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Dehydrogenative Coupling of Methane by Use of Thermal Diffusion Column

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By using a thermal diffusion column as reactor, the dehydrogenative coupling of methane was investigated over electrically heated tungsten wire at 1000-1400 °C. Besides hydrogen, the main product by the downward flow of methane was C_2 hydrocarbon, although that by the upward flow was aromatic oil.

In 1941 Hirota reported the formation of oily aromatic hydrocarbons and hydrogen from methane by use of Clusius-Dickel type thermal diffusion column with the upward flow of the reactant gas.$^{1-3)}$ His success in getting the oil in a better yield was attributable to prevent from the recombination reaction by the instant separation of produced hydrogen from hydrocarbon residues owing to thermal diffusion effect.

We traced out his experiments with a vertically held pyrex-glass column of 1 m in length and 2 cm in inner-diameter, which was cooled with running water, centering a straight tungsten wire of 70 cm in length and 0.5 mm in diameter, which was electrically heated at 1000-1400 °C. The temperature of the heated surface was measured pyroptically in advance of the methane feeding, and the electric voltage to give the desired temperature was maintained throughout the reaction period. The duration was usually 4 h. The resulting gaseous products were collected and analysed by gas chromatography, and the oily products were collected from the bottom of the column and weighed. The composition of the aromatic oil has not been determined. Yields of the gaseous products and the oil were calculated on the basis of mole and weight, respectively, of methane feeded.

As shown in Figs. 1 and 2, the results were quite different with the direction of flow of the reactant gas. The main product by upward flow was oily hydrocarbon coincidently with Hirota's results especially at lower flow rate (Fig. 1 a), and its maximum yield was obtained at 1300 °C (Fig. 2 a). However, with downward flow, we found that the main product was C_2 hydrocarbon accompanying negligible amount of oil (Fig. 1 b). The maximum of C_2 yield was obtained at 1300 °C. The production of carbonaceous substance depressed the yield at 1400 °C (Fig. 2 b).

The selectivity of ethylene in C_2 hydrocarbon was affected with the surface temperature. More than 90% selectivity of ethylene was obtained at 1200 °C. However, the predominancies of ethane and acethylene over ethylene were observed at 1000 °C and 1400 °C, respectively. This could be understood on the basis of thermodynamical data. Further polymerization of C_2 hydrocarbon which occurred by the recycling to the high temperature surface may be limited because its downward direction along with the cold wall is with the current when the overall feed flow is downward. Further theoretical considerations on the results will be stated elsewhere.

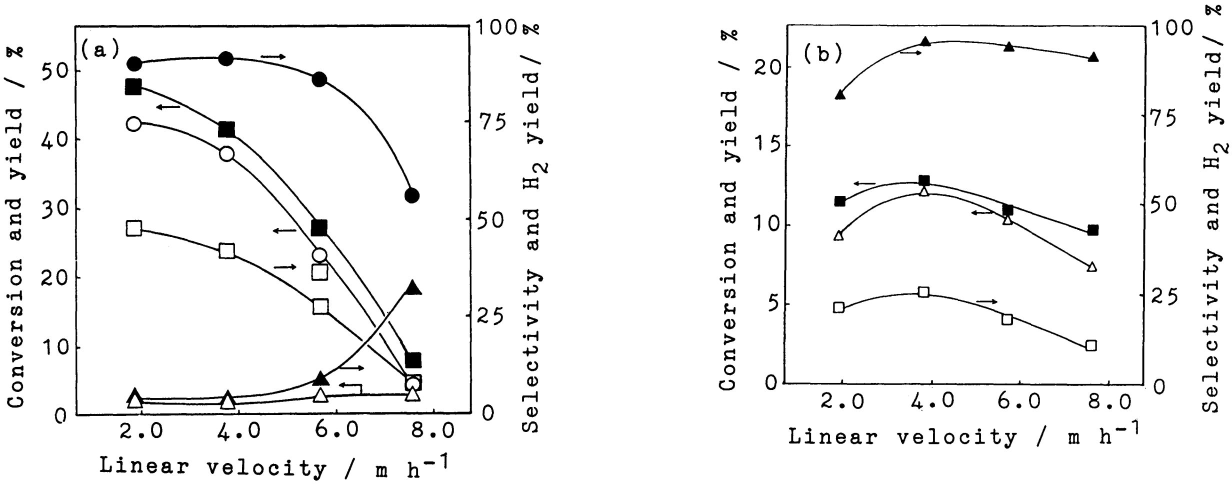

Fig. 1. Dependence of yields and selectivities on the flow rate.
(a) upward flow at 1200 °C; (b) downward flow at 1300 °C
■:methane conversion, ●:oil selectivity, ○:oil yield,
▲:C_2 selectivity △:C_2 yield, □:H_2 yield

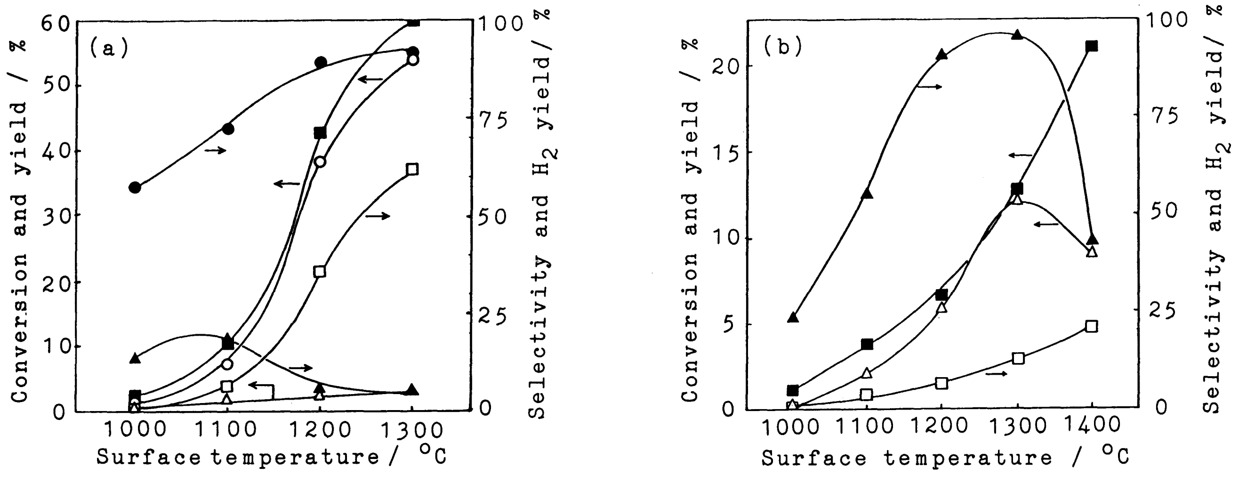

Fig. 2. Dependence of yields and selectivities on the surface temperature.
(a) upward flow of 3.8 m h^{-1}; (b) downward flow of 3.8 m h^{-1}
■:methane conversion, ●:oil selectivity, ○:oil yield,
▲:C_2 selectivity △:C_2 yield, □:H_2 yield

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References

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