NOTES *Bull. Chem. Soc. Jpn., 61, 2649—2650 (1988)*

Selective Synthesis of Ethylene by Dehydrogenative Coupling of Methane by Use of Thermal Diffusion Column

Tatsuaki YAMAGUCHI* and Chiaki SAITO
Laboratory of Organic Chemistry, Chiba Institute of Technology,
Tsudanuma, Narashino-shi, Chiba 275
(Received February 8, 1988)

Synopsis. Ethylene was found to be obtained dehydrogenatively from methane in extremely high selectivities (91.5% at 9.4% conversion of methane) with the downward introduction to the modified thermal diffusion column with electrically heated tungusten wire at 1200 °C.

From the challenging viewpoint of the utilization of natural gas, the partial oxidative conversion of methane into more useful chemicals such as ethylene[1] and methanol[2] has been investigated more and more extensively. Nevertheless, less attention has been now taken on the direct dehydrogenative coupling of methane to ethylene because it requires temperatures higher than 1000 °C. But the by-production of hydrogen is the advantage of this process over the oxidative one.

$$2CH_4 \longrightarrow CH_2=CH_2 + 2H_2$$

Half a century ago, Clusius and Dickel invented a powerful separation column based on thermal diffusion and thermal convection.[3] A few years later Hirota applied this separation column to the thermal polymerization of methane and succeeded in getting condensed hydrocarbon oil in a good yield.[4]

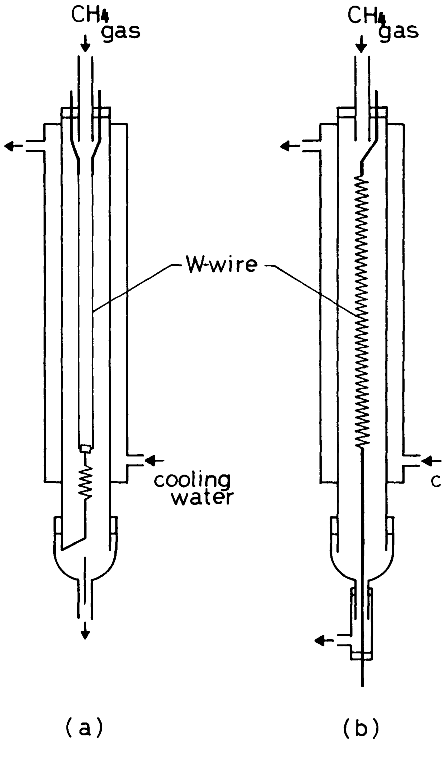

Fig. 1. Clusius-Dickel type thermal diffusion column reactor. The tungsten wire is modified in a) U-type, b) spiralled type.

By the upward flow (linear velocity 3.8 m h^{-1}) of methane in a water-cooled Pyrex-glass column of 1 m in length and 2 cm in diameter centering a straight tungsten wire of 70 cm in length and 0.5 mm in diameter, which was heated electrically at 1200 °C on surface, we could fully reproduce Hirota's results obtaining hydrocarbon oil in the yield of 62% of methane feeded. However, the operation in downward flow of methane with the similar apparatus in the same conditions was found to give a quite different result. Thus, ethylene was obtained in the yield of 5.4% with 90% selectivity at 1200 °C accompanying with far less amount of oily matter.[5]

With intent of enhancing the methane conversion, the shape of the tungsten wire is now modified from a straight line to a U-type (Fig. 1a) or a spiral (Fig. 1b) in this paper.

Experimental

Deoxygenated methane gas was introduced from the top of the thermal diffusion column (Fig. 1, length 40 cm, inner diameter 2.0 cm) without preheating under ordinary pressure, and the out-let gas from the bottom was analyzed by a gaschromatograph (Shimadzu GC-9A). The surface temperature of the tungsten wire was measured pyroptically by a radiation pyrometer (Minolta IR-120). And the amount of the alternating current was measured by a clamp tester (SOAR Model 2220).

Results and Discussion

The results are summarized in Table 1 with experimental details. In the case of Run 1, substantially 100% selectivity to total C_2 compounds was obtained. But in other cases oily matter condensed on the cold wall of column as by-products. Especially carbonaceous product was observed in Run 7. This means too much heating of the gas phase causes unfavorable results on ethylene selectivity. As expected, increasing the contact chance of methane molecule on the high-temperature tungsten surface gave the favorable effect increasing the methane conversion and the hydrogen yield with high selectivities of ethylene (Runs 1—3). The ethane yields were as low as 0.3% in every run.

Figure 2 shows variations of the product yields with the linear velocity of gas flow in the column with U-type tungsten wire. The higher linear velocity resulted in decrease of the methane conversion and increase of the ethylene selectivity. The maximum of the ethylene yield was given around 6 m h^{-1} with this type of reactor. The ethane productions were limited in a very low yield in this case again.

Table 1. Results with the Modified Column

Run No.	W wire length	Heating zone	Electric power	Methane conv.	Ethylene yield	Ethylene selec.	Ethane yield	Ethane selec.	Hydrogen yield
	cm	cm	W	%	%	%	%	%	%
1	30	30	150	2.6	2.3	89.5	0.3	10.5	5
2	60a)	30	450	9.4	8.6	91.5	0.3	3.4	27
3	120b)	30	675	14.2	12.6	88.8	0.3	2.0	43
4	30c)	24	150	3.5	2.9	82.1	0.3	8.6	8
5	30c)	18	150	4.2	3.8	90.6	0.3	6.6	11
6	30c)	12	150	9.1	7.1	78.1	0.3	2.9	23
7	30c)	6	150	26.1	15.0	58.1	0.2	0.7	56

Methane feed rate $1.8\,\mathrm{dl\,h^{-1}}$, linear velocity $5.76\,\mathrm{m\,h^{-1}}$, average surface temperature of W wire 1200 °C. Values for selectivities were based on the methane conversion. Yields of ethylene and ethane were defined as the product of the conversion and the selectivity. Hydrogen yields were calculated from the molar ratio of produced hydrogen to methane feeded. a) Folded in U-type. b) Folded in W-type. c) Spiralled 4 mm in diameter.

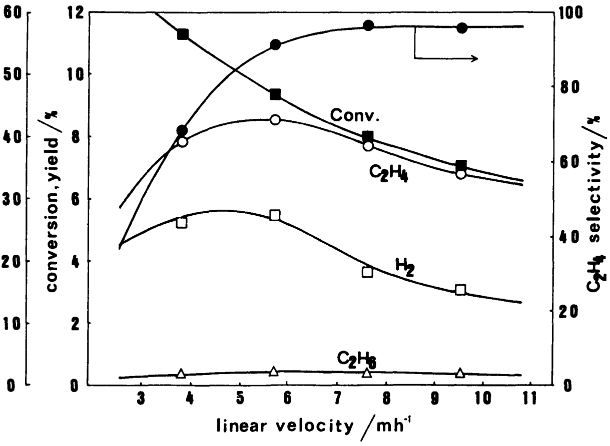

Fig. 2. The influence of the linear velocity of methane in the column.
Tungsten wire 0.5 mm×60 cm, U-type (heating zone 30 cm), surface temperature 1200 °C. Methane conversion: ■. Ethylene selectivity: ●. Yields: ○, ethylene; △, ethane; □, hydrogen.

The phenomenon giving high selectivity of ethylene production may be understood in terms of two theoretical considerations. First, the thermodynamic data give the favorable free energy change for the gas-phase conversion of methane to ethylene at 1200 °C over that to ethane. This is suggested from the fact of the very low yield of ethane throughout the experiments at this temperature. Secondly, the thermal diffusion due to the temperature gradient between the surfaces of the heated tungsten wire and the cold wall of the column permits the produced ethylene molecule, which is of the highest molecular weight in the system, to leave the heated surface for the cold wall. Following by the thermal convection the ethylene molecule is driven downward along with the cold wall and the hydrogen molecule driven upward as pointed out by Clusius. The observation of less brightness in the upper part of the tungsten wire suggests a higher concentration of hydrogen around this part of the column. By this effect the produced ethylene may be prevented from the recombination with hydrogen. Further polymerization of ethylene which occured by its recycling to the high-temperature surface may be limited because its downward direction along the cold wall is with the current when the overall feed flow in the column is downward.

From the practical viewpoint, it should be noted that the electric power required in this procedure would be rather low since it is not necessary to heat the whole gas phase up to 1200 °C.

References

1) a) G. E. Keller and M. M. Bhasin, *J. Catal.*, **73**, 9 (1982); b) T. Ito and J. H. Lunsford, *Nature (London)*, **314**, 721 (1985); c) E. Iwamatsu, T. Moriyama, N. Takasaki, and K. Aika, *J. Chem. Soc., Chem. Commun.*, **1987**, 19; d) K. Otsuka and T. Komatsu, *J. Chem. Soc., Chem. Commun.*, 1987, 388.

2) a) H. D. Gesser and N. R. Hunter, *Chem. Rev.*, **85**, 235 (1985); b) R. Pitchai and K. Klier, *Catal. Rev. Sci. Eng.*, **28**, 13 (1986).

3) K. Clusius and G. Dickel, *Naturwiss.*, **26**, 546 (1938).

4) K. Hirota, *Bull. Chem. Soc. Jpn.*, **16**, 274 (1941).

5) T. Yamaguchi, A. Kadota, and C. Saito, *Chem. Lett.*, **1988**, 681.