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Selective Pyrolysis of Ethane over Pitch Based Carbon Fiber

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Ethane was found stationally and selectively pyrolyzed into ethylene in first order over a pitch based carbon fiber (CF) by the contact time of 4 second at 948 to 1023 K, which was lower by 200 K than that for the convensional pyrolyses without the fiber. The selectivity tended to decrease moderately with sharp increase of the conversion at higher temperatures, being 97 to 93%, respectively, at the conversions of 2 and 33% at 948 and 1023 K, respectively.

Ethylene, a major source for petrochemicals, is currently produced through the pyrolysis of naphtha. Ethane as a major by-product in the natural gas or naphtha cracking can be an excellent feed for ethylene, and its dehydrogenation into ethylene has been industrialized.[1)] Rather small capacity of ethane compared to that of naphtha in japanese petrochemical industry is looking for its more selective and efficient process.

The present authors reported in previous papers that pitch based carbon fiber accelerated the thermal coupling of methane into ethane and ethylene at 1223 K in a rather selective manner (C_2 selectivity >90%) with a little production of carbon on the fiber surface when the conversion was below 10%.[2,3)]

In the present letter, pyrolysis of ethane was studied on an isotropic pitch based carbon fiber in a temperature range of 948 to 1073 K, which is certainly lower by 100-200 K than that of the conventional pyrolysis without any catalytic substances. The surface of the carbon fiber is expected to initiate the fission of C-C and C-H bonds of ethane, to propagate the radical chain reaction, and to transfer the heat to the gaseous substrate efficiently, providing better selectivity at high conversions at lower temperatures.

A pitch based carbon fiber (CF) (KCF-100, Kureha Chemical Industrial Co.) was used in the present study. Cut-fiber was carefully placed in the quartz tube reactor. The weight of CF was 0.2 g when the length of packed CF was 40 mm. Fiber was pretreated in helium at 1173 K for 60 min. Ethane-helium mixture (C_2H_6:10-100%, flow rate:60 cm$\cdot$min^{-1}) was preheated to 873 K at the upper part of the furnace and then sent to the reaction zone (isothermal zone:120 mm) of the prescribed temperature. The carbon fiber was packed in both zones. The gaseous products were analyzed and quantified by a gaschromatograph (column:Apiezon grease L) and the amount of carbon product was measured by weighing the used fiber. No tary product was found in the reactor. Conversion and selectivity were definded by following equations.

$$\text{Conversion } /\% = 100 \cdot (1 - \text{unreacted } C_2H_6/\text{fed } C_2H_6) \quad (1)$$

$$\text{Selectivity } /\% \text{ for } C_k \text{ hydrocarbon} = 100 \cdot (C_k / \sum_i C_i) \quad (2)$$

where C_k and C_i are amounts of k and i kinds of hydrocarbon produced, respectively.

Figure 1 illustrates the conversion of ethane and selectivity for ethylene on KCF-100 of 0.2 g at 1023 and 1073 K. The pyrolysis over CF was very stable at 1023 K, providing stationary conversion (19%) and selectivity (95%) for longer than 14 h. In contrast, the conversion increased with the time on stream at 1073 K, increasing from 45% at 1h after the reaction started to 60% after 9 h, while the selectivity decreased from 92 to 85%. Without CF or with kish graphite grains or quartz wool in the reaction zone, no reaction was observed at 1073 K by the same contact time, suggesting catalytic roles of CF for selective pyrolysis of ethane.

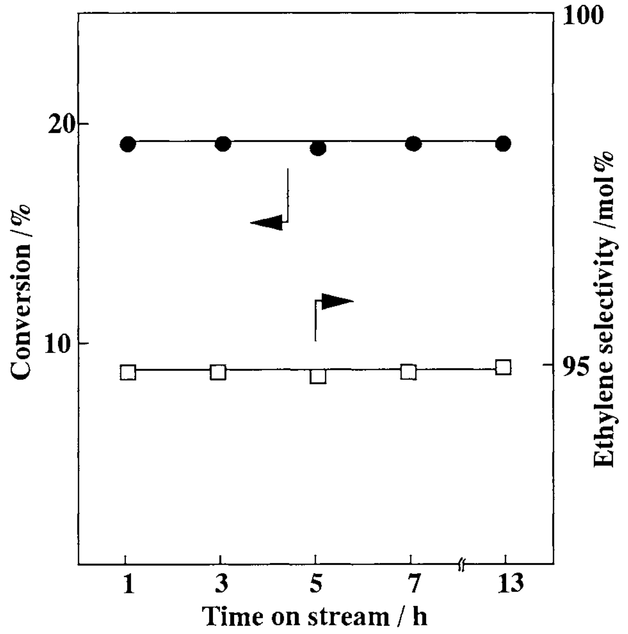

Fig. 1-a. Pyrolysis of ethane over carbon fiber at 1023 K.

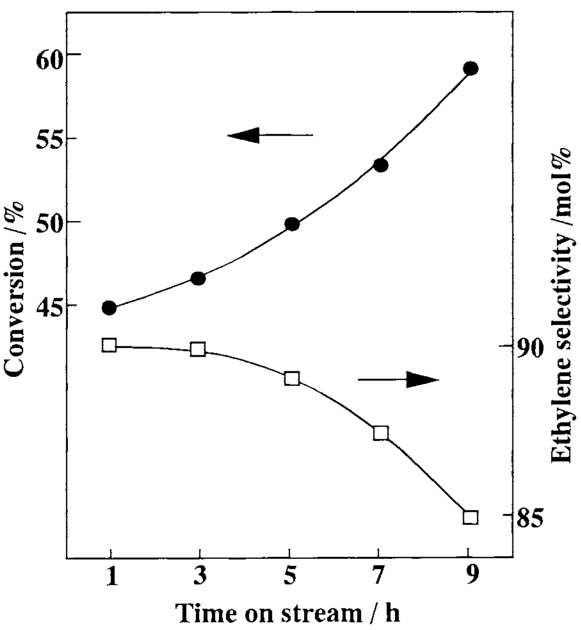

Fig. 1-b. Pyrolysis of ethane over carbon fiber at 1073 K.

Table 1 summarizes the product distribution except for hydrogen in mole percent by the pyrolysis over CF of 0.2 g at 948 to 1028 K where the reaction was stationary. The reaction was very selective at 948 to 1028 K, giving high selectivity of 97 to 93% at the conversion level of 2 to 37%. The higher reaction temperature increased the conversion sharply at a moderate sacrifice of the ethylene selectivity. Major by-product was methane, suggesting minor contribution of successive reaction of ethylene.

Table 1. Conversion and product distribution in ethane pyrolysis

React.temp.	Conversion	Product distribution /mol%					
K	%	CH_4	C_2H_4	C_2H_2	C_3H_6	C_4^+	carbon
948	2	3	97	0	0	0	0
973	4	3	97	0	0	0	0
998	8	3	96	1	-	-	0
1023	19	3	95	1	-	1	0
1048	37	5	93	1	1	-	0

Table 2 summarizes the conversion and product distribution over CF at 1023 K when the ethane concentration was varied from 10 to 100%. The conversion and product distribution were essentially unchanged regardless of the ethane concentration. First order reaction in ethane is suggested.

Table 2. Influences of ethane concentration on the conversion and product distribution a)

Ethane conc.	Conversion	Product distribution/mol%					
vol%	%	CH_4	C_2H_4	C_2H_2	C_3H_6	C_4^+	carbon
10	18	4	94	1	-	1	0
30	19	3	95	1	-	1	0
50	18	3	93	2	-	2	0
70	17	3	94	1	1	1	0
100	15	3	93	2	-	2	0

a) Flow rate:1 cm/s; carbon fiber: 0.2 g, 40 mm; reaction temperature: 1023 K.

The present study revealed that an isotropic pitch based carbon fiber enhanced the selective pyrolysis of ethane at lower temperatures by 150-200 K at least than that of unpacked quartz tube. Since the pyrolysis is endothermic, a role of CF as a good heat-transferring media may not be ruled out. However, packed substances such as kish graphite grains or quartz wool do not always accelerate such a selective pyrolysis. The surface of CF may participate in the radical chain reaction of ethane at its initiation and chain propagation stages. Acceleration by pyrolytic carbon produced on CF suggests also the surface participation in this reaction.

$$C_2H_6 \longrightarrow 2\,CH_3 \tag{3}$$

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \tag{4}$$

$$C_2H_5 \longrightarrow C_2H_4 + H \tag{5}$$

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5 \tag{6}$$

The fisson of the C-C bond in ethane is believed the initiation step of ethane pyrolysis according to energetic consideration, 4,5) providing two methyl radicals as shown by Eq.3, since the bond energies of C-H and C-C bonds in ethane are reported 409.1 and 365.9 kJ/mol, respectively. The radical reacts with ethane to produce methane and an ethyl radical, the latter of which decomposes into ethylene and a hydrogen atom (Eqs.4,5). Hydrogen atom reacts with ethane, forming H_2 and an ethyl radical (Eq.6). Equations 5 and 6 are chain propagation steps, producing ethylene without methane formation. Some successive reactions of ethylene are postulated to explain the production of higher hydrocarbons including tar and carbon.

The first order reaction in ethane is compatible with the scheme as far as the chain propagation defines the rate while the remaining ethane is still dominant. According to this scheme, methane should be inevitably produced because of the initiation. Hence the selectivity is determined by the ratio of initiation vs. propagation. The successive reactions are very minor under the present conditions, producing very limited amount of higher hydrocarbons. No production of tar and carbon is a large advantage of the present pyrolysis in the practical application.

The CF surface may accelerate the fission of C-C bond in ethane at a temperature range of 948 to 1048 K, where the non-catalyzed fission is very slow. At the same time CF surface may facilitate the propagation step by adsorbing both H and ethane, to maintain the excellent selectivity. More optimization of kinetic conditions in terms of flow rate, reaction temperature, kinds, amounts, packed length, density and arrengement of CF are expected to allow better performance of higher selectivity around 90% at a higher conversion up to 60%, which may be commercially acceptable.

The pyrolysis at 1073 K produces certainly carbon on the CF. It is very interesting that such a carbon markedly accelerates the pyrolysis. Unfortunately such carbon lowers the selectivity, probably due to limited acceleration of propagation. Control of the CF surface is suggested to improve the selectivity at a higher conversion.

References

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