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NOVEL CATALYSTS FOR METHANE ACTIVATION

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SUMMARY

Fullerenes are a recently discovered allotrope of carbon that possess unusual properties, some of which may be ideal for methane activation. This project is designed to evaluate these carbon-based materials for conversion of methane into higher hydrocarbons. The project is divided into three technical tasks. Task 1 deals with synthesis and characterization of the fullerenes and fullerene soots, Task 2 with testing of the catalysts, and Task 3 with evaluation of the results and technical reporting. The results and accomplishments for this quarter are summarized below.

Task 1. Synthesis and Characterization of Fullerenes

- A lithium-doped soot was prepared.
- A palladium promoted soot was doped with potassium.
- A nickel promoted soot was doped with potassium.

Task 2. Testing of Catalysts

- K-doped soots of 6%, 12%, and 24% concentrations were compared to determine relative selectivities. The K-soots with higher K concentrations (12 and 24 wt%) were found to have higher activities and selectivities to C₂-C₄ hydrocarbons than either the 6% K-soot or the fullerene soot without potassium incorporation. The selectivities of all the K-soots were higher than the fullerene soot at a given conversion level.
- The Li-doped soot was tested for methane activation. The selectivity for C₂ hydrocarbons from the methane conversion catalyzed by this soot was found to be similar to that observed for the K-soot but had a slightly lower selectivity for C₃-C₄ hydrocarbons.
- The nickel and palladium promoted K-doped soots were tested. In each case, the selectivity for higher hydrocarbons was found to be higher than that for fullerene soot, but was lower than that for the K-soot without the metal.
- The palladium promoted K-doped soot was examined for methane activation in the presence of co-feeds of either ethane or ethylene and compared to the activity of the K-doped soot and fullerene soot. The ethylene co-feed was found to promote methane activation at lower temperatures and give higher selectivities when catalyzed by the palladium K-soot than observed under similar conditions with either K-soot or fullerene soot.

PROJECT OBJECTIVES

GENERAL OBJECTIVES

Methane is one of the most abundant sources of energy and is found naturally in underground reservoirs and as a by-product of indirect liquefaction processes. Although methane is useful as a fuel, it is not easily stored or transported, and for that reason, the efficient direct conversion of methane to higher hydrocarbons is essential to provide an economical alternative energy source. However, because the C-H bond of methane is stronger than that of the higher hydrocarbons, high pyrolytic temperatures are needed, and the products tend to rapidly polymerize to coke and unwanted hydrocarbons.^{1,2}

This project is designed to evaluate the feasibility of using fullerene materials as methane activation catalysts. Fullerenes are a new allotrope of carbon consisting of closed shells of sixty or more atoms.³ The full scope of the reactivity of these novel materials is not yet known. However, SRI and others have demonstrated that fullerenes have unique properties, including the ability to stabilize methyl radicals, shuttle H atoms, and act as electrophiles.^{4,5} Fullerenes have been found to act as "radical sponges" that readily accommodate organic radicals. Thus we expect that fullerenes or fullerene-based catalysts may be ideal for methane activation, and since these catalysts are easily produced in soot, they can potentially be inexpensive catalysts and make the direct conversion of methane into higher hydrocarbons inexpensive and environmentally sound.

In this project, novel fullerene-based catalysts are being synthesized and examined for their ability to convert methane into olefins and other higher hydrocarbons. They will be examined using a short-contact-time reactor to minimize any by-product formation due to free-radical polymerization reactions. The primary objectives of this project are to synthesize and examine the reactivities of fullerene-based catalysts and to develop an understanding of these catalysts in terms of hydrogen activation, polymerization of methane into higher hydrocarbons, and minimizing of coke formation.

PROJECT OBJECTIVES FOR THIS QUARTER

We had two objectives for this quarter. The first objective was to complete our study of the K-doped fullerene soots to include the selectivity of these materials as a function of methane

conversion. The second objective was to identify and evaluate other metal promoters, and the combination of transition and alkali metals to enhance the selectivity of the methane conversion process and hopefully reduce the temperature of reaction.

TASK 1: PREPARATION OF CATALYSTS

The objectives of this task are to synthesize and characterize fullerenes, fullerene soots, and catalysts based on these materials. One of the novelties of these fullerene preparations is that other atoms can be incorporated into the structure: inside the cage, outside the cage, or within the framework itself. During this quarter, we continued to study the effect of modifying a fullerene soot (from Terrasimco, Inc.) with various alkali metals and combinations of alkali and group 8 transition metals with the goal of achieving the selectivity found with the alkali metal, and the lower temperatures of reaction found with the transition metals.

PREPARATION OF METAL-MODIFIED FULLERENE SOOTS

During this quarter we prepared Li, K/Pd, and K/Ni containing soots. The Li containing soot was prepared in a manner similar to that of the K-soot as described in Quarterly Report 8. In this preparation, Li_2CO_3 (0.256 g) was dissolved in 100 mL of a water:methanol 9:1 mixture, and the solution slowly added to 4 g of fullerene soot with proper stirring. The solvents were evaporated under flowing nitrogen, and the product dried under vacuum to remove the residual solvent and leave the Li-doped soot. The concentration of the Li_2CO_3 was 6.4% which is equivalent on a molar basis to the 12% K_2CO_3 doped soot.

The K-doped palladium soot and K-doped nickel soot were prepared in a similar manner. The transition metal was added to the fullerene soot as a water:methanol solution of either PdCl_2 or $\text{Ni}(\text{NO}_3)_2$. The mixture was well stirred, and the solvent then evaporated and dried under vacuum. The metal soots were then subjected to reducing conditions under flowing hydrogen at 350°C for 12 hours. The metal content (Ni or Pd) of these reduced catalysts was formulated to be 1% by weight. The potassium carbonate was then added as described above and dried to give a 12% K_2CO_3 doped soot.

TASK 2: METHANE ACTIVATION

The objectives of this task are to evaluate and compare the soots and promoted soots for their reactivities, selectivities, and coking propensities during the methane activation experiment. The emphasis during this quarter was to explore the effect of alkali metals and combinations of the alkali metals and group 8 transition metals to enhance the selectivity of the soots towards higher hydrocarbons. The catalysts tested or compared during this quarter are listed in Table 1. Since the alkali metal reactions were found to require a period of activation, all experiments included a long duration run at 950°C until steady state was reached.

Table 1

SOOTS INVESTIGATED DURING THIS QUARTER

Catalyst	Description
Fullerene soot	Terrasimco fullerene soot
K-soot	Terrasimco fullerene soot doped with 6%, 12%, and 24% K_2CO_3
K-AB	Acetylene Black doped with 12% K_2CO_3
Li-soot	Terrasimco fullerene soot doped with 6.4% Li_2CO_3
Cs-soot	Terrasimco fullerene soot doped with 28.3 % Cs_2CO_3
K-doped palladium soot	1% Pd; 12% K_2CO_3
K-doped nickel soot	1% Ni; 12% K_2CO_3

K-soot studies

Last quarter we reported results on methane activation for Terrasimco fullerene soot with several potassium concentrations. However, at that time we were not able to report a good mass

balance due to problems with one of our gas chromatographs. This quarter we were able to obtain more complete data and the product selectivity could be obtained as a function of both temperature and conversion. Table 2 shows the activities and selectivities for the 6%, 12%, and 24% K doped soots for the methane activation experiment conducted at 950°C with methane flow rates of 150 mL/min. Noted in these figures is that the 12% and 24% K promoted soots are quite similar in reactivities and selectivities, and the 6% promoted soot gives is slightly more active but less selective. Note also that a comparison of the K doped acetylene black catalyst does not give such high selectivities.

Table 2. Effect of K loading on methane activation.^a

Catalyst	Selectivity			Conversion
	C2	C3-C4	Total Selectivity	
Fullerene Soot	20%	--	20%	6%
12% K-AB ^b	20%	--	20%	6%
6% K-Soot	35%	8%	43%	5%
12% K-Soot	58%	10%	68%	3%
24% K-Soot	50%	15%	65%	3%

^aReaction conditions, temperature 950°C, flow rate 150 mL/min.

^bPotassium doped acetylene black.

One of the advantages of the K-soot over the non-promoted soot is that we can conduct these experiments at higher temperatures to increase the conversions without excessive coking. Table 3 lists the results from experiments conducted at 1000°C as a function of flow rate. Note that at these higher temperatures, the selectivity is still quite high, and both the conversions and selectivities are higher for the K-doped soot than for the fullerene soot.

Table 3. Reactions of 12% K-soot on methane activation at 1000°C

Flow Rate	Selectivity			Conversion
	C2	C3-C4	Total Selectivity	
100 mL/min	32%	7%	39%	12%
150 mL/min	42%	13%	55%	7%
200 mL/min	48%	19%	67%	5.3%

Comparison of alkali metals on methane activation

Given the promising results with potassium, efforts were made this quarter to examine the effect of other alkali metals on methane activation. Mixtures of alkali carbonates mixed with carbon have been reported in literature to exhibit high reactivities for gasification reactions, and were reported to show the presence of free radicals when heated to high temperatures in helium.⁶ Among the alkali metal carbonates, the magnitude of the effect decreased in the following order: $\text{Cs}_2\text{CO}_3 > \text{Li}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{no additive}$. During this quarter we wanted to examine the effects of the most active of these alkali metals, Cs, Li, and K. Since the K-soot was found to require an activation period at 950°C, these alkali soots were tested at this temperature until a stable reactivity profile was observed. The amount of the alkali metals was adjusted so that they all had the same molar concentration and were the molar equivalent of the 12% K_2CO_3 doped soot (i.e. 0.87 mmoles alkali metal carbonate/gram of soot). The activities and selectivities of these materials are compared at 950°C in Table 4. The order of selectivity was found to be $\text{K} > \text{Li} \gg \text{Cs} > \text{no additive}$ while the activity was the reverse order. For instance, both the K and Li doped soots were extremely selective, and C2 selectivities were in the range of 50-60%. The K-soot exhibited C3 selectivities in the range of 10-15%, for a total of approximately 70% selectivity to higher hydrocarbons while the Li-soot was less selective towards C3-C4 higher hydrocarbons and only gave a selectivity of 5% towards the higher hydrocarbons, for a total of 55% C2-C3. In contrast, the Cs-doped soot gave only 35% C2 and an additional 5% C3-C4 hydrocarbons. In comparison, fullerene soot catalyzed reactions exhibited approximately 20% selectivity to C2 hydrocarbons, with essentially no C3-C4 hydrocarbons. In terms of total yield (selectivity x conversion) we find

fairly similar conversions for the alkali metal soots, with the order being Cs > Li > K >> no additive.

The interaction of the alkali metals with carbon materials and hydrocarbons at high temperatures is not clear, although it is obvious that at high temperatures the alkali carbonates can be reduced to the molecular element. Lithium can react with carbon or hydrogen to form stable carbides or hydrides (the hydride is stable to 900°C).⁶ Potassium and cesium can also react with carbon, but give non-stoichiometric interstitial compounds. There are several possible roles that the alkali metals may provide to increase the selectivity in the methane activation experiment. One possibility is that these metals form free radicals at these high temperatures causing the increase in selectivity to higher hydrocarbons. Alternatively, they may provide a similar role to that found in Fischer-Tropsch chemistry, or in the examples of two-stage methane activation, where metal carbides, or some sort of carbanaceous species, react with hydrogen and/or C1 species to form higher hydrocarbons.⁷⁻¹⁰

Table 4. Reactivity of alkali-soots for methane activation at 950°C.^a

Catalyst	Selectivity			Conversion
	C2	C3-C4	Total Selectivity	
Fullerene Soot	20%	--	20%	6 %
K-Soot	58%	10%	68%	3 %
Li-Soot	50%	5%	55%	4 %
Cs-Soot	35%	5%	40%	6%

^aMethane flow rate 150 mL/min.

Effect of K on transition metal promoted soots

We have seen that the presence of potassium increases the selectivity to higher hydrocarbons, while at the same time group 8 metals are well known to facilitate the activation of C-H bonds at moderate temperatures.^{11,12} Therefore we conducted several experiments where we

modified metal promoted soots with potassium so that we could determine if any synergetic effects could be found. Table 5 shows the effect of the potassium on a Ni and Pd promoted soot. In previous experiments we found that the Ni-soot exhibited similar activity to that of fullerene-soot while Pd-soot was very active towards methane conversion, but produced considerable amounts of carbon and hydrogen, but very little higher hydrocarbons. As seen in this table, the K-Ni-soot gives similar reactivity to that of the fullerene-soot, although with increased C3-C4 yields, and the K-Pd-soot gives both poorer reactivity and poorer selectivity to higher hydrocarbons than the fullerene-soot.

Table 5. Reactivity of metal soot catalysts on methane activation at 950°C.^a

Catalyst	Selectivity			Conversion
	C2	C3-C4	Total Selectivity	
Fullerene Soot	20%	--	20%	6 %
K-Soot	58%	10%	68%	3 %
K-Ni-Soot	18%	4%	22%	8 %
K-Pd-Soot	3%	1%	4%	5%

^aMethane flow rate 150 mL/min.

Effect of co-feeds on methane activation.

One method that has been discussed in literature to further increase yields and lower the temperature threshold of the methane activation experiment, is to use a co-feed of ethylene.¹³⁻¹⁶ However under the literature conditions, the overall conversion is too low to be of economical significance, and at the higher temperatures required to increase the conversion, the ethylene undergoes substantial decomposition. We hoped that some of our catalysts would be more active under these co-feed conditions. During this quarter we compared fullerene soot, K-soot, and K-Pd-soot under ethylene co-feed conditions. For these experiments, we used a co-feed of 10% ethylene and a temperature regime of 500°C to 900°C. The results from these experiments are listed in Table 6. The C2, C3, and C4 columns list the % increase or decrease of the respective

gases found in the product stream. Column 6 refers to the percentage methane that has been converted, while the last column lists the selectivity of higher hydrocarbon formation based on the methane conversion. In cases where there is a loss of ethylene feed, the loss in ethylene is subtracted from the higher hydrocarbon formation, and if the value is negative, the selectivity is simply stated as zero. As seen in this table, the fullerene soot itself rapidly destroys the ethylene at temperatures of 600°C and above, and gives no increase in hydrocarbon formation under these conditions. The K-soot behaves somewhat differently, in that loss of ethylene is insignificant until temperatures of 800°C are reached, but at the same time produces C3 and C4 hydrocarbons so the selectivity to higher hydrocarbons is as high as 60% at these temperatures. However, the conversion is only 0.3% under these conditions. In contrast, the Pd-K-soot catalyzed reaction shows methane conversion of 1.2% at temperatures as low as 500°C, with essentially 100% selectivity. At 700°C conversions as high as 2.15% and selectivities of 88% are achieved. Above these temperatures the conversion increases further, but the selectivity drops down to negative values. Thus we see that although these may not be the optimal catalysts or reaction conditions, co-feeds can be used to enhance the selectivities and activities, and exhibit methane activation at low temperatures with high selectivities.

Table 6. Effect of 10% ethylene co-feed on methane activation. Flow rate 100 mL/min

Catalyst	Temperature	C2 ^a	C3	C4	Conv	Select (%)
Soot	500	0	0	0	0	0
	600	-0.25	0	0	0	0
	700	-1.2	0	0	0	0
	800	-3.1	0	0	1.5	0
K-Soot	500	0	0	0	0	0
	600	0	0	0	0	0
	700	0	0.1	0.03	trace	100
	800	-1.5	0.7	0.3	0.3	100
	850	-3.5	0.8	0.3	1	0
Pd-K-Soot	500	0.6	0	0	1.2	100
	600	0.6	0	0	1.3	92
	700	0.95	0	0	2.15	88
	800	-1.4	0	0	3.5	0

^aC2 values refer to amounts above or below the initial ethylene co-feed.

Conclusions

Our efforts during this quarter were to investigate promoters and initiators to decrease the temperature threshold of the methane activation step and increase the selectivity to higher hydrocarbons. Of the 3 alkali metals tested this quarter, Li and K proved to be most useful in improving the selectivity of reaction to higher hydrocarbons. The use of C₂ hydrocarbons as initiators gave variable results. With the K-soot was able to increase the yield to C₃-C₄ hydrocarbons; however, the net selectivity was not improved due to concurrent decomposition reactions at the higher temperatures. However, in the case of K-Pd-soot we were able to reduce the threshold temperature to as low as 500°C and give high selectivities, so there can be a potential for this method. However, at this time, we need to continue our screening efforts to determine which types of catalysts are the most promising for the methane activation. From the results so far, it appears that the promoters that can react with methane to form carbanaceous species give better selectivities to the higher hydrocarbons. For instance, nickel can react with methane to form nickel carbide while palladium does not form carbides, and nickel is found to give better conversions to higher hydrocarbons than does palladium (unless potassium is added as a co-promoter). This result is consistent with chain growth tendencies for Fischer-Tropsch reactions with these two metals. We are not sure at this time if such an explanation also applies to the alkali metals. Next quarter we will investigate other metals with emphasis on Fischer-Tropsch catalysts such as cobalt.

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