"Design, Synthesis, and Characterization of Novel Fine-Particle, Unsupported Catalysts for Coal Liquefaction"

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Catalyst Synthesis

A series of iron carbonyl-based homogeneous catalyst precursors has been prepared.

These species include:

$\text{Fe(CO)}_4\text{PPh}_3$

$\text{Fe(CO)}_3(\text{PPh}_3)_2$

$\text{Fe(CO)}_2(\text{PPh}_3)_2\text{CS}_2$

$\text{S}_2\text{Fe}_2(\text{CO})_6$

$\text{S}_2\text{Fe}_3(\text{CO})_9$

$\text{Fe(CO)}_4\text{PPh}_3$ was prepared by a combined photochemical and thermal route from triphenylphosphine (PPh_3) in iron pentacarbonyl (Fe(CO)_5), following the synthesis procedure of Conder and Darensbourg¹. This preparation procedure, which is selective to the monosubstituted product, is outlined below:

Thus 3 g of PPh₃ (0.011 mole) was added to 28 ml of Fe(CO)₅ (0.208 mole) under a dry N₂ atmosphere. The stirred solution was irradiated with a 100-Watt long-wave UV lamp for 2 hours. The lamp was then turned off and the solution was held at reflux conditions (100°C) for 1 hour, followed by an additional hour of reflux with the UV lamp turned back on. At the end of the reaction sequence, excess Fe(CO)₅ was removed in vacuo. The residue was extracted with 50 ml THF and chromatographed on a neutral alumina column, eluting with 75 ml THF. 50 ml of distilled water was then added, and the solution volume reduced under vacuum to precipitate pale yellow crystals which were collected by filtration and purified by recrystallization from heptane. The above procedure gave a 24% yield of Fe(CO)₄PPh₃ (based on PPh₃).

Fe(CO)₃(PPh₃)₂ was prepared from Fe(CO)₅ and PPh₃ in refluxing cyclohexanol, following the procedure of Clifford and Mukherjee². In this synthesis, 2 ml of Fe(CO)₅ (0.015 mole) and 5 g of PPh₃ (0.018 mole) were added to 100 ml of cyclohexanol which had been distilled under N₂ over 4A molecular sieve to remove oxygen and water. The solution was then refluxed (161°C) for 1 hour under N₂. 100 ml of hexane was added to the reaction solution which was then cooled, giving a yellow precipitate. This relatively straightforward procedure gave a 38.9% yield (based on Fe(CO)₅) of the disubstituted product, Fe(CO)₃(PPh₃)₂, with a small amount of the monosubstituted derivative, Fe(CO)₄PPh₃, present.

$\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{CS}_2$ was prepared from diiron nonacarbonyl ($\text{Fe}_2(\text{CO})_9$) and PPh_3 in refluxing (46°C) carbon disulfide (CS_2), as outlined by Baird et al.³ A mixture of 1.5 g of $\text{Fe}_2(\text{CO})_9$ (0.004 mole) and 3 g of PPh_3 (0.011 mole) in 25 ml of CS_2 was refluxed under N_2 for 40 minutes. The solution was cooled, and the rust-red precipitate, $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{CS}_2$, was filtered off (48% yield based on $\text{Fe}_2(\text{CO})_9$).

$\text{S}_2\text{Fe}_2(\text{CO})_6$ and $\text{S}_2\text{Fe}_3(\text{CO})_9$ were prepared from $\text{Fe}(\text{CO})_5$ and Na_2S_5 , as described by Seyferth et al.⁴ In this procedure, 8 ml of $\text{Fe}(\text{CO})_5$ (0.06 mole) and 16 ml of 50% aqueous KOH (w/v) were added to 40 ml of degassed methanol at 0°C . An aqueous solution equivalent to 83 mmol of Na_2S_5 was then added, and the mixture was stirred at 0°C for 2 hours. The reaction mixture was then acidified by slow addition of 80 ml of degassed 18.5% HCl solution which gave a brown precipitate. The brown precipitate was collected by filtration and twice extracted with pentane. The pentane was then removed in vacuo to give a reddish-brown solid. Sublimation of the solid at 40.5°C for 10 hours yielded dark ruby-red crystals of $\text{S}_2\text{Fe}_2(\text{CO})_6$ (5% yield based on $\text{Fe}(\text{CO})_5$). The remaining solid ($\text{S}_2\text{Fe}_3(\text{CO})_9$ and decomposition products) was dissolved in 50 ml pentane and passed through a 4 cm bed of silica gel in a filter funnel to remove decomposition products. Subsequent pentane removal (in vacuo) gave brown $\text{S}_2\text{Fe}_3(\text{CO})_9$ at a yield of 7% (based on $\text{Fe}(\text{CO})_5$).

Identification of the products was made by comparison of their color and infrared spectra with literature values, as shown in Table 1.

Table 1

Compound	Medium	CO stretching frequency (cm ⁻¹)		
Fe(CO) ₄ PPh ₃	CH ₂ Cl ₂	2051	1974	1939
	CHCl ₃ ⁵	2059	1978	1938
Fe(CO) ₃ (PPh ₃) ₂	CH ₂ Cl ₂	1882		
	CHCl ₃ ⁵	1887		
Fe(CO) ₂ (PPh ₃) ₂ CS ₂	CH ₂ Cl ₂	1990	1929	
	CH ₂ Cl ₂ ³	1989	1929	
S ₂ Fe ₂ (CO) ₆	CH ₂ Cl ₂	2083	2042	2003
	CCl ₄ ⁶	2081	2042	2005
S ₂ Fe ₃ (CO) ₉	CCl ₄	2063	2043	2020
	CCl ₄ ⁶	2063	2045	2024

Currently these compounds are being tested as catalysts/catalyst precursors with coal or model compounds in the tubing bomb reactors to provide information relating catalytic activity to catalyst structure and properties. These catalyst precursors are expected to decompose to some form of sulfur-containing iron species at reaction conditions, and the various compounds we have prepared are designed to examine several different precursor properties and their effect on the form of the final active species. Addition of the PPh₃ ligand to the iron carbonyl coordination sphere increases the thermal stability of the iron carbonyl, and testing of the compounds Fe(CO)₄PPh₃ and Fe(CO)₃(PPh₃)₂ is expected to yield information regarding catalytic activity and catalyst particle size versus thermal stability of the precursor. The compound Fe(CO)₂(PPh₃)₂CS₂ is designed to look at the additional effect of having sulfur within the iron coordination sphere. It is possible that readily available sulfur in the iron coordination sphere may lead to very fine-particle iron sulfides upon decomposition of the species. S₂Fe₂(CO)₆ and S₂Fe₃(CO)₉ examine the effect of metal-metal bonds on the morphology of the iron sulfide species formed. Thermal decomposition studies of all the above catalyst precursors are planned to determine their decomposition rates in solution upon heating and to examine the particle size and other properties of the compounds formed by decomposition of the precursors.

Catalyst Characterization

BACKGROUND

Tubing Bomb reactors are being employed to characterize the activity of catalysts through kinetic analysis. Currently, a coal model compound, Dibenzyl Ether (DBE), is being used to characterize the catalysts. We have established the testing conditions as 275 °C under atmospheric Nitrogen (before heat up). The reactor is charged with 1 g DBE, 3 g Tetralin, ~0.05 g catalyst, ~0.04 g Triphenylphosphine and 50 μ L Carbon Disulfide.

SUMMARY OF CURRENT WORK

We have tested various Iron based, homogeneous catalysts under these conditions, and the rate data, in the form of pseudo-first order rate constants, are summarized in Table 2.

Some of the kinetic data obtained in these experiments are shown in Figure 1. The $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{CS}_2$ catalyst showed a remarkably higher activity for cracking the DBE than did the other Iron based and AmocatTM catalysts. In all of the cases, the same major products were identified: Benzaldehyde, Benzyl Alcohol and Toluene. We plan to test the Hydrogenation ability of these catalysts using different model compounds (Bibenzyl for example) in a Hydrogen atmosphere. In addition, we will test some of them on coal in both Tubing Bomb Reactors and the Short Contact Time Reactor. We will continue to run all of these tests on new catalysts as they are synthesized.

CATALYST	1ST ORDER RATE CONSTANT AT 275°C (MIN ⁻¹ g CATALYST ⁻¹)	
	Atmospheric Nitrogen 50 µL Carbon Disulfide	Atmospheric Nitrogen 50 µL Carbon Disulfide Excess of PPh ₃
Amocat™ NiMo / Alumina	3.92	
Fe(CO) ₃ (PPh ₃) ₂	1.89	8.22
Fe(CO) ₄ (PPh ₃)	5.28	
Fe(CO) ₂ (PPh ₃) ₂ CS ₂		78.01
NONE		No Reaction at 8 min

Table 2: Pseudo first-order rate constants for DBE in the presence of various catalysts.

First Order Rate Laws for the Disappearance of DBE

Figure 1: Pseudo-first order rate constants for the catalytic cracking of DBE at 275°C in an excess of Tetralin. The catalysts used were Amocat™ (NiMo / Al₂O₃), Fe(CO)₃(PPh₃)₂, and Fe(CO)₂(PPh₃)₂CS₂. The values of the rate constant were 3.92, 8.22, and 78.01 (min*g cat.)⁻¹ respectively. All three of the catalysts were run in an excess of CS₂ and the Fe(CO)₃(PPh₃)₂ and Fe(CO)₂(PPh₃)₂CS₂ catalysts were run in an excess of PPh₃.

Coal Flash Pyrolysis Studies

The total organic oxygen content as determined directly by fast neutron activation analysis (FNAA) is compared with oxygen functional group contents as determined by chemical and flash pyrolysis techniques.

There are a number of analytical methods for carboxyl, hydroxyl, and carbonyl groups in coal. For our work, we chose Blom and Schafer's chemical methods. Ethers (internal and external) were estimated by difference. Kjeldahl nitrogen runs as part of the carbonyl determination were run by Micro Analysis Inc. However, we must remember that reacting a solid with a liquid as is the case with these methods involve mass transfer difficulties. Before using these chemical methods, all of the coal samples were ground under nitrogen to minus 200 mesh and then dried in the vacuum oven overnight. Coal was also treated

with aqueous HCl to remove labile metal ions and analyses were run under reflux for 1-3 days. The carboxyl analysis was confirmed by an alternative pyrolysis methods. The pyrolysis experiments were conducted on the Beulah-Zap and Wyodak samples at 625-930°C with 74-105 μm fractions in a continuous fluidized sand bed pyrolyzer.

The percent oxygen as carboxyl, hydroxyl, carbonyl, and ether (by difference) in each sample is shown in Table 3. Carboxylic groups are found in considerable concentration in the low-rank coals. The percent oxygen in carboxyl groups decreases with increasing rank and approaches zero for coals of higher rank. The percent oxygen as hydroxyl and carbonyl show similar trend with increasing rank, but carbonyl shows greater variability. There is significant amounts of ether oxygen (by difference) in all samples. Illinois #6 coal, however, seems to be somewhat lower in ether oxygen than might be expected for its rank. Other samples of Illinois #6 are being analyzed to see whether they also show low ether oxygen. In the case of Wyodak and Beulah-Zap samples, carboxyl content as determined by CO₂ evolution from flash pyrolysis technique agrees closely with chemical analysis indicating that carboxyl groups pyrolyze quantitatively to CO₂.

Low-rank coals contain the large concentration of exchangeable metal ions associated with the carboxyl groups. In the case of Wyodak and Beulah-Zap samples, the comparison of % low temperature ash of the original and acid forms show significant concentrations of associated metal ions, as shown in Table 4.

Table 3. Determination of Organic Oxygen Contents by Chemical and Pyrolytic Analyses of Argonne Premium Coal Samples (dry, wt. %)

Coal	Beulah- Zap	Wyodak- Anderson	Illinois # 6	Blind Canyon	Pittsburgh # 8	Lewiston- Stockton	Upper Freeport	Pocahontas # 3
Rank C(dmmf)	Lig. 74.05	Subb. 76.04	HVB. 80.73	HVB. 81.32	HVB. 84.95	HVB. 85.47	MVB. 88.08	LVB. 91.81
Total Organic O by FNAA (1)	17.21	14.31	7.41	9.76	6.74	5.75	2.90	1.59
% O as CO ₂ H by Chemical Method (2)								
	3.81	3.33	0.23	0.23	0.16	0.20	0.14	0.05
% O as CO ₂ H by Pyrolysis Method								
	3.94	3.14						
% O as OH by Chemical Method (3)								
	9.16	7.68	5.68	5.22	4.32	2.70	1.96	0.98
% O as C=O by Chemical Method (4)								
	1.96	0.74	0.93	0.63	0.18	0.18	0.44	0.32
% O as Ether by Difference (1) - (2) - (3) - (4)								
	2.28	2.56	0.57	3.68	2.08	2.67	0.36	0.24

Table 4. Metal Ions Associated with Low-Rank Coals

Anderson (wt %)	Coal	Beulah-Zap	(wt %)	Wyodak-
	Low Temperature Ash on Raw Coal	11.88	11.51	
	Low Temperature Ash on Acid Form	2.87	5.7	
	Associated Metal Ions	9.01	5.81	

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