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Pyrolysis of Methane into Higher Hydrocarbons on Carbon Fibers

Isao MOCHIDA,* Yusuke AOYAGI, and Hiroshi FUJITSU
Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816

Pyrolysis of methane over pitch based carbon fibers at 1173-1273 K produced rather selectively C_2 hydrocarbons (selectivity up to 67%) at a stational conversion of 20% with limited deposition of carbon (18%).

Since methane is one of major hydrocarbon resources endowed on the earth, its broad utilization is most expected in the next decade.[1] Its direct conversions into chemical feedstocks have been extensively searched. Oxidative coupling into higher hydrocarbons and oxidation into methanol are reported to be promising,[2-4] but yields are still limited.

In the present letter, pyrolytic conversion of methane into higher hydrocarbons was examined on the surface of carbon fibers(CF). Surface of CF may be active to produce radicals from methane, enhance their coupling and terminate their chain reactions at the appropriate length.

PAN based (M40, Toray; surface area < 10 m^2/g), pitch based (KCF and KGF, Kureha; both < 10 m^2/g), active CF (ACF, Toho Rayon; 1090 m^2/g) and quartz wool were used. Cutted fiber (0.3 g, 40 mm long) was placed in the reaction tube (quartz: 15 mm diameter). IR image furnace was used for heating. After fiber was pretreated in helium at 1273 K for 30 min, helium-methane mixture (10 vol% CH_4, 30 ml min^{-1}) was introduced at prescribed temperatures. The products were analyzed by gas-chromatography and weighing CF.

Methane was pyrolyzed on fibers at 1273 K at constant conversions for 20 h except for first 1 h, while the conversion decreased from 80 % to stational one. The product selectivities on CF were essentially unchanged during this transient region. Table 1 summarizes the stational conversion and selectivity of methane pyrolysis at 1173 and 1273 K on CF and quartz wool. Only pitch based KCF and KGF exhibited remarkable selectivities for

total hydrocarbons as high as 73 to 82%, ethylene and acetylene being the major hydrocarbon products with their selectivities of 34 and 33%, respectively. A variety of $C3^+$ hydrocarbons, principally propylene and 2-butene, was produced at their total yield of 12-13%. The pyrolytic carbon was also produced on CF.

Table 1. Methane pyrolysis on CF

CF	Temp	Conv.	Selectivity/%[a]					
	K	%	C_2H_6	C_2H_4	C_2H_2	C_3^+	$\sum$Ci	PC
KCF	1273	20	2	34	33	13	82	18
	1173	5	24	47	13	8	92	8
KGF	1273	20	2	26	33	12	73	27
	1173	5	16	48	16	9	89	11
ACF	1273	20	1	18	16	2	37	63
	1173	5	23	44	11	4	82	18
M40	1273	12	2	18	11	-	31	69
QW[b]	1273	15	1	16	13	8	38	62

a) $\sum$Ci:Sum of hydrocarbons, PC: Pyrolytic carbon.
b) Quartz wool.

ACF, PAN-based CF, and quartz wool produced the carbons as a principal product.

Conversion at 1173 K was as low as 5% on KCF, KGF, and ACF. Ethylene was the major product with its selectivity of as high as 45-50%, and ethane and acetylene followed at their selectivities around 20%. Production of pyrolytic carbon was reduced very much.

The reaction mechanism and roles of the fiber surface in the present pyrolysis are not clarified. The pyrolysis may be initiated by the radical fission of methane either on the surface or in the gas phase into methyl radicals which are coupled on the surface first into C_2 species and then to higher ones and finally pyrolytic carbon. Marked decrease of the conversion in the first 1 h may indicate the participation of the surface in the activation of methane. The semi-graphitic surface of pitch-based CF may provide sites for produced hydrogen to terminate the consecutive reaction for high selectivity. The detail kinetics and characteristic features of fiber surface are targets of future study.

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