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High-Power Pulsed Radio-Frequency and Microwave Catalytic Processes: Selective Production of Acetylene from the Reaction of Methane over Carbon

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Methane is converted to acetylene, ethylene, and ethane over carbon at atmospheric pressures using pulsed high-power radio-frequency or microwave radiation. By judicious use of experimental variables, selectivity of acetylene in hydrocarbon products can be >90%. The concentration of hydrogen has been shown to be important. To obtain a clearer understanding of the role of carbon in this system, experiments have been conducted using amorphous ^{13}C. A mechanism is postulated to explain the contribution of carbon and hydrogen to the formation of higher hydrocarbons.

INTRODUCTION

Acetylene is synthesized industrially via the transformation of inorganic feedstocks such as carbon dioxide and hydrogen (Fischer–Topsch synthesis) (1, 2), or via calcium or lithium carbide and water (3). These processes are becoming increasingly undesirable to the chemical industry due to the high energy consumption and concern over the environmental consequences. An alternative technique, which is highly selective toward acetylene and is both environmentally attractive and economically more viable, would be very beneficial. Such a process could utilize methane due to the fact that there are significant natural gas reserves in the world, of which methane is the major constituent. Since methane is relatively inexpensive, there has been considerable investigation and study dedicated to converting it to more useful, and hence more expensive, hydrocarbons, such as acetylene, via a relatively inexpensive route. Methane is thermodynamically the most stable hydrocarbon at standard temperatures and pressures, and current methods of converting it to more valuable products are very costly. In the last 15 years, there has been extensive research into the conversion of methane, particularly heterogeneous catalytic methane oxidation utilizing processes such as oxidative methane coupling and partial methane oxidation (4, 5). However, despite the considerable progress and enormous effort in this field, there has not yet appeared a system that exhibits both suitable activity and selectivity to desired products which can be developed on an industrial level.

There have been a growing number of articles accumulating in the literature concerning microwave radiation as an alternative form of heating. An excellent review of the application of this technology to chemical synthesis has been made by Mingos and Baghurst (6). One of the areas where microwave irradiation appears to have a beneficial effect is heterogeneous catalysis (7, 8), where one of the most studied reactions is the conversion of methane. Several researchers (9–14) have used microwave plasma methods for the catalytic conversion of methane to higher hydrocarbons at low pressures. Conversion of methane gave ethane, ethylene, and acetylene. Selectivity was influenced by the power, flow rate, and presence/absence of a catalyst. Microwave studies have been conducted on the oxidative coupling of methane onto oxide catalysts by directly heating the catalyst with microwave irradiation (8, 15). Increased production of ethane and ethylene have been reported and a high ethylene to ethane ratio has been observed. In previous studies conducted in this laboratory, the catalytic conversion of methane to higher hydrocarbons under microwave radiation has been studied using a different experimental procedure (16, 17). The catalyst (nickel powder or pellets) was heated under pulsed microwave radiation (typically millisecond pulses) at atmospheric pressure. Pulsed microwave heating of the catalyst gave C_2 and C_3 hydrocarbons depending on the power and duration of the pulses.

The present paper describes the decomposition of methane over carbon, using both radio-frequency (RF) and microwave irradiation. The major product from both systems was acetylene. Methods employing this microwave-induced catalytic technology, using inexpensive reagents

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such as carbon and water, have demonstrated that production of acetylene can be highly selective (18). Higher conversions and selectivities have been obtained from the production of acetylene from benzene (19). However, this research has been directed toward an understanding of the participation of carbon in the decomposition of methane to produce acetylene. Conventional studies using solid carbon for the production of hydrocarbons include the pyrolysis of methane over carbon fibers producing ethylene as the major hydrocarbon product (20), and the reaction of hydrogen with thin films of carbon producing methane, ethane, and ethylene (21). There are various reasons for using carbon in RF–microwave studies. Methane is known to chemisorb well on carbon at high temperatures (22, 23), and it has been observed that carbon is an excellent absorber of incident microwave energy and can efficiently convert this electromagnetic energy into thermal energy (18, 24). This is particularly advantageous since high temperatures are required for direct conversion of methane to higher hydrocarbons. With this in mind, experiments were performed with amorphous ^{13}C using both radio-frequency and microwave technology to obtain a clear understanding of the role of carbon in the decomposition of methane.

METHODS

Reagents and Catalysts

Methane (purity 99.995%) and hydrogen (purity 99.99%) were obtained from Canadian Oxygen Ltd.; acetylene (purity 99.6%) was obtained from Matheson. All reagent gases were used as received. The catalysts used in this study were activated carbon, Norit RB 10.6 pellets, supplied from Aldrich Chemical Co., and amorphous carbon, (^{13}C 99%), supplied from Cambridge Isotope Laboratories. The catalysts were either used as received or pretreated thermally at 300°C under flowing nitrogen.

Radio Frequency Unit and Gas System

Radio-frequency (RF) experiments were carried out using a "RFC Macrowave Unit" (Model 961) manufactured by Radio Frequency Co., Inc. operating at a frequency of 40 MHz. The power and pulse control circuits of the instrument were modified in order to allow operation at a peak power of 2.5 kW, with a pulse duration of 1 to 20 ms,and a duty cycle of 0.001 to 1 (duty cycle = $t_p/(t_p + t_r)$ where t_p is the pulse time and t_r is the rest time between pulses). In a typical experiment, a Pyrex reactor of 3.7-mm inner diameter tubing was filled with 0.3 g of activated carbon or 0.1 g of ^{13}C, and mounted inside the applicator chamber of the RF unit as shown in Fig. 1. The ground electrodes were installed 100 mm from the high-voltage electrode. A flow of methane, or a mixture of methane and hydrogen, was introduced into the reactor at a pressure of 100 kPa. Before the experiments, the sample was pretreated under a flow of dry nitrogen using 1-ms RF pulses at the repetition rate of 10 Hz in order to remove adsorbed water, the presence of which reduced the selectivity of acetylene formation. All RF experiments were carried out at an incident power of 2.5 kW at a fixed duty cycle of 0.05.

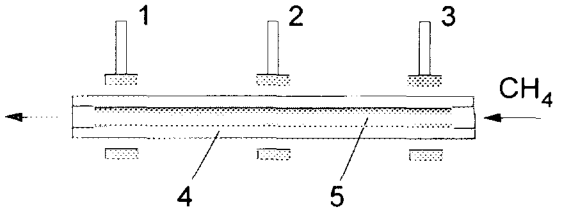

FIG. 1. Schematic diagram of the RF reactor: 1, ground electrode; 2, high voltage electrode; 3, ground electrode; 4, Pyrex tube; 5, solid carbon.

Microwave Apparatus and Gas System

The details of the microwave apparatus that was used in this study have been described previously (17). A Cober variable 3-kW, 2.45-GHz magnetron, Model S3F/4091 was used as a power source. A custom-built pulse controller was used to control the period, duty cycle, as well as the power level in a reproducible manner. The reaction cavity was essentially a modified section of the waveguide where a Pyrex reaction cell (6 cm long and 1.7 cm in diameter) could be inserted so that its long axis was perpendicular to the direction of the microwave propagation and to the electric field so as to maximize exposure to the incident microwave radiation. Controlled microwave experiments were performed in a batch gas system in which the reactants and products were recirculated through the catalyst bed at 10 ml/min using a peristaltic pump (Masterflex Model 7014-52). In a typical experiment, 4 g of activated carbon or 1 g of ^{13}C was packed into the reactor and the reactor was then placed in the reaction cavity and connected to the gas lines. After the microwave system had been tuned under a helium atmosphere, the batch gas system was then evacuated for 5 min, and then methane was introduced at a pressure of 100 kPA. The catalyst was subjected to 500-ms pulses of microwave (MW) irradiation at an incident power of 2 kW followed by a rest period of typically 25 s.

Analysis of Products

Gas sampling of products was achieved by use of online 6-port gas sample valves using fixed 100-μl sample loops. The products were analyzed using Hewlett–Packard 5890A gas chromatographs (GC) with flame ionization (FID) and thermal conductivity detectors (TCD). Identification of products was performed using a Finnigan automated 4000 gas chromatograph/mass spectrometer (GC/MS) system. Products were separated using a 6 ft × ⅛ in. stainless-steel column packed with Porapak N.

As hydrogen was one of the expected products, GC–TCD was employed for quantitative measurements; however, simultaneous quantitative determination of hydrogen and methane using the TCD detector was complicated due to the relatively close values of their retention times and the negative polarity of the hydrogen peak. As a result, the accuracy of the TCD determination of these species was not sufficient for a reliable calculation of mass balance in the system under investigation. To achieve a more precise determination of the hydrogen content, simultaneous GC–FID analysis and measurements of the sound velocity in the gas products using a microwave-induced acoustic (MIA) technique (25, 26) were conducted. The microwave-absorbing material used in the MIA measurements was a carbon filament, 3 mm in length. Microwave pulses of 2 μs duration at a repetition rate of 5 Hz were produced by a Varian Model SFD 367 coaxial magnetron. A MIA cell was used which consisted of a Pyrex tube of 3.7-mm inner diameter with a microphone mounted hermetically close to its outlet. This was installed in series with the GC sampling loop. The sound velocity in the gas product was determined by dividing the distance between the carbon filament and the microphone by the time of acoustic wave propagation.

The sound velocity V_s in a gas mixture can be represented as

$$V_s^2 = \gamma^* RT/M^*, \qquad [1]$$

where

$$\gamma^* = \sum_{i=1}^{N} C_p^i x_i / \sum_{i=1}^{N} C_v^i x_i$$

is the ratio of averaged heat capacity at constant pressure to that at constant volume; x_i is the relative mole concentration of an ith product ($i = 1, 2, \ldots, N$); R is the gas constant; T is the temperature; and

$$M^* = \sum_{i=1}^{N} M_i x_i / \sum_{i=1}^{N} x_i,$$

the averaged molecular weight.

When the relative concentrations of the hydrocarbons were known from the GC-FID measurements, Eq. [1] was used to determine the hydrogen concentration, assuming that

$$\sum_{i=1}^{N} x_i = 100\%.$$

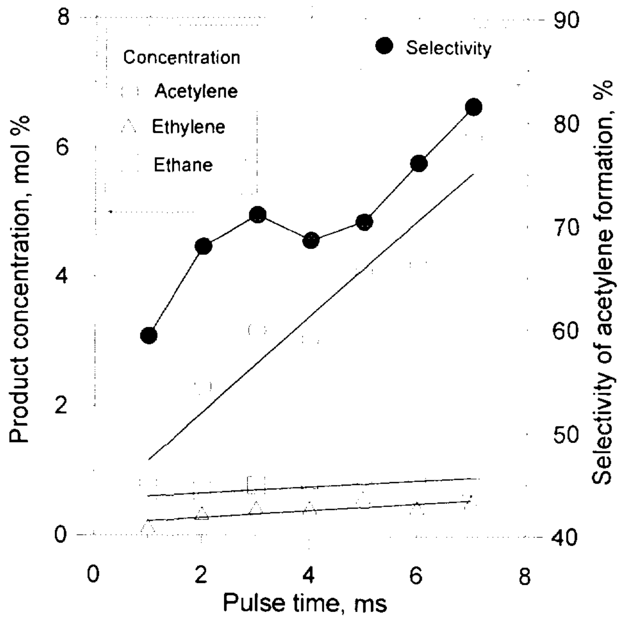

FIG. 2. Reaction of methane over activated carbon using pulsed RF irradiation at a duty cycle of 0.05 with a methane flow rate of 0.5 ml/s.

Using these data, it was possible to calculate the stoichiometric coefficients of methane and carbon, α and β, in the reaction:

$$\alpha CH_4 + \beta C = x_1 H_2 + x_2 CH_4 + x_3 C_2H_2 + x_4 C_2H_4 + x_5 C_2H_6 + x_6 C_3H_8 + \cdots \qquad [2]$$

RESULTS

The main products obtained from the reaction of methane over activated carbon using RF and MW irradiation were acetylene, ethylene, and ethane. Traces of C_3 and C_4 hydrocarbons, on the order of 0.02–0.1 mol%, were also detected. It was found that the concentration of acetylene in the products linearly increased with increasing pulse duration at a constant duty cycle under RF irradiation in a flow system (Fig. 2). In a circulating system under MW irradiation, the product concentration increased with increasing irradiation time (Fig. 3). Under RF conditions, with a constant pulse duration of 7 ms and duty cycle of 5%, the concentration and the selectivity of acetylene formation increased with decreasing methane flow rate, whereas the yield of ethane and ethylene decreased as shown in Fig. 4a. The selectivity to acetylene in hydrocarbons can be as high as 92% under RF irradiation, and 96% under MW irradiation.

In the pulsed systems under consideration, the reaction rate varies according to the time dependence of the supplied electromagnetic energy. For example, the data pre-

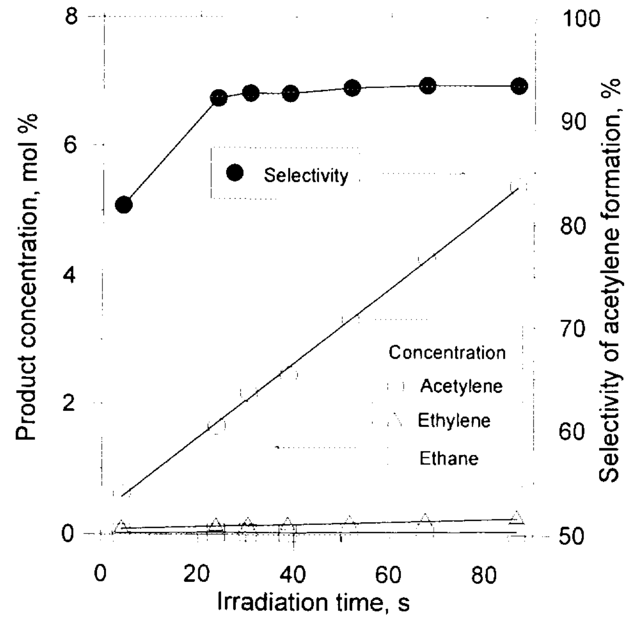

FIG. 3. Reaction of methane over activated carbon with MW irradiation time at 2 kW.

sented in Fig. 4a were obtained with a RF pulse width of 7 ms followed by a rest period of 133 ms, with a pulse period of 140 ms. Therefore the reaction rates were evaluated as methane conversion per RF pulse. These values were calculated using the following procedure. First, an averaged residence time, τ, of methane in the reactor was evaluated by dividing the effective reactor volume, which is equal to the empty space in the reactor containing the catalyst, by the volume gas flow rate. The number of RF pulses which irradiate the catalyst during this residence time was obtained by dividing τ by the pulse period. The conversion rates presented in Fig. 4b were calculated by dividing the methane conversion by the number of RF pulses. It was found that the conversion rates per RF pulse do not considerably change with methane volume flow rate; whereas the number of RF pulses varied from 1 to 4 for methane flow rates presented in Figs. 4a and 4b. However, the selectivity of acetylene formation decreased with decreasing residence time.

In the experiments using methane over activated carbon, we have found that the coefficient β in Eq. [2] was negative. This result was consistent with the observations of a carbonaceous deposit on the reactor walls after the experiments. Formation of this carbonaceous deposit can proceed through the consecutive removal of hydrogen atoms from methane molecules and some stages of this process could be reversible. Further experiments were conducted to study the influence of the hydrogen concentration on the reaction stoichiometry. Figure 5 shows the dependence of the mole ratio between reacting carbon and methane, $\beta/(\alpha - x_2)$, on the input ratio H_2/CH_4 (in this case, hydrogen was also included in the left-hand side of Eq. 2 as γH_2). As shown in Fig. 5, the β coefficient became almost 0 when a feed of composition 60% CH_4–40% H_2 was employed. The selectivity of acetylene formation was still 90%, and the methane conversion was 10%. In the mixtures of 40% CH_4–60% H_2, the selectivity of acetylene formation was 90% and the methane conversion was 19%. In this case we obtained a positive value of β. With increasing hydrogen concentration, the participation of solid carbon in light hydrocarbon formation increased. The selectivity of acetylene formation remained at the level of 85–90%.

In order to form a mechanistic picture of the reaction of methane over carbon catalysts in these systems, we have studied the isotope distribution in the hydrocarbon products when amorphous ^{13}C was used instead of activated carbon. The results are presented in Table 1.

DISCUSSION

The thermodynamics of the products formed in the carbon–hydrogen system, in particular the decomposition of methane are well known (27). The thermal decomposition of methane takes place at temperatures above 1200–1400 K giving rise to the formation of acetylene (28). However, the most stable species at these temperatures are graphite and hydrogen and thus decomposition into the elements competes with the rate of acetylene formation. Nonequilibrium processes utilizing plasma technology can increase the yield of acetylene by product quenching. In thermal decomposition of methane, the presence of a solid surface can influence selectivity in the product formation (29).

The experiments with RF or MW heating of the carbon–methane system show that acetylene has the highest selectivity among gaseous hydrocarbons obtained in this system (Figs. 2, 3, and 4b). This result is in contrast with the results of van der Zwet *et al.* (29), where the yield of acetylene was lower than that of ethylene and the main product from the reaction was coke. This contradiction can be related to the different chemical composition of the catalysts used by these workers (typically metals supported on Al_2O_3) and in our work, and to the different nature of electromagnetic and thermal heating. In microwave- or RF-induced catalysis, the heat is liberated on the surface of a catalyst, which usually consists of a relatively low conducting material, and then transferred to the gas stream. If the catalyst structure consists of randomly oriented particles or pellets, then the temperature distribution over the surfaces and edges of these particles or pellets is not uniform due to interaction with the electromagnetic field. As a result, a highly nonequilibrium system is created, where chemical intermediates formed on the

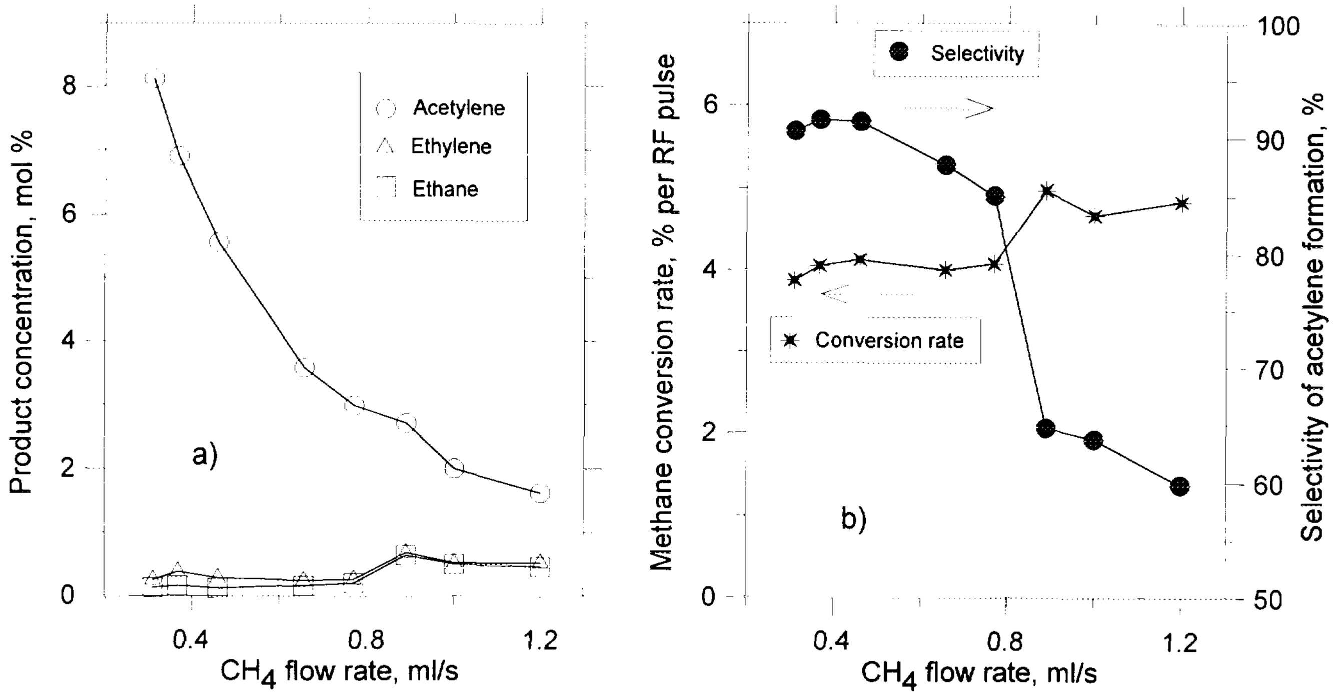

FIG. 4. (a) Product concentration vs methane flow rate; (b) Methane conversion rate and acetylene selectivity vs methane flow rate. Conditions: RF irradiation using 7-ms pulses at a duty cycle of 0.05.

catalyst surface are thermally desorbed from the catalyst surface during the RF or microwave pulse absorption and quenched in a relatively cold gas phase, so the reaction paths can considerably differ from a system with normal conventional thermal heating. Thus, a temperature manifold exists in the reaction system including the nonuniform surface temperature, bulk temperature, and the gas-phase temperature with a high gradient close to the catalyst surface. Due to the nonequilibrium nature of RF and microwave catalysis, the determination of the surface temperature, which is a very important parameter in the reaction mechanism, is not feasible. This temperature is mainly determined by the energy absorbed during a pulse of irradiation. Figure 2 shows an increase in the acetylene concentration and selectivity when the RF pulse duration increased from 1 to 7 ms at a constant duty cycle (and, therefore, at a constant average energy input). This effect is attributed to higher temperatures developed during longer pulses, where the energy absorbed per pulse was higher. Longer pulse durations were not possible because of damage to the Pyrex reactor. At a constant RF pulse duration of 7 ms (Fig. 4b), the methane conversion per single pulse was almost constant, whereas the residence time of methane in the reactor changed four times due to a different gas flow rate. This means that the primary active species, such as hydrocarbon radicals, are formed on the catalytic surface under the same conditions in each pulse. However, the selectivity of acetylene formation is highly influenced by the residence time (the number of the RF pulses). This increase in the acetylene yield at higher residence times originates from the decomposition of ethane and ethylene formed from methane.

The results on the methane–carbon system obtained in this work with the electromagnetic heating, as well as the literature data obtained with thermal heating (28) demonstrate that the formation of coke accompanies acetylene production, so the expectation is that acetylene formation should be due to methane decomposition. However, the presence of $^{13}CH^{12}CH$ above the natural isotopic level, which was detected in experiments B and C with amorphous ^{13}C (Table 1), is clear evidence that solid carbon is involved in this system.

In the decomposition of methane leading to coke formation, a considerable amount of hydrogen is evolved. The mechanism of hydrogen interaction with carbon has been investigated using thermal methods (21) and with atomic hydrogen (30) using a molecular beam technique. We assume that hydrogen evolved in the methane decomposition can react with the surface atoms of the solid carbon resulting in the formation of acetylene and other hydrocarbons as postulated by Balooch and Olander (30).

Table 1 shows that the I_{27}/I_{26} mass peak ratio in the acetylene GC/MS peak measured in A with experiments on activated carbon (^{12}C) coincides with the natural level

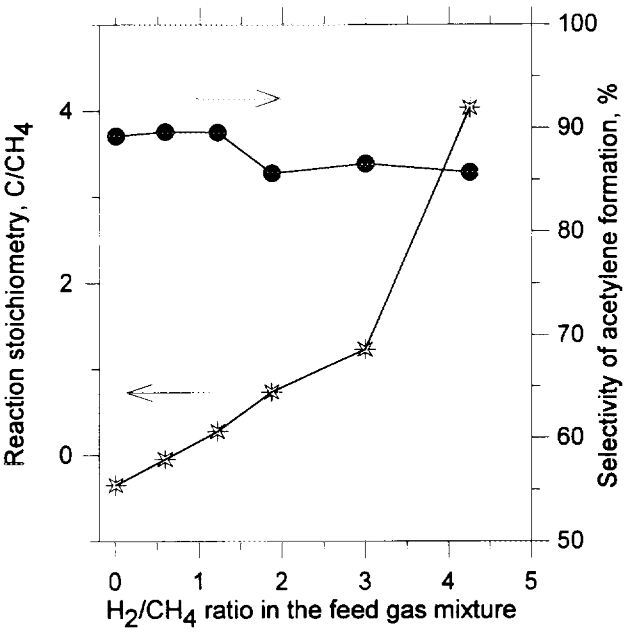

FIG. 5. Dependence of the mole ratio between reacting carbon and methane on the input ratio H_2/CH_4 under RF conditions (7-ms pulses at a duty cycle of 0.05). The gas flow rate is 0.5 ml/s.

of the isotope distribution. This was confirmed by measurements using commercially available acetylene. This ratio increased when experiments on ^{13}C were conducted. The experiments (B to E) indicate a correlation between the concentration of $^{13}CH^{12}CH$ and the concentration of hydrogen in the mixture feed. Thus, the increased I_{27}/I_{26} mass peak ratio in B and C as compared to A can be attributed to the interaction of the ^{13}C with hydrogen evolved in the decomposition of methane.

The results obtained with ^{13}C agree with the data presented in Fig. 5; however, the mass spectra data for D and E presented in Table 1 are considerably smaller than the values expected from the results in Fig. 5. As shown in Fig. 5, with a H_2/CH_4 ratio of 4, the reacting carbon to methane ratio is 3 : 1. Under these conditions, the participation of carbon in the reaction should increase so we should have observed a much higher I_{27}/I_{26} mass peak ratio for acetylene over ^{13}C in the mass spectra data. There was also a decrease in selectivity to acetylene, which was typically 40–50% of hydrocarbon products with experiments using ^{13}C, as compared with a selectivity of 90% using activated carbon. The main reason for this discrepancy is probably due to the different geometry of the carbon particles in the two samples. The amorphous ^{13}C produced a more compact medium than the activated carbon pellets. As a result, a smaller surface of the ^{13}C sample was in contact with a flow of the gas mixture, which reduced the efficiency of the reaction with solid carbon and increased the gas-phase formation of acetylene from methane.

TABLE 1

Mass-Spectral Peaks Ratio in the Acetylene GC/MS Peak

Mode of irradiation	Experiment	Catalyst	H_2/CH_4 (mole ratio)	I_{27}/I_{26} (%)
MW or RF	A	^{12}C	0	2.7
MW	B	^{13}C	0	4.9
RF	C	^{13}C	0	4.7
RF	D	^{13}C	3.8	12
RF	E	^{13}C	4.4	33

The reaction mechanism is postulated as follows.

Generation of Hydrogen Atoms

$$CH \rightarrow CH_3 + H \quad [3]$$

$$CH_3 \rightarrow CH_2 + H \quad [4]$$

$$CH_2 \rightarrow CH + H \quad [5]$$

$$CH \rightarrow C + H. \quad [6]$$

Atomic hydrogen can also be generated from molecular hydrogen which is present in the gas phase as a result of the methane decomposition or from hydrogen that was added to the feedstock (H–H and $H–CH_3$ bond energies have similar values (31)).

Atomic hydrogen can recombine on the solid carbon to form molecular hydrogen, but can also interact with solid carbon to form the CH radical, as suggested by Balooch and Olander (30).

Hydrogenation of the Surface Carbon Atoms

$$C_{(S)} + H_{(ads)} \rightarrow CH_{(ads)} \quad [7]$$

The CH radicals in Eq. [7] can react with methane or hydrogen:

$$CH + CH_4 \rightarrow C_2H_5 \quad [8]$$

or

$$CH + H_2 \rightarrow CH_3. \quad [9]$$

The C_2H_5 radicals can undergo further decomposition producing ethylene and acetylene. Ethane can be formed by recombination of methyl radicals obtained by Eq. (9). The ethylene and ethane which accumulated can undergo thermal decomposition giving rise to acetylene. This process is facilitated by increasing temperature and residence time. The reaction of methyl radicals obtained by Eq.

(9) with acetylene resulting in the formation of the C_3H_5 radical can explain the subsequent formation of C_3 and C_4 hydrocarbons. However, the CH_3 and CH radicals formed from the decomposition of methane (Eqs. [4] and [6]) can also participate and react with hydrogen or methane. This conclusion is based on the observation of a noticeable amount of acetylene containing ^{12}C in the experiments with the ^{13}C (Table 1).

In the experiments with ^{13}C and methane–hydrogen mixtures we did not see any noticeable amount of $^{13}CH^{13}CH$ in the products (acetylene containing two ^{13}C atoms, as well as $^{13}CH_4$, was obtained only in experiments with pure hydrogen). Our data show that the recombination of CH radicals in the systems under consideration is less preferable than their reaction with molecules in the gas phase. This is due to a lower concentration of radicals, compared to the concentration of molecules, as a result of a relatively high pressure used in this work as compared with the experiments on atomic hydrogen (30) or with microwave plasma experiments (9–14).

In this system it is possible to achieve a stoichiometry close to

$$CH_4 + 3C \rightarrow 2C_2H_2, \qquad [10]$$

when the feeding gas mixture contains approximately 20% methane and 80% hydrogen. In this case the amount of hydrogen in the products remains the same as in the feedstock, and it can be considered a catalyst in the reaction.

CONCLUSION

This study shows that it is possible to convert methane to higher hydrocarbons using RF or microwave energy. The major products are C_2 hydrocarbons, with a high selectivity towards acetylene. The role of hydrogen and carbon in the reaction was observed to be crucial. Judicious use of experimental variables such as incident power, irradiation time, initial methane and hydrogen pressure can result in obtaining high acetylene production and selectivity.

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