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

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Technical Progress Report

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I. Catalyst Synthesis/Characterization

A. Fine-Particle Iron Sulfides

An investigation aimed at devising a procedure for preparing alkyl- or aryl-capped iron sulfide particles continues. An initial attempt to prepare fine-particle, aryl-capped iron sulfides (S-31) involved the competitive reaction of thiophenol (PhSH) and sodium sulfide (Na₂S) with Fe(II). The idea was that PhS⁻ would cap the growth of the iron sulfide particles formed by reaction of Fe(II) and S²⁻, and so by varying the ratio [PhSH]/[Na₂S] some size control of the iron sulfide particles prepared could be attained. However, SEM examination of the particles formed by this procedure indicated that no size control had been attained, and that the particles were relatively large (~1-10 micron). It was thought that the phenyl group of thiophenol was not bulky enough to prevent thiolate bridging and consequent particle size growth of the metal sulfide. So the bulkier thiol 1-adamantanethiol was synthesized and used in synthesis S-33 in the next attempt to prepare fine-particle, capped iron sulfides.

In S-33, a methanol/water solution of Fe(NH₄)₂(SO₄)₂·6H₂O was added with stirring to a solution containing NaSAda and Na₂S in methanol/water. The NaSAda solution was prepared from 1-adamantanethiol (HSAda) and sodium methoxide (NaOMe) in methanol/water. As in S-31, the ratio [RS⁻]/[S²⁻] was varied between 0 and 10 in preparations S-33A, B, and C. This procedure resulted in flocculated particles with little or no solubility in heptane, THF, or acetone. Some difficulty was encountered in getting all the reactants to dissolve in the same solvent solution, so different iron salts will be tried in future preparation attempts. Also, the reaction rates of S²⁻ and AdaS⁻ with Fe(II) may not be competitive at room temperature, so elevated temperatures will also be tried.

B. Bench-Top Reactor Tests

A series of tests has been run to examine possible interactions (e.g., metal-arene complex formation) between metal precursors and the model compound naphthyl bibenzyl methane (NBBM). The tests were performed using the ReactIR instrument,

which allows on-line IR spectra to be taken as the reactions are run. In test T-10, 0.2 g NBBM and 0.2 ml $\text{Fe}(\text{CO})_5$ were added to 50 ml heptane (deoxygenated by bubbling with N_2), which was then irradiated by a 100-Watt long-wave UV light. After 3 hours of irradiation, no significant difference was seen between the evolving spectra of the T-10 reaction solution and that of a blank run, T-12, which was run under identical conditions but without addition of NBBM. Thus the changes in the spectra could be attributed to conversion of $\text{Fe}(\text{CO})_5$ to $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$. It is possible that not enough UV light penetrated the reaction glassware to promote reaction (i.e., loss of sufficient CO) adequately, so the experiment was repeated using thermal activation in test T-14.

In test T-14, 0.2 g NBBM and 0.2 ml $\text{Fe}(\text{CO})_5$ were added to 50 ml heptane (deoxygenated by bubbling with N_2). The reaction mixture was then held at 80°C for 2.5 hrs, after which the temperature was raised to 90°C for an additional 2.5 hrs. No change in the spectrum of the reaction solution was noted over the course of the experiment.

In test T-15, the compound $\text{Fe}(\text{CO})_4\text{PPh}_3$ was used in place of $\text{Fe}(\text{CO})_5$. Thus, 0.2 g NBBM and 0.27 g $\text{Fe}(\text{CO})_4\text{PPh}_3$ were added to 45 ml heptane. The reaction solution was heated to 80°C for 3 hrs, followed by a 20 hr hold at 85°C . No significant change in the spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_3$ was observed, suggesting that no interactions between $\text{Fe}(\text{CO})_4\text{PPh}_3$ and NBBM were occurring.

The above tests seem to indicate that the iron precursors used are not reactive enough to interact with the weakly ligating aromatic p-systems of NBBM. To provide a more reactive iron carbonyl species, the compound benzylideneacetoneiron tricarbonyl ($\text{BDAFe}(\text{CO})_3$) has been prepared following the synthesis procedure of Brookhart et al¹, with slight modification. $\text{BDAFe}(\text{CO})_3$ is a source of the $\text{Fe}(\text{CO})_3$ moiety, which is often used to trap unstable 1,3-diene species. It may be possible to use $\text{BDAFe}(\text{CO})_3$ to ligate the naphthalene fragment of NBBM in an h^4 - fashion:

¹Charles R. Graham, Gary Scholes, and Maurice Brookhart, "Selective Trapping of Dienes by Benzylideneiron Tricarbonyl. Synthetic and Mechanistic Studies of the Reactions of 1,3,5-Cyclooctatriene and its Derivatives with Benzylideneacetone Tricarbonyl", *J. Am. Chem. Soc.*, **99**, 1180 (1977).

II. Catalyst Testing

A. Shaken Micro-Batch Reactors

Our recent model compound work has been confined to the reaction of dibenzyl ether in a hydrogen donating solvent (Tetralin). We are now expanding our scope to include a new model compound, naphthyl bibenzyl methane (NBBM) which has been examined in the literature as a model compound for the purpose of modeling coal liquefaction².

The model compound NBBM was also reacted thermally and in the presence of a catalyst precursor ($\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{CS}_2$ in this case), at a temperature of 420°C for 60 minutes. In this case, the conversion of NBBM was 10% without addition of the precursor, and 15% with the addition of the precursor. In subsequent reactions, however, it was found that at this high temperature (420°C), the walls of the stainless steel micro-batch reactor were being sulfided and that the iron sulfide derived from the catalyst precursor was also plating to the reactor walls. To avoid this problem our experimental procedure has been altered. The reactants are now sealed in a 1mL glass ampule, and the ampule is placed inside the steel micro-batch reactor and packed with glass wool. The reactor is shaken, as before, during reaction to effect good mixing and catalyst contact in the reaction mixture.

Employing this new experimental procedure, we have performed reactions with NBBM in the presence of our iron carbonyl based catalyst precursors. The results are listed in Tables 1 and 2.

Table 1

<u>Precursor</u>	<u>Conversion</u>
$\text{Fe}(\text{CO})_4\text{PPh}_3$	23.4
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	21.9
$\text{Fe}(\text{CO})_2(\text{PPh}_3)_3\text{CS}_2$	21.3

²Farcasiu, M., and Smith, C., "Modeling Coal Liquefaction. 1. Decomposition of 4-(1-Naphthylmethyl)bibenzyl Catalyzed by Carbon Black", *Energy and Fuels*, 5, 83-87 (1991).

The conversions and the relative yields of the products obtained for the three precursors are virtually the same, implying that the active species derived from the precursors are similar or identical species.

Table 2

Molar Product Yields (x100)

	$\text{Fe(CO)}_4\text{PPh}_3$	$\text{Fe(CO)}_3(\text{PPh}_3)_2$	$\text{Fe(CO)}_2(\text{PPh}_3)_2\text{CS}_2$
9.7	11.8	11.4
8.3	9.5	1.0
---	---	---
1.1	1.4	---
4.7	4.8	4.5
2.1	2.1	1.9
0.6	0.8	---
0.4	0.6	---
4.8	4.8	5.4
---	---	---
7.7	8.2	9.4
1.7	1.7	---

--- = below detection limits

The model compound NBBM was reacted thermally in an excess of 9,10-dihydrophenanthrene (DHP) at 420°C for times ranging from 15 to 150 minutes. A plot of NBBM conversion versus time is shown in Figure 1. When performing catalytic reactions with our iron carbonyl based precursors, we have been adding CS₂ as a sulfur source in order to form iron sulfides during the reaction. In order to understand the effect of the sulfur source itself on the reaction of NBBM we performed reactions involving NBBM in an excess of DHP in the presence of 50 microliters of CS₂ under the same temperature and time conditions. The conversion versus time data for this experiment is also summarized in Figure 1. In addition, similar experiments were performed involving NBBM in an excess of DHP with 50 microliters of CS₂ and 0.25 wt. % iron of the Fe(CO)₃(PPh₃)₂ precursor (with an excess of PPh₃). These results are also summarized in Figure 1.

Conversion versus Time for NBBM in 9,10-Dihydrophenanthrene

Figure 1: Conversion versus time for thermal, thermal + CS₂, and catalytic reaction of NBBM in an excess of DHP (10 mg NBBM, 325 mg DHP, 6 mg precursor, 6 mg PPh₃).

The results in Figure 1 show the thermal conversion of NBBM rising to approximately 60% after 150 minutes. The addition of CS₂ only does not show an effect on the conversion of NBBM. However,

when the precursor is added the conversion of NBBM is not enhanced. In fact, the conversion is suppressed. The selectivities from the thermal and catalytic reactions are shown in Figures 2 & 3. There are no large discrepancies between the selectivities of the two reactions except for the large amount of benzene formed in the catalytic case. This is, presumably, derived from the PPh_3 added to the reaction mixture for precursor stability.

Cumulative Yields for the Products of NBBM in DHP 420°C, No Catalyst

Figure 2: Cumulative yields of products for the thermal reaction of NBBM in an excess of DHP at 420°C.

Cumulative Yields for the Products of NBBM in DHP420°C, Fe(CO)₃(PPh₃)₂

Figure 3: Cumulative yields of products for the catalytic reaction of NBBM in an excess of DHP at 420°C (0.25 wt.% Fe of Fe(CO)₃(PPh₃)₂).

In future work, we plan to explore the reasons for the conversion suppression by the catalyst precursor. We are currently working on a mathematical model to describe the thermal reaction of NBBM. This model, in conjunction with the physical properties of the catalyst precursor and any suspected active species, will be used to attempt to explain this phenomenon, and hopefully predict the effect of other similar catalytic materials.

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