal which, in many cases, proves to be an effective catalyst for coal liquefaction. In this case, at the usual temperature of coal liquefaction, free radicals are formed by the splitting of various covalent bonds and the catalysts aid in the capping of these reactive species with hydrogen.

It is important to be aware of these two very different modes of action of transition metal carbonyl complexes in the catalytic liquefaction of coal.

It is possible to employ both methods of using transition metal complexes, that is, hydrogenate susceptible bonds in coal at low temperatures using the transition metal complex and then use conventional coal liquid catalysts such as cobalt molybdate to complete the liquefaction of coal. In some cases, this works quite well.

Introduction

Coal may be considered as consisting of polynuclear aromatic and hydroaromatic clusters joined together or cross-linked by various types of linkages such as aliphatic bridges or ether, carbonyl, sulfide, and biphenyl-type bridges. Heteroatom constituents, sulfur, nitrogen, and oxygen may occupy ring positions or exist in side chains and bridges. Direct liquefaction of coal under a high pressure of hydrogen at elevated temperatures induces the thermal degradation of coal into fragment radicals (Petrakis and Grandy, 1981; Petrakis et al., 1983). The free radicals are reactive and can repolymerize very rapidly. However, the free radicals can be stabilized by donor hydrogen (from solvent, catalyst, or coal) and by other small coal-derived fragments (e.g., CH_3) to yield liquid fuels (or gases). This stage of free radical stabilization requires suitable catalytic circumstances, such as good contact between coal radicals and catalysts or good hydrogen donors.

A large number of catalysts for coal liquefaction have been investigated with the aim of improving coal conversion to light oils. The physical distribution of catalyst has been found to be important for high catalytic activity (Guin et al., 1978; Grag and Givens, 1984). Mineral matter in coal (e.g., pyrite) acts catalytically in coal liquefaction, but the catalytic activity of pyrite was found to depend on particle size and the method of pyrite addition. Weller and Pelipetz (1951) studied the effects of the addition of catalysts on coal conversion and reported that only impregnated iron sulfate showed high catalytic activity. Similarly, Mitra et al. (1984) compared iron oxide catalysts for hydrogenation of coal and concluded that the efficiency of the deposited form of catalyst was superior to the mixed type.

Over the last decade homogeneous catalysis has been explored to achieve better contact between catalysts, coal, hydrogen, and solvent. Several researchers (Suzuki et al, 1982; Yamada et al., 1985; Cox et al., 1976; McCabe and Orchin, 1976; Holy et al., 1977) have reported the use of transition metal carbonyls for the preparation of dispersed metallic catalysts during coal liquefaction. Since a good dispersion state of the catalyst can be achieved with the use of a transition metal carbonyl as a catalyst precursor, the soluble transition metal complex can penetrate into the pores of the coal; this may facilitate strong interaction between the coal and the catalyst and improves the dissolution of coal.

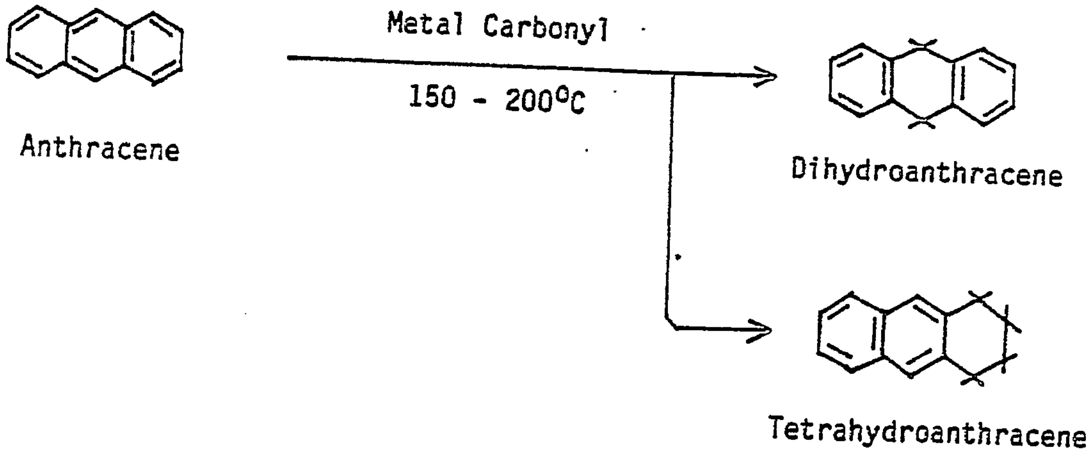
This study will present an overview of the advantages, limitations, and significance of homogeneous catalysts such as iron carbonyls and other transition metal complexes for coal liquefaction, furnishing a perspective as to where innovations in this type of coal liquefaction catalysis are likely to occur. Several transition metal complexes will be evaluated for their effectiveness in the hydroliquefaction of coal under mild conditions. Emphasis will be placed on the use of various iron carbonyl complexes, e.g., $Fe(CO)_5$, for obtaining good coal conversion and distillate yields. The subject of transition metal catalysts for coal liquefaction covers a large amount of published material as well as ongoing research. Attention is also given to homogeneous catalytic hydrogenation of coal model compounds that could lead to a better understanding of the reaction mechanisms affecting the selectivity of the homogeneous catalyst in coal liquefaction. This kind of information is extremely useful, as it could be applied to advantage in the design of more selective catalysts for new, more efficient processes in the development of direct coal liquefaction.

Hydrogenation of Model Coal Constituents Using Transition Metal Carbonyl Catalysts

Hydrogenation of Polynuclear Aromatic Hydrocarbons

Considerable efforts have been made in the past to investigate hydrogenation of model coal constituents using metal carbonyls as catalysts. Literature references on metal carbonyl-catalyzed hydrogenation of polynuclear aromatic compounds have been reported by Wender and coworkers using cobalt carbonyl in the presence of carbon monoxide and hydrogen (Wender et al., 1950; Friedman et al., 1959). Project SEACOKE (conducted by the Atlantic-Richfield Chemical Company, 1966) has demonstrated the homogeneous catalytic hydrogenation of coal model compounds as well as coal-derived products using metal carbonyls as catalysts. Lynch et al. (1982; 1984) hydrogenated model compounds by using iron pentacarbonyl and Fish et al. (1982) investigated a number of polynuclear aromatic compounds under various homogeneous catalytic hydrogenation conditions with transition metal carbonyl hydrides.

Anthracene, representing an important constituent in coal, can be hydrogenated at comparatively low temperatures to give 9, 10-dihydroanthracene and 1, 2, 3, 4-tetrahydroanthracene, depending on the types of metal carbonyl catalysts used and the hydrogenation conditions employed. Generally, hydrogenation of anthracene proceeds in good yields to dihydroanthracene (which contains isolated benzenoid rings) as the major product. A more active metal carbonyl could convert anthracene to tetrahydroanthracene.



(1)

Typical results using various transition metal carbonyl catalysts for hydrogenation of anthracene are summarized in Table II-1. Very high conversions to dihydroanthracene were observed at temperatures below 200°C under synthesis gas ($1H_2$: 1CO) conditions. Cobalt, iron, chromium, tungsten, and molybdenum carbonyls all showed high catalytic activity for anthracene hydrogenation in the presence of carbon monoxide and hydrogen. In contrast, much lower conversions were obtained under water-gas shift (CO, H_2O, base) conditions where hydrogen needed for reactions comes exclusively from water (Fish et al., 1982). The instant availability of hydrogen with synthesis gas enhances the hydrogenation of anthracene compared to that under water-gas shift conditions.

The conversion of anthracene to tetrahydroanthracene is below 8% (as shown in Table II-1), except when $Ru(Cl)_2(CO)_2(Ph_3P)_2$ was used as a catalyst. Interestingly, Fish et al. (1982) found that, with this catalyst in the presence of hydrogen and a base (e.g., KOH), the reduction of anthracene

Table II-1

Hydrogenation of Anthracene Using Transition Metal Carbonyls as Catalysts

Catalyst	Temp. °C	Conditions	Pressure, psi	Products (wt%)		Reference
				Dihydroanthracene	Tetrahydroanthracene	
$Co_2(CO)_8$	135	H_2/CO	2900	99	–	b
$CoCO_3$[a]	185	H_2/CO	2800	93	7	c
$Fe(CO)_5$	185	H_2/CO	2800	90	3	c
$Cr(CO)_6$	185	H_2/CO	2800	89	4	c
$W(CO)_6$	185	H_2/CO	2800	85	5	c
$Mo(CO)_6$	185	H_2/CO	2800	81	–	c
$Fe(CO)_5$	150	$CO/H_2O/KOH$	500	25	–	d
$Fe(CO)_5$	300	$CO/H_2O/KOH$	400	32	–	d
$Ru(Cl)_2(CO)_2(Ph_3P)_2$	180	H_2/KOH	350	–	30	e

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a. Basic cobaltous carbonate used.
b. Friedman et al., 1959.
c. ARCO - SEACOKE, 1966.
d. Lynch et al., 1982.
e. Fish et al., 1982.

was quite selective and gave 1, 2, 3, 4-tetrahydroanthracene in 30% yield without the formation of 9, 10-dihydroanthracene as the intermediate or final product.

Lynch et al. (1982, 1984) have compared several iron carbonyl complexes as catalysts for the hydrogenation of anthracene to dihydroanthracene under water-gas shift conditions. The results are presented in Table II-2. All the iron complexes exhibited some activity but none were as effective as $Fe(CO)_5$. The capability of providing a reduction potential sufficient for electron transfer to a reactive substrate, followed by protonation, has been suggested as the main reaction pathway (Lynch et al., 1984; Murr and Chaloyard, 1982; Bond et al., 1977).

In Table II-3, a number of polynuclear aromatic hydrocarbons are compared under synthesis gas (H_2:CO 1:1) conditions using $Co_2(CO)_8$ as the catalyst. The data showed that anthracene can be hydrogenated readily to dihydroanthracene, but phenanthrene is hardly reduced. Similarly, naphthacene is largely hydrogenated to dihydronaphthacene compared to the hydrogenation of chrysene or triphenylene, indicating linear aromatic compounds are much more reactive than non-linear aromatics such as phenanthrene. Importantly, the metal carbonyls have little or no activity for the reduction of isolated aromatic rings (e. g., fluorene).Polynuclear aromatic hydrocarbons tend to hydrogenate to form products with isolated benzene rings: Carbonization of coal produces a large number of polynuclear condensed aromatic hydrocarbons in the coal tar products.

The phenanthrene-like structure is more resistant to hydrogenation than other substrates at the lower temperatures and pressures. However, in the SEACOKE project (ARCO, 1966), over 90% of phenanthrene conversion was obtained using cobalt carbonyl at temperatures above 200°C and pressures over 6000 psi of CO/H_2. Because of the high resistance to hydrogenation, phenanthrene was

Table II-2

Comparison of Iron Complexes as Catalysts for Hydrogenation of Anthracene[a] (Lynch et al., 1984)

Promoter Iron Catalyst	Additive	Turnover[b]
$Fe(CO)_5$	Bipyridyl	17.1
$Fe_2(CO)_9$	Bipyridyl	8.8
$Fe_3(CO)_{12}$	Bipyridyl	3.4
$Fe(CO)_5$	-	14.2
$Fe(C_8H_8)(CO)_3$	Bipyridyl	0.7
$Fe(C_8H_8)(CO)_3$	-	7.1
$Fe(terpy)(CO)_2$	Bipyridyl	0.8

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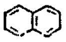
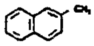
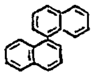
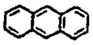
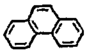
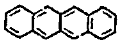
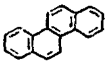
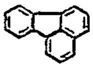
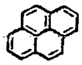
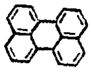
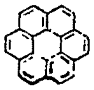
a. Experimental conditions: 300°C, CO 400 psi, H_2O 167 mmol, iron complex 0.76 mmol, and KOH 42 mmol.

b. Molar equivalent of anthracene hydrogenated to 9, 10-dihydroanthracene.

Table III-3

Hydrogenation of Polynuclear Aromatic Hydrocarbons Using Dicobalt Octacarbonyl (Friedman et al., 1959;)

Compound	Structure	Substrate / Catalyst (g/g)	Temp. (°C)	(CO/H_2) Pressure (psi)	Yield of Hydrogenated Products (wt%)
Naphthalene		26.7	200	3100	16
2-Methylnaphthalene		25.8	200	3500	43
1,1-Dinaphthyl		0.7	200	3500	ND[b]
Acenaphthene		4.4	200	3500	45
		8.7[a]	185	2800	82
Fluorene		4.1	200	3600	ND[b]
Anthracene		95.8	135	2900	99
		7.5[a]	185	2800	93
Phenanthrene		4.6	200	3500	8
		7.5[a]	185	2800	31
Naphthacene		20.5	140	3000	70
Chrysene		0.4	150	3500	ND[b]
		0.7	200	3000	24
Fluoranthene		1.2	200	3200	54
Triphenylene		0.2	200	3200	ND[b]
Pyrene		0.9	150	3600	ND[b]
Perylene		1.1	200	3000	69
		0.3	150	3000	72
Coronene		0.2	200	2800	ND[b]

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a. Reference from ARCO SEACOKE Project (1966).
b. Not detectable.

also chosen as a model compound to compare the catalytic activity of cobalt carbonyl with that of a cobalt molybdate catalyst. The results as shown in Table II-4 indicate that dicobalt octacarbonyl possesses a high degree of hydrogenation activity at low temperatures; however, much higher temperatures (and pressures) are required for cobalt molybdate to reach high conversions of phenanthrene. Cobalt carbonyl is active at a lower temperature than is cobalt molybdate for the hydrogenation of condensed aromatic hydrocarbons. In addition, cobalt carbonyl is also more selective with respect to partial hydrogenation (to dihydro derivatives) than is cobalt molybdate. The cobalt molybdate gives greater quantities of fully hydrogenated products, while the cobalt carbonyl would be expected to give a product which would permit subsequent hydrogenation and catalytic cracking to yield a high content of alkylbenzenes, suitable for the production of high octane gasoline.

Hydrogenation of Polynuclear Oxygenated Compounds

Dicobalt octacarbonyl is also quite active in the hydrogenation of naphthols to either tetrahydronaphthols or tetrahydronaphthalenes, but it fails to interact with diphenyl ether or polynuclear oxygenated aromatics such as dibenzofuran (SEACOKE Project, ARCO, 1966). A summary of the hydrogenation of heterocyclic oxygen compounds is listed in Table II-5. For naphthols, cobalt carbonyl is more active than molydenum carbonyl or cobalt metal on carbon. In general, a metal carbonyl is not an active catalyst for the hydrogenation of polynuclear oxygenated aromatic compounds.

Hydrogenation of Polynuclear Sulfur-Containing Compounds

The reactivities of iron carbonyls for the desulfurization of organic sulfur compounds have been investigated (Alper and Paik, 1977; Porter et al., 1981; Kaesz et al., 1960). As discussed in the reaction scheme below, thiophene, which represents a model for an unreactive organosulfur functional groups found in coal, can react with iron carbonyls to give iron-metalated complexes (Kaesz et al., 1960; King, 1963; Nametkin et al., 1978),

Table II-4
Hydrogenation of Phenanthrene
(ARCO SEACOKE Project, 1966)[a]

Catalyst	Temp. (°C)	CO/H_2 or H_2 Pressure (psi)	Product Distribution				Conversion(wt%)
			Dihydro-	Tetrahydro-	Octahydro-	Perhydro-	
$Co_2(CO)_8$	185	4200, H_2/CO	34.1	6.9	5.2	2.7	48.4
$Co_2(CO)_8$	232	4200, H_2/CO	37.8	5.6	5.3	4.4	52.6
$Co_2(CO)_8$	371	4250, H_2/CO	29.9	9.2	5.5	6.3	50.4
$Co_2(CO)_8$	185	6500, H_2/CO	49.1	7.4	10.6	6.1	72.8
$Co_2(CO)_8$	232	6000, H_2/CO	68.8	2.1	7.2	13.7	94.0
Co-Mo	232	4200-5000, H_2	7.9	4.9	1.0	-	15.3
Co-Mo	260	4200-5000, H_2	45.7	11.3	6.9	4.6	70.8
Co-Mo	288	4200-5000, H_2	53.7	9.1	14.0	9.2	88.7
Co-Mo	316	4200-5000, H_2	41.8	2.4	24.0	24.6	96.5
Co-Mo	371	4200-5000, H_2	3.2	0.6	37.0	53.7	99.8

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[a] Experiments using dicobalt octacarbonyl were under CO/H_2 (1:1); experiments using cobalt molybdate were under H_2 pressure

Table II-5

Hydrogenation of Polynuclear Oxygenated Aromatics[a]
(ARCO SEACOKE Project, 1966)

Compounds	Catalyst	Recovered Starting Compound	Hydrogenated Products (wt %)
1-Naphthol	$Co_2(CO)_8$	4.9	95.1
	$CoCO_3$[b]	9.0	91.0
2-Naphthol	$Co_2(CO)_8$	-	100.0
	Co on Carbon	74.7	25.3
	$Mo(CO)_6$	62.0	38.0
Diphenyl Ether	$CoCO_3$[b]	>99.9	-
Dibenzofuran	$CoCO_3$[b]	97.3	2.7

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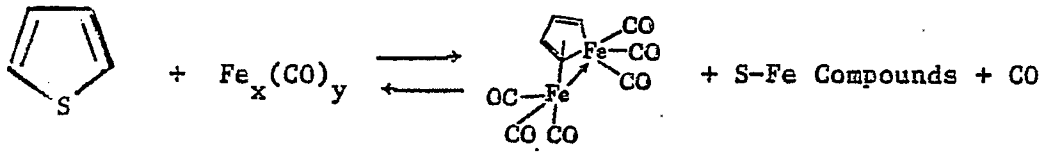
a. Conditions: initial pressure, 2800 psi of $1H_2 + 1CO$, 185°C, 16 hr; toluene used as solvent.

b. Basic cobaltous carbonate is converted to $Co_2(CO)_8$ under reaction conditions.



(2)

where x = 1, y = 5 is iron pentacarbonyl ($Fe(CO)_5$); x = 2, y = 9 is diiron enneacarbonyl ($Fe_2(CO)_9$); x = 3, y = 12 for triiron dodecacarbonyl ($Fe_3(CO)_{12}$). Sulfur usually forms pyrrhotite-like ($Fe_{1-x}S$) structures, or reacts with iron carbonyls to give as products dithiodiironhexacarbonyl ($S_2Fe_2(CO)_6$) and dithiotriironnonacarbonyl ($S_2Fe_3(CO)_9$).

Nametkin et al. (1978) have conducted a series of experiments to study the reactivity of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ with sulfur, hydrogen sulfide, and various organosulfur compounds. It was found that elementary sulfur reacts with iron carbonyls in benzene solution at 80°C in one to two hours, to give predominantly FeS. When passing H_2S in benzene solutions over $Fe_3(CO)_{12}$ at 50-55°C, $S_2Fe_2(CO)_6$ is obtained as the primary product. Relative reactivities were investigated for a series of alkyl and aryl organosulfide compounds with the iron carbonyls; it was found that $Fe_3(CO)_{12}$ is the most active while $Fe(CO)_5$ is the least reactive yielding bis(alkyl- and arylthioirontricarbonyls), $(RSFe(CO)_3)_2$ (Table II-6). This is the reverse of the results observed by Lynch et al. (1984) (Table II-2) where $Fe(CO)_5$ was found most active in the hydrogenation of anthracene to dihydroanthracene under water-gas shift conditions at 300°C. Although the nature of the reducing species and mechanisms involved in the iron carbonyl reactions is not well understood, it has been suggested that the activity of iron carbonyls at low temperatures depends on the rate of formation of the intermediate compound ($Fe(CO)_4^{2-}$). However under severe conditions (e.g., high temperature, high pressure) the formation of either carbonyl hydrides

Table II-6
Reactions of Some Organosulfur Compounds with Iron Carbonyls
(Nametkin et al., 1978)

	$Fe(CO)_5$		$Fe_2(CO)_9$		$Fe_3(CO)_{12}$	
Organosulfur Compound	Time (h)	Yield[a] (%)	Time (h)	Yield[a] (%)	Time (h)	Yield[a] (%)
RSH[b]	22	59-61	11	90-93	1	92
RSSR[c]	34	54-59	19	65-67	5	72
RSR[d]	36	23-25	24	50-54	18	60

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a. Formation of $[RSFe(CO)_3]_2$.

b. R = ethyl, n-butyl, n-hexyl, n-octyl, n-dodecyl, phenyl, benzyl.

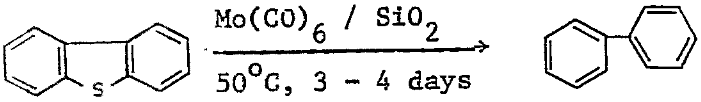
c. R = n-butyl, n-pentyl, n-hexyl, n-dodecyl

d. R = methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-dodecyl, cyclopentyl, phenyl.

(e.g., hydridotetracarbonyl ferrate anion, $HFe(CO)_4^-$) in the water-gas shift conditions or colloidal iron (Fe^0) becomes important.

The promising desulfurization results using iron carbonyl catalysts have not been obtained with other metal carbonyls. Early work carried out in the SEACOKE project (1966) indicated that cobalt carbonyl was unreactive with dibenzothiophene under an initial pressure of 2800 psi of H_2 and CO at 185°C (Table II-7).

Alper and Blais (1980) studied the removal of sulfur from dibenzothiophene with carbonyl complexes. They observed that no desulfurization occurred when dibenzothiophene was exposed to molybdenum hexacarbonyl in tetrahydrofuran, but if the metal carbonyl is first modified by adsorption onto silica, then the resultant molybdenum species is active as a desulfurization agent.



(3)

Dibenzothiophene was desulfurized to biphenyl at 50°C using $Mo(CO)_6$ preadsorbed on silica (see Table II-7). It was also claimed that mercaptans such as 2-naphthalenethiol could be desulfurized in this way to give naphthalene (Alper and Blais, 1980).

Table II-7

Hydrogenation of Dibenzothiophene

Catalyst	[Sub]/[Cat.]	Temp (^{o}C)	Time (hr)	Hydrogenated Product (%)	Reference
$Co_2(CO)_8$[a]	7.3	185	16	4	ARCO (1966)
$Mo(CO)_6/SiO_2$[b]	0.3	50	72 - 96	83	Alper and Blais (1980

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a. Initial pressure, 2800 psi of $1H_2 + 1CO$.

b. $Mo(CO)_6$ on silica in THF for 3 - 4 days at 50°C.

Hydrogenation of Polynuclear Nitrogen-Containing Compounds

Nitrogen heterocycles are found (Lynch et al., 1984; Abasyes and Alper, 1977; Fish et al., 1982) to be most susceptible to hydrogenation by using transition metal carbonyl catalysts under synthesis gas (1CO : $1H_2$) or water-gas shift (CO, H_2O, base) conditions. A comparison of the hydrogenation of acridine using various transition metal carbonyls as catalysts under synthesis gas conditions is shown in Table II-8. Cobalt and manganese carbonyl complexes provide 100% of reduced products; other transition metal carbonyls (e.g., Mo, Cr, W, Rh) hydrogenated the substrate to 85 to 95% of reduced products. Dicobalt octacarbonyl was a very effective catalyst for the hydrogenation of acridine to mainly octahydro-products, especially when the cobalt carbonyl was prepared from basic cobaltous carbonate.

Under hydrogen pressure, but without carbon monoxide added to the system, Fish et al. (1982) found that high yields of hydrogenated products could be obtained from the reduction of heteroaromatic nitrogen compounds with ruthenium carbonyl complexes as catalysts (Table II-9). For example, acridine was reduced to dihydroacridine and quinoline to tetrahydroquinoline in 74 and 100% yields, respectively. They also found that tetrahydridotetraruthenium dodecacarbonyl ($H_4Ru_4(CO)_{12}$) was an excellent catalyst for the reduction of acridine and quinoline, but was relatively inactive for the reductions of benzoquinoline and phenanthridine.

Products and yields from the treatment of several nitrogen heterocyclic compounds with $Fe(CO)_5$ under water-gas shift conditions are listed in Table II-10. Using a feed (substrate) to catalyst ($Fe(CO)_5$) weight ratio of two to one, the nitrogen-containing rings in quinoline and in acridine are completely hydrogenated to 1, 2, 3, 4-tetrahydroquinoline and 9, 10-dihydroacridine, respectively.

Table II-8

Hydrogenation of Acridine With Synthesis Gas ($1CO + 1H_2$)
(ARCO SEACOKE Project, 1966; Fish et al., 1982)

Catalyst	Substrate / Catalyst (wt%)	Temp. (°C)	$CO + H_2$ Pressure (psi)	Time (hr)	Product (Wt %)			Reference
					Dihydro-	Tetrahydro-	Octahydro-	
$Co_2(CO)_8$	7.5	185	2800	16	–	17	80	a
$Mo(CO)_6$	–	185	2800	16	54	–	36	a
$Cr(CO)_6$	–	185	2800	16	61	–	32	a
$W(CO)_6$	–	185	2800	16	65	–	29	a
Rh on Carbon	–	185	2800	16	96	–	–	a
$Mn_2(CO)_6(Bu_3P)_2$	20	200	700	2	100	–	–	b
$Co_2(CO)_6(Ph_3P)_2$	20	200	700	2	100	–	–	b

---

a. ARCO SEACOKE Project (1966).
b. Fish et al. (1982).

Table II-9

Hydrogenation of Polynuclear Nitrogen-Containing Compounds With Hydrogen[a] (Fish et al., 1982)

N-Compound	Catalyst	Temp. (°C)	Product	wt% Product
5, 6-Benzoquinoline	$Ru(Cl)_2(CO)_2(Ph_3P)_2$	180	Tetrahydro-	92
7, 8-Benzoquinoline	$Ru(Cl)_2(CO)_2(Ph_3P)_2$	180	Tetrahydro-	72
9, 10-Phenanthridine	$Ru(Cl)_2(CO)_2(Ph_3P)_2$	180	Dihydro-	15
Acridine	$Ru(Cl)_2(CO)_2(Ph_3P)_2$	180	Dihydro-	74
Quinoline	$Ru(Cl)_2(CO)_2(Ph_3P)_2$	180	Tetrahydro-	100
5, 6-Benzoquinoline	$H_4Ru_4(CO)_{12}$	150	Tetrahydro-	75
7, 8-Benzoquinoline	$H_4Ru_4(CO)_{12}$	150	Tetrahydro-	8
Phenanthridine	$H_4Ru_4(CO)_{12}$	150	Dihydro-	15
Acridine	$H_4Ru_4(CO)_{12}$	150	Dihydro-	100
Quinoline	$H_4Ru_4(CO)_{12}$	150	Tetrahydro-	100

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[a] Experimental conditions: 350°C for 2 hours and [Sub]/[Cat.] = 10.

Table II-10

Hydrogenation of Polynuclear Nitrogen-Containing Compounds Under Water-Gas Shift Conditions (Lynch et al., 1982; Fish et al., 1982)

N-Compound	Catalyst	[Sub]/[Cat.]	Temp. (^oC)	CO Pressure (psi)	Time (hr)	Product	% Product	Reference
Acridine	$Fe(CO)_5$	2	150	600	15	Dihydro-	100	a
	$Fe(CO)_5$	10	180	800	2	Dihydro-	100	b
	$Mn_2(CO)_8(Bu_3P)_2$	10	200	350	2	Dihydro-	38	b
Quinoline	$Fe(CO)_5$	2	150	600	15	Tetrahydro-	100	a
	$Fe(CO)_5$	10	180	350	2	ND[c]	0	b
	$Mn_2(CO)_8(Bu_3P)_2$	20	200	350	5	Tetrahydro-	4	b
Isoquinoline	$Fe(CO)_5$	2	150	600	15	Tetrahydro-	100	a
4, 7-Phenanthroline	$Fe(CO)_5$	2	150	600	15	Tetrahydro-	75	a
1,10-Phenanthroline	$Fe(CO)_5$	2	150	600	15	Tetrahydro-	50	a
5, 6-Benzoquinoline	$Mn_2(CO)_8(Bu_3P)_2$	20	200	350	5	Tetrahydro-	4	b
	$Fe(CO)_4(Bu_3P)$	10	180	350	5	Tetrahydro-	1	b
7, 8-Benzoquinoline	$Mn_2(CO)_8(Bu_3P)_2$	20	200	350	2	ND[c]	0	b
Phenanthridine	$Mn_2(CO)_8(Bu_3P)_2$	20	200	350	2	Dihydro-	1	b

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a. Lynch et al. (1982).
b. Fish et al. (1982).
c. Not detectable.

isoquinoline is both hydrogenated and N-formylated to 1,2,3,4-tetrahydro-2-quinoline carboxaldehyde, also in 100% yield. In the phenanthrolines (4, 7 or 1, 10), hydrogenation of only one of the two nitrogen-containing rings is observed. The yields of tetrahydrophenanthrolines varied from about 50 to 75%.

It is important to note cases in which only the nitrogen ring is hydrogenated using $Fe(CO)_5$ as catalyst under water-gas shift conditions. This is probably due to the lower reduction potential of the nitrogen-containing ring for hydrogenation compared to the carbon analogs. The regioselectively reduced nitrogen-containing ring is important in the view of removing nitrogen from polynuclear heterocyclic nitrogen compounds existing in synthetic fuel processing. Several studies have identified hydridoiron tetracarbonyl anion ($HFe(CO)_4^-$) as the reactive species in basic solution,

$$Fe(CO)_5 + OH^- \rightleftharpoons HFe(CO)_4^- + CO_2 \qquad (4)$$

The catalytic cycle proposed for the iron-base carbonyl system is shown in Figure II-1. There are numerous paths by which a metal hybride can cause hydrogenation (Alper, 1975; Lynch et al. 1984; Wada and Matsuda, 1973). Here, the participation of the anionic hydride reagent involves an unpaired electron transfer from $HFe(CO)_4^-$. Carbon monoxide is needed to regenerate $Fe(CO)_5$ and produce atomic hydrogen. The participation of aromatic hydrocarbons or polynuclear heteroaromatic compounds in such electron-transfer paths and their conversion to hydrogenated products has been extensively discussed elsewhere (Lynch et al., 1984; Alper and Paik, 1977).

It was also suggested (Lynch et al, 1984) that the observed hydrogenation of only one ring of polynuclear aromatic compounds indicates that an electron-

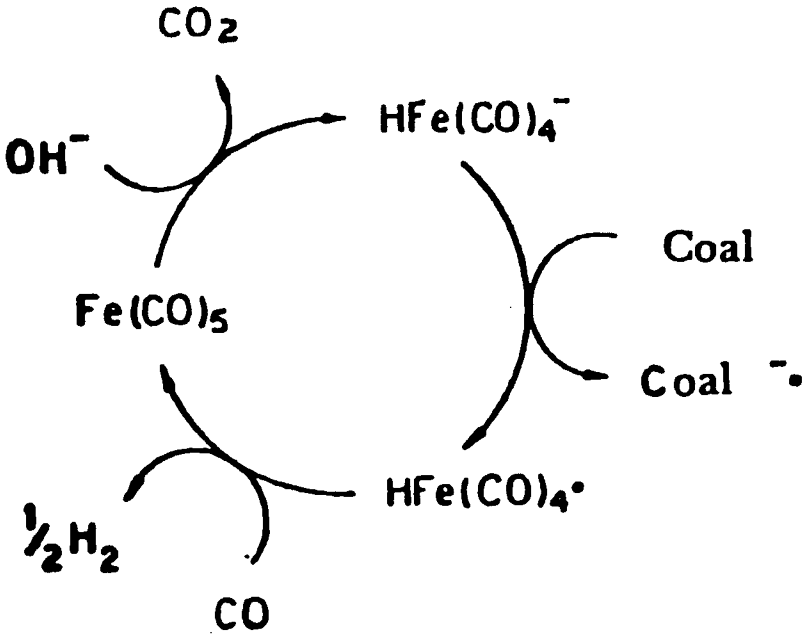

Figure II-1: Catalytic Cycle Proposed for the Iron-Base Carbonyl System. (Modified from Lynch, et al., 1984) transfer (followed by protonation) mechanism is likely involved in the reaction pathway. A correlation between reduction potentials (Meiter and Zuman, 1977) of polynuclear hydrocarbons and heteroatomic aromatics with their ability or resistance to undergo hydrogenation can be plotted as in Figure II-2. Polynuclear hydrocarbons such as anthracene and naphthacene that are relatively easy to hydrogenate have low reduction potentials, -1.93 V and -2.08 V, respectively, compared to unreactive compounds such as dinaphthyl, fluorene, phenanthrene, chrysene, triphenylene, and coronene, all of which have reduction potentials more negative than -2.25 V. Similarly, substrates such as the heteroaromatics that are easy to hydrogenate, have lower reduction potentials: acridine, -1.68; quinoline, -2.08; isoquinoline, -2.15; and phenanthroline, -2.17V. Unreactive heteroatomic aromatics such as pyridine, dibenzothiophene, and diphenyl ether have high negative reduction potentials.

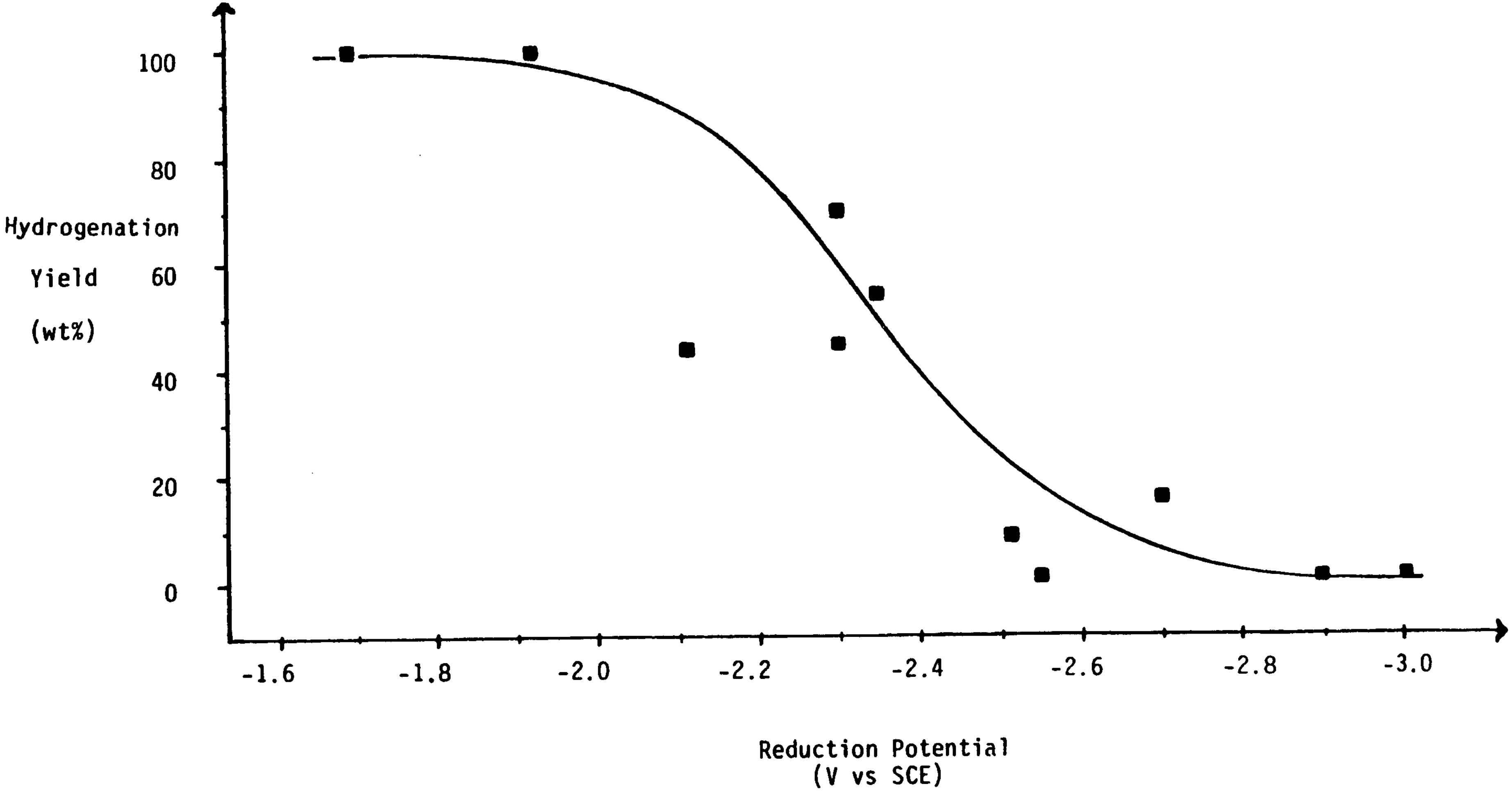

Figure II-2: Correlation Between Reduction Potentials of Polynuclear Aromatic Compounds and Hydrogenation Yields Using $Co_2(CO)_8$ under CO/H_2 (1:1).

Hydrogenation of Coal-Derived Products Using Transition Metal Carbonyl Complexes as Catalysts

Cobalt carbonyl systems have been applied to a variety of charge stocks in the SEACOKE project (ARCO, 1966) which investigated homogeneous catalytic hydrogenation of coal-derived products. Several feedstocks containing coal-derived products were employed including (a) SEACOKE liquids (products produced from a low-temperature carbonization of coal), (b) lignite tar, (c) de-ashed coal extract, (d) coker distillate-coal tar blends, and (e) Illinois No. 6 coal tar.

The results and operating conditions of consecutive hydrogenations of the coke gas oil-coal tar mixture with different combinations of cobalt carbonyl and cobalt molybdate are summarized in Table II-11. In a mild treatment of feed with cobalt carbonyl at 185°C, a partial hydrogenation saturates nitrogen-containing rings, but no nitrogen is removed at this stage. However this treatment has made the products more susceptible for further hydrodenitrogenation. The results (shown in Table II-11) indicate 68% of nitrogen removal for the cobalt carbonyl-cobalt molybdate combination compared to 45% for two successive cobalt molybdate hydrotreatments.

Two series of hydrogenations of the Illinois coal tar have also been tested; one with cobalt carbonyl under synthesis gas conditions, the other with pure hydrogen and cobalt molybdate. The comparison of hydrogenation selectivity of the two catalyst systems was made by determining the amount of partially hydrogenated coal tars which could be further catalytically cracked to useful products. Data for the hydrogenation of Illinois No. 6 coal tar and subsequent cracking of the hydrogenated products are given in Table II-12. The results show that, for a given hydrogen consumption, the cobalt carbonyl and the cobalt molybdate systems, on catalytic cracking, present approximately equivalent selectivities for gasoline and coke yields.

Table II-11

Hydrogenation of Coker Distillate - Coal Tar Blend[a]
(ARCO SEACOKE, 1966)

Run No.	Feed Charge	Catalyst	Temp. (°C)	Pressure (psi)	Analysis of Liquid Products					Per Cent Removal		
					C	H	N	O	S	N	O	S
1	Blend	$Co_2(CO)_8$	185	3000 $CO + H_2$	82.50	10.33	0.25	3.26	3.05	0	-	8
2.	Product from Run 1	Co-Mo	400	1500 H_2	87.99	11.58	0.07	0.36	0.47	68	75	86
3.	Blend	Co-Mo	400	1500 H_2	87.22	11.38	0.19	0.34	0.96	14	76	71
4.	Product from Run 3	Co-Mo	400	1500 H_2	87.11	12.34	0.12	0.21	0.00	45	85	100

---

a. Coker distillate - coal tar blend: C, 84.6%; H, 9.9; N, 0.22; O, 1.44; S, 3.30.
b. Experiments were run for 4 hours.

Table II-12

Hydrogenation of Illinois Coal Tar
(ARCO SEACOKE Project, 1966)

Catalyst	Temp. (°C)	Pressure (psi)	Time (hr)	H_2 Consumption (ft^3/bbl)	Cracking Product[a] Coke Selectivity	Gasoline Selectivity
$Co_2(CO)_8$	204	5000 H_2 + CO	16	1790	0.544	0.350
$Co_2(CO)_8$	232	8000 H_2 + CO	100	2000	0.488	0.485
CoMo	204	2500 H_2	69	NG[b]	-	-
CoMo	370	3000 H_2	67	1650	0.466	0.521

---

a. Cracking Conditions: 140 g silica-alumina, 24 cc feed charge, 482°C, 12 min.
b. Negligible.

The data from these tests showed the following characteristic features of transition metal carbonyl systems:

(1) Cobalt carbonyl is active at temperatures lower than those at which cobalt molybdate may be used.

(2) Cobalt carbonyl is relatively more effective in removing nitrogen heteroatoms when hydrogenation with cobalt carbonyl was followed by hydrogenation with cobalt molybdate, than for two successive cobalt molybdate treatments.

(3) Overall, cobalt carbonyl and cobalt molybdate show about equal effectiveness, per unit of hydrogen consumption, in producing a cracking stock.

(4) Cobalt carbonyl may be used with a low-cost mixture of hydrogen and carbon monoxide (synthesis gas).

Coal Liquefaction Using Transition Metal Carbonyl Catalysts

Mild Coal Liquefaction (at $T < 250^{\circ}C$)

As described above, soluble transition metal complexes are active homogeneous hydrogenation catalysts; it has been demonstrated that polynuclear aromatic molecules can be hydrogenated under mild conditions with these catalysts. Hydrogenation of sulfur and nitrogen-containing compounds has also been demonstrated under mild conditions. In view of the striking catalytic activities of soluble transition metal complexes, attempts have been made by several investigators (Holy et al., 1977; Cox et al., 1976; Larson, 1977) to evaluate the effectiveness of metal carbonyl catalysts in liquefying coal under mild conditions.

Holy et al. (1977) tested several soluble transition metal complexes including rhodium and iridium carbonyl complexes for the liquefaction of coal at temperatures below 170°C and pressures of 0.1 - 3.96 MPa (14 - 575 psig). The experimental results (Table II-13) indicated that in no case did the coal appreciably liquefy or consume hydrogen. It was suggested that the coal deactivates the catalyst by either adsorption or absorption of this catalyst and alters its electronic or steric requirements.

Cox et al. (1976) have also tested the homogeneous catalytic hydrogenation of complex substrates including hvA bituminous coal and coal-derived materials such as solvent-refined coal and COED pyrolyzate. The results showed that no significant hydrogenation activity occurred at 200°C when the experiments were carried out using $Co_2(CO)_8$, $Ni[(PhO)_3P]_2(CO)_2$, or $Fe_3(CO)_{12}$. It was suggested that the failure to obtain coal hydroliquefaction was in part due to the inaccessiblity of the catalyst to the coal matrix.

Table II-13

Low Temperature Coal Liquefaction Using Transition Metal Carbonyl Catalysts[a] (Holy et al., 1977)

Catalyst	[Coal]/[Cat.] (Wt Ratio)	Temp. (^{o}C)	H_2 Pressure (psi)	Time (h)	THF-Solubles (wt %)
Rh(CO)(2, 3-pyrazine-dicarboxylic acid)	21.8	75	58	20	10.6
$Rh(CO)_2$ (acetylacetonate)	25.0	60	58	20	11.1
$IrCl(CO)(PPh_3)_2$	71.4	100	300	16	2.6

---

[a] Experiments used Kentucky No. 11 bituminous coal (Fries Mine, Island Creek Coal Company).

Larson (1977) has made an attempt to carbonylate coal with $Cu(CO)_4^+$ in $BF_3 \cdot H_2O$, but little coal depolymerization was found although the sulfur content was reduced in the treated coal. Derencsenyi and Vermeulen (1979) reported the use of transition metal carbonyl complexes such as $Mn_2(CO)_8(PBu_3)_2$ as potential co-catalysts with molten $ZnCl_2$ in coal liquefaction. The catalysts again appeared unable to activate H_2 adequately for coal liquefaction.

The failures of early experiments, carried out by Holy et al. (1977), Cox et al. (1976), and others, could be due to the absence of bond breaking and thus a lack of reactive fragments from coal at these low temperatures. Coal starts swelling at relatively low temperatures (175 - 200°C), but breaking significant amounts of linkages such as aliphatic, ether and other covalent bonds occurs only at temperatures close to or above its mesophase formation temperature. The requirement of higher reaction temperatures between coal and transition metal carbonyl complexes can be illustrated more clearly in a discussion of coal desulfurization using iron carbonyl treatment and coal liquefaction at temperatures above 375°C in the following sections; under these conditions, the complex is decomposed to the metal.

Coal Desulfurization

Sulfur is a recognized undesirable constituent in coal. The inorganic sulfur in coal is principally tied up with iron mainly as pyritic sulfur (pyrite or marcasite, FeS_2) along with small amounts of sulfate (hydrates of ferrous or ferric sulfate). The majority of the organic sulfur in coal is contained in ring thiophenes and possibly in thiol, sulfide, and disulfide functionalities.

Many physical and chemical methods have been developed for removal of sulfur from coal. Among them, the Magnex Process (Porter and Goens, 1979; Porter, et al., 1981) has used an iron carbonyl treatment as one of the key steps for removing sulfur from coal. In the Magnex Process (Figure II-3), the crushed (minus 14 mesh), hot coal is treated with the vapor of iron pentacarbonyl at about 170°C, followed by a magnetic separation. It is postulated that iron pentacarbonyl decomposes in the presence of the hot coal with zerovalent iron forming crystallites which attach to the ash particles for magnetic separation. It has been estimated that 17 pounds of iron pentacarbonyl per ton of coal is required to achieve a clean coal containing 1.2 pounds of SO_2 emission per million Btu (Porter and Goens, 1979). It was claimed that iron pentacarbonyl is an economically accessible reagent for desulfurization of coal with the process feasibility of regenerating the iron pentacarbonyl.

The results of desulfurization tests for a Pennsylvania coal (minus 14 mesh) using various dosages of iron pentacarbonyl per ton of coal are summarized in Table II-14. Using 40 pounds of iron pentacarbonyl per ton of coal (Test C in Table II-14), the clean coal yield was 81.0% with a total sulfur content of 0.66% and 1.01 lb of SO_2 emission per million Btu, compared to the feed coal having 1.27% total sulfur and 1.97 lb of SO_2 emission.

Other desulfurization tests for an Ohio No. 6 seam coal with iron pentacarbonyl are summarized in Table II-15. The results indicated no significant change in forms of sulfur or total sulfur content when a coal having minus 14 mesh was reacted with $Fe(CO)_5$ in a methanol slurry at its reflux temperature (as shown in Test 1 of Table II-15). In Test 2, a significant reduction of organic sulfur content was obtained by treatment of a minus 200 mesh coal with intense stirring. Under water-gas shift condition

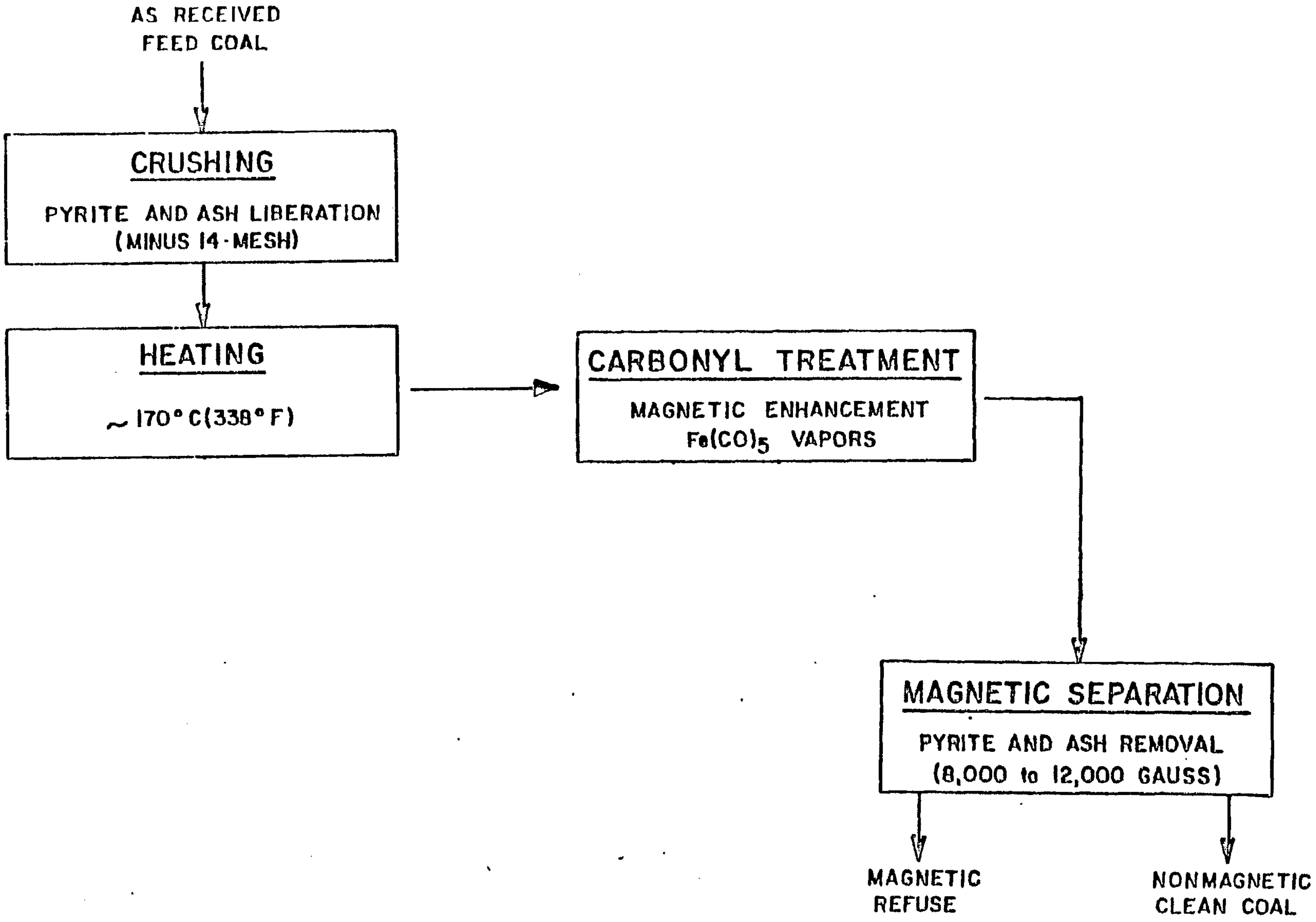

Figure II-3: The Magnex Process for Coal Desulfurization.
(Porter and Goens, 1979)

Table II-14

Desulfurization of Coal by Treatment with Iron Pentacarbonyl

(Porter and Goens, 1979)

	Feed[a] Coal	Test Numbers A	Test Numbers B	Test Numbers C
Carbonyl Treatment				
Temp. (°C)		170	170	170
Dosage (lb/ton)		2.5	10	40
Clean Coal				
Yield (%)		96.4	86.4	81.0
Ash (%)	12.7	11.6	11.8	10.7
Total Sulfur (%)	1.27	1.08	0.89	0.66
Inorganic Sulfur (%)	0.71	0.34	0.24	0.09
Heating Value (Btu/lb)	12,376	12,992	12,964	13,160
Emissions (lb $SO_2/10^6$ Btu)	1.97	1.66	1.38	1.01

---

a. Feed coal was obtained from the Allegheny Group of Pennsylvania (Sample No. 10442)

Table II-15

Desulfurization Tests with an Ohio No. 6 Coal Using Iron Pentacarbonyl (Porter et al. 1981)

	Feed Coal	Test Number		
		1	2	3
Carbonyl Treatment				
Coal Particle Size (mesh)		< 14	< 200	< 200
Conditions		• Gentle mixing with N_2 purge. • At reflux temp. of methanol	• Intense mixing with N_2 purge • At reflux temp. of methanol	• At water-gas shift conditions.
Clean Coal				
Pyritic Sulfur (%)	0.72	0.81	0.77	0.52
Sulfate Sulfur (%)	0.53	0.53	0.41	0.91
Organic Sulfur (%)	1.03	0.96	0.45	0.13
Total Sulfur (%)	2.29	2.30	1.63	1.56

(Test 3), the results showed that pyritic sulfur was apparently reduced or altered and the organic sulfur content was substantially reduced, but the sulfate sulfur content was increased from 0.53% in the feed coal to 0.91% in the product. This could be attributed to the undesirable adsorption of decomposed iron from iron carbonyl on the sulfate surface.

Coal Liquefaction Using Transition Metal Carbonyl Complexes as Catalyst Precursors

As shown by the above results, it seems that the decomposition of metal carbonyl complexes into finely dispersed metals in conjunction with cleaving coal linkages at higher temperatures is required in order to have a significant effect on coal desulfurization or liquefaction using transition metal carbonyl catalysts. This can be seen more clearly as described in a series of coal liquefaction tests carried out by Porter et al. (1981). The conditions and results of four coal liquefaction tests with an Ohio No. 6 seam coal under water-gas shift conditions at various temperatures and pressures are summarized in Table II-16. Substantial higher conversions of coal to THF-solubles were obtained at 400°C and 2600 psig pressure compared to these obtained at lower temperatures and lower pressures. This further indicates the importances of coal fragmentation at high temperatures and metal carbonyl decomposition to well-dispersed metals during the coal liquefaction. The total sulfur content in the THF-soluble product was reduced to only 0.056%, compared to 2.29% in the feed coal. It was also claimed that the hydrogen to carbon ratios of the THF-soluble fraction in the product was increased significantly.

McCabe and Orchin (1976) have made attempts to liquefy coal with chemically-bonded metal carbonyls. The chemically-bonded metal carbonyls on coal were prepared via chloromethylation followed by phosphorylation; then the phosphorylated coal was equilibrated with transition metal carbonyls (e.g.,

Table II-16

Coal Liquefaction Under Water-Gas Shift Conditions[a]

(Porter et al., 1981)

	Test Number			
Liquefaction Conditions	1	2	3	4
Temp. (°C)	140	225	230	400
Pressure (psig CO)	550	550	1200	2600
Time (hours)	2	2	2	2
Conversion Results				
THF-Solubles (%)	6.9	30.8	28.8	93.3
% Total Sulfur in THF-Soluble Fractions	Trace	ND[b]	ND[b]	0.056
H/C Atomic Ratio[c]				
THF-Solubles	-	-	1.53	-
THF-Solubles/Pentane Insolubles	-	-	0.89	-

---

a. Feed coal: Ohio No. 6 seam.

b. Not detected.

c. The H/C atomic ratio of the feed coal was 0.84.

dicobalt octacarbonyl). The hydrogenation of a bituminous coal (Elkhorn Mine, Kentucky) was conducted for one hour at 390°C with an initial pressure of 2000 psi of hydrogen (Table II-17). With decalin as solvent, the presence of cobalt (where dicobalt octacarbonyl was added as such) enhanced the hydrogenation but the increase in liquefaction (conversion to benzene-soluble products) was not significant. The effect on liquefaction was much more pronounced in the presence of tetralin. In reactions using chemically-bonded $Co_2(CO)_{8-x}$, the results were obviously superior for hydrogenation and liquefaction compared to $Co_2(CO)_8$ added neat to the system, with the benzene-soluble products reaching 74 wt%. It is likely that the bonded dicobalt octacarbonyl was converted to metallic cobalt which served as an active catalytic site well within the coal matrix.

More recent work reported by Suzuki and coworkers (Suzuki et al., 1982, 1984, 1985a, 1985b: Watanabe et al., 1984; Yamada et al, 1985) indicated that $Fe(CO)_5$, soluble in organic solvents, could serve as an excellent catalyst for coal hydroliquefaction. The finely dispersed metallic iron derived from $Fe(CO)_5$ seems to give high catalytic activity. The catalytic ability of transition metal carbonyls, when reduced to the finely divided, well-dispersed metal, promotes hydrogen transfer from molecular hydrogen to coal fragment radicals and is also important during coal liquefaction under relatively mild conditions (375-400°C).

Some striking results of these investigations are discussed and summarized as follows:

(i) Effect of Reaction Temperature - The conversion of coal to THF-soluble fractions has been investigated extensively over the range 375° to 480°C. The hydroliquefaction of several coals, Taiheiyo (Japanese), Mi-ike (Japanese), Wandoan (Australian), and Illinois No. 6 (analytical

Table II-17

Comparison of Coal Hydrogenation Using Unbonded and Bonded Dicobalt Octacarbonyl as Catalyst Precursors[a]
(McCabe and Orchin, 1976)

Catalyst[b]	Vehicle	H_2 Consumed (mol)	Liquefaction Benzene-Solubles (wt %)
None	Decalin	0.057	20.8
None	Tetralin	0.051	32.2
$Co_2(CO)_8$	Decalin	0.166	27.7
$Co_2(CO)_8$	Tetralin	0.179	54.4
$-Co_2(CO)_{8-x}$, bound	Decalin	0.242	51.1
$-Co_2(CO)_{8-x}$, bound	Tetralin	0.217	73.8

(Hydrogenation Conditions: 390°C, 1 hr., and 2000 psi initial H_2 pressure)

[a] Feed coal: 100 mesh, Elkhorn Mine, Kentucky; C, 79.1; H, 5.3; N, 1.3; S, 1.0; ash, 5.3.

[b] 13 mmol of cobalt carbonyl was used for 10 gm coal.

data for coals are given in Table II-18) was carried out using iron pentacarbonyl under a hydrogen pressure in either a hydrogen donating solvent, tetralin, or a non-hydrogen donating solvent, 1-methylnaphthalene. The results of effects of reaction temperature are summarized in Table II-19. In the liquefaction of Taiheiyo coal, the presence of $Fe(CO)_5$ and tetralin resulted in increases in the amount of THF-soluble fractions (coal conversion) from 65.7 to 84.5% at 375°C and from 90.9 to 99.7% at 425°C. In the case of Mi-ike coal, the THF-soluble fraction increased from 96.0 to 100%. Increases in coal conversion, however, are not distinctive at 425°C in the presence of an excellent hydrogen donor solvent such as tetralin. In the presence of $Fe(CO)_5$ and a non-hydrogen donor solvent, 1-methylnaphthalene, coal conversion increased from 54.5 to 84.8% at 425°C and from 53.8 to 81.5% at 460°C for the Taiheiyo coal. It appears that coal conversion decreased slightly at 460°C compared to its conversion at 425°C. This is probably due to coking at high temperatures.

In the hydroliquefaction of Illinois No. 6 coal with 1-methylnaphthalene (Table II-19), the conversion to THF-soluble products varied little throughout the temperature range from 425° to 480°C in the presence of $Fe(CO)_5$. The coal conversion (THF-solubles) was 92.2% at 425°C, 95.0% at 460°C, and 93.9% at 480°C, respectively. At high temperatures, coal conversions do not change appreciably, but significant internal changes of products among preasphaltene, asphaltene, and oil fractions do occur.

Table II-18

Analyses of Coal Samples Used in Hydroliquefaction with Transition Metal Carbonyls as Catalyst Precursors
(Suzuki et al., 1985b; Yamada, et al., 1985)

Coal	C (%)	H (%)	Total Sulfur (%)	Ash (%)	VM[a] (%)
Mi-ike	83.9	5.4	1.9	8.2	43.2
Taiheiyo	77.2	6.7	-	16.1	46.0
Wandoan	76.8	6.7	0.2	7.7	43.0
Illinois No. 6	76.8	5.6	4.0	11.2	42.2

---

a. Volatile matter.

Table II-19

Coal Hydroliquefaction Using Iron Carbonyl Complexes as Catalyst Precursors[a]

(Suzuki et al., 1982; Watanabe et al., 1984; Suzuki et al., 1984; Suzuki et al, 1985[a])

Coal	Catalyst	Temp. (°C)	Solvent[b]	Conversion (THF-Solubles) (%)	Product Distribution (%)		
					Oils	Asphaltenes	Preasphaltenes
Taiheiyo	None	375	T	65.7	14.5	13.9	37.3
	$Fe(CO)_5$	375	T	85.4	26.1	12.3	47.0
	$[Fe(CO)_2Cp]_2$	375	T	75.1	22.6	11.7	40.8
	None	425	T	90.9	56.1	18.2	16.6
	$Fe(CO)_5$	425	T	99.7	56.3	25.9	17.5
	None	425	MN	54.5	34.9	11.7	7.9
	$Fe(CO)_5$	425	MN	84.8	46.8	22.2	15.8
	None	460	MN	53.8	41.3	8.7	3.8
	$Fe(CO)_5$	460	MN	81.5	59.1	14.1	8.3
Mi-ike	None	425	T	96.0	38.8	35.5	21.7
	$Fe(CO)_5$	425	T	~100	45.4	39.8	14.8
	None	445	T	97.2	49.8	33.4	14.0
	$Fe(CO)_5$	445	T	~100	57.5	32.5	10.0
Illinois No. 6	None	425	MN	56.7	26.5	19.2	11.0
	$Fe(CO)_5$	425	MN	92.2	44.0	30.4	17.8
	None	460	MN	69.7	37.2	20.4	12.1
	$Fe(CO)_5$	460	MN	95.0	53.1	30.5	11.4
	None	480	MN	61.2	34.9	16.2	10.1
	$Fe(CO)_5$	480	MN	93.9	50.4	29.5	14.0

---

a. Experimental conditions: coal, 2 gm; Fe, 2 mmol; initial H_2 pressure, 700-1150 psi; reaction time, 60 min.

b. T, tetralin; MN, 1-methylnaphthalene.

(ii) Effect of Various Metal Carbonyls - The catalytic activity of metal carbonyl complexes of chromium, molybdenum, tungsten, manganese, iron, cobalt, and nickel in the liquefaction of coal has also been investigated by Suzuki and his coworkers. The carbonyl compounds of molybdenum, tungsten, iron, cobalt, and nickel acted as highly active catalyst precursors for the liquefaction of Illinois No. 6 coal as shown in Table II-20. The results indicate that high coal conversions (> 90%) and high oil yields (> 32%), were obtained using transition metal carbonyl complexes as catalyst precursors, under a hydrogen pressure of 710 psi with a non-hydrogen donating solvent at 425°C for 60 minutes. Among the catalysts employed, the decomposition products from $Mo(CO)_6$ gave the highest oil yield (57.7%) and the largest amount of hydrogen transferred to coal (3.1 wt% of coal). Chromium hexacarbonyl and manganese carbonyl complexes were less effective catalysts for hydroliquefaction.
However, the molybdenum and tungsten carbonyls did not exhibit high catalytic activity (Table II-21) for low sulfur Wandoan coal (total sulfur 0.2% as shown in Table II-18). On the other hand, the addition of sulfur to the carbonyl system increased coal conversion significantly from 72.5 to 90.3% for $Mo(CO)_6$ and 52.3 to 93.9% for $W(CO)_6$. In the case of $Fe(CO)_5$, the conversion increased slightly from 85.2 to 94.4% with the addition of sulfur. But decomposition products from cobalt and nickel carbonyls showed high catalytic activity regardless of the amount of sulfur present in the reaction system. It was suggested (Suzuki et al., 1985b) that iron carbonyl was converted into pyrrhotite-like material when sulfur was present, but into iron oxides in the absence of sulfur.

Table II-20

Hydroliquefaction of Illinois No. 6 Coal
Using Various Transition Metal Carbonyl Complexes as Catalysts[a]
(Yamada et al., 1985)

		Distribution of Products			
Catalyst[b]	Conversion (%)	Oil (%)	Asphaltenes (%)	Preasphaltenes (%)	H_2 added to Coal (wt% of coal)
None	56.7	22.1	19.2	11.0	0.5
$MnCpMe(CO)_3$[c]	75.8	20.0	27.7	22.4	1.3
$Cr(CO)_6$	77.3	25.9	25.3	19.8	1.4
$W(CO)_6$	91.6	33.0	33.0	19.4	2.2
$Mo(CO)_6$	92.1	57.7	26.0	3.8	3.1
$Fe(CO)_5$	92.2	44.0	30.4	17.8	2.2
$[FeCp(CO)_2]_2$[d]	92.9	32.6	39.0	14.5	2.5
$Co_2(CO)_8$	93.3	37.9	32.8	16.6	2.3
$Ni(CO)_4$	94.1	32.4	35.3	21.1	2.2

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a. Experimental conditions: 2 gm Illinois No. 6 coal, 4.0 ml 1-methylnaphthalene, initial H_2 pressure 710 psi, 425°C and 60 min.

b. 1 wt% of coal as metal.

c. Methylcyclopentadienylmanganese tricarbonyl.

d. Cyclopentadienyliron dicarbonyl dimer.

Table II-21

Hydroliquefaction of Wandoan Coal
Using Transition Metal Carbonyls and Sulfur Compounds as
Catalyst Precursors[a]
(Yamada et al., 1985)

	Product Distribution				
Catalyst[b]	Conversion wt (%)	Oils (%)	Asphaltenes (%)	Preasphaltenes (%)	H_2 added to Coal (wt% of coal)
None	48.6	22.3	12.6	5.9	0.2
$W(CO)_6$	52.3	14.2	16.2	14.6	0.7
$Mo(CO)_6$[c]	72.5	26.5	18.6	17.9	1.5
$Fe(CO)_5$	85.2	35.5	21.0	21.8	1.5
$[FeCp[CO)_2]_2$	89.3	31.3	32.2	17.9	2.4
$Ni(CO)_4$	92.9	48.8	22.1	13.8	2.5
$Co_2(CO)_8$	93.5	48.1	26.5	12.6	2.9
$W(CO)_6$-S	93.9	56.6	27.1	3.2	3.4
$Mo(CO)_6$-S[c]	90.3	39.9	27.1	12.7	2.7
$Fe(CO)_5$-S	94.4	48.6	24.8	11.5	2.8
$[FeCp(CO)_2]_2$-S	94.9	41.0	29.6	15.0	2.7
$Ni(CO)_4$-S	92.3	50.9	25.2	6.4	2.6
$Co_2(CO)_8$-S	91.1	50.0	24.4	7.9	2.4

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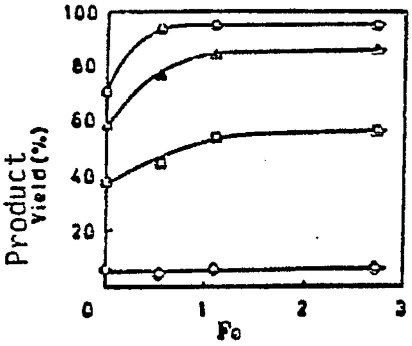
a. Experimental Conditions: 2 gm Wandoan coal, 4.0 ml 1-methylnaphthalene, initial H_2 pressure 710 psi, 425°C and 60 min.

b. 0.4 mmol of metal and 1 mmol of sulfur used.

c. 0.04 mmol of Mo used.

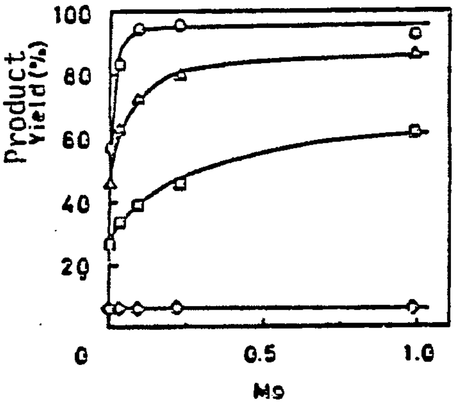
(iii) Effect of Metal Carbonyl Concentrations - The effects of $Fe(CO)_5$, $Co_2(CO)_8$, and $Mo(CO)_6$ catalyst levels on the liquefaction of Illinois No. 6 are summarized in Figure II-4. Coal conversion increased from 70 to 93% when 0.6 wt% Fe (based on coal) was used and only slightly increased with further addition of the catalyst up to 2.8%. Constant oil and asphaltene yields were observed when more than 1% Fe was added as $Fe(CO)_5$. In the case of $Co_2(CO)_8$, the conversion and yields of liquefaction products gradually increased with increasing amounts of catalyst. More than 1.6% of cobalt was needed to obtain maximum conversion and oil yield. On the other hand, addition of about 0.1% of Mo gave almost maximum values of coal conversion. The addition of a larger amount of Mo increased the conversion of preasphaltenes and asphaltenes into oils, with no effect on the overall coal conversion.

(A)



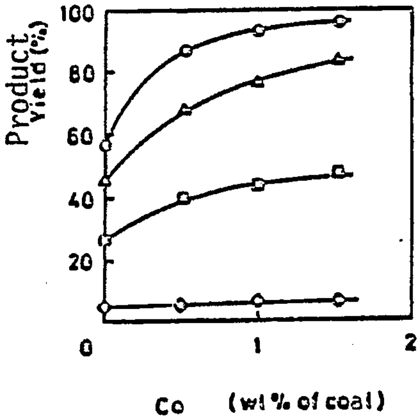
Reaction conditions: initial hydrogen pressure 1140 psi, at 460^{o}C for 20 min., in 1-methylnaphthalene.

(B)



Reaction conditions: initial hydrogen pressure 710 psi, at 425^{o}C, for 60 min., in 1-methylnaphthalene.

(C)



Reaction conditions: initial hydrogen pressure 710 psi, at 425^{o}C, for 60 min., in 1-methylnaphthalene.

Figure II-4:. Effects of Zerovalent Metal Concentrations from Decomposition of Metal Carbonyls on Liquefaction of Illinois No. 6 Coal (References of (A) From Suzuki et al., 1985a, and (B) and (C) from Yamada et al., 1985) Preasphaltenes, Asphaltenes, Oils, and Gas in Descending Order of Curves.

Conclusions and Recommendations

As discussed on the work of coal conversion, soluble transition metal complexes, in particular metal carbonyls, serve as excellent catalyst precursors for coal hydroliquefaction. The unique properties of transition metal carbonyls lie in their relatively easy decomposition to yield finely dispersed metals which can penetrate the coal pores to give high catalytic activity. The ability of transition metal carbonyls to promote hydrogen transfer from molecular hydrogen to coal fragment radicals at temperatures above coal mesophase formation is also important during coal liquefaction. This could partially explain the failure of early experiments conducted by Holy et al. (1977) and Cox et al. (1976) to obtain any significant amount of coal conversion or hydrogen transfer to coal. They both employed a lower reaction temperature (below 200°C) for liquefaction. In general, metal carbonyl complexes are more active at a low temperature than is a cobalt molybdate catalyst for the partial hydrogenation of condensed aromatic hydrocarbons. The complex is also more selective than is the molybdate, The carbonyl gives a partly reduced compound with isolated aromatic ring structures remaining.

It has often been pointed out that the most critical factors for the selection of coal liquefaction catalysts are thermal and chemical stabilities. Thermal stability is the ability of a material to maintain physical and mechanical integrity at various reaction conditions. Chemical stability indicates the ability of a material to withstand coal liquefaction conditions without bulk chemical transformation. The second criterion (chemical stability) is the most difficult for most materials to meet, especially at the high level of hydrogen sulfide, ammonia, and water expected in coal liquefaction. In the case of transition metal carbonyl catalysis, thermal decomposition of metal carbonyls seems to provide finely divided reduced metal to disperse evenly on to coal particles; meanwhile, H_2S could promote the catalytic activity of metal carbonyl.

Based on this review of coal liquefaction using transition metal carbonyl complexes as catalysts, the following recommendations are made with respect to potential areas of development for future study.

(1) A multimetal catalyst composed of group VI and VIII transition metal carbonyls should be investigated to possibly obtain higher catalytic activity and product selectivity. The addition of a small amount of a second metal carbonyl complex to the primary metal complex may result in a synergistic effect, with increases in both yields and hydrogen utilization efficiency.

(2) Anchoring homogeneous catalysts on solid supports has been attempted to combine the advantages of homogeneous and heterogeneous catalysts to maximum thermal and chemical stabilities. Metal carbonyl catalysts with high selectivity and thermal stability can be prepared by either the use of polymer supports, such as cross-linked polystyrene-divinylbenzene, as well as silica or alumina. Several physical and chemical methods are suitable for preparing supported metal carbonyl catalysts including impregnation, ion exchange, or acid base treatment. While this approach has been rather thoroughly studied, it has, so far, not proved fruitful.

(3) Research efforts should also focus on the applications of transition-metal carbonyl hydrides by reacting metal carbonyls with hydroxide ion or methanol in bases under water-gas shift conditions. Hydridic carbonyl complexes of transition metals can affect a variety of interesting transformations including the room temperature reduction of aromatic

nitro compounds to amines. Hydrogenation of polynuclear heteroatom-containing compounds could be achieved catalytically with transition metal complexes.

(4) Attempts should also be made to modify the homogeneous metal carbonyl complex systems to improve catalyst performance by either adding a phase-transfer agent or replacing one of the carbon monoxide groups with a polar ligand. A phase-transfer agent, such as a tetraalkylammonium halides or a crown ether, would improve the phase contact between metal carbonyl ions and coal polynuclear aromatics which usually have hydrophobic properties. A polar ligand, such as a dibutylphenylphosphine ligand, would preferentially complex with polycyclic heteroatoms in the coal constituent.

(5) A strong coal bond-breaking agent, such as a molten halide, would give reactive coal fragments which might repolymerize to a refractory structure unless H_2 or a stabilization agent is present. Hence, the study of the possibility of using a homogeneous co-catalyst such as a metal carbonyl complex and a bond-cleaving agent should be investigated, so that the intermediate fragments could be hydrogenated immediately by the surrounding transition metal complex catalysts.

(6) Endeavor to synthesize transition metal complexes of high thermal stability which are catalytically active at high temperatures. Ferrocene is a very stable complex but it is not catalytically active. Another way of operating at high temperatures with metal carbonyl complexes is to raise the CO pressure so that the complex does not decompose. However, this may well require pressures above 5000 psi. The use of a metal carbonyl at 450°C under high pressure would preserve the identity of the complex perhaps providing an excellent catalytic system.

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