

Direct synthesis of acetylene from methane by direct current pulse discharge

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In non-catalytic direct conversion of methane to acetylene by using direct current pulse discharge under conditions of ambient temperature and atmospheric pressure, the selectivity of acetylene from methane was >95% at methane conversion ranging from 16 to 52%; coexisting oxygen was very effective in removing deposited carbon and stabilized the state of discharge.

Methane, which is a major constituent of natural gas, is so stable that high reaction temperatures such as 1273 K or higher are required for its pyrolysis to ethylene or acetylene.¹ Although high reaction temperature is favorable for high conversion, higher temperature promotes the consecutive decomposition of the products to carbon.^{1,2} Recently, direct conversion of methane to higher hydrocarbons using plasma technology has been studied to improve the selectivity and yield of the desired products.^{3–8} For example, in microwave plasma reaction, acetylene was produced with a selectivity of >90% from methane at as low a reaction pressure as 4.5 kPa.⁶ The plasma catalytic conversion of methane by using dc corona discharge was also found to produce acetylene with high selectivity and yield under atmospheric pressure in the temperature range 343–773 K. The nature of the catalyst surface in contact with the plasma was very important for homogeneous activation of methane and NaY zeolite gave the highest yields of C₂ hydrocarbons. The highest yield of C₂ hydrocarbons (32%) was obtained in a hydrogen-containing plasma at a flow rate of 10 cm³ min⁻¹.⁷ In this study, dc pulse discharge was applied to non-catalytic direct conversion of methane at ambient temperature and under atmospheric pressure to prepare C₂ hydrocarbons selectively, with high methane conversion.

A flow type reaction apparatus which was composed of a Pyrex glass tube of 4.0 mm internal diameter was used as the reactor. Reactant gas which was premixed at a given ratio was fed at a constant flow rate. Stainless steel electrodes of 2 mm diameter were inserted from each end of the reactor as shown in Fig. 1 and the distance between the electrodes was 1.5 mm. A dc pulse discharge was initiated by supplying a negative high voltage with a dc power generator. The wave signal was observed by a digital oscilloscope and the pulse duration was *ca.* 10 ms. All the reactions were conducted at atmospheric pressure and ambient temperature without any catalyst and all products were analyzed by gas chromatography. Product selectivity was

defined as follows; selectivity (%) = yield of the product (Carbon mmol)/sum of all the products (Carbon mmol) × 100.

Upon dc pulse discharge, methane was activated readily to form acetylene with a selectivity of >90% in the absence of catalyst. Fig. 2 shows methane conversion, yield of C₂ hydrocarbons and selectivity of acetylene, ethylene and ethane *vs.* supplied power. While methane conversion increased up to 52% by the increasing power supply, acetylene selectivity was very stable at *ca.* 95%. Applying a discharge for methane activation thus led to the selective formation of acetylene with high C₂ yield and stable selectivity, not observed in conventional homogenous gas phase reactions. Other hydrocarbon products such as prop-1-yne and buta-1,3-diyne were at <1%. Some carbon deposition occurred on both electrodes and the reactor wall during the reaction and eventually resulted in unstable discharge and sometimes in cessation.

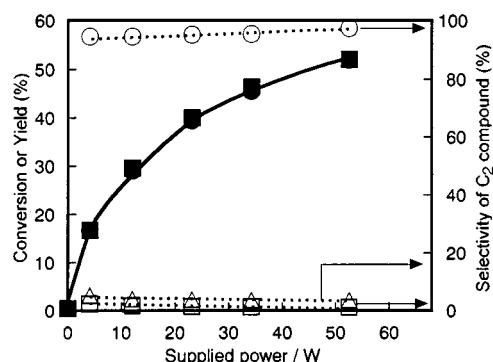


Fig. 2 Effect of supplied power on conversion and selectivity. Reaction conditions: pure methane, 10 cm³ min⁻¹ (NTP) flow rate, ambient temperature, 0.1 MPa, 1.5 mm electrode distance, (■) methane conv., (●) C₂ yield, (○) acetylene selectivity, (△) ethylene selectivity, (□) ethane selectivity.

In order to prevent carbon deposition during discharge, O₂ and Ar were added to give a resultant feed gas composition CH₄-O₂-Ar = 5 : 1 : 4. Reaction results under a flow of 10 cm³ min⁻¹ at normal temperature and pressure (NTP) and 25 W power supply are given in Table 1. Carbon monoxide was produced as well as carbon dioxide (selectivity <1% to CO₂), in addition to C₂ compounds. Comparing results with those of the reaction with pure methane, there was little difference in C₂ yield, which indicates that the increased methane conversion was essentially due to the carbon monoxide formed. Additionally, the composition of C₂ compounds was not much affected. In the reaction using pure methane, the C₂ yield was 40.6% and the amount of acetylene in the C₂ products was 94.4%, while the reaction in the presence of O₂ gave 91% acetylene selectivity in terms of non-CO/CO₂ carbon products with yields of C₂ compounds and CO of 38 and 20%, respectively. These results suggest that the precursor of the deposited carbon is converted to carbon monoxide by reaction with oxygen. Also the reaction in the presence of O₂ led to stable discharge.

The effect of total flow rate (from 3 to 225 cm³ min⁻¹ in the presence of O₂) with a supplied power of *ca.* 25 W is also shown in Table 1. Methane and oxygen conversion was remarkably

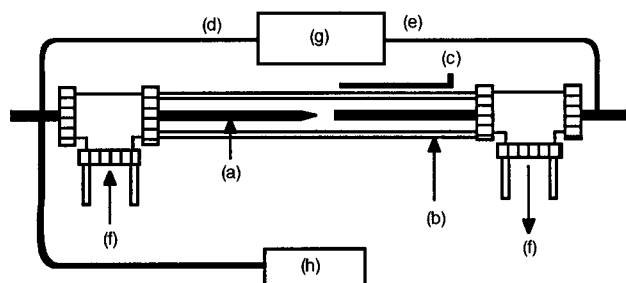


Fig. 1 Schematic diagram of the reactor. (a) 2.0 mm diameter stainless steel electrode, (b) 4.6 mm internal diameter quartz tube, (c) thermocouple, (d) negative high voltage, (e) ground, (f) direction of the flow gas, (g) direct current high voltage power supply, (h) digital oscilloscope.

Table 1 Effect of coexisting oxygen and total flow rate^a

| Feed gas | Flow rate (NTP)/ cm ³ min ⁻¹ | Conv. (%) | | Yield (%) | | Selectivity (%) | |
|---|--|-----------------|----------------|----------------|------|-------------------------------|------|
| | | CH ₄ | O ₂ | C ₂ | CO | C ₂ H ₂ | CO |
| CH ₄ | 10 | 40.6 | — | 39.9 | — | 94.4 | — |
| CH ₄ -O ₂ -Ar (5:1:4) | 3 | 83.9 | 100.0 | 49.6 | 33.8 | 56.2 | 40.3 |
| CH ₄ -O ₂ -Ar (5:1:4) | 10 | 58.9 | 69.9 | 38.1 | 20.2 | 58.9 | 33.8 |
| CH ₄ -O ₂ -Ar (5:1:4) | 225 | 6.8 | 9.7 | 4.9 | 1.9 | 62.3 | 27.9 |

^a Reaction conditions: ambient temperature, 0.1 MPa, 1.5 mm electrode distance, 25 W supplied power.

affected by the total flow rate. At 3 cm³ min⁻¹ total flow rate, oxygen conversion reached 100% and methane conversion was 84%. On the other hand, the selectivity towards acetylene was scarcely affected while the C₂ yield increased to ca. 50%. The selectivity to carbon monoxide increased slightly as the total flow rate was decreased. If carbon monoxide was formed by a chain reaction, its selectivity should increase more drastically with decreasing flow rate. Thus, the behavior of carbon monoxide selectivity to the total flow rate indicated that carbon monoxide formation was separate from C₂ compound formation and derived from a coke precursor.

We also attempted to stabilize the discharge by using hydrogen as the coexisting gas, since using oxygen caused the formation of carbon monoxide which decreased the selectivity to C₂ compounds. The reaction results were much the same as for pure methane, and H₂ did not stabilize discharge as well as O₂. However, dilution of methane by hydrogen such that CH₄:H₂ = 1:4 was effective for stabilization of the discharge.

Table 2 shows methane conversion, C₂ yield and selectivities to each C₂ compound at various H₂ concentrations from 0 to 90%. Up to 50% hydrogen concentration, a marked effect of H₂ was not observed. However as the hydrogen concentration was

increased, methane conversion and C₂ yield increased from 44% (pure methane) to 57% (CH₄:H₂ = 1:2). At 80% hydrogen concentration, methane conversion and acetylene selectivity decreased slightly, and selectivity towards ethane and ethylene increased. At conditions of > 80% hydrogen concentration, the excessive concentration of hydrogen interfered with electron attack on methane, leading to drastic reduction in methane conversion and to an increase in ethane selectivity.

In conclusion, when a dc pulse discharge was applied for methane activation, acetylene was produced directly and selectively. Oxygen removed deposited carbon by oxidation to form carbon monoxide, and stabilized the state of discharge. Dilution of methane with hydrogen up to 80% also stabilized the state of discharge without changing the product selectivity. We assume that the formation of acetylene is *via* dimerisation of CH radicals which form by dc discharge, and that the high selectivity to acetylene is a characteristic feature of short range pulse discharge.

Notes and references

- 1 F. G. Billaud, F. Baronnet and C. P. Gueret, *Ind. Eng. Chem. Res.*, 1993, **32**, 1549.
- 2 A. Holmen, O. Olsvik and O. A. Rokstad, *Fuel Process. Technol.*, 1995, **42**, 249.
- 3 M. S. Ioffe, S. D. Pollington and J. K. S. Wan, *J. Catal.*, 1995, **151**, 349.
- 4 C. Liu, A. Marafee, B. Hill, G. Xu, R. Mallinson and L. Lobban, *Ind. Eng. Chem. Res.*, 1996, **35**, 3295.
- 5 A. Marafee, C. Liu, G. Xu, R. Mallinson and L. Lobban, *Ind. Eng. Chem. Res.*, 1997, **36**, 632.
- 6 K. Onoe, A. Fujie, T. Yamaguchi and Y. Hatano, *Fuel*, 1997, **76**, 281.
- 7 C. Liu, R. Mallinson and L. Lobban, *J. Catal.*, 1998, **179**, 326.
- 8 K. Thanyachotpaiboon, S. Chavadej, T. A. Caldwell, L. L. Lobban and R. G. Mallinson, *AIChE J.*, 1998, **44**, 2252.

Table 2 Effect of hydrogen concentration on conversion and selectivity^a

| H ₂ concentration (%) | CH ₄ conv. (%) | C ₂ yield (%) | Selectivity (%) | | |
|--|------------------------------|-----------------------------|-------------------------------|-------------------------------|-------------------------------|
| | | | C ₂ H ₆ | C ₂ H ₄ | C ₂ H ₂ |
| 0 | 44.3 | 44.2 | 0.6 | 2.8 | 94.6 |
| 50 | 46.3 | 46.2 | 1.1 | 4.4 | 94.2 |
| 67 | 57.4 | 57.1 | 1.2 | 5.7 | 92.7 |
| 80 | 47.0 | 46.6 | 2.9 | 8.1 | 88.2 |
| 90 | 11.8 | 11.4 | 17.7 | 15.2 | 63.7 |

^a Reaction conditions: 10 cm³ min⁻¹ (NTP) flow rate, ambient temperature, 0.1 MPa, 1.5 mm electrode distance, 4 mA dc.

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