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Final Report - 11 June 1996

NOVEL CATALYSTS FOR METHANE ACTIVATION

By: A. S. Hirschon, Senior Research Chemist
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Chemistry and Chemical Engineering Laboratory

Prepared for:

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

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EXECUTIVE SUMMARY

This final report summarizes the results of our research under Contract No. DE-AC22-92PC92112, Novel Catalysts for Methane Activation. In this research we prepared and tested fullerene soots for converting methane into higher hydrocarbons. We conducted the methane conversions using dehydrocoupling conditions, primarily in the temperature regimes of 600°-1000°C and atmospheric pressures. The research was divided into three sections. The first section focused on comparing fullerene soots with other forms of carbon such as acetylene black and Norit-A. We found that the fullerene soot was indeed more reactive than the other forms of carbon. However, due to its high reactivity, it was not selective. The second section focused on the effect of metals on the reactivity of the soots, including both transition metals and alkali metals. We found that potassium could enhance the selectivities of fullerene soot to higher hydrocarbons, but the effect was unique to fullerene soot and did not improve the performance of other forms of carbon. The third part focused on the use of co-feeds for methane activation to enhance the selectivities and lower the temperature threshold of methane activation. The principal findings of this project are summarized below and in the Appendix.

- Fullerene soot can promote methane conversion at temperatures more than 200°C lower than other carbons.
- Addition of certain transition metals to the fullerene soot increased both the activities and selectivities for methane conversion to C2 hydrocarbons.
- Alkali metals, particularly potassium, increased the C2-C4 hydrocarbon formation and increased the ability of the soot to promote dehydrogenation reactions.
- Co-feeds of ethylene decreased the temperature threshold for methane activation when fullerene soot was doped with certain combinations of alkali and transition metals.
- These fullerene-based catalysts allow us to significantly lower the temperature threshold for methane activation. However, the conversions are limited by secondary reactions. Proper reactor configuration will be essential for practical use of these fullerene-based catalysts.

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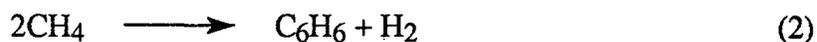
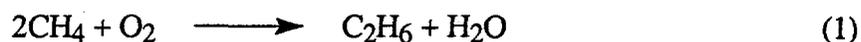
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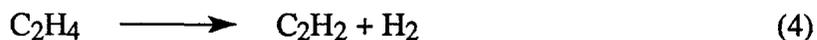
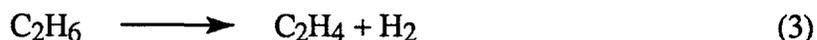
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INTRODUCTION

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 and direct conversion of methane to higher hydrocarbons is essential to provide an economical alternative energy source. Two possibilities exist for dehydrocoupling of methane to higher hydrocarbons: oxidative coupling to ethane/ethylene and water (equation 1) and thermal dehydrocoupling to produce higher hydrocarbons and hydrogen (equation 2).



The primary difficulty with conversion of methane to more useful products is of strong C-H bonds (BDE = 105.1 kcal/mole¹). Other hydrocarbons and particularly the desirable products of methane activation have weaker C-H bonds and therefore react more quickly (for example, the C-H BDE of ethane = 98.2). Thus at the high pyrolytic temperatures needed to activate the methane, the products tend to rapidly dehydrogenate and polymerize to coke and unwanted hydrocarbons (equations 3-5).^{2,3}



Although oxidative methods are facile, the over oxidation to CO₂ makes the process inefficient and increases environmental problems such as the greenhouse effect.

The purpose of this project was to use fullerene soots to overcome these problems and make these pyrolysis reactions more economically feasible for direct conversion of methane into higher hydrocarbons. The use of carbon materials for methane pyrolysis has already been demonstrated. For instance, the use of carbon fibers as catalysts was found to increase the

selectivity to ethylenes and decrease coke formation.⁴ Unlike other forms of carbon, fullerenes are soluble in solvents like benzene and toluene. All carbon atoms in fullerenes are sp^2 and form a three-dimensional fully conjugated system. The full scope of the reactivity of these novel materials is not yet known, but they have been shown to have many intriguing properties. For instance, SRI and others have demonstrated that fullerenes can stabilize methyl radicals, shuttle H atoms, and act as electrophiles.⁵⁻⁸ Fullerenes have been found to act as "radical sponges" that readily accommodate organic radicals. Because methyl radicals are generated during the methane activation process, we expected fullerenes or fullerene-based catalysts to be ideal for methane activation.

The key structural feature that gives fullerenes many of its characteristics is the presence of a pentagon surrounded by hexagons. When radicals are added to the fullerenes, this combination of pentagons and hexagons results in stable aromatic resonance structures. The fullerene soot formed during the arc process is thought to result from carbon clusters that did not close on themselves completely and hence went on to combine with other such clusters with dangling bonds. Thus the fullerene soot will most likely contain pentagons in a hexagonal lattice, and these sites will give the soot the desired chemical attributes of strong electrophilic nature and an ability to stabilize the radicals necessary for methane activation. Economic analyses suggest that this fullerene soot, when produced on large scale, could be an inexpensive catalyst support. Therefore, we are investigating this material for several types of reactions including methane activation.

OBJECTIVES

Fullerene-based catalysts were synthesized and examined for their ability to convert methane into olefins and other higher hydrocarbons. They were 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 were 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. Task 1 dealt with synthesis and characterization of the fullerenes and fullerene soots, and Task 2 dealt with testing of the catalysts. The objectives of the individual technical tasks are described below.

Task 1: Synthesis and Characterization of Fullerenes

The objectives of this task were (1) to prepare and modify fullerene soots so that we could compare the effects of the soluble fullerenes (i.e., C₆₀, C₇₀) and the effects of variations of surface areas on the reactivities of the soots and (2) to prepare fullerene soots with promoters, including transition metals known for their methane activation abilities as well as alkali metals known for their ability to alter selectivities during hydrocarbon conversions.

Task 2. Testing of Catalysts

In this task we tested the various fullerene-based catalysts and compared them for their abilities to convert methane to higher hydrocarbons. The objectives were (1) to compare various forms of fullerene soots with other forms of carbon for their relative methane activation abilities, (2) to test soots promoted with various transition metal and alkali metals to determine their relative effects on methane conversion, and (3) to determine the effect of co-feeds such as hydrogen and ethylene on the performance of the various catalysts.

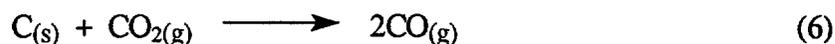
TASK 1: SYNTHESIS AND CHARACTERIZATION OF FULLERENES

Fullerene soot contains 10%-20% soluble fullerenes such as C₆₀ and C₇₀. The insoluble portion of the soot is believed to consist of either larger fullerenes or cross-linked, smaller, imperfect fullerenes. Thus the soot itself may also present a unique fullerene-like surface and hence may have properties similar to fullerene itself, in particular, the ability to stabilize radicals. In this task we prepared various modifications of this fullerene soot to compare the effects of surface area and soluble fullerene content. In addition, metals may behave in a unique manner once they are either bound or close to the fullerene-type surface of the soot. For instance, methyl radicals, produced at the active metal site, may spill-over to the fullerene surface where they will reside long enough to encounter other methane (or methyls) and be converted to higher hydrocarbons. Alternatively, the metals may react with the hydrogen liberated during the methane activation process and provide a partial pressure of hydrogen to prevent the activated methane from coking during the conversion process. Thus there are many rationales for the use of fullerenes and fullerenes containing metals, and we therefore prepared soots or fullerenes that contained various types of metals to compare their effects on methane activation. The details of preparing these catalysts are described below. Their respective performance for methane activation is described in Task 2.

PREPARATION OF FULLERENES AND FULLERENE SOOTS

Many laboratories including SRI have been developing large-scale syntheses of fullerenes. Typical methods for producing fullerene soot include passing a high voltage through carbon electrodes and laser pyrolysis of carbon in an inert atmosphere to form a soot containing 10%-20% of C₆₀ (buckminsterfullerene) with small amounts of the 70 carbon fullerene (C₇₀). SRI synthesizes the fullerenes and fullerene soot by the method of Krätschmer et al.,⁹ and the soot generally contains about 15% C₆₀. Pure C₆₀ is readily obtained by chromatography, although for the methane activation work, the soot itself is used as a catalyst material. However, for this project it was more cost efficient to purchase the fullerene soot or fullerenes from companies producing these materials in large scale and use our synthesis apparatus to prepare specialty soots such as those that contain metals or carbon nanotubes.

Fullerene soot was modified in three ways to test the effect of variations in surface area and soluble fullerene content on performance during the methane activation experiments. The first modification was to treat the soot with toluene to remove the soluble fullerenes (i.e., C₆₀ and C₇₀) to produce an extracted (or C₆₀/C₇₀ depleted) soot. This extracted soot has a slightly higher surface area and more open structure than the original soot. The second modification was to add C₆₀ to an extracted soot. The third modification was to treat the soot with carbon dioxide as described by Tsang et al. to produce a high surface area soot.^{10,11} In this method, the soot is oxidized with carbon dioxide at 850°C as shown in Equation 6.



This reverse Boudouard reaction has an equilibrium constant of 1.76 at these reaction temperatures so it is a facile reaction. The final product is reported to give a microporous carbon with a high surface area and a fullerene type structure that is inert to further oxidation by carbon dioxide. Thus this material is of high interest for this methane activation project and other possible applications, since it has high surface area and may behave similarly to the extractable fullerenes.

The details of the modifications of the fullerene soots and their resultant physical properties are described below.

Extracted or C₆₀/C₇₀ Depleted Soots

An example of the preparation of an extracted soot is as follows: Under nitrogen, 3.00 g of the fullerene soot was stirred with 500 mL of toluene at room temperature for 24 hours. The mixture was then filtered and dried at 60°C for 24 hours to yield 2.51 g of extracted soot, or a loss of 16.3% of extractable material. Since the extraction process can alter the pore structure of the soot, a C₆₀/C₇₀ depleted soot was also prepared by subliming the volatile fullerenes from the fullerene soot under 25 mL/min of flowing helium at 850°C for 5 hours. The soot exhibited a weight loss of 16%.

Reconstituted Fullerene Soot

Under nitrogen, C₆₀ was added to a sample of the extracted soot by dissolving C₆₀ (0.12 g) in 100 mL of toluene and adding the solution to 1 g of extracted soot. The mixture was stirred for 24 hours, and the toluene removed under vacuum to produce the reconstituted fullerene soot.

CO₂ Modified Soot

The fullerene soot was treated with carbon dioxide by suspending the soot on a fritted disc in an upflow quartz reactor heated in a tube furnace. The soot was then treated with carbon dioxide (20 mL/min) and the reactor was heated at 850°C for 5 hours. The weight loss during the CO₂-activation was 20.3 wt%. A sample of the activated fullerene soot was subjected to a toluene extraction experiment to analyze for C₆₀/C₇₀; however, no soluble fullerenes were observed. The nitrogen BET surface area of the product was approximately 600 m²/g. Similar results were obtained when extracted soot was subjected to the CO₂ treatment.

PREPARATION OF FULLERENES AND FULLERENE SOOTS CONTAINING METAL

We prepared three classes of fullerenes or fullerene soots containing metal. The first class incorporated the metal directly during the synthesis of the soot during the arc process. The feasibility of this process depends upon the choice of metal substrate and its volatility under the reaction conditions. A wide range of metal contents were achieved and a wide range of particle sizes. Metal fullerenes were also made is the direct derivatization of the fullerenes by transmetalation reactions such as with metal allyls shown in Equation seven. Methods such as reactions of the metal allyls or carbonyls have been shown to react with fullerenes (Equation 7).¹²⁻¹³



R = Alkyl, CO, PR₃, etc.
M = Pt, Ni etc.

This type of method would allow the metal to be added on a molecular scale. However, this method would be used only after the optimal metals are determined during the screening tests. Due to lack of time and money, the first two classes were not tested for methane activation.

The majority of the efforts to produce fullerene soots containing metal involved conventional incipient wetness methods, where metal salts were added to the soot, and then reduced to their elemental forms. Examples of the synthesis methods for these three types of catalysts are described below.

Preparation of Metallized Soots by Arc-Method

The preparation of metallized soots by the arc-method is similar to that used for production of normal fullerene soot with graphite electrodes. In a typical example, a hole is drilled through the graphite anode and the reactor electrode's hole is packed with the metal of interest or, in case the metal is very volatile, with a suitably refractory compound like the carbide or oxide. After the rods are packed, the ends are capped with a plug of graphite. A graphite rod is used as the stationary cathode.

During the run the gap between the electrodes was maintained between 5 and 8 mm; the current varied between 125 and 150 A, and the potential difference was about 30 V. The yield of extractable fullerenes under these conditions is generally low (1%-2%), mainly because of the presence of oxygen. Using this setup, we prepared metallized soot from the first row transition metals, including Ni, Fe, Cu, Cr, V and Mn.

The metal content was determined by oxidizing the soot using a thermogravimetric analysis (TGA) and recording the remaining ash (metal oxide). The soot was oxidized in synthetic air using a temperature ramp of 10°C/min from room temperature to 1000°C with a hold time of 60 minutes at 750°C to ensure a controlled and complete oxidation. Table 1 lists the ash contents for these soots as determined by this method. Assuming the state of the metal as listed in this table, the final Wt% of the metal was determined to range from 10.6% for V to 18.1% for Ni, or at.% of 2.7% to 4.3%, respectively.

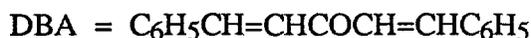
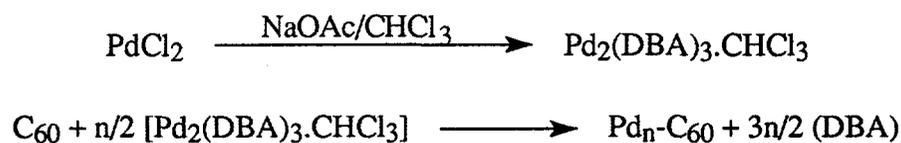
Table 1
TGA ANALYSES OF METALLIZED SOOTS

Metal	At. Wt	Oxide (valency)	Mol Wt	Residue, Wt%	Wt %	At %
V	50.9	5	181.8	18.9	10.6	2.7
Cr	52.0	3	152.0	20.3	13.9	3.6
Fe	55.9	3	159.7	17.1	12.0	2.8
Ni	58.7	4	90.7	27.9	18.1	4.3
Cu	63.5	2	79.5	20.3	16.2	3.5

Preparation of Fullerene Metal Complexes

Fullerene complexes of nickel and palladium were prepared. Both these metals have been investigated for methane activation and have been reported to complex with fullerenes. These preparations are described below.

Preparation of Pd-C₆₀ Complex. The Pd-C₆₀ complex by the method of Nagashima et al.¹⁴ was chosen because it is known to cleave C-H bonds in a facile manner,¹⁵ and this particular preparation yields a Pd-C₆₀ complex with no ligands other than C₆₀ itself. In this preparation, a solution of Pd dibenzylideneacetone (prepared by the method of Ukai and Kwazura¹⁶) is mixed with a solution of C₆₀ to give oligomers (Scheme 1). Excess of C₆₀ does not appear to give simple dimers, but rather an apparent oligomer with a 1:1 ratio of Pd to C₆₀.



Scheme 1. Preparation of Pd-C₆₀

We prepared complexes using Pd:fullerene ratios of 2:1 and 4:1. These materials are insoluble and difficult to characterize; however, we were able to subject them to analysis using SRI's surface analysis by laser ionization (SALI) instrument. Although they were found to form considerable amount of fragmentation during the analysis, we found mass spectral evidence of Pd-C₆₀ for the 4:1 product, and both Pd-C₆₀ and Pd-(C₆₀)₂ for the 2:1 product. Thus we confirmed that we indeed have a Pd-C₆₀ complex; however, the fact that the dimer fragment was found for the 2:1 product and not for the 4:1 product was unexpected.

Preparation of [(Et₃P)₂Ni]₆η²C₆₀. The nickel C₆₀ complex was synthesized by the method of Fagan et al.¹³ In this preparation, tetrakis(triethyl)phosphine nickel(0) was prepared by the method of Schunn¹⁷ from nickel cyclooctadiene (Equation 8).



Under nitrogen, the nickel phosphine complex (0.6 g, 6 equiv.) was dissolved in 10 mL of toluene and mixed with a toluene solution of C₆₀ (0.1 g, 1 equivalent), as shown in Equation 9.



The toluene was evaporated to produce the red-brown product. The nickel is thought to be bound to the C_{60} through the double bond-like structure of the fullerene, in much the same way that the metal would bind with an olefin.

Preparation of Fullerene Catalysts by Incipient Wetness Techniques

Various alkali, alkaline earth, lanthanide, and transition metals were added to the fullerene soots by impregnation with respective metal salts and tested in Task 2 for methane activation to determine their relative effects on the performance of the soot for methane activation. General procedures for preparing these catalysts are described below.

Preparation of Fullerene Soots Doped with Transition Metals. Fullerene soots doped with transition metals were prepared using the method of Domingo-Garcia et al.¹⁸ and Prado-Burguete et al.¹⁹ In a typical example, the desired amount of metal salt (i.e., 0.035 g PdCl_2) was dissolved in 10 mL of a toluene/ethanol 4:1 mixture, and this solution was slowly added to 2 g of fullerene soot. The mixture was stirred, and the solvents were evaporated under flowing nitrogen and then dried under vacuum to remove the residual solvent to give a Pd-doped soot with approximately 1% metal loading. By similar methods, we obtained soots doped with Ni, Pd, Pt, Ru, V, Cr, Mn, Fe, Co, and Ni. The Pd, Pt, and Ru metals were in the chloride form, the Ni and Co were used as the nitrates, and the rest were the acetylacetonates. The solvents were adjusted as necessary due to the solubilities of the respective metal salts. The metallized soots were reduced under flowing hydrogen at 300°C before testing.

Preparation of Fullerene Soots Doped with Nontransition Metals. The desired amount of alkali metal carbonate was dissolved in 100 mL of a water:methanol 9:1 mixture. This solution was then slowly added to approximately 4 g of fullerene soot. The mixture was stirred for 24 hours and then warmed to approximately 50°C and dried under flowing nitrogen. The soot was then dried further under vacuum at 76°C to yield the alkali doped soot. We prepared K-soot with concentrations of 6%, 12%, and 24% K_2CO_3 , which correspond to 3.4, 6.8%, and 13.6% K metal loading, respectively. We also prepared Cs and Li-doped soots to see whether other alkali metals have a similar effect on the catalytic activity of the soot (the concentration of these metals was adjusted to be equivalent to the 12% K_2CO_3 loading on a molar basis). Ca and La doped soots were prepared in a similar manner, with metal loadings of 1% and 5%, respectively.

TASK 2: TESTING OF CATALYSTS

The objective of this task was to evaluate and compare the fullerene-based catalysts for conversion of methane into higher hydrocarbons. Thermal dehydrocoupling rather than oxidative conditions were used because of the nature of the carbon support. The experiments were run in the temperature regimes of 600°C to 1000°C and at atmospheric pressures. We found that the fullerene soots were active under these conditions for methane activation. Addition of transition metals promoted these reactions even at lower temperatures, but required higher temperatures to produce significant amounts of upgrading activities. For most experiments, we chose 950°C as the optimal temperature to compare our catalysts.

The following four sections summarize the results from the fullerene catalysts for methane activation. The first section describes the reactor. Since the products derived from the methane are more reactive than methane itself, they must be removed from the high temperature reactor as quickly as possible. Thus a short contact time reactor is essential for reducing further reactions and coke formation.

The second section compares the reactivity of fullerene soots with other forms of carbon and with an uncatalyzed/thermal methane activation process. These carbon-based materials were compared as a function of temperature, contact time, and hydrogen co-feeds. All these parameters have been shown to affect the methane conversion process. The objective of this comparison was to determine if the fullerene-based materials do indeed have any unique reactivities compared with other forms of carbon.

The third part of this task involved testing the effects of metals on the soot with the goal of using the metals to activate the methane at reduced temperatures under conditions such that the fullerene structures can direct these activated methyl radicals to couple into higher hydrocarbons. The last section describes our efforts to test the most active fullerene catalysts with co-feeds of ethane or ethylene to lower the threshold of methane activation and to react with methane radicals to give higher activity during the methane conversion process. Due to the enormous scope of possible variations and methods of preparations for these new materials, we were able to make or screen only some of these possibilities; thus further work would be required to optimize and realize the full potential of these materials for methane activation or other hydrocarbon processing.

REACTOR CONFIGURATION

Many elaborate reactor configurations are found in literature or could be envisioned for methane conversion. However, for our project where we desired a rapid screening apparatus, we chose to use a simple configuration using a high temperature furnace with a very short heating zone to minimize the contact time at high temperatures. Flow controllers were used to control the flow rates of methane and other gases such as hydrogen or diluent gases such as helium. The catalyst (approximately 1.5 g) was supported on a fritted disk in a quartz reactor which was placed within a set of furnaces placed in tandem.

The methane was first preheated in the lower furnace (at 600°C) and then passed into the high temperature furnace (which heats the catalyst bed). For reactions conducted at temperatures lower than 600°C, the preheating furnace was adjusted accordingly. The high temperature furnace contains a short heating zone (4 inches) which leads to a cool quenching zone to minimize any possible thermal reactions after conversion. The gaseous products were analyzed using a Carle 500 gas chromatograph equipped with a thermal conductivity detector. Argon (7 vol%) was used in the methane gas stream as an internal standard. Higher hydrocarbons were determined using a HP 5890 gas chromatograph equipped with a flame ionization detector. We found that the temperature ranges of 600° to 1000°C were satisfactory, with most experiments conducted at 950°C.

COMPARISON OF SOOTS AND OTHER CARBONS

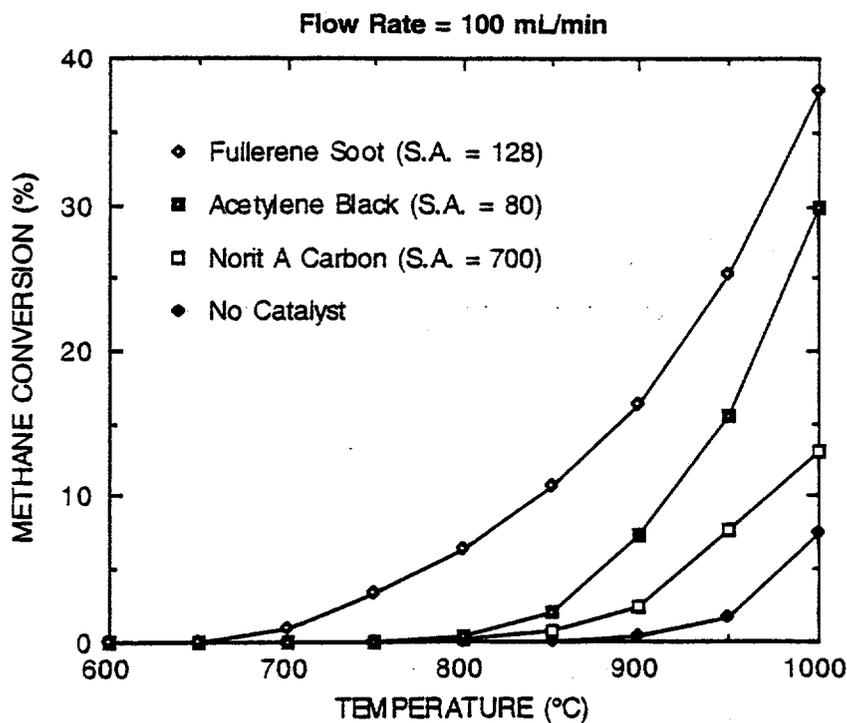
The first priority of our work was to determine if the fullerene soots did indeed exhibit any enhanced activities or selectivities over other carbon materials or a simple thermal conversion of methane. Figure 1 compares various carbons for the methane conversion process. As seen in this figure, the onset of the methane activation in the absence of any catalyst was found to occur at 900°C, while the onset was observed to be approximately 800°C in the presence of the acetylene black and Norit-A carbons, and as low as 600°C in the presence of the fullerene soot. The acetylene black has a lower surface area than the fullerene soot, whereas the Norit-A has a higher surface area. Thus the fullerenes are more active for methane activation and the increased reactivity cannot be attributed to differences in surface areas. The activity of the soot was found to be reproducible and did not vary at temperatures up to 900°C. Soots obtained from several commercial sources were also examined, and although some differences in reactivity were found, all these fullerene soots were found to be active for methane activation at temperatures as low as 600°C.

After reaction a sample of the fullerene soot was analyzed using a surface analysis by laser ionization (SALI) instrument. In this technique, surface species are desorbed by an IR laser, and the neutrals are then photoionized using a vacuum UV laser (118 nm). The single-ion photoionization eliminates fragmentation of the resulting ion and thus gives a true molecular weight distribution of the desorbed species.

As shown in Figure 2, analysis shows evidence of masses due to C_{60} , as well as masses due to methylated derivatives, $C_{60}(CH_3)_n$. These results suggest that the methane activation occurs on the surface of the soot, although we cannot rule out concurrent gas phase reactions. The fullerene soot that remains at the end of the methane activation experiments does not contain any extractable fullerenes. However, the fact that we see C_{60} and methylated C_{60} species in the SALI experiments suggests that there are indeed C_{60} fragments within the soot, and the presence of methylated or ethylated C_{60} fragments suggests that these fullerenes are involved in the methane activation step.

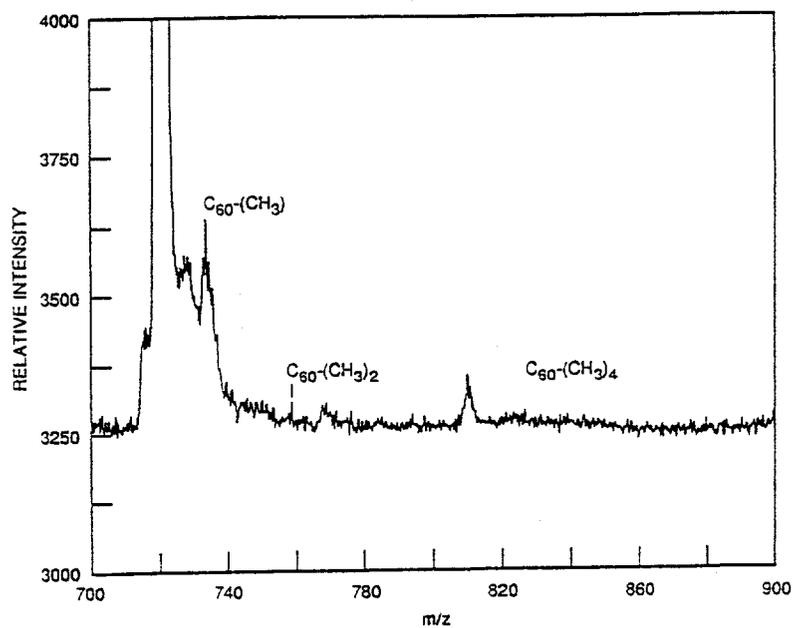
Figure 3 compares the effect of methane flow rate on the product selectivity for the thermal reaction and the fullerene-soot catalyzed reaction at $950^\circ C$. For the soot reaction, the only hydrocarbon products observed were C_2 gases, while for the thermal methane conversion, tars and condensables were also observed. Also, an increased flow rate decreased the yield of C_2 gases for the thermal reaction, while the higher flow rate increased the C_2 production in the soot-catalyzed case. These results are consistent with the fullerene soot not only being active for methane conversion, but also being active for later reactions of the products such as ethane and ethylene. For instance, the fullerene soot facilitates the conversion of methane to ethylene, but at the same time it enhances dehydrogenation reactions (Equations 4-5), giving lower C_2 yields at the lower flow rates. Thus a short contact time reactor or a low temperature catalyst is essential to avoid these secondary reactions that lead to coke.

We prepared and tested several forms of soot designed to vary surface areas and soluble fullerene content. Figure 4 shows the relative activities and selectivities of these fullerene soots. Included in this comparison are a fullerene soot, an extracted soot, a CO_2 activated soot, and a reconstituted soot. The CO_2 -activation increased the surface area of the fullerene soots from $128\text{ m}^2/\text{g}$ to over $600\text{ m}^2/\text{g}$. The extraction process removes the soluble fullerenes like C_{60} and C_{70} , allowing us to observe the reactivity of the residual soot. Although this process removes the soluble fullerenes, it also may change the physical properties of the fullerene soot. For instance, the surface area of the material increases from approximately $125\text{ m}^2/\text{g}$ to $185\text{ m}^2/\text{g}$; thus it does



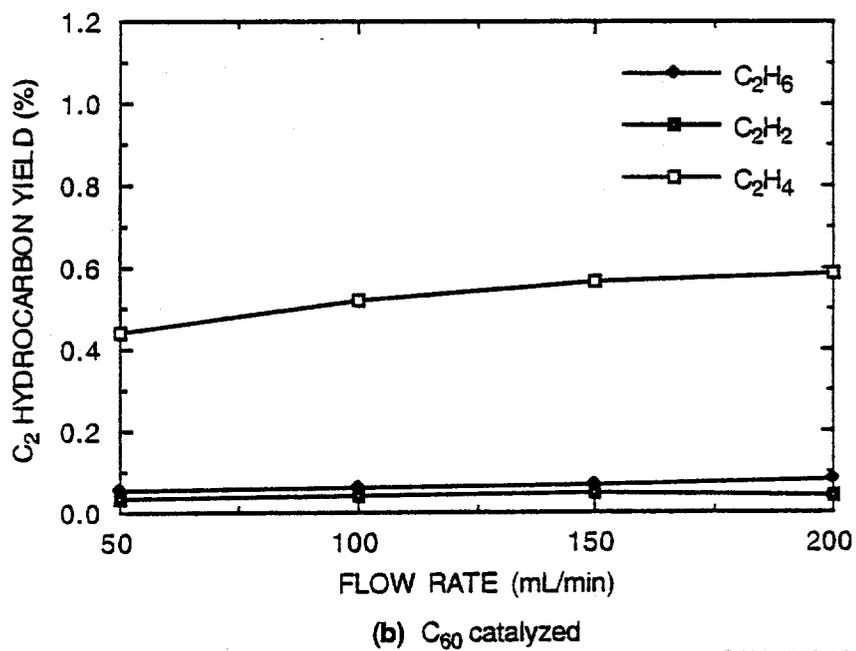
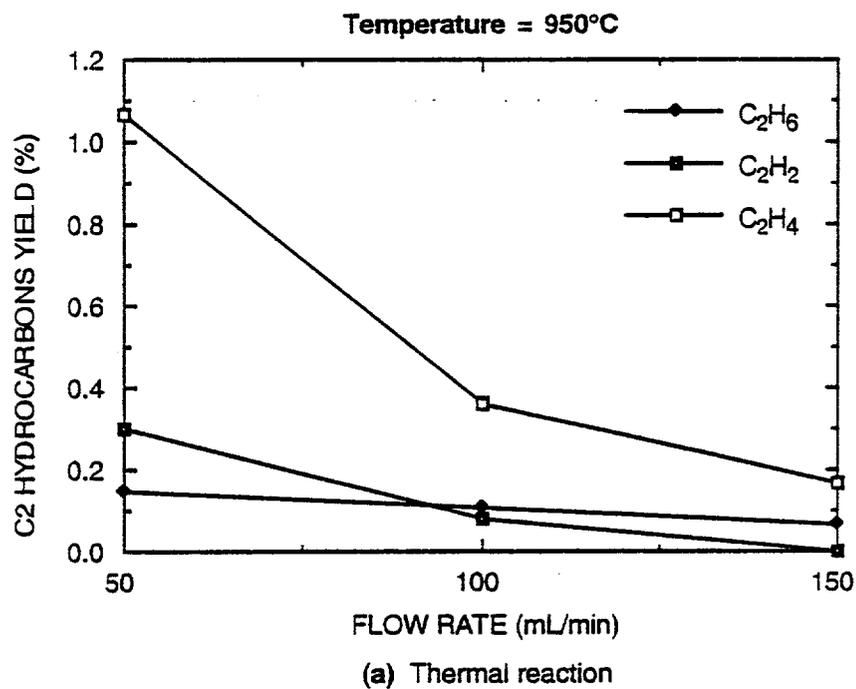
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Figure 1. Methane conversion as a function of catalyst.
Methane flow rate 100 mL/min.



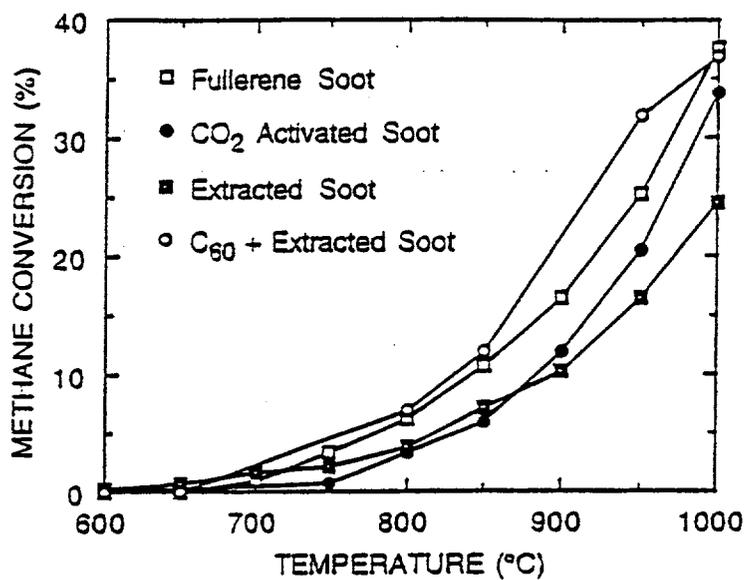
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Figure 2. SALI spectrum of soot treated with Methane at 900°C.

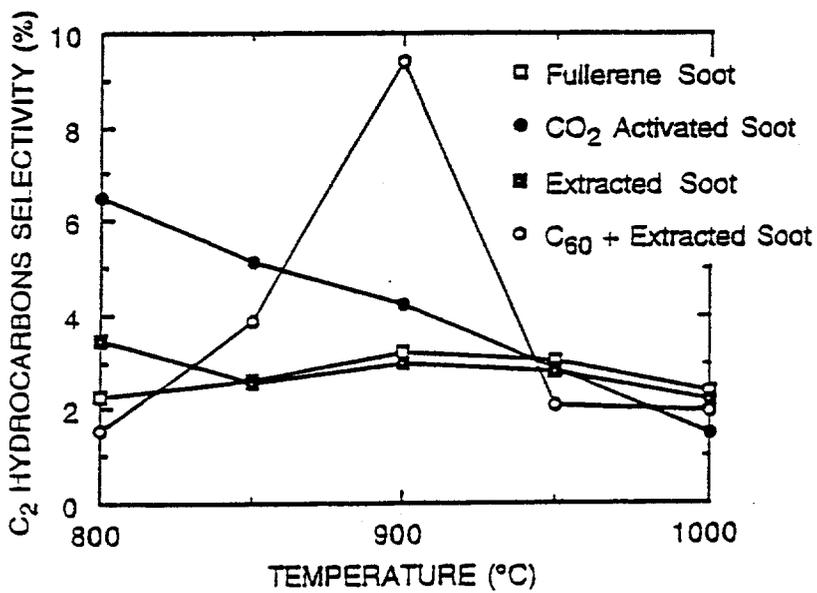


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Figure 3. Effect of flow rate on C₂ products at 950°C.



(a) Methane conversion



(b) Selectivity

CAM-4069-20

Figure 4. Methane conversion and selectivity as a function of pretreatment.

not necessarily compare only the effects of the soluble fullerenes on the methane activation experiment.

To complete this study, a reconstituted soot (C_{60} added to an extracted soot) was tested for methane activation; however, no significant differences in either activity or selectives were observed with the exception of slightly higher selectivities for the reconstituted soot. At $950^{\circ}C$ and above, the differences were negligible. Thus we conclude that the soot is extremely reactive even without the presence of C_{60} and the reactivity is not limited by surface area.

Despite the high activities of the fullerene soots, their selectivities to higher hydrocarbons were lower than observed for the other carbon materials, acetylene black and Norit-A, and for the thermal case. Thus we initiated a series of experiments to see if we could increase the selectivities of the fullerene-catalyzed reactions to take advantage of their high reactivities toward methane activation. One method was to use a co-feeds of hydrogen, which has been shown to increase the selectivity to C_2 hydrocarbons.²⁰⁻²² One possible explanation of this effect is that the hydrogen reacts with coke precursors, thus increasing the amounts of useful hydrocarbons and reducing the amounts of coke. However, since hydrogen is also a diluent, it will lower the partial pressure of methane and may alter the product reactivity profile. Therefore, for comparison, we also tested the effect of added helium, which is an inert diluent.

To better compare these catalysts, we prepared a series of scatter plots under the various reaction conditions and with the different catalyst materials. These types of plots allow us to better compare the results from a wide range of experiments under different reaction conditions and can aid in determining trends and limitations during the catalyst development process.²³ Figures 5 through 8 illustrate the conversion as a function of selectivity and diluent. These figures combine the results of reactions ranging from $800^{\circ}C$ to $1100^{\circ}C$ and flow rates from 50 mL/min to 200 mL/min at STP.

Figure 5 compares the fullerene soot, Norit-A, and thermal reaction for methane conversion to C_2 hydrocarbons in the absence of diluent. As seen in this figure, the selectivity for all systems drops dramatically with increase in conversion. The order of selectivity to C_2 hydrocarbons is thermal > Norit-A > fullerene soot.

Figure 6 illustrates the effect of hydrogen and helium on the selectivity during the thermal conversions and shows a positive effect for these diluents in terms of selectivity.

Figure 7 likewise shows the effect of diluents for the Norit-A catalyzed conversions. At low conversions hydrogen appears to give very high selectivity to C_2 hydrocarbons, but high

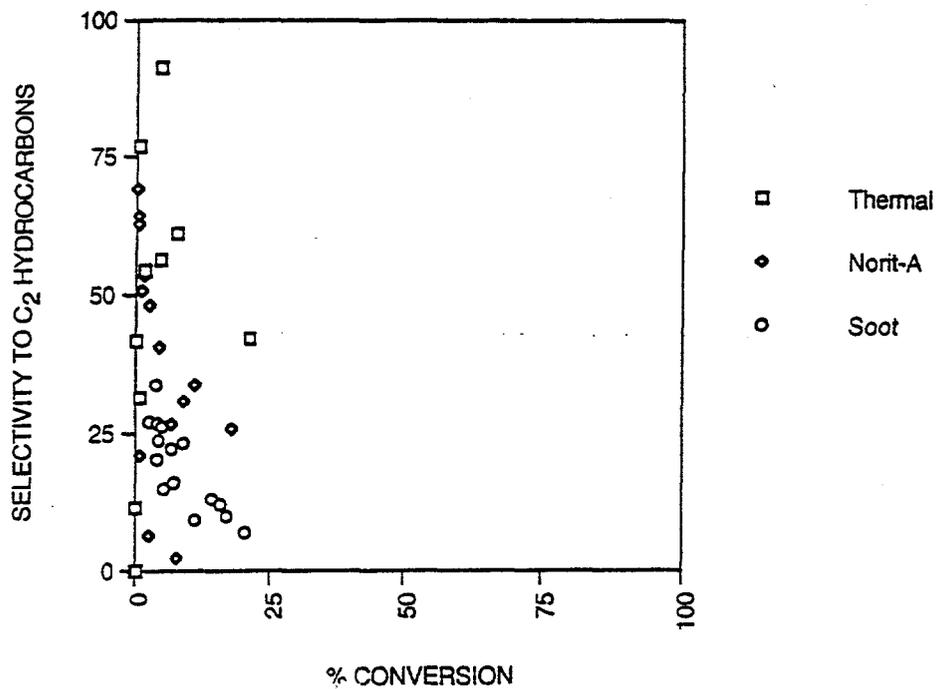


Figure 5. Effect of catalyst on methane conversion. Scatter plot of conversion versus selectivity.

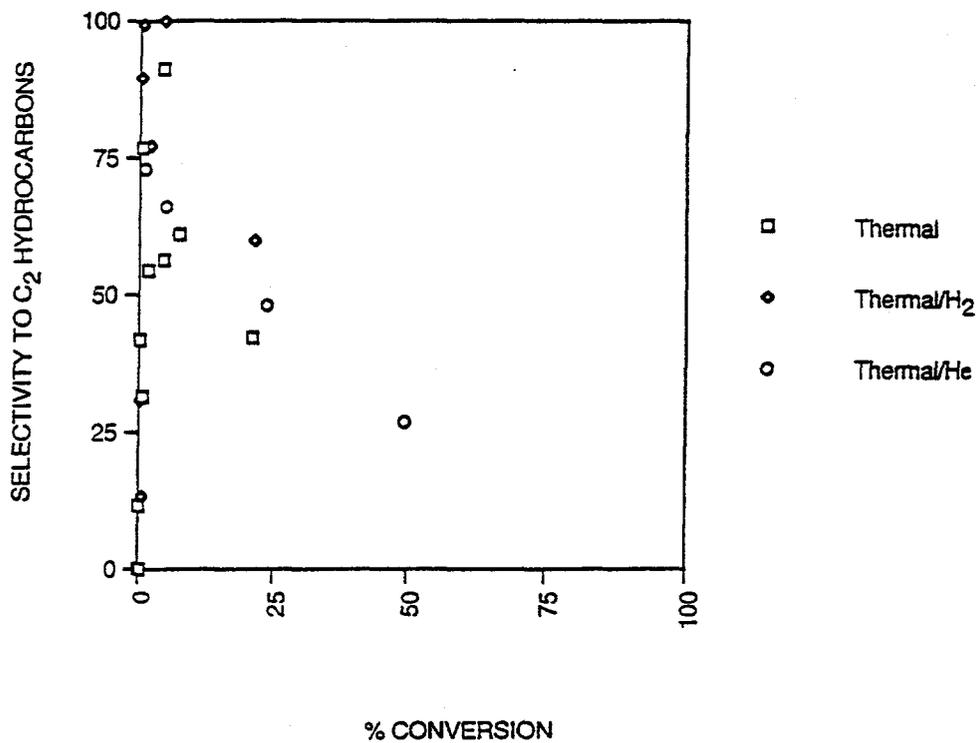


Figure 6. Effect of hydrogen and helium on thermal methane conversion. Scatter plot of conversion versus selectivity.

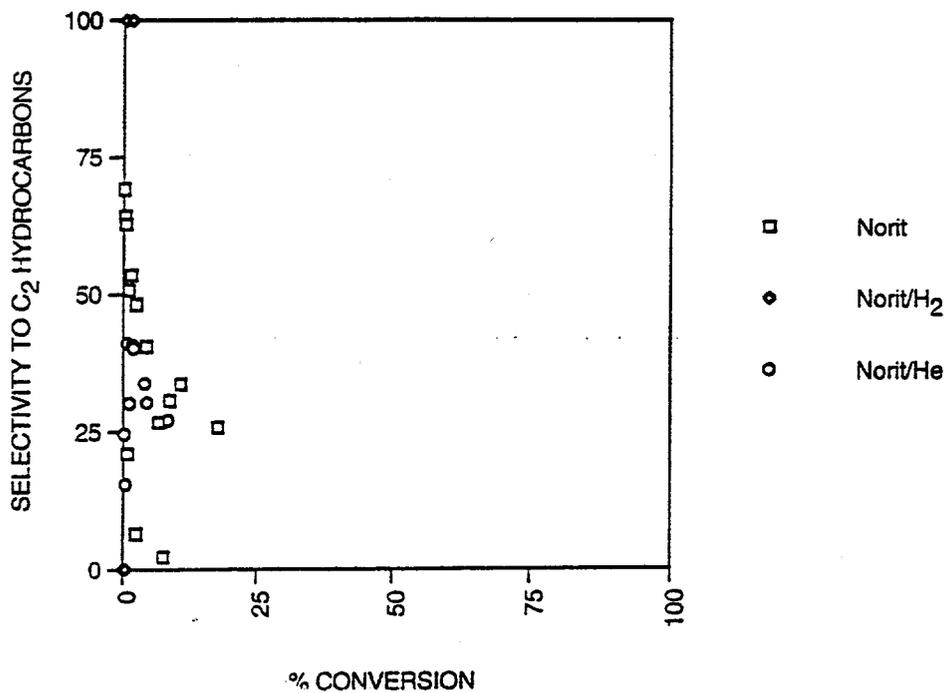


Figure 7. Effect of diluents on Norit-A catalyzed methane conversion. Scatter plot of conversion versus selectivity.

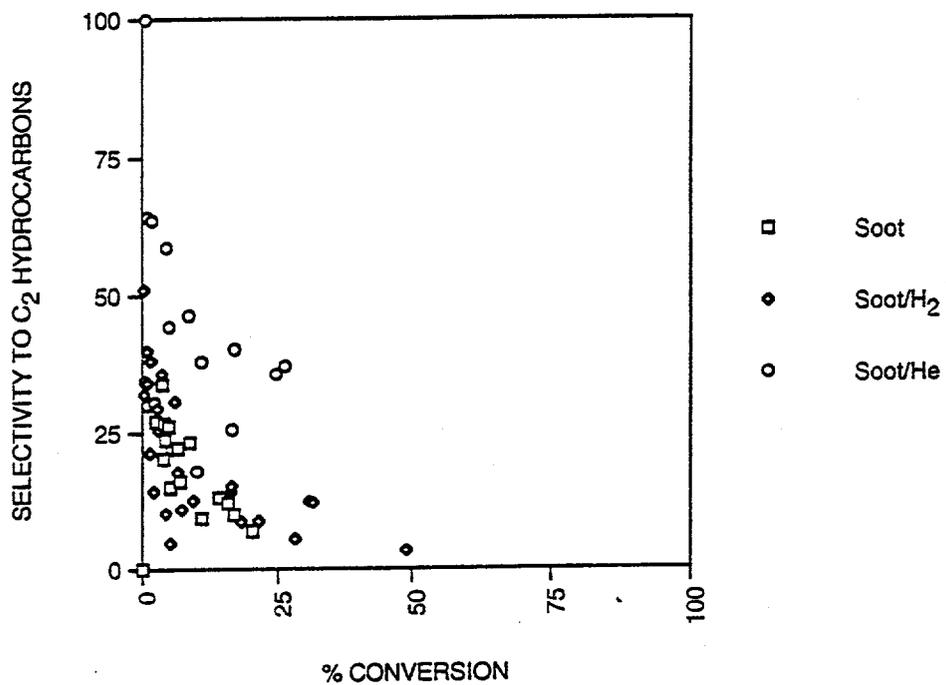


Figure 8. Effect of diluents on fullerene-soot-catalyzed methane conversion. Scatter plot of conversion versus selectivity.

conversions could not be achieved for the Norit-A even at higher temperatures under these conditions. In contrast, with the fullerene soot (Figure 8), there appears to be only a minor effect with hydrogen, but a much more pronounced and positive effect with helium. We are not sure of the reason for this effect with helium and the lack of effect with the hydrogen. One possibility is that the hydrogen reacts with the fullerene soot in much the same way as does the methane (since they have similar bond strengths), and therefore there is a competitive effect for the methane activation sites, decreasing the extent of reaction, as well as a diluent effect that may increase the extent of reaction.

INCORPORATION OF METALS INTO FULLERENE SOOTS

We attempted to enhance the performance of the fullerene soots by incorporating metals into the soot. As was described in Task 1, metals can be incorporated into the soots by many ways, including an *in-situ* incorporation by the arc method, by reacting the fullerene soot with metal complexes, or by conventional incipient wetness techniques. For this project, we tested only soots prepared by the conventional incipient wetness techniques where the metal was added as its salt. Catalysts that were tested included soots impregnated with alkali metals, alkaline earth metals, lanthanides, and transition metals. Concentrations of 1-2 wt% appeared to be adequate to differentiate between the transition metals, although the amounts were not optimized. For the alkali metals, we found that the optimal amount of promoter was higher, for instance in the range of 6 wt%, for the potassium-doped soot. Doping of the soot with these alkali materials had a dramatic and beneficial effect.

Transition Metal Doped Soots

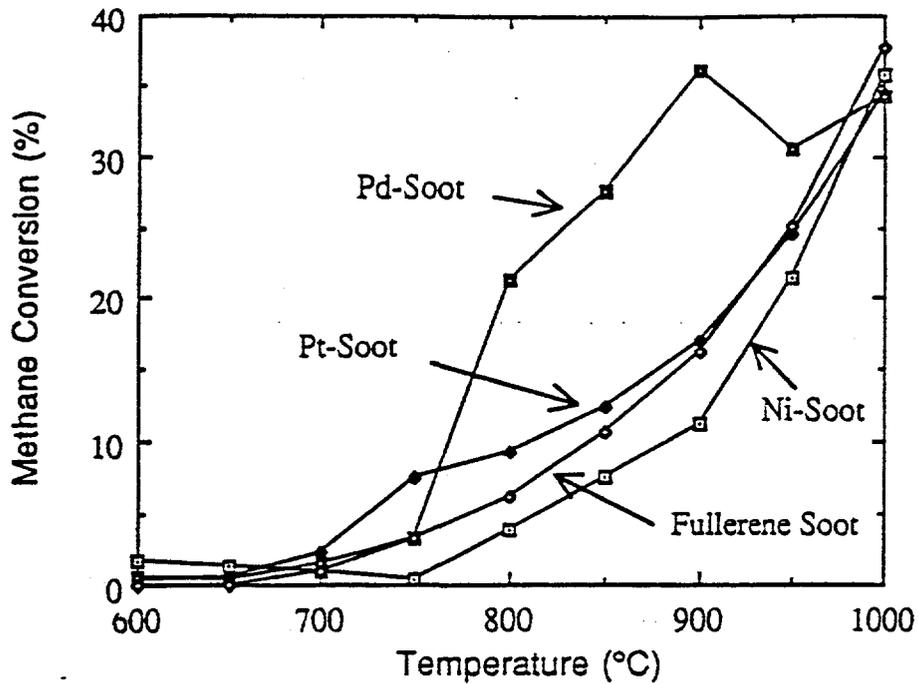
C-H activation by transition metals has been studied for many years both experimentally and by using theoretical calculations. In general, all metals will activate the C-H bond of methane, although at different rates and with a large variation in threshold temperatures. The key question when using transition metals for methane activation is what will happen in the next step. Ideally, one would like the methyl radicals to couple into ethane and be released in the gas phase. However, in reality, the activated methane reacts further to form either coke or metal carbides. Workers have been able to overcome this problem with certain metal carbides by using a two-step sequence in which the metal first reacts with methane to form the metal carbide or carbonaceous materials (this carbide formation is favored at higher temperatures), and then this metal carbide is treated with hydrogen to form hydrocarbons (this hydrogenation reaction is favored at lower

temperatures).²⁴⁻²⁹ Since we are impregnating metals on fullerene soot that has unique H-transfer abilities and can stabilize radicals, we postulated that perhaps the nature of the carbide or carbonaceous material may be altered and perhaps more easily upgraded into higher hydrocarbons. Note that carbonaceous material can also be formed by nonthermal routes, and this material may also contribute to the methane activation process.³⁰

Of the transition metals we tested, we examined the Pt group the most thoroughly and determined their respective reactivity as a function of temperature. As shown in Figure 9, the Pd, Ni, and Pt soots all show activity toward methane activation at temperatures below 600°C, with the Pd soot being more active. Attempts were made to hydrogenate the products after reaction as shown in the literature. However, no higher hydrocarbons were observed after hydrogenation. As seen in Figure 10, the Pd soot exhibits the lowest selectivity, with a greater degree of coking than the Pt and Ni soots, while the Ni soot appears to have a selectivity pattern similar to that of the original soot.

We surveyed a series of catalysts prepared by impregnating fullerene soot with various first row transition metals. Although in certain cases high initial activity was observed at modest temperatures, no catalyst sustained a high activity for long term reactions. The optimal temperature to test these catalysts was the same as the temperature for the soots not containing transition metals, 950°C. Figure 11 shows the results obtained at 950°C and flow rates of 100 mL/min. Conversions ranged from 3% to 8% and selectivities ranged from 25% to 80% of higher hydrocarbons. Surprisingly, the higher conversions in some cases also resulted in higher selectivities, so there appears to be a positive effect of some metals. As seen in this figure, Cr- and Fe-doped soots had low activities (approximately 3%) and had selectivities to higher hydrocarbons in the range of 50%.

In comparison, the rest of the metals exhibited higher activities (6%-8%) with a range of selectivities from 25% to 80%. Since Ca readily forms carbides we had anticipated selectivity similar to that of the alkali metals, but perhaps it requires higher concentrations of Ca to be as effective as the alkalis. Of all the metals, we expected Co to have high activities and selectivities, since it is often used in Fischer-Tropsch chemistry and has a tendency to dimerize C1's to C2's. However, under our conditions, the Mn soot had both the highest activity and selectivity, with a activity of 7%-8% and selectivity to higher hydrocarbons of at least 80% at temperatures of 950°C and methane flow rates of 100 mL/min (STP). However, due to lack of funds, we were not able to explore these interesting leads.



*Flow rate 100 mL/min

Figure 9. Activity of Pd, Ni, and Pt.

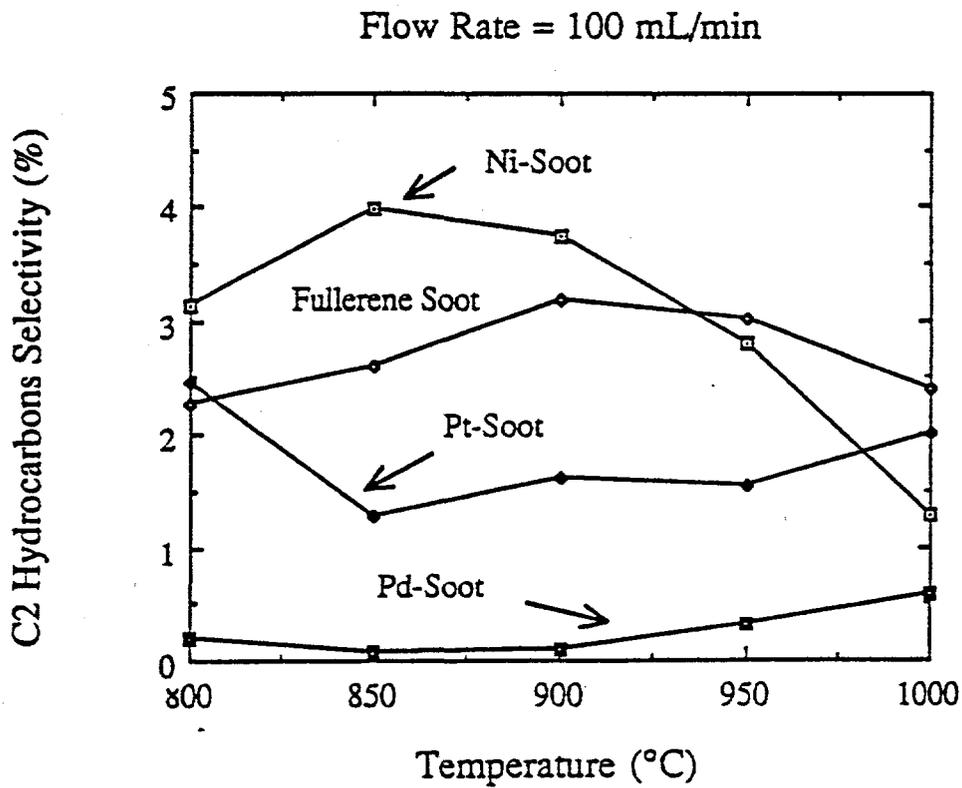


Figure 10. Selectivity of Pd, Ni, and Pt.

EFFECT OF METAL ON REACTIVITY

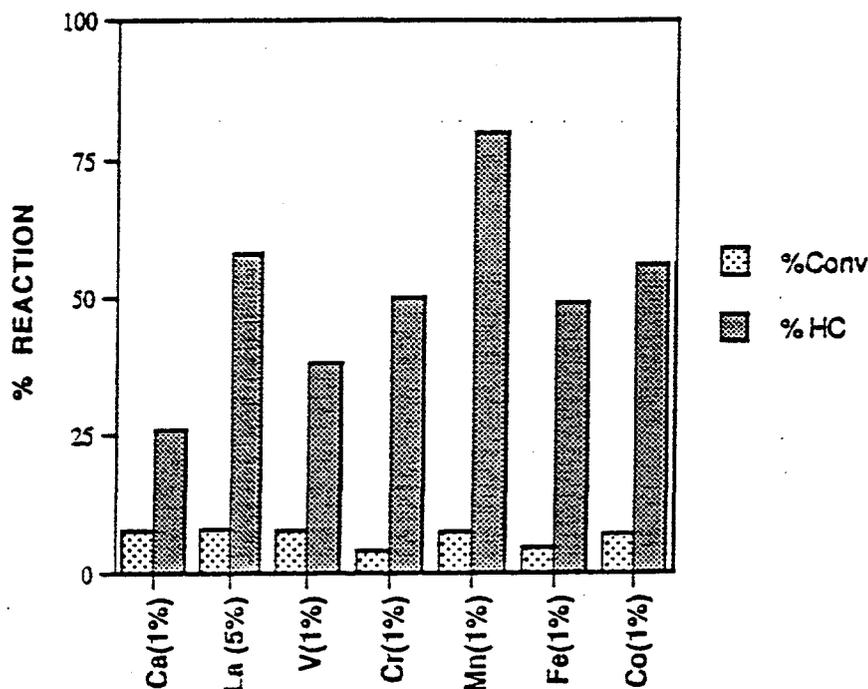


Figure 11. Methane conversion at 950°C at a flowrate of 100 mL/min.

Alkali Metals

Our flow rate studies on the reactivity of the fullerene soots and transition metal soots showed that the low selectivity is due to secondary reactions, such as the decomposition of the products ethane and ethylene. Thus these fullerene-based reactions are not "reactivity" limited but limited by later reactions, and efforts to reduce these secondary reactions that lead to coke are essential. One approach to limiting these secondary reactions is to modify the catalysts by some agent that can block or limit the C₂ decomposition reactions. A recent paper showed that the presence of potassium on a platinum catalyst decreases the decomposition of ethylene.³¹ Thus we began a study to determine the effects of alkali metals on fullerene soots and on metallized fullerene soot to attempt to provide a path to reducing the secondary decomposition reactions.

The soots were doped with varying amounts of the alkali carbonate. A potassium-doped soot (containing 6.8 wt% K) was investigated to determine its reactivity as a function of temperature. During this testing, we found a dramatic change in reactivity at higher temperatures, in particular, 950°C, and therefore monitored the extent of methane conversion as a function of time at this temperature. As seen in Figure 12, a very dramatic drop in methane conversion was exhibited after several hours on stream. Under these reaction conditions fullerene soot and potassium-doped acetylene black both showed a slow decrease in reactivity for methane conversion until they appeared to stabilize at approximately 15 hours. However, in the case of the potassium soot, an immediate decrease in methane conversion was observed concurrent with an increase in C2 hydrocarbons. Thus the K-Soot shows an increase in selectivity to C2 hydrocarbons from approximately 5% to 55%, while the fullerene soot and K-acetylene black show only a maximum selectivity of 20% (Figure 13). In addition to the C2 production, the K-soot also produces significant quantities of C3-C4 hydrocarbons, so its overall selectivity to useful hydrocarbons under these conditions approaches 70%. Interestingly, the effect of potassium promotion for the acetylene black was much less significant and does not exhibit the C3-C4 production as does the K-Soot. The role of potassium is unclear at this time, but based on data from alkali gasification experiments,³² the potassium is thought to form molecular potassium at this temperature, and perhaps this form of potassium is involved in the active activation catalyst.

Table 2 shows the activities and selectivities for the 3.4%, 6.8%, and 13.6% K doped soots for the methane activation experiment conducted at 950°C with methane flow rates of 150 mL/min. The 6.8% and 13.6% K promoted soots are similar in reactivities and selectivities, and the 3.4% promoted soot is slightly more active but less selective. The K-doped acetylene black catalyst gives only 20% selectivity.

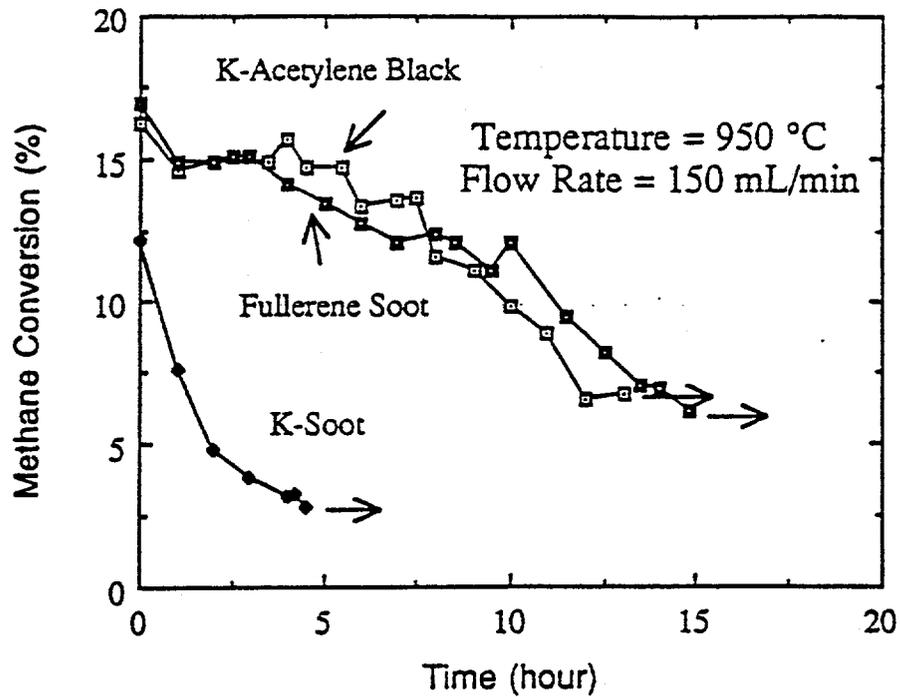


Figure 12. Methane conversion as a function of time.

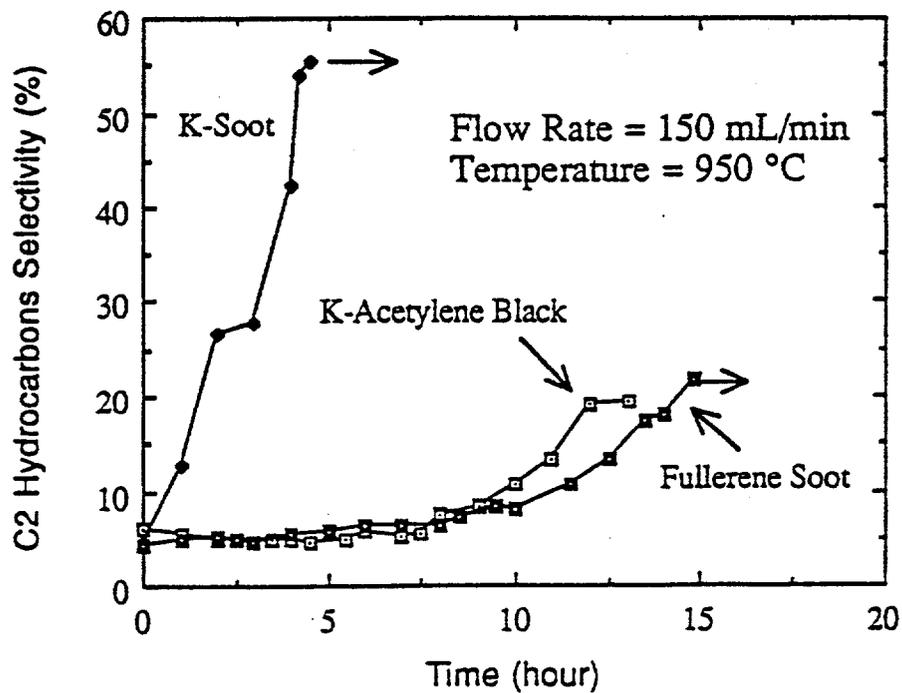


Figure 13. Selectivity as a function of time.

Table 2
EFFECT OF K LOADING ON METHANE ACTIVATION^a

Catalyst	Selectivity			Conversion
	C2	C3-C4	Total Selectivity	
Fullerene soot	20%	-	20%	6%
6.8% K-ABb	20%	-	20%	6%
3.4% K-soot	35%	8%	43%	5%
6.8% K-soot	58%	10%	68%	3%
13.6% 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 nonpromoted 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. At these higher temperatures, the selectivity is still high, and both the conversions and selectivities are higher for the K-doped soot than for the fullerene soot.

Table 3
REACTIONS OF 6.8% 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%

Effects of Alkali Metals on Methane Activation

Given the promising results with potassium, we examined the effect of other alkali metals on methane activation. Alkali carbonates mixed with carbon have been reported to exhibit high reactivities for gasification reactions and to show the presence of free radicals when heated to high temperatures in helium.³² Among the alkali metal carbonates, the magnitude of the effect decreased in the following order: $\text{Cs}_2\text{CO}_3 > \text{Li}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{no additive}$. Therefore, 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 6.8% K_2CO_3 -doped soot (i.e., 0.87 mmole alkali metal carbonate/gram of soot).

The activities and selectivities of these materials are compared at 950°C in Table 4. Surprisingly, the reactivity was in a different order than observed with the gasification reactions, with the order of selectivity now being $\text{K} > \text{Li} \gg \text{Cs} > \text{no additive}$. 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 toward C3-C4 higher hydrocarbons and gave a selectivity of only 5% toward 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. The conversions under these conditions were similar, in the range of 3%-6%.

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.

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).³² Potassium and cesium can also react with carbon, but give nonstoichiometric interstitial compounds.

There are several possible roles that the alkali metals may play 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 carbonaceous species react with hydrogen and/or C1 species to form higher hydrocarbons.²⁵⁻³⁰ One of the unique properties of the fullerenes is that the K metal may be able to donate an electron to the fullerene structure, forming stable aromatic structures, and this property may be the one that gives the K-fullerene soot its unique reactivity toward methane activation.

Effect of K on Transition Metal Promoted Soots

We have seen that the presence of potassium increases the selectivity to higher hydrocarbons, whereas group 8 metals are well known to facilitate the activation of C-H bonds at moderate temperatures.¹⁵ Therefore, we conducted several experiments in which we modified metal-promoted soots with potassium so that we could determine any synergistic effects. 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 activity similar to that of fullerene-soot, while Pd-soot was very active toward methane conversion, but produced considerable amounts of carbon and hydrogen and very little higher hydrocarbons. As seen in this table, the K-Ni-soot gives reactivity similar 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. Thus under these conditions the combination of transition metals and alkali metals did not give a suitable beneficial effect.

Table 5

**REACTIVITY OF MIXED-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 C2 HYDROCARBONS ON METHANE ACTIVATION

Researchers recently investigated the use of higher hydrocarbon co-feeds such as ethane and ethylene to initiate the methane activation reaction.³³⁻³⁶ These co-feeds have been used both for thermal reactions and for the two-stage transition-metal-catalyzed reactions. In a postulated mechanism, ethylene, introduced directly or through the dehydrogenation of ethane, undergoes a disproportionation reaction to yield C_2H_3 and C_2H_5 radicals that can consume methane or can undergo reactions forming H radicals that can react with methane to form methyl radicals. These methyl radicals can then either abstract a hydrogen or add to an olefin such as ethylene to form higher hydrocarbons such as illustrated. Concurrently, the C2 hydrocarbons can also couple to form C4 isomers. Thus many reaction pathways are possible. Reports of using C2 co-feeds show that, in the temperature regime of 500° to 750°C, additional amounts of C2-C4's have been observed, although they are formed at very low rates. The presence of methane was found to produce C3 hydrocarbons as the most predominate higher hydrocarbon product, and at the reaction temperature of 750°C, more methane than ethylene was consumed. These reports, however, were on batch and not on continuous systems, as is ours, and we felt that perhaps under our conditions and using our catalysts we could use these types of initiation steps to increase our yields and selectivities.

For our experiments, we used a co-feed of 10% ethane or ethylene and a temperature regime of 500°C to 900°C. When fullerene soot was used as a catalyst and ethane was used as a co-feed, the ethane underwent both dehydrogenation and decomposition reactions at temperatures

as low as 700°C. In contrast, in the presence of the K-soot, no decomposition reactions were observed up to 800°C. At this temperature, the ethane was almost quantitatively dehydrogenated into ethylene, with no decomposition observed. Thus the K-soot could be very useful as a selective dehydrogenation catalyst. Since the ethane was either converted to ethylene in the case of the K-soot or decomposed in the case of the fullerene soot, we concentrated on ethylene as a co-feed.

The results from the ethylene experiments are listed in Table 6. 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 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. This observation is consistent with the suggestion that K doping can decrease the ethylene decomposition (or secondary decomposition reactions) and thereby enhance the selectivity to C₃ and C₄ hydrocarbons. 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.

Thus we see that co-feeds when used in combination of certain catalysts can be used to enhance the selectivities and activities and exhibit methane activation at low temperatures with high selectivities. Although a 2% conversion is not as nearly as high as we would like, the conversion and selectivity are far greater than observed from Pd-soot, and perhaps testing of the more active catalysts such as Mn or Co in combination with alkali promotion and ethylene co-feeds would also significantly increase their respective conversions and yields.

Table 6

EFFECT OF 10% ETHYLENE CO-FEED ON METHANE ACTIVATION
(Flow Rate 100 ml/min)

Catalyst	Temperature	C2 ^a (%)	C3 (%)	C4 (%)	% Methane Converted	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

We found that the fullerene soots and modified soots all have high activities toward methane conversion, and show reactivities at temperatures as low as 600°C, compared with 800°C for other forms of carbon and 900°C for a purely thermal reactions. We also showed that the methane or perhaps ethane is incorporated into the soot itself, which is consistent with surface catalyzed reactions rather than gas phase reactions. However, the selectivity of these catalysts must be improved before these materials can be used for methane conversions for commercial applications.

During our screening studies, we found that with incorporation of certain promoters such as alkali metals and some transition metals, the selectivities can be dramatically improved. For instance, selectivities to higher hydrocarbons can be increased from approximately 20% with no promotion to 80% with 1% Mn promoter. Furthermore, the use of certain co-feeds such as ethylene to certain catalysts can lower the temperature threshold of reaction to as low as 500°C.

FUTURE WORK

It is evident that these reactions are not reactivity limited, but rather limited by reactor configuration. Several workers have shown the improvements that can be achieved by use of novel reactors. For instance, Broutin et al. studied the thermal coupling of methane using short contact time reactors and, by using high temperatures and short residence times, was able to convert methane to higher hydrocarbons at prices they claim are comparable to those of naphtha steam cracking.²⁰ Likewise, Marcelin et al.³⁷ reported good success in methane conversions using their short contact time reactor with rapid quenching. Thus we expect that using improved reactor technology and optimized fullerene-soot-based catalysts, we could likewise produce more competitive methane conversions with high selectivities.

REFERENCES

1. J. Cox and G. Pilchem, *Thermochemistry of Organic and Organometallic Compounds* (Academic Press, 1970).
2. J. Lee and S. Oyami, *Cat. Rev. Sci. Eng.* **1988**, *230*, 249-280.
3. P. Broutin, C. Busson, J. Weill, and F. Billaud, *Novel Production Methods for Ethylene, Light Hydrocarbons, and Aromatics*, L. Albright, B. Crynes, and S. Nowak, Eds. (Marcell Dekker, New York, 1992), pp. 239-258.
4. I. Mochida, Y. Aoyagi, S. Yatsunami, and H. Fujitsu, *Anal. Appl. Pyro.* **1992**, *21*, 95-102.
5. F. Wudl, A. Hirsch, K. C. Khemani, and C. Suzuki, in *Fullerenes*, G. S. Hammond and V. J. Kuck Eds. (ACS Symposium Series, Washington, DC, 1992), p. 161.
6. C. N. McEwen, R. G. McKay, and B. S. Larsen, *J. Am. Chem. Soc.* **1992**, *114*, 4412-4414.
7. R. Malhotra, D. F. McMillen, D. S. Tse, D. C. Lorents, R. S. Ruoff, and D. M. Keegan, *Energy Fuels* **1993**, *7*, 685-686.
8. R. Malhotra, D. Tse, and D. McMillen, U. S. Patent 5,336,828 (August 9, 1994).
9. W. Krätschner, K. Fostiropoulos, D. R. Huffman, and L. D. Lamb, *Nature* **1990**, *347*, 354.
10. S. C. Tsang, P.J.F. Harris, J. B. Claridge, and M.L.H. Green, *J. Chem. Soc. Chem. Commun.*, **1993**, 1519-1522.
11. S. C. Tsang, P.J.F. Harris, and M.L.H. Green, *Nature*, **1993**, *362*, 520-522.
12. S. A. Lerke, B. A. Parkinson, D. H. Evans, and P. J. Fagan, *J. Am. Chem. Soc.* **1992**, *114*, 7807-7813.
13. P. J. Fagan, J. C. Calabrese, and B. Malone, *Acc. Chem. Res.* **1992**, *25*, 134-142.
14. H. Nagashima, and A. Nakaoka, *J. Chem. Soc. Chem. Commun.*, **1992**, 377-379.
15. F. Solymosi, A. Erdohelyi, and J. Cserenyi, *ACS Petrol. Prep.*, **1994**, *39*, 279.
16. T. Ukai and H. Kwazura, *J. Organomet. Chem.*, **1974**, *65*, 253-266.
17. R. A. Schunn, *Inorg. Chem.* **1976**, *15*, 208-212

18. M. Domingo-Garcia, I. Fernandez-Morales, and F. J. Lopez-Garzon, *App. Catalysis A*: **1994**, *112*, 75-85.
19. C. Prado-Burguete, A. Linares-Solano, F. Rodriguez-Reinoso, C. Salinas-Martinez de Lecen. *J. Catal.* **1991**, *128*, 397-404.
20. P. Broutin, C. Busson, J. Weill, and F. Billaud, "Thermal Coupling of Methane," in *Novel Production Methods for Ethylene, Light Hydrocarbon, and Aromatics*, L. F. Albright, B. L. Crynes, and S. Nowak, Eds. (Marcel Dekker, New York, 1992), Chapter 12, pp. 239-258.
21. O. A. Rokstad, O. Olsvik, B. Jenssen, and A. Holmen, "Ethylene, Acetylene, and Benzene from Methane Pyrolysis" in *Novel Production Methods for Ethylene, Light Hydrocarbons, and Aromatics*, L. F. Albright, B. L. Crynes, and S. Nowak, Eds. (Marcel Dekker, New York, 1992), Chapter 13, pp. 259-272.
22. F. Billaud, and F. Baronnet, *Ind. Eng. Chem. Res.* **1993**, *32*, 1549-1554.
23. Personnel Communication, J. McCarty, 1993.
24. T. Koerts, M. Deelen, and R. Van Santen, *J. Catal.*, **1992**, *138*, 101-114.
25. T. Koerts and R. Van Santen, *J. Chem Soc., Chem. Comm.*, **1991**, 1281-1283.
26. T. Koerts, P. Leclercq, and R. Van Santen, *Am. Chem. Soc.*, **1992**, *114*, 7272-7278; T. Koerts and R. Van Santen, *J. Molecular Catalysis.*, **1991**, *70*, 119-127.
27. M. Belgued, P. Pareja, A. Amarigillo, and H. Amariglio, **1991**, *352*, *Nature*, 789-790.
28. A. Amariglio, P. Pareja, M. Belgued, and H. Amariglio, *J. Chem Soc. Chem. Comm.*, **1994**, 561-562.
29. M. Koranne, D. Goodman, and G. Zajac, *Catal. Let.* **1995**, *30*, 219-234.
30. C. Gueret, F. Billaud, B. Fixari, and P. Le Perchec, *Carbon*, **1995**, *33*, 159-170.
31. R. C. Windham and B. E. Koel, *J. Phys. Chem.* **1990**, *94*, 1489-1496.
32. N. Wood, and K. Sancier, *Catal. Rev.-Sci. Eng.*, **1984**, *26*, 233-279.
33. A. Bossard and M. H. Back, *Can. J. Chem.* **1990**, *68*, 37-42.
34. A. Bossard and M. H. Back, *Can. J. Chem.* **1990**, *68*, 1401-1407.
35. I. Loffler, W. Maier, J. Andrade, I. Thies, and P. von Rague Schleyer, *J. Chem Soc., Chem. Comm.*, **1984**, 1177-1179.
36. T. Koerts and R. Van Santen, *J. Chem Soc. Chem. Comm.*, **1992**, 345-346.
37. G. Marcelin, R. Oukaci, and R. Migone, *Coal Liquefaction and Gas Conversion Contractors' Review Conference Proceedings*, Pittsburgh, PA, September 7-8, 1994.