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The Effect of the Coexistent Gases on the Thermal Reaction of Toluene or Methane in a Clusius–Dickel Type Thermal Diffusion Column

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The thermal reactions of toluene or methane in a Clusius–Dickel type thermal diffusion column was investigated in the temperature range from 1300 K to 1470 K under atmospheric pressure from the viewpoint of the effect of coexistent gases to clarify the effect of thermal diffusion on the reactions. The addition of hydrogen accelerated the hydrogenolysis of toluene resulting in the high selectivity of benzene. Contrarily, by the addition of either helium or nitrogen, the reactions were retarded. On the other hand, the reactions of methane were promoted by the addition of nitrogen, and retarded by the addition of helium. This difference of the effect of coexistent gases of helium and nitrogen shows that the partial separation of reaction mixture due to thermal diffusion and convection actually occurs and has a great influence on the reaction results in a Clusius–Dickel type thermal diffusion column.

Thermal diffusion arises when a mixture is subjected to a temperature gradient making the partial separation of the components, promoted by convection synergistically.[1] In this process, the component of low molecular weight concentrates in the hot region. In a reactor, which has a large temperature gradient, the partial separation of the components of the reaction mixture due to thermal diffusion effect prevents such side reactions as reverse reactions and successive reactions. By such a reactor, the reaction products are expected to be different from those in the conventional ones. For example, Hirota carried out the dehydrogenative coupling of methane to obtain oily aromatic hydrocarbons and hydrogen.[2–4] His success in getting the oil in a high yield could be accounted for by the prevention of the recombination reaction by the instant separation of produced hydrogen from hydrocarbon residues owing to thermal diffusion and convection effect caused by the temperature gradient.

The thermal reactions of simple aromatic hydrocarbons in a temperature gradient system have been investigated in this laboratory.[5–11] In a previous paper,[11] we reported the thermal reactions of toluene in a Clusius–Dickel type thermal diffusion column, in which toluene underwent hydrogenolysis without the addition of hydrogen as a reactant, thanks to the concentration of the hydrogen, which evolved during the reaction, around the heater due to thermal diffusion and convection.

The present paper discusses the role of thermal diffusion and convection in a reactor with a large temperature gradient through the effect of coexistent gases on the thermal reactions of toluene and methane.

Experimental

Toluene. The reactor used for the thermal reactions of toluene is schematically shown in Fig. 1. The reactor is a modification of a Clusius-Dickel type thermal diffusion column for the reactions, consisting of a Pyrex glass-made Liebig condenser (60 cm in length, and 20 mm in inner diameter) and a heater made of a nickel chromium steel wire (42 cm in length and 1.0 mm in diameter) mounted at the axis of the condenser. The inlet of toluene was placed at the level 2 cm lower from the top of the heater. The reactions were carried out under atmospheric pressure, in the temperature range from 1300 K to 1470 K. The air in the reactor was first replaced by nitrogen and cooling water was supplied. The power of the heater was then turned on. The temperature of the heater was measured by a radiation pyrometer (Minolta IR-120) and set at a desired reaction temperature before the toluene feeding. Toluene was vaporized by a preheater and

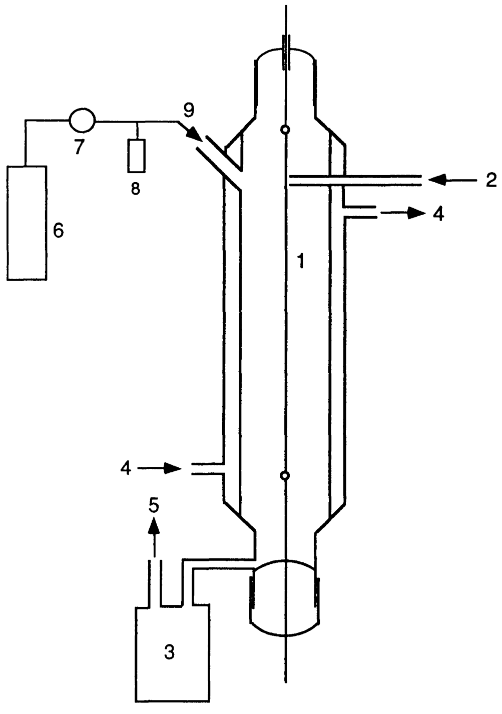

Fig. 1. Systematic diagram of a Clusius–Dickel type separator as a reactor.
1: Heater, 2: Toluene, 3: Liquid products, 4: Cooling water, 5: Gaseous products, 6: Gas container, 7: Control valve, 8: Flow meter, 9: Gas inlet.

charged downward parallel to the heater at the constant rate of 0.1 mol h^{-1}, and the surface temperature of the heater was adjusted to the desired temperature. Coexistent gases were then charged downward, at the rate of 0.04 mol h^{-1}, and were maintained at the rate by the control valve according to the reading of the flow meter. During the reaction the heater was kept at the temperature by controlling the voltage and the currency of the electric current. The duration was usually 2 h. The reaction products were identified by GC-MS and GC-IR analysis by using authentic samples. Liquid products were sampled every 30 min and analyzed by gas chromatography. The result of the sample for the last 30 min was usually employed for each run.

Methane. The thermal reactions of methane were carried out in the same type of reactor (80 cm in length and 20 mm in inner diameter). A mixture of methane and a coexistent gas in the desired ratio was charged at the rate of 40 ml min^{-1} under atmospheric pressure in the temperature range from 1270 K to 1570 K. The surface temperature of the heater and the flow rate of the reactant gas were controlled by the same way for the reactions of toluene. The duration was also 2 h. The reaction products were identified and analyzed by gaschromatography.

Results and Discussions

The Role of Thermal Diffusion and Convection in the Thermal Reactions of Toluene. Table 1 includes the results of the thermal reactions of toluene in a Clusius–Dickel type thermal diffusion column of 20 mm in diameter. As reported in the previous paper,[11] the thermal reactions of toluene without a coexistent gas in a diffusion column are characterized by the high selectivity of benzene in the reactions with the high conversion of toluene. This is in contrast to the result of the pyrolysis of toluene carried out in a conventional tubular reactor at 970 K, in which the selectivity of benzene and bibenzyl was 39% and 15%, respectively, when toluene conversion was as much as 6.5%.[11]

Another characteristics of the reaction was a remarkable change in the selectivity of benzene and bibenzyl with the conversion of toluene. High conversion of toluene resulted in the high benzene selectivity, and the low bibenzyl selectivity. On the other hand, the benzene selectivity declined and the bibenzyl selectivity increased as the toluene conversion decreased.

These two features should be attributable to thermal diffusion and convection. Thermal diffusion arises when a mixture is subjected to a temperature gradient making the partial separation of the components, promoted by convection synergistically. In this process, the component of low molecular weight concentrates in the hot region. In the thermal diffusion reactor of our experiment, molecular hydrogen or atomic hydrogen, evolved in the course of reactions, are separated and concentrated on the surface of the heater due to thermal diffusion effect. This process is further accelerated by convection. They could retard the formation of benzyl radical, and promote the production of benzene by hydrogenolysis of toluene, resulting in the high selectivity of benzene and low selectivity of bibenzyl. In other words, in the thermal diffusion column, toluene appears to have undergone hydrogenolysis due to the concentration of hydrogen, without supplying hydrogen as a reactant. Therefore, the selectivity of benzene is indicative of hydrogenolysis of toluene and the degree of hydrogen concentration on the surface of the heater. Accordingly, it can be said basically that the higher is the toluene conversion, the more is the hydrogen formation with the higher selectivity of benzene. On the other hand, when the toluene conversion is low, hydrogen is not produced enough to carry out hydrogenolysis of toluene and benzyl radicals give bibenzyl by combination reaction.

Furthermore, almost no carbonaceous products were formed during the course of thermal reactions of toluene, which can also be accounted for by thermal diffusion and convection.

The Effect of Coexistent Gases in the Thermal Reactions of Toluene. Hydrogen: Figure 2 shows the effect of coexistent gases, i.e. diluent gases with regard to the toluene conversion and the benzene selectivity. The addition of only small amount of hydrogen, (40% of toluene on molar basis) resulted in an increased conversion of toluene at the same reaction temperature, and a higher benzene selectivity at the same benzene conversion. The selectivity of benzene was as high as 98% even with the low toluene conversion of 1.9%. However, the selectivity of benzene decreased with the increase of toluene conversion. This means that the amount of hydrogen added as a diluent gas was not sufficient enough to undergo the hydrogenolysis of toluene significantly especially when toluene conversion

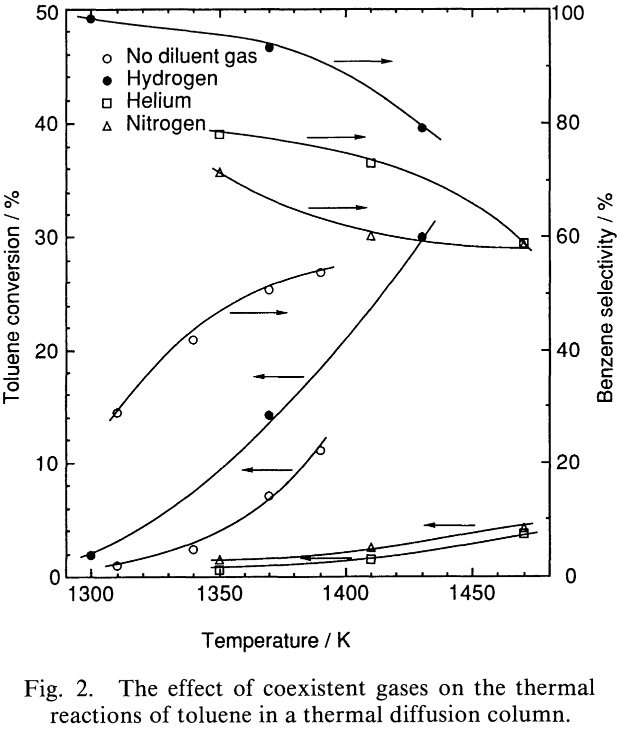

Fig. 2. The effect of coexistent gases on the thermal reactions of toluene in a thermal diffusion column.

Table 1. The Effect of Diluent Gases on Thermal Reactions of Toluene

Reaction Temperature/K	1310	1340	1370	1390	1300	1370	1430	1350	1410	1470	1350	1410	1470
Flow rate/mol h^{-1}	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Diluent gas	—	—	—	—	H_2	H_2	H_2	He	He	He	N_2	N_2	N_2
Gas rate/mol h^{-1}	—	—	—	—	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Conversion/%	1.0	2.4	7.1	11.1	1.9	14.3	30.0	0.6	1.6	3.7	1.5	2.6	4.3
Weight selectivity of liquid products/%													
Benzene	29.0	42.0	50.7	53.9	98.4	93.2	79.2	78.2	73.0	59.1	71.5	60.3	58.7
Ethylbenzene	8.0	7.8	7.3	4.5	0	1.6	5.9	7.6	6.3	5.9	7.8	6.2	6.1
Xylenes	5.3	6.4	5.9	4.6	Trace	2.3	3.6	6.9	5.6	6.4	6.5	5.8	6.0
Styrene	Trace	3.8	6.6	6.6	0	Trace	0.9	0	0.6	2.9	0	1.9	2.9
Indan	0.5	0.5	1.4	1.4	0	0	0.5	0	0	0	0	0	0
Indene	1.5	1.6	4.1	5.3	0	0	Trace	0	0	0	0	0	0
Naphthalene	Trace	Trace	1.4	2.5	0	0	0	0	0	0	0	0	0
Biphenyl	0.2	0.5	1.1	1.5	0	0	4.0	0	0	0	0	0	0
Methylbiphenyls	0.9	3.2	3.2	3.4	0	1.5	3.5	0	0	0	0	0	0
Dimethylbiphenyls	5.1	6.0	3.6	3.6	0	Trace	0.1	0	0	0	0	0	0
Diphenylmethane	1.3	1.6	1.2	1.4	0	0.3	0.8	0	0	0	0	0	0
Phenyltolylmethanes	5.4	5.1	2.7	2.8	0	0	0	0	Trace	Trace	Trace	Trace	Trace
Bibenzyl	41.9	18.3	3.8	1.6	1.6	1.1	1.1	7.3	14.5	25.7	14.2	25.8	26.3
Stilbene	Trace	0.2	0.3	0.2	0	0	0	0	0	0	0	0	0
Phenanthrene	Trace	0.5	0.6	0.7	0	0	0	0	0	0	0	0	0
Anthracene	Trace	0.4	0.4	0.6	0	0	0	0	0	0	0	0	0
Others	0.9	2.1	5.7	5.4	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Yield of gaseous product/ml h^{-1}	12	29	91	142	—	—	—	—	—	—	—	—	—
Composition of gaseous product/mol%													
H_2	55.4	35.0	24.3	18.2	—	—	—	—	—	—	—	—	—
CH_4	43.6	63.3	73.4	79.2	—	—	—	—	—	—	—	—	—
Others	1.0	1.6	2.3	2.6	—	—	—	—	—	—	—	—	—

was large. In the conventional flow type reactor without a temperature gradient, the amount of hydrogen, which is necessary to carry out the hydrogenolysis substantially, is at least five times as much as that of toluene on molar basis.[12] In this experiment, the employment of that much hydrogen was avoided, because the addition of small amount of hydrogen might be advantageous for the evaluation of the effect of the coexistent gas.

Helium: The addition of 40% of helium to toluene on molar basis decreased the conversion of toluene considerably. Even at the reaction temperature of 1470 K, the toluene conversion was only 3.7%. Such a sharp decrease of toluene does not occur in the conventional reactor without a temperature gradient, in which toluene conversion is generally reduced in accordance with the decrease of the residence time. Thermal diffusion should be responsible for this sharp decline of toluene conversion. An inert gas of helium, which is lighter than toluene, is concentrated in the vicinity of the heater due to thermal diffusion and convection. In this case, far smaller toluene concentration around the heater is attained than when two gases are mixed homogeneously, resulting in the considerable decrease of toluene conversion.

Nitrogen: The addition of nitrogen retarded the thermal reactions of toluene as well as that of helium. Nitrogen, which is lighter than toluene, is concentrated in the vicinity of the heater due to thermal diffusion and convection, and prevents the thermal reactions of toluene. The difference of molecular weight between nitrogen and toluene is smaller than that between helium and toluene. Therefore, nitrogen is less readily concentrated around the heater than helium. This can account for the result in Fig. 2 that the decline of toluene conversion is smaller in the addition of nitrogen than in that of helium.

The Effect of Coexistent Gas on the Thermal Reactions of Methane. Thermal reactions of methane were investigated by a few researchers. Oily aromatic hydrocarbons, hydrogen, and C_2 compounds such as ethane, ethylene and acetylene were main products from methane in these studies.[2–4,12,13] Fig. 3 indicates the effect of hydrogen, helium, nitrogen and argon on the thermal reactions of methane with regard to methane conversion.

The addition of hydrogen resulted in the sharply decreased conversion of methane. On the other hand, conversion of methane remained almost the same by the addition of helium up to 30% of methane. However, the addition of 50% of helium reduced the conversion of methane, although less substantially than that of toluene. These results can be explained by thermal diffusion effect and convection. Drickamer, Downey and Pierce[14] tried to calculate the thermal diffusion factor for the mixture of hydrogen and methane in a Clusius–Dickel type thermal diffusion column, and showed that methane was concentrated in the hot region. Therefore, the component of smaller molecular weight (hydrogen or helium) also concentrated around the heater in our experiments. In this process, hydrogen, which is smaller in molecular weight than helium is more easily concentrated and prevents the reactions of methane more substantially.

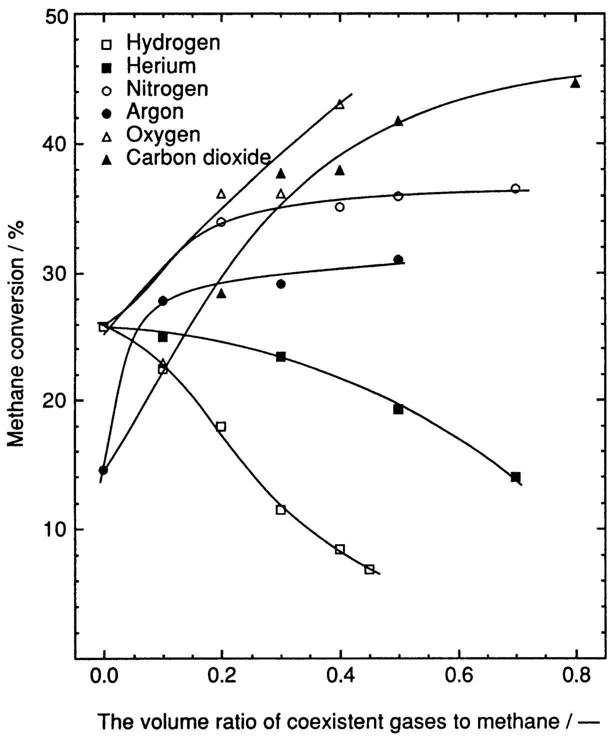

Fig. 3. The effect of coexistent gases on the thermal reactions of methane.
Temperature: ●, ▲: 1470 K, ○, □, ■, △: 1570 K, Flow rate: 40 $\mathrm{ml\,min^{-1}}$., Reactor diameter: 20 mm, Heater: tungsten wire (40 cm×2).

The addition of 20% of nitrogen or 10% of argon to methane enhanced the conversion of methane. These results are one of the characteristics of a Clusius–Dickel type thermal diffusion column. In a conventional flow type reactor without a temperature gradient, the conversion of a reactant cannot be increased by the addition of a coexistent gas. This increase of methane conversion can be accounted for by thermal diffusion and convection. When a mixture of methane and nitrogen is charged in a reactor with a significant temperature gradient, methane, which is the smaller in molecular weight, is concentrated around the heater thanks to thermal diffusion effect and convection, and is led to a higher conversion. As for a mixture of methane and hydrogen, the thermal diffusion factor was obtained by Pal, Bhattacharyya and Baura.[15] Their study supports the concentration of methane around the heater. The effect of argon can also be explained in the same manner.

The addition of oxygen or carbon dioxide to methane also increased the conversion of methane.[13] In these cases, however, the reactions between methane and either of the added gases occurred and almost no C_2

compounds such as ethane, ethylene and acetylene were produced.

The Comparison of the Effect of Coexistent Gas between the Reactions of Toluene and Methane. The conversion of toluene in a thermal diffusion column was decreased by both the addition of helium and nitrogen. On the other hand, the conversion of methane was decreased by the addition of helium, and increased by the addition of nitrogen. This difference of the effect of coexistent gases can be explained in the following manner. In regard of a mixture of toluene with helium or nitrogen, both helium and nitrogen, which are smaller in molecular weight than toluene, are concentrated around the heater and prevent the thermal reactions of toluene.

As for the thermal reactions of methane, helium gathers around the heater and retards the reaction, in a mixture of methane and helium. However, in a mixture of methane and nitrogen, methane concentrates around the heater, resulting in a higher conversion.

It can be said from these results that the separation of ingredients of a reaction mixture actually occurs and affects the reaction results in a Clusius–Dickel type thermal diffusion column.

Conclusions

The addition of helium, which is smaller in molecular weight than both methane and toluene, prevents the thermal reactions of both of them. On the other hand, the addition of nitrogen, which is smaller in molecular weight than toluene and larger than methane, retards the reaction of the former, and promotes that of the latter. This difference of the effect of coexistent gases on the thermal reactions of toluene and methane shows that the partial separation of reaction mixture due to thermal diffusion and convection actually occurs and has a great influence on the reaction results in a Clusius–Dickel type thermal diffusion column.

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