

IN SITU CONVERSION OF COAL

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## INTRODUCTION

This project was a search for catalysts which would allow the liquefaction of coal under very mild conditions. The most ambitious goal for liquefaction processes is to develop one which will operate in situ, which will bring about the liquefaction of coal in the seam. There are a number of excellent reasons for embarking on this formidable task. Not only would the safety and environmental problems of present deep mining practices be neutralized, but a large cost advantage exists if the coal does not have to be dug from the ground. In spite of the obvious advantages, few groups have been bold enough to undertake such development. The reason is the traditional view that coal is unreactive and requires high pressures and temperatures for conversion. The latter half of this statement has not yet been proved false, but it is quite apparent that coal is not unreactive. In fact, the problem may be that it is too reactive, with most liquefying reactions occurring in competition with polymerizing reactions. If one searches for reactions which will go under the mild conditions demanded by in situ conversion and fails, one may still have developed process chemistry which is an improvement over the extreme conditions used in the processes now under development. The situation is that probability of success is very low, but the results of success so enormous that the attempt must be made. In our case, the attempt failed in its original aim, but succeeded in the development of a reaction capable of the rapid and highly selective removal of sulfur from coal.

One of the factors which encouraged us to search for very mild liquefaction conditions was the reported existence of a variety of catalysts capable of causing the hydrogenation of aromatics at room temperature or slightly above and at hydrogen pressures of one or two atm. A number of such systems are described in James book.<sup>1</sup> All were developed recently, and no publications describing their application to coal or heavy ends had appeared. Accordingly,

we undertook to test each promising system with coal. Our results can be summarized briefly; nothing worked. We then started designing our own systems, happily with better results.

### Tulupov Catalysts

Among the most unusual and promising catalysts for the homogeneous hydrogenation of olefins and aromatics are the transition metal stearates reported by Tulupov.<sup>2-5</sup> They appeared to have the dual advantages of high reactivity and low cost. The reaction mechanisms have been explored<sup>6,7</sup> and two reviews on the reaction published.<sup>8</sup> Tulupov reported the reduction of cyclohexene in ethanol by H<sub>2</sub> at 1 atm pressure at room temperature in the presence of stearate salts of Ni(II), Cu(II), Co(II), Cr(III), Fe(III), Sc(III), Ti(IV), and Zn(II). More important for our purposes, he also reported the hydrogenation of benzene in the presence of Ni(II), Co(II), Fe(III), and Pb(II) stearates. A literature search revealed no attempts to repeat Tulupov's studies.<sup>9</sup> We attempted to repeat Tulupov's work and failed. Some of our attempts are summarized in Table I.

Table I. Attempted Catalytic Hydrogenation of Cyclohexene Using Tulupov's Catalysts

Rxn	"Catalyst"	Solvent	Temp, °C	H <sub>2</sub> pressure, psia	Rxn. time, h	pressure drop, psi
1	Ni(II) stearate	Hexanes	~23	37	48	0
2	Ni(II) stearate	Hexanes	60	38	60	0
3	NiCl <sub>2</sub>	Ethanol	~23	45	37	0
4	NiCl <sub>2</sub> ·6H <sub>2</sub> O	Ethanol	~23	47	43	0
5	NiCl <sub>2</sub> /stearic acid <sup>2</sup>	Ethanol	~23	45	36	0
6	NiCl <sub>2</sub> ·6H <sub>2</sub> O/stearic acid	Ethanol	~23	35	24	0
7	Cu(II) stearate	Isobutyl alcohol	50	38	28	0
8	CoCl <sub>2</sub>	Ethanol	~23	46	67	0
9	CoCl <sub>2</sub> /stearic acid	Ethanol	~23	47	36	0
10	Ni(II) stearate <sup>a</sup>	Hexanes	~23	49	42	0

<sup>a</sup>The olefin used was norbornene.

In addition to the failure to observe any hydrogenation, our samples of Ni(II) stearate, which had correct chemical analyses, were insoluble in anhydrous ethanol. Tulupov<sup>3</sup> reported the solubility to be  $4.21 \times 10^{-3}$  M/l. Cu(II) (reported solubility<sup>4</sup>  $4.02 \times 10^{-4}$  M/l) behaved similarly although it was slightly soluble in hot ethanol. These results raise the possibility that Tulupov was not working with the stearates. However, neither the stearates or anything else likely to be present in the stearates is an active hydrogenation catalyst under the conditions reported by Tulupov. There seemed little to be gained by further study of this system, and so we initiated studies of Muetterties catalyst.

## MUETTERTIES CATALYST

The most active hydrogenation catalyst for benzene yet developed is  $n^3\text{-C}_3\text{H}_5\text{Co[P(OCH}_3)_3]_3$ , prepared originally by Muetterties.<sup>10-12</sup> A survey of the activity of this catalyst with a variety of substituted aromatics has been carried out.<sup>13</sup> We had experimental difficulties in carrying out the synthesis of this catalyst. Our experimental procedure; which is a minor modification of Muetterties procedure, has been published.<sup>14</sup> We carried out a number of reactions using a low pressure Parr hydrogenator. Products were isolated by gas chromatography and structures verified using mass spectrometry. Our data are given in Table 2. It is notable that as the size of the polycyclic aromatic to be hydrogenated increases, the effectiveness of the catalyst decreases. The catalyst is destroyed by compounds having acidic hydrogen. We felt this might be the reason why coal and asphaltenes failed to react. We examined this possibility methylating using dimethyl sulfate and base in order to remove active hydrogen. The methyl ethers and esters are known to react.<sup>13</sup> Again no reaction was observed. The reason for this is not clear.-

In addition to the Muetterties catalyst, the N-phenylanthranilic acid complex of Rh(I) readily catalyzes the hydrogenation of benzene at 1 at  $\text{H}_2$  and room temperature.<sup>15-18</sup> We were able to verify the reported behavior, but this catalyst was not effective with coal. A more thorough study of this system obtained the same results.<sup>19</sup>

TABLE 2. Attempted Catalytic Hydrogenation of Unsaturated Compounds Using the Muetterties' Catalyst

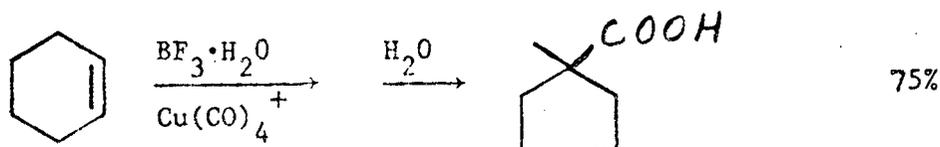
Compound	Solvent	Amount of Catalyst used (mg)	Temp°C	H <sub>2</sub> Pressure <sup>a</sup> psi	Rxn time h	Pressure drop, psi	Product <sup>b</sup> Yield (%)
Naphthalene (3.2g)	THF (50 ml)	250	21.5	45.8	96	4.6	55
Anthracene (1.9g)	THF (50 ml)	200	19	45.7	95	0.9	23
Phenanthrene (1.9g)	THF (50 ml)	400	24	44.7	98	2.0	42
Thiophene (4.9g)	THF (50 ml)	200	31	45.2	42	0	
Phenol (2.4g)	THF (50 ml)	200	21	45.2	72	0	
Pyrene (2.1g)	THF (50 ml)	350	26	45.0	46	0	
Benzofuran (2.2g)	THF (50 ml)	200	23	46.4	91	0	
Coal (Bruceton passed 300 mesh) (9.3g)	THF (90 ml)	900	24	25.2	168	0	
Coal Asphaltenes (Mobil) (3.9g)	THF	600	24	44.6	48	0	
Petroleum Asphaltenes (Exxon) (2.6g)	THF (50 ml)	800	19	45.2	71	0	
Methylated Coal Asphaltenes (Mobil, 2.2g)	THF (70 ml)	350	19	45.5	50	0	

<sup>a</sup> The final pressures of hydrogenation were connected for temperature change. <sup>b</sup> The yields were determined by comparison of the amount of hydrogenation substrate in solution before and after hydrogenation using gc.

## CARBONYLATION

One of the most efficient methods for converting coal to a soluble, easily handled material is Heredy-Neuworth depolymerization.<sup>20</sup> Formally, the reaction is the generation of a carbonium ion in the coal by protonation followed by attack on the ion by phenol resulting in cleavage of the methylene bridges which link the aromatic units in coal. The reaction is not commercially useful due to the high cost of phenol. However, if phenol could be replaced by a cheap reagent capable of trapping carbonium ions, the chemistry involved in Heredy-Neuworth depolymerization might form the basis of an economical liquefaction scheme.

An excellent cheap carbonium ion trap is carbon monoxide. Is it possible to cleave coal via carbonium ion processes and trap the carbonium ions with coal using CO? While our initial results were not favorable, we feel this idea is worth continued study and are trying a few other approaches. Our initial approach was an attempt to take advantage of some elegant carbonylation chemistry developed by Souma and Sano.<sup>21</sup> These workers showed that a variety of olefins could be carbonylated rapidly at room temperature using  $\text{Cu}(\text{CO})_4^+$  or  $\text{Au}(\text{CO})_2^+$  in  $\text{BF}_3 \cdot \text{H}_2\text{O}$ . Alkanes could be carbonylated



under the same conditions if some olefin was present. We sought to take advantage of the catalytic effect of the copper carbonyl and tried these reaction conditions on Bruceton coal. The results, while interesting, did not meet our original goals.

TABLE 3. Results of Carbonylation of Bruceton Coal

Bruceton Coal	Treated with $\text{BF}_3 \cdot \text{H}_2\text{O}$	Treated with $\text{BF}_3 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{CO})_4^+$	
% C	79.4	76.5	75.98
% H	5.4	5.3	4.9
% N	1.7	1.41	1.66
% O	8.4		
% S	0.9	0.73	0.70
Pyridine Extractability			
	21%	17%	12%

It is clear from the table that little depolymerization occurred. If it had, the pyridine extractability should have increased. It is interesting that treatment with  $\text{BF}_3 \cdot \text{H}_2\text{O}$  decreases the sulfur content somewhat. Since almost all the sulfur is organic, some sulfur removal reaction must be occurring. Its identity remains mysterious. The nmr of the pyridine soluble fraction of carbonylated coal contained peaks in the region where vinyl protons normally absorb. These peaks were not present in either the parent coal or in the coal treated with  $\text{BF}_3 \cdot \text{H}_2\text{O}$ . We have no explanation for their appearance.

## IONIC HYDROGENATION

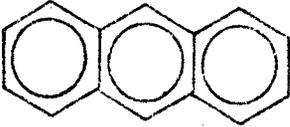
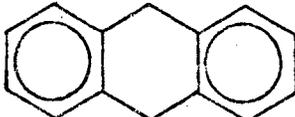
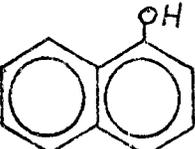
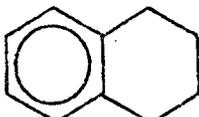
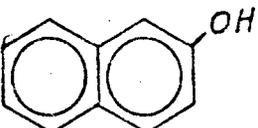
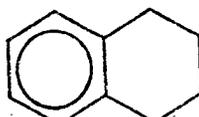
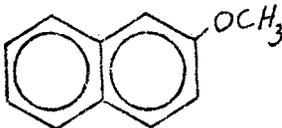
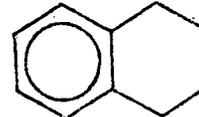
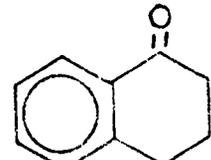
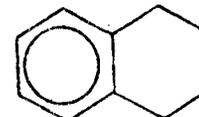
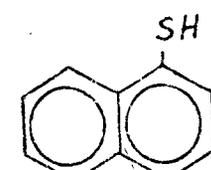
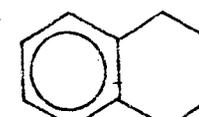
Intermolecular hydride transfer from a variety of compounds to carbonium ions is a well known, well studied reaction and has been reviewed.<sup>22</sup> A recently developed hydride transfer reduction has proven to be synthetically useful, principally for reducing ketones to alcohols.<sup>23</sup>



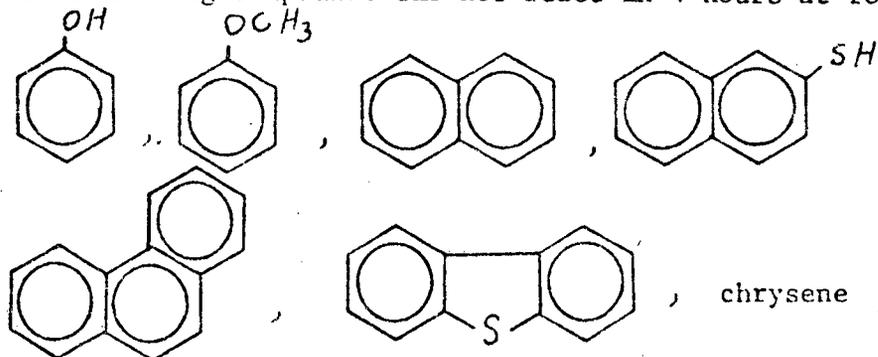
We have developed an extension of this reaction which is useful for reducing heteroatom substituted polycyclic aromatics and is capable of removing organic sulfur from coal. The reaction uses  $\text{BF}_3 \cdot \text{H}_2\text{O}$  as the acid and  $\text{Et}_3\text{SiH}$  as the hydride donor. The organic compound to be reduced is protonated by the  $\text{BF}_3 \cdot \text{H}_2\text{O}$  to give a carbonium ion which then hydride abstracts from the  $\text{Et}_3\text{SiH}$ . Thus, half of the hydrogen introduced comes from water and the other half from the hydride donor. Several examples of this reaction are given in the Table. All were carried out at  $25^\circ$  using  $\text{BF}_3 \cdot \text{H}_2\text{O}$  and  $\text{Et}_3\text{SH}$ . When a co-solvent was used it is indicated. The reaction mixture was extracted with carbon tetrachloride and yields were measured by nmr using the addition of a known amount of anisole to the  $\text{CCl}_4$  solution. No attempts have yet been made to maximise yields.

Table 4.

Ionic Reduction with  $\text{BF}_3 \cdot \text{H}_2\text{O}$  and  $\text{Et}_3\text{SiH}$  at  $25^\circ\text{C}$ 

Compound	Time (hrs)	Product	Yield (%)
	3		97
	2		76
	4		36
	4		49
	4		71
	4		12

The following compounds did not react in 4 hours at room temperature:



The results with several coals are shown in the next table.

Table 5. Ionic Hydrogenation of Coals and Asphaltenes With  $H_2O \cdot BF_3$  and  $Et_3SiH$

Coal (MAF)					Product				Pyridine Extractability	
%C	%H	%N	%S		%C	%H	%N	%S	Coal	Product
84.8	5.5	1.8	1.0	(Bruceton)	75.68	5.37	1.44	0.61	21	31
89.7	4.6	1.3	0.7	(Pocahontas)	72.04	4.13	0.85	0.77	3	16
72.3	4.4	1.0	1.5	(Lignite)	61.32	4.67	0.83	0.79	13	13
				Petroleum Asphaltene					pentane solubility unchanged	

There are two features of this reaction to which we wish to draw attention. One is that it is a very mild reduction of aromatics which should find synthetic utility. The other is that some sulfur is removed from coals under very mild conditions together with some conversion of bituminous coals. We are exploring the synthetic scope and utility of this reaction, exploring its application to coals, and looking for other, cheaper, hydride donors to replace triethylsilane.

## ALKYLATION USING METATHESIS CATALYSTS

Friedel Crafts alkylation of coals apparently causes a cross linking competitive with the alkylation.<sup>20</sup> We sought to avoid this by alkylating coal with an olefin in the presence of a metathesis catalyst prepared from  $WCl_6$  and  $EtAlCl_2$ . This catalyst is known to bring about the rapid alkylation and trans alkylation of aromatics.<sup>24</sup> The reaction was carried out on Bruceton coal. The pyridine extractability of the coal did not change. The sulfur content was reduced to 0.56% by an unknown mechanism. We feel this technique is worth further exploration.

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