

THE INVESTIGATION OF FULLERENE BASED CATALYSTS FOR METHANE ACTIVATION

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ABSTRACT

Prompted by the interesting and unusual chemical activities exhibited by fullerenes, we began an investigation of fullerenes and fullerene soots for converting methane into higher hydrocarbons. We plan to ultimately study fullerene supported metal catalysts for this purpose. However, currently we are investigating the reactivity of various fullerene materials without metals for methane activation. These materials include a fullerene soot, a fullerene soot which has been extracted to remove the soluble fullerenes, like C₆₀ and C₇₀, CO₂-activated soot, as well as other carbons such as a Norit-A carbon. We found that fullerene soot activates the C-H bond of methane, allowing methane conversion at lower temperatures (lower by 250°C) than found under purely thermal conditions. Furthermore, soot catalysis appears to produce a minimal amount of aromatic hydrocarbons. The extraction of C₆₀/C₇₀ from the fullerene soot was found to reduce the selectivity for C₂ hydrocarbons, while the CO₂ activation of soot does not appear to alter the catalytic activity of the soot. The effect of reaction conditions such as temperature, residence time, added hydrogen and inert gas on the reactivity and selectivity of these materials are presently being studied.

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 coal liquefaction and petroleum processes. However, methane has not been successfully utilized because of difficulties in storage and transportation. Conversion of methane into higher hydrocarbons would substantially increase its utilization, and intense efforts have been directed towards this goal. The main difficulty in converting methane is the production of undesirable side products. Oxidative methods easily convert methane to higher hydrocarbons, but over oxidation to CO₂ makes it an uneconomical method. Alternatively, simple thermal decomposition of methane also makes higher hydrocarbons; however, the production of liquid fuels from methane by this method is not yet economically feasible because of the high C-H bond strength of methane compared with that of reaction products (i.e. 98.2 kcal/mol for ethane). At the high temperatures required to activate methane, the C₂ products formed will further decompose and produce still higher hydrocarbons, aromatics, and coke.

Direct coupling of methane can be achieved thermally without catalyst. The key to these pyrolysis reactions is to generate methyl radicals, which then polymerize into higher hydrocarbons. However, current methods are thought to produce the radicals in the gas phase, which may lead to indiscriminate reactions and coke formation. In contrast, fullerenes, which have a great affinity for radicals, are expected to add methyl radicals and thereby provide for more selective reactions.¹ Another attribute of these fullerenes is that they can easily incorporate metals either inside or outside the cage structure.^{2,3} Some of these metals may impart to the fullerenes properties that will aid in producing methyl radicals. A second reason why fullerenes may be effective catalysts for methane activation is their strong electrophilic character. Recent work shown by Sen et al.⁴ has shown that methane may be activated by electrophilic agents. C₆₀ and C₇₀ fullerenes display remarkable electrophilic characteristics including direct amination with primary and secondary amines and a very low first reduction potential of -0.5 V (vs. NHE). Wudl⁵ has characterized fullerenes as, "electrophiles par excellence." In the present study we are evaluating the feasibility of using fullerene based catalysts for methane activation. The full scope of the reactivity of these novel materials is not yet known. Because of the reasons cited above, we believe that catalysts based on C₆₀ and other fullerenes will provide a facile pathway to convert methane into higher hydrocarbons.

In the arc process for preparing fullerenes, one obtains C₆₀, C₇₀ and other extractable fullerenes along with a much larger amount of an insoluble soot. This soot most likely results from carbon clusters that did not close into fullerenes, but instead continued to grow into large particles. We therefore suspect that the soot so generated also has a fullerene like structure and exhibits many of its properties. We report here the preliminary results on the methane activation catalyzed by this arc generated soot containing C₆₀ and C₇₀ and compare the results with those obtained with activated carbon (Norit A). We also report on the effect of extracting the soot with toluene, or activating it by partial oxidation with CO₂.

Batch hydrogen and methane activation experiments were conducted by charging a 5 mL tubular reactor with soot and 500 to 1000 psig of gaseous material for 2 hours. The methane activation experiments were conducted using flowing methane at atmospheric pressures. The catalyst was supported on a fritted disk in a quartz reactor. The exit of the reactor was fitted with a quenching zone through which cooling gases could be introduced. The catalyst was heated using a dual furnace reactor system where the methane was first heated in a preheating furnace (at 600°C) and then passed into a high temperature furnace with a short heating zone (4"), leading to the cool quenching zone to minimize any possible thermal reactions after conversion. Soot (containing 12 % C₆₀/C₇₀) was obtained from Ulvick Industries, Inc. Toluene-Extracted soot was obtained from Materials & Electrochemical Research (MER) Corporation. Norit A activated carbon was obtained from Aldrich (750 m²/g). Carbon dioxide activation was carried out using the procedure described by Tsang et al⁶ by treating the fullerene soot or extracted soot with CO₂ (20mL/min) at 850°C for five hours. Surface area of the materials were measured by BET method using N₂. Surface area of the soot and extracted soot were determined to be 125 m²/g and 185 m²/g, respectively. The surface areas of the CO₂-activated fullerene soot and extracted soot were found to approximately 600 m²/g for each material. The gaseous products were analyzed by a Carle CGC 500 gas chromatograph using a TCD detector. Argon was used in the methane gas stream as an internal standard. Fullerene soot, which was subjected to either methane or hydrogen, was analyzed using a surface analysis by SRT's surface analysis by laser ionization instrument (SALI).

RESULTS AND DISCUSSION

The batch experiments were conducted in order to determine the reactivity of the fullerene soot to methane and hydrogen. Analysis by SALI showed that the hydrogen reacted with the C₆₀ contained in the soot to produce various hydrogenated C₆₀ species; however, no evidence was found for addition of methane to the C₆₀ under these conditions. However, since C₆₀ was able to "activate" the 104-kcal/mol H-H bond, it seems reasonable that C₆₀, and other fullerenes, can also activate the 105-kcal/mol C-H bond in methane. One possible explanation for the lack of detection of methylated species is that any methane that does react with the fullerene in this batch system will be further decomposed to carbon and not be observed. Thus a continuous reactor system would be a better test of the reactivity of fullerenes for methane activation.

In order to test the effect of fullerenes, we used a high temperature flow through reactor with a minimal heating zone in order to prevent subsequent reactions of the reaction products. For these tests we used fullerene soot and, for comparison, an activated carbon (Norit A) under typical methane activation conditions (600°C to 1100°C). Carbons have been noted to have catalytic activity for methane activation and thus would provide a good comparison for the effect of fullerenes and fullerene soot.⁷ During the thermal pyrolysis of methane without catalysis, the formation of tar in addition to coke and gaseous products was observed. However, in the case of fullerene soot or Norit catalyzed methane activation, no tar was observed. Figure 1 shows the extent of methane conversion for the soot, Norit A, and the thermal case (no catalyst) when subjected to flowing methane gas at 100 mL/min. As seen in this figure, when induced by thermal pyrolysis without catalyst, the onset of the methane activation was 900°C, while the onset was observed to be approximately 800°C for the Norit-A and as low as 600°C for the fullerene soot. It is interesting to note that the fullerene soot with a substantially lower surface area (ca. 120 m²/g compared to 750 m²/g for Norit A carbon) lowered the onset temperature for methane conversion over that found for Norit A. Hence, the surface area of the carbon is not the discriminating factor. SALI analysis of the fullerene soot after exposure to methane under these reaction conditions, (Figure 2) shows evidence of methylated C₆₀, further demonstrating the capability of soot to activate methane.

The selectivities of C₂ hydrocarbon observed for methane activation at 950°C under different reaction conditions are summarized in Table 1. In order to alter the selectivities we conducted the methane activation experiments in the presence of hydrogen, and for comparison, the presence of an inert gas, helium. The effect of hydrogen dilution is generally recognized to increase the yield and selectivity of C₂ hydrocarbons.⁸⁻¹⁰ These trends are consistent with the observation for the methane activation conducted without catalyst or with Norit carbon as catalyst. In contrast, with the fullerene soot, there appears to be only a minor effect with hydrogen, but a much more pronounced and positive effect with helium. This effect may be key to determining the role that fullerene-soot plays in methane activation.

The comparison of methane conversions catalyzed by fullerene soot and extracted fullerene soot as well as these respective soots treated by CO₂ is shown in Figure 3. The extracted soot was prepared by room temperature toluene extraction of fullerene soot. This extraction process removes the soluble fullerenes like C₆₀ and C₇₀. However, in the preparation of the soot by arc process, a large amount of large molecular weight fullerene like structures and incomplete fullerene structures are thought to be present. Most research has focused on the soluble part of the soot and very little information of the insoluble soot is available. As seen in this figure both extracted soot and fullerene soot can activate methane at ca. 600°C, with the extracted soot catalyzing more methane conversion than does the fullerene soot. However, as shown in Figure 4, the selectivity for C₂ hydrocarbons is lower in the case of extracted soot than for the fullerene soot, which suggests more coke formation in the methane activation catalyzed by extracted soot.

The reason for this difference is not clear but it could be attributed to the presence of C₆₀/C₇₀ in fullerene soot. It might be argued that C₆₀/C₇₀ will evaporate at the temperature that methane activation is carried out. But the possibility that C₆₀ undergoes reactions with methane and becomes nonvolatile at this temperature can not be excluded. Alternatively, the process of extraction may alter the behavior of the fullerene soot by an as yet unknown manner. Contact with solvents does markedly increase the apparent density of the material. The reason for this anomaly is now under study.

Tsang et al⁶ recently reported that treating extracted soot at 850°C with CO₂ leads to the formation of microporous carbon with high surface area. We therefore prepared the CO₂-activated fullerene soot and CO₂-activated extracted soot in the same manner. The weight loss during the CO₂-activation was 20.3 wt% for the fullerene soot and 19 wt% for the extracted soot. The CO₂-activation was found to increase the surface areas of the soots to over 600 m²/g from 120 m²/g for the fullerene soot and from 185 m²/g for the extracted soot. The methane activation study of these pretreated soots is shown in Figures 3 and 4. We found that although CO₂-activation procedure increases the surface area of the soot dramatically, the methane activation catalyzed by CO₂-activated soot does not show higher conversions under these conditions. On the other hand, the selectivity for C₂ hydrocarbon is slightly improved. The CO₂-activated extracted soot does not show any difference from extracted soot in terms of methane conversion and C₂ hydrocarbon selectivity. Comparing the effect of CO₂ activation with extraction suggests that the difference of surface area is not as important as the nature of the catalyst in the catalytic activities and selectivities for methane activation.

CONCLUSIONS

These results obtained so far show that both activated carbon and fullerene soot appear activate the C-H bond of methane and convert it into higher hydrocarbons, albeit to different extents. Both fullerene soot and extracted soot can lower the onset temperature for methane by ca. 250°C compared to the case without catalyst. This activity provides a good ground for the future work on the catalytic application of fullerene-based materials. We plan to explore these differences for both fullerene and metallized fullerenes in future work on the upgrading of natural gas and related work.

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Table 1 The Pyrolysis of Methane at 950°C and 100 mL/min

Catalyst Employed	Co-feed Gas (Vol%)	CH ₄ Conversion (%)	Selectivity (%)			
			C ₂ H ₄	C ₂ H ₆	C ₂ H ₂	Total
No Catalyst	None	1.7	36	11	8	55
No Catalyst	H ₂ (50%)	0.3	76	14	0	90
No Catalyst	He(50%)	1	73	0	0	73
Norit	None	7.6	23	2	3	28
Norit	H ₂ (50%)	0.6	87	6	0	93
Norit	He(50%)	7.3	24	3	3	30
Soot	None	16.9	8	1	1	10
Soot	H ₂ (50%)	7.4	11	0	0	11
Soot	He(50%)	5	32	5	7	44

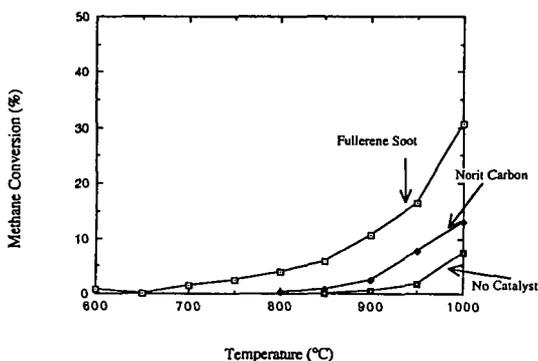


Figure 1. Methane conversion as a function of catalyst. Methane flow rate 100 mL/min.

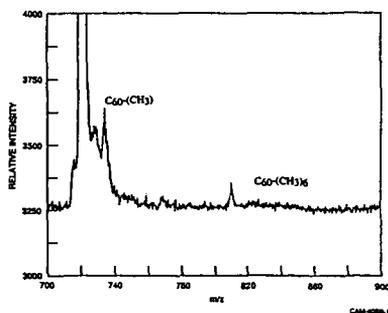


Figure 2. SALI spectrum of fullerene soot treated with methane at 900°C.

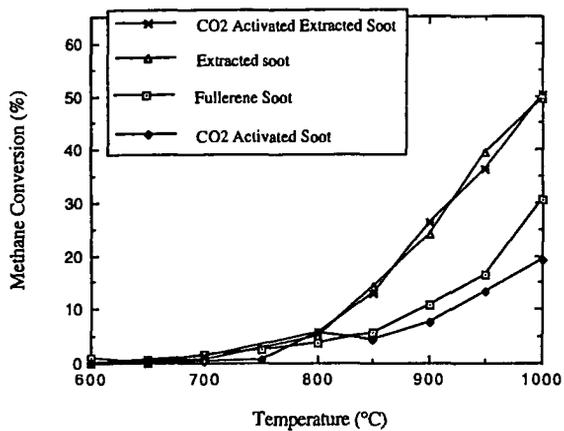


Figure 3. Effect of pretreatment of fullerene soot on methane conversion. Methane flow rate 100 mL/min.

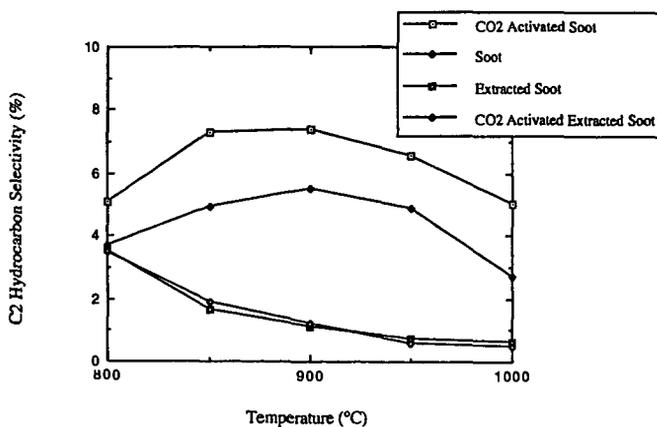


Figure 4. Effect of pretreatment of fullerene soot on C₂ selectivity. Methane flow rate 100 mL/min.