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ARTICLE

Pyrolysis of Mixtures of Methane and Ethane: Activation of Methane with the Aid of Radicals Generated from Ethane

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Direct chemical conversion of methane (CH_4) has been actively researched in order to use natural gas as a chemical resource. However, the high stability of CH_4 molecules hinders the chemical conversion of CH_4. In this study, we investigated pyrolysis of mixtures of CH_4 and ethane (C_2H_6) at 973~1073K. Even though CH_4 alone did not react in the temperature range, mixtures of CH_4/C_2H_6 and of Ar/C_2H_6 showed different pyrolysis behaviours; the co-existence of CH_4 significantly increased yields of propylene (C_3H_6), propane (C_3H_8) and toluene. Mass spectrometry analysis using ^{13}C-labeled CH_4 revealed that carbon contained in CH_4 was incorporated into the pyrolysis products. The results suggested that CH_4 was activated with the aid of C_2H_6. We assumed that CH_4 was attacked by radical species generated from pyrolysis of C_2H_6 and was converted into methyl radicals. The CH_4-derived methyl radicals were incorporated into pyrolysis products via radical reactions. This study clarified that CH_4 can be activated by radicals generated from co-existing molecules without the help of catalysts or extremely high temperature.

Introduction

Innovations in shale gas extraction technology are boosting the use of natural gas in various fields. Natural gas is expected to play an active role as a raw material for the chemical industry. This is because petroleum, which is a fossil resource that plays a major role in the current chemical industry, is depleting rapidly. Methane (CH_4), a main component of natural gas, is industrially used to produce synthesis gas via steam reforming. In addition, ethane (C_2H_6), a secondary component of natural gas, can be converted to ethylene (C_2H_4) via thermal cracking. Steam reforming and thermal cracking are typical examples of methods of chemical conversion of natural gas, however, although industrial interest in natural gas conversion has intensified, most natural gas is presently used as fuel for thermal power generation etc. In other words, natural gas plays a more limited role in the current chemical industry compared with petroleum.

The reason is attributed to the high stability of the CH_4 molecule; the high stability of CH_4 hampers the chemical conversion processes for natural gas[1]. Thus, the development of technology to convert natural gas into essential chemicals is being intensively researched. In particular, direct conversion processes of CH_4 such as coupling to produce lower olefins[2-7] and aromatization[8, 9] are being rigorously explored.

In contrast, Periana et al. developed a catalyst for the selective oxidation of mixtures of CH_4, C_2H_6 and C_3H_8 to alcohol esters.[10] Such direct conversion of CH_4-based hydrocarbon mixtures is interesting from the viewpoint of direct utilization of natural gas because natural gas is a CH_4-based hydrocarbon mixture (C_2H_6 and C_3H_8 are present as secondary and tertiary components). In related works, dehydrogenative conversion of lower olefins containing CH_4 using zeolite-supported catalysts has also been investigated.[10-15]

However, the chemical conversion of CH_4-based hydrocarbon mixtures is not easy because the reactivities of CH_4 and other hydrocarbons are quite different; in brief, CH_4 is much more stable than other hydrocarbons. Pyrolysis of CH_4 has been intensively investigated,[16-20] and among various hydrocarbons, CH_4 requires extreme high temperatures (> approx. 1473 K) for pyrolysis reactions.[1, 18] However, such high temperatures are too severe for other hydrocarbons. For most hydrocarbons, coke should be formed by deep dehydrogenation under the conditions appropriate for pyrolysis of CH_4. Conversely, reaction conditions suitable for pyrolysis of other hydrocarbons such as C_2H_6 and C_3H_8 are too mild to activate CH_4 molecules, indicating CH_4 does not react.

So far, most studies have focused on catalysts that enable the direct activation of CH_4. However, indirect activation routes would be feasible; for example, OH radicals generated from H_2O on a molten salt catalyst activate CH_4 molecules and promote the coupling of CH_4.[21, 22] In addition, CH_4 activation by gas phase atomic clusters has been investigated.[23] Thus, if active radical species can be generated, CH_4 would be activated with the aid of the radicals. In this study, pyrolysis of mixtures of CH_4 and C_2H_6 was examined. We clarified that CH_4 was activated by C_2H_6-derived radicals; as a result, even under mild conditions where CH_4 alone did not react, CH_4 molecules played a role in the pyrolysis reaction and were incorporated into pyrolysis products.

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Experimental

Pyrolysis reactions

Schematic diagram of reactor system is shown in Fig. 1. Pyrolysis reactions were carried out with a quartz reactor (i.d. = 10 mm, o.d. = 12 mm) that was heated with an electric furnace. The temperature profile for the furnace is shown in Fig. 1. Flow rates of CH_4 (99.999%), C_2H_6 (99.7%), and Ar (99.99%) were controlled by using mass flow controllers. The reactor was purged by flowing Ar for 10 min, and then heated to reaction temperature (973~1073 K). By introducing mixtures of CH_4 and C_2H_6 or of Ar and C_2H_6, pyrolysis was carried out for 1h. Hereafter, mixtures of CH_4 and C_2H_6 and of Ar and C_2H_6 will be denoted as CH_4/C_2H_6 and Ar/C_2H_6, respectively. Volume fractions of C_2H_6 in the gas mixtures were adjusted to 0.17, 0.25, and 0.50, and flow rates of the gas mixtures were controlled at 10, 30, and 50 mL min^{-1}. The flow rates of the outlet gas were measured by a soap film flowmeter.

During the pyrolysis reaction, outlet gas of 0.5 mL was collected with a gas-tight syringe and injected into gas chromatographs every 15 min. For H_2, CH_4, and C_2H_6, a gas chromatograph (Shimadzu GC-8A, TCD) equipped with a packed column (Active carbon) was used at 473 K (injection/detector) and 443 K (column) under flowing Ar as a carrier gas. For C_2H_4, C_2H_2, and C_3 hydrocarbons, a gas chromatograph (Shimadzu GC-8A, FID) equipped with a packed column (Unibeads 1S) was used at 453 K (injection/detector) and 383 K (column) under flowing N_2 as a carrier gas. To quantify gaseous products, calibration curves for all products were prepared by injecting different volume of the gases. The gases were collected from a gas cylinder (99.999% H_2, 99.999% CH_4, and 99.7% C_2H_6) or a gas can (GL Science Inc; 99.5 % C_2H_4, 0.100% C_2H_2, 99.5% C_3H_6, and 99.5% C_3H_8). Formation rates of the products were calculated based on the flow rates and the GC analysis.

Aromatics (benzene, toluene, styrene, and naphthalene) formed by the pyrolysis were collected in a glass trap cooled with a dry ice/ethanol bath. After the reaction, the trapped aromatics were dissolved in acetonitrile and then 30 mM butyl acetate in acetonitrile (1 or 2 mL) was added as an internal standard. The obtained solution was injected into a gas chromatograph (Shimazu, GC-18A) equipped with a capillary column (Shinwa chemical industries ltd., ULBON HR-1, 0.25 mm i.d., 30 m) under flowing N_2 as a carrier gas. Temperature for injection/detector was settled at 523 K and temperature for column was raised from 313 K to 473 K at 10 K min^{-1}. To quantify the aromatics, solutions containing different amounts of benzene (99.5%, Kanto Chemical Co., Inc.), toluene (99.5%, Kanto Chemical Co., Inc.), styrene (99.0%, Kanto Chemical Co., Inc.), naphthalene (98.0%, Kanto Chemical Co., Inc.), and butyl acetate (99.0%, FUJIFILM Wako Pure Chemical Corporation) in acetonitrile (99.5%, Kanto Chemical Co., Inc.) were prepared and calibration curves were prepared by injecting the solutions into the GC.

Conversions of CH_4 and C_2H_6 were calculated based on gas composition analysed by GC and flow rates of mixture gas. Mass balance was calculated from ratios of carbon atoms for components of feed and outlet gases and trapped solutions.

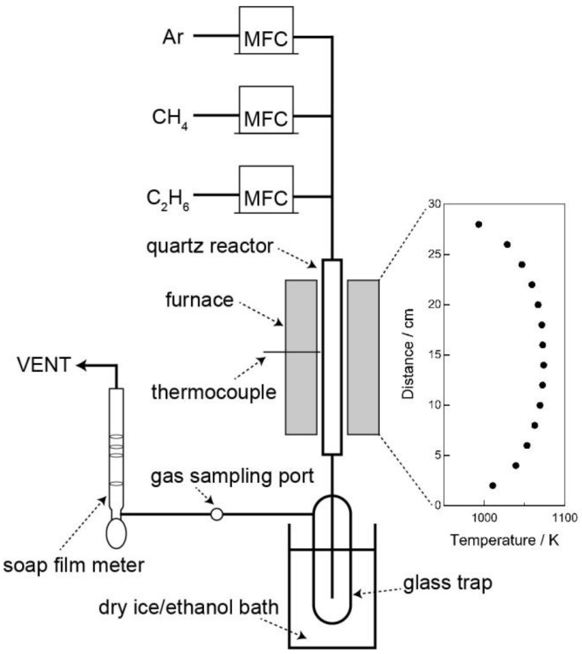

Fig. 1 Schematic diagram of reaction system and the temperature profile for the furnace.

Equilibrium conversion and standard free energy of formation for hydrocarbons (ΔG_f°) was calculated using HSC Chemistry (Outotec).

Pyrolysis reactions using ^{13}C-labeled CH_4

Pyrolysis reactions using ^{13}C-labeled CH_4 ($^{13}CH_4$; Watari Co. Ltd.) were carried out on a closed gas-circulation system (224 mL) equipped with an electric furnace. The closed gas-circulation system was mainly made of Pyrex glass and a reactor that was heated with an electric furnace was made of quartz glass. After evacuating the closed gas-circulation system, $^{13}CH_4/C_2H_6$ (20 kPa/20 kPa) or He/C_2H_6 (20 kPa/20 kPa) were introduced. The reactor was heated to 1073 K under circulating the gas mixtures and maintained for 2 h. During the reaction, the aromatics were collected in a glass trap cooled with a dry ice/ethanol bath. After the reaction, the trapped aromatics were dissolved in acetonitrile and mass spectra of the aromatics were obtained with GC-MS (Bruker, SCION SQ) equipped with a capillary column (Bruker, BR-5ms, 0.25 mm i.d., 30 m).

Table 1 All results of pyrolysis reactions in this study.

entry	reaction temp. / K	reactant gas	volume fraction of C_2H_6	flow rate / mL min^{-1}	yield / µmol h^{-1}											conv.[b)] / %		mass balance / %
					H_2	CH_4[a)]	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_6H_6	C_7H_8	C_8H_8	$C_{10}H_8$	CH_4	C_2H_6	
1	973	Ar/C_2H_6	0.5	10	5011	731	6978	4258	11	4	76	20	2	1	0.3	n/a	43.9	94.2
2	973	CH_4/C_2H_6	0.5	10	5138	13356	7444	4496	13	12	109	16	2	1	0.4	-1.7	42.3	96.7
3	1023	Ar/C_2H_6	0.5	10	7457	2010	3360	5418	28	7	121	182	14	14	12	n/a	73.1	85.1
4	1023	CH_4/C_2H_6	0.5	10	7900	15746	3607	5668	29	16	181	202	15	12	12	-20.1	72.0	93.2
5	1073	Ar/C_2H_6	0.5	10	8764	5831	1238	3882	57	3	60	508	20	31	62	n/a	90.1	80.5
6	1073	CH_4/C_2H_6	0.5	10	9648	18610	1524	4204	54	7	109	522	30	34	58	-44.7	88.0	89.8
7	973	Ar/C_2H_6	0.25	10	2898	319	3346	2678	11	1	32	6	0.4	n.d.	n.d.	n/a	47.5	97.9
8	973	CH_4/C_2H_6	0.25	10	2710	19680	3393	2481	12	8	63	5	0.4	n.d.	n.d.	2.1	46.8	96.0
9	1023	Ar/C_2H_6	0.25	10	4494	1559	1157	3364	26	2	52	88	5	6	7	n/a	79.6	89.5
10	1023	CH_4/C_2H_6	0.25	10	4590	20406	1485	3331	25	9	123	86	8	5	5	-1.2	76.8	94.2
11	1073	Ar/C_2H_6	0.25	10	5280	1819	311	2463	50	1	28	239	8	14	30	n/a	94.3	73.0
12	1073	CH_4/C_2H_6	0.25	10	6029	21788	612	2672	47	4	90	251	17	15	24	-8.4	90.4	92.7
13	973	Ar/C_2H_6	0.17	10	1916	165	1953	1771	10	0.4	15	4	0.3	n.d.	n.d.	n/a	53.7	91.1
14	973	CH_4/C_2H_6	0.17	10	1873	22490	2259	1619	9	6	47	2	0.3	n.d.	n.d.	1.2	46.1	97.2
15	1023	Ar/C_2H_6	0.17	10	3071	811	693	2238	24	1	25	60	2	2	4	n/a	83.5	85.3
16	1023	CH_4/C_2H_6	0.17	10	3404	23104	947	2382	26	6	103	47	6	4	3	-0.9	77.4	97.3
17	1073	Ar/C_2H_6	0.17	10	3599	1571	209	1667	47	0.2	14	129	3	6	14	n/a	95.0	75.7
18	1073	CH_4/C_2H_6	0.17	10	4568	23411	334	1984	48	3	81	154	12	9	16	-2.2	92.0	94.4
19	973	Ar/C_2H_6	0.5	30	9882	473	27007	8797	25	2	68	1	n.d.	n.d.	n.d.	n/a	26.2	98.7
20	973	CH_4/C_2H_6	0.5	30	10149	39915	26705	8386	25	16	103	1	n.d.	n.d.	n.d.	-1.5	27.3	97.9
21	1023	Ar/C_2H_6	0.5	30	20085	3170	13316	17459	80	17	332	132	5	3	3	n/a	61.7	96.0
22	1023	CH_4/C_2H_6	0.5	30	21066	41303	13881	16799	82	43	450	123	12	7	3	-5.9	61.3	94.8
23	1073	Ar/C_2H_6	0.5	30	27284	7769	5463	17287	209	13	314	756	17	24	34	n/a	84.9	81.9
24	1073	CH_4/C_2H_6	0.5	30	27551	47205	5678	18353	206	33	537	736	24	27	28	-20.6	84.1	92.1
25	973	Ar/C_2H_6	0.25	30	5687	227	12796	5395	24	1	28	n.d.	n.d.	n.d.	n.d.	n/a	31.0	98.8
26	973	CH_4/C_2H_6	0.25	30	5152	59286	13357	4871	24	16	68	n.d.	n.d.	n.d.	n.d.	1.9	30.1	97.7
27	1023	Ar/C_2H_6	0.25	30	12473	1368	6223	10941	74	5	133	68	7	5	2	n/a	65.7	101.4
28	1023	CH_4/C_2H_6	0.25	30	11930	59433	6637	9604	64	29	299	46	6	3	0.8	1.3	65.1	95.0
29	1073	Ar/C_2H_6	0.25	30	16412	4165	2047	10793	199	3	130	292	3	6	12	n/a	88.6	89.8
30	1073	CH_4/C_2H_6	0.25	30	17353	62212	2355	10650	185	18	385	252	7	7	19	-3.3	87.5	93.2
31	973	Ar/C_2H_6	0.17	30	3817	137	8570	3838	23	0.4	16	n.d.	n.d.	n.d.	n.d.	n/a	32.7	98.4
32	973	CH_4/C_2H_6	0.17	30	3214	64877	9227	3024	22	11	47	n.d.	n.d.	n.d.	n.d.	-0.4	27.8	99.4
33	1023	Ar/C_2H_6	0.17	30	8998	1045	3574	7723	68	3	23	46	3	3	1	n/a	76.8	88.8
34	1023	CH_4/C_2H_6	0.17	30	9164	64408	4536	7323	62	22	263	33	4	2	0.5	-0.8	68.9	98.3
35	1073	Ar/C_2H_6	0.17	30	11468	2966	987	7602	185	1	19	202	2	4	15	n/a	99.1	77.5
36	1073	CH_4/C_2H_6	0.17	30	13015	64175	876	8141	167	13	353	180	6	5	10	-0.7	94.3	94.0
37	973	Ar/C_2H_6	0.5	50	12156	415	50438	11555	41	1	53	n.d.	n.d.	n.d.	n.d.	n/a	20.5	98.4
38	973	CH_4/C_2H_6	0.5	50	12481	67289	50763	11319	38	20	84	n.d.	n.d.	n.d.	n.d.	-0.3	19.3	99.4
39	1023	Ar/C_2H_6	0.5	50	32276	2931	29434	28272	112	20	412	49	3	1	0.6	n/a	53.3	94.9
40	1023	CH_4/C_2H_6	0.5	50	33106	69008	29123	27750	112	70	596	49	2	1	0.6	-2.8	53.4	96.0
41	1073	Ar/C_2H_6	0.5	50	46302	8525	11065	34253	391	25	599	611	10	12	20	n/a	82.3	83.6
42	1073	CH_4/C_2H_6	0.5	50	48454	76300	12148	34998	390	64	972	594	14	14	20	-13.6	80.7	92.4
43	973	Ar/C_2H_6	0.25	50	7165	215	25122	7180	37	0.5	25	n.d.	n.d.	n.d.	n.d.	n/a	23.7	98.5
44	973	CH_4/C_2H_6	0.25	50	6892	98540	24831	5894	37	20	61	n.d.	n.d.	n.d.	n.d.	1.1	24.1	97.1
45	1023	Ar/C_2H_6	0.25	50	19571	1796	12678	16951	101	7	171	37	2	2	0.5	n/a	61.5	94.0
46	1023	CH_4/C_2H_6	0.25	50	18142	100294	14487	13050	85	46	333	20	2	1	n.d.	-0.6	55.8	94.9
47	1073	Ar/C_2H_6	0.25	50	27145	5836	4560	19518	315	7	239	278	2	4	11	n/a	86.1	86.6
48	1073	CH_4/C_2H_6	0.25	50	28294	103283	5319	19925	312	39	722	231	5	4	7	-5.4	83.3	98.0
49	973	Ar/C_2H_6	0.17	50	4429	148	14111	4620	36	0.2	12	n.d.	n.d.	n.d.	n.d.	n/a	32.2	90.4
50	973	CH_4/C_2H_6	0.17	50	3599	105133	16386	3948	34	15	95	n.d.	n.d.	n.d.	n.d.	2.7	23.7	96.4
51	1023	Ar/C_2H_6	0.17	50	12528	936	7243	10989	87	3	81	23	0.7	1	0.3	n/a	65.2	91.0
52	1023	CH_4/C_2H_6	0.17	50	11820	109066	9741	10206	73	37	305	8	0.3	n.d.	n.d.	-0.5	54.9	99.0
53	1073	Ar/C_2H_6	0.17	50	18047	3318	1941	13027	303	2	113	192	0.9	2	10	n/a	90.6	85.0
54	1073	CH_4/C_2H_6	0.17	50	19563	109098	3235	13611	266	24	595	125	3	2	4	-0.7	85.0	96.2
55	1073	CH_4	0	10	n.d.[c)]	n/a	3	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.002[d)]	n/a	102.0

[a)] CH_4 yields for CH_4/C_2H_6 conditions contained not only formed CH_4 but also feed CH_4; [b)] average value in pyrolysis for 1h; [c)] although C_2H_6 and C_2H_4 was formed by dehydrogenation reactions, H_2 could not be detected because hydrocarbon was analysed by using GC-FID at the highest sensitivity but H_2 was analysed by using GC-TCD; [d)] the CH_4 conversion was calculated on the basis of the yields of C_2H_6 and C_2H_4.

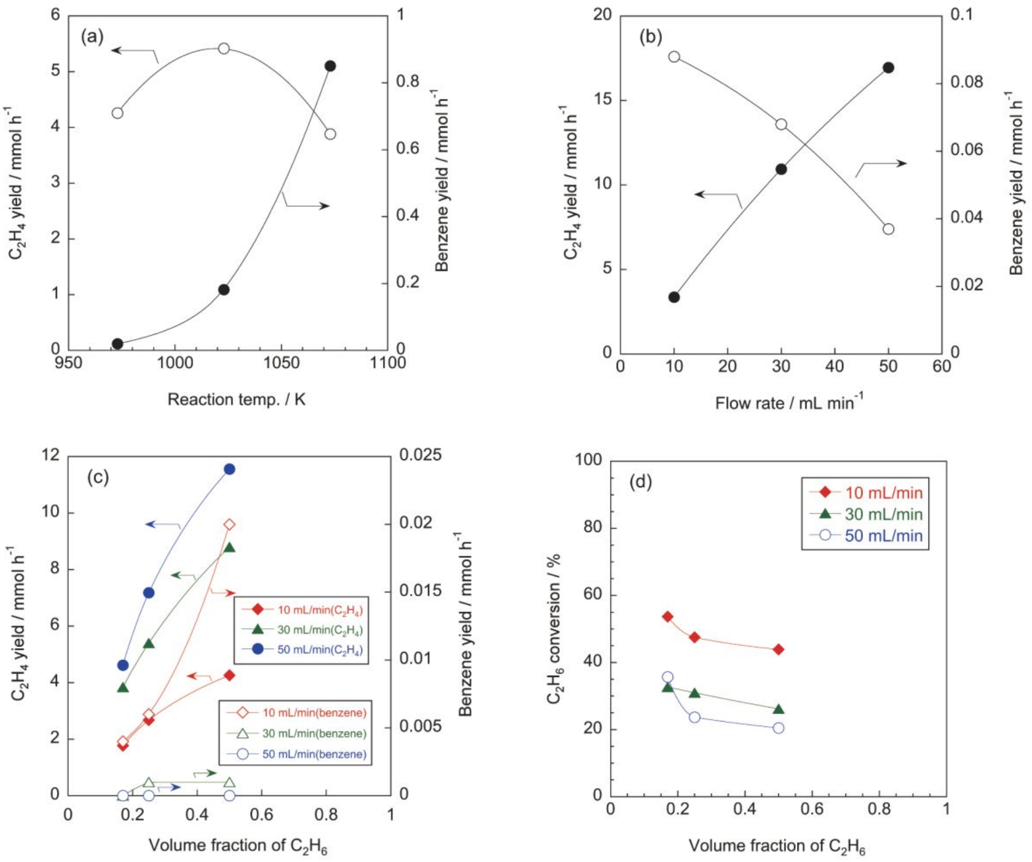

Fig. 2 C_2H_4 and benzene yields for Ar/C_2H_6 condition at different (a) reaction temperatures, (b) flow rates and (c) volume fractions of C_2H_6. (d) C_2H_6 conversion at different flow rates and volume fractions. (a) flow rate: 10mL min^{-1}, volume fraction of C_2H_6: 0.5; (b) reaction temperature: 1023K, volume fraction of C_2H_6: 0.25; (c, d) reaction temperature: 973 K.

Results and discussion

In this study, pyrolysis reactions of two different gas mixtures (i.e., CH_4/C_2H_6 and Ar/C_2H_6) were carried out by controlling three reaction parameters: (1) reaction temperature, (2) gas flow rate, and (3) gas composition. Consequently, 55 experimental results were obtained and are summarized in Table 1. In these reactions, the pyrolysis products were hydrogen (H_2), CH_4, C_2H_4, acetylene (C_2H_2), propylene (C_3H_6), C_3H_8, benzene (C_6H_6), toluene (C_7H_8), styrene (C_8H_8), and naphthalene ($C_{10}H_8$). Coke was also produced depending on the reaction conditions. Note that CH_4 conversions under CH_4/C_2H_6 conditions were calculated based on the amount of CH_4 in the inlet and the outlet gases, therefore, when CH_4 was formed from C_2H_6 (Eqs. 1 and 2), the amount of CH_4 in the outlet gas increased so that the CH_4 conversion became negative.

$$C_2H_6 \rightarrow 2\ CH_3\cdot \qquad (1)$$

$$CH_3\cdot\ + C_2H_6 \rightarrow CH_4 + C_2H_5\cdot \qquad (2)$$

Before considering the main subject (i.e., activation of CH_4 with the aid of C_2H_6), the basic effects of the reaction parameters on the pyrolysis behaviour will be considered.

Effect of reaction temperature

To discuss the effect of reaction temperature, we used several results of Ar/C_2H_6 conditions as examples (entries 1, 3, 5 in Table 1). C_2H_6 conversions increased to 44, 73, and 90% as reaction temperature increased to 973, 1023, and 1073 K, which is because the pyrolysis reactions are endothermic. Fig. 2a shows C_2H_4 and benzene yields at different reaction temperatures. Because C_2H_4 and benzene were the main products in the reaction, their yields may become higher with increasing C_2H_6 conversion with the reaction temperatures. While the benzene yield increased with the reaction temperatures, the C_2H_4 yield dropped at 1073 K. As for the formation of H_2, dehydrogenation of C_2H_6 to C_2H_4 mainly contributed at 973 K. For example, in entry 1, the yields of C_2H_4 and H_2 was 4258 and 5011 µmol h^{-1}; the amounts C_2H_4 and H_2 were similar. At higher temperature, the formation of benzene and coke also contributed to the formation of H_2.

According to previous studies on CH_4 pyrolysis,[24, 25] benzene is formed by the recombination of propargyl radicals ($C_3H_3\cdot$), which are generated via H abstraction reactions of C_2H_6.

$$C_2H_6 + H\cdot \rightarrow C_2H_5\cdot + H_2 \qquad (3)$$

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot \quad (4)$$

$$C_2H_4 + H\cdot \rightarrow C_2H_3\cdot + H_2 \quad (5)$$

$$C_2H_3\cdot \rightarrow C_2H_2 + H\cdot \quad (6)$$

$$C_2H_2 + CH_3\cdot \rightarrow C_3H_4 + H\cdot \quad (7)$$

$$C_3H_4 + H\cdot \rightarrow C_3H_3\cdot + H_2 \quad (8)$$

$$C_3H_3\cdot + C_3H_3\cdot \rightarrow C_6H_6 \quad (9)$$

In addition, there is another model that cyclopentadienyl radical is an important intermediate.[26, 27]

Considering that C_2H_4 is the primary product in the pyrolysis of C_2H_6,[28] C_2H_4 concentration should increase at high reaction temperatures because C_2H_6 conversion increased with the reaction temperature. Furthermore, as shown in Eqs. 3-9, benzene is formed via C_2H_4; therefore, it is likely that benzene formation is enhanced with increasing C_2H_4 concentration at high temperature. Consequently, the C_2H_4 yield was suppressed apparently by consuming C_2H_4 to form benzene. This is the reason why the C_2H_4 yield dropped at 1073 K.

Mass balance for carbon atoms was shown in Table 1. At 973 K, the mass balance was approx. 100%, while the mass valance decreased as increasing reaction temperature. This is because the formation of coke, indeed, the wall of the quartz reactor became black after the pyrolysis reaction at high temperature.

Effect of gas flow rate

The effect of gas flow rate on the pyrolysis of Ar/C_2H_6 was considered by using entries 9, 27, 45 in Table 1 as typical examples. As the flow rate of the reactant gas increased to 10, 30, and 50 mL min^{-1}, C_2H_6 conversions decreased to 80, 66, and 62%, respectively. The high flow rate means a short residence time of reactant gases in the reactor, which should result in the decrease in C_2H_6 conversion. Yields of lower hydrocarbons such as C_2 and C_3 increased when the flow rate was high, and conversely, yields of aromatics decreased. As typical examples, the effect of the flow rate on yields of C_2H_4 and benzene is shown in Fig. 2b. With increasing gas flow rates, the C_2H_4 yields increased and the benzene yields decreased. As described above, benzene is formed via the recombination of propargyl radicals that are successively formed by H abstraction reactions of C_2H_6. Such a successive reaction is likely to be affected by the residence time of reactant gases; long residence time is favourable for the formation of benzene. Therefore, high flow rate, that is, short residence time, resulted in increasing yield of the intermediate product, namely C_2H_4.

Effect of volume fraction of C_2H_6

The volume fraction of C_2H_6, that is the concentration of C_2H_6, is a reaction parameter in this study. As shown in Table 1, product yields became higher with higher C_2H_6 concentrations, and product distributions were almost the same regardless of the C_2H_6 concentration. Fig. 2c shows C_2H_4 and benzene yields at different volume fraction of C_2H_6 and flow rates. C_2H_4 and benzene yields tended to increase as a function of the volume fraction of C_2H_6. As described above, H abstraction from C_2H_6 provides C_2H_4 and benzene. Thus, it is reasonable that increase in volume fraction of C_2H_6 contributed to the formation of C_2H_4 and benzene. In addition, similar to Fig. 2b, as increasing flow rates, C_2H_4 yield increased and benzene yield decreased regardless of volume fraction of C_2H_6.

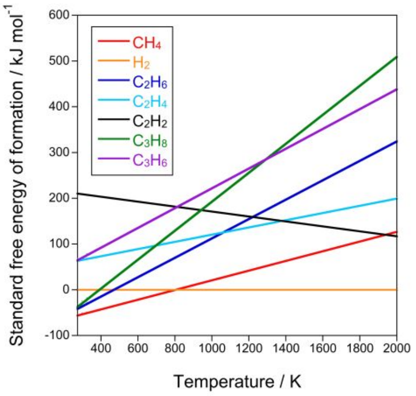

Fig. 3 Standard free energy of formation (ΔG_f^o) of hydrocarbons as a function of temperature.

Fig. 2d shows C_2H_6 conversion at different volume fractions of C_2H_6 in Ar. C_2H_6 conversion was in inverse proportion to the volume fraction of C_2H_6. The dominant reaction in the pyrolysis of C_2H_6 is the dehydrogenation of C_2H_6 into C_2H_4 ($C_2H_6 \rightarrow C_2H_4 + H_2$). The equilibrium conversions for the reaction are as follows: 71, 67, and 62% for the volume fractions of 0.17, 0.25, and 0.5, respectively. This order is in accordance with the tendency of C_2H_6 conversion shown in Fig. 2d.

Pyrolysis of CH_4/C_2H_6 mixtures

A CH_4 molecule is so stable that CH_4 alone did not react under the reaction conditions in this study. Even under the most severe condition (i.e., the highest temperature and the lowest flow rate), the CH_4 conversion was approximately 0% (entry 55 in Table 1). Thermodynamic data also suggest that CH_4 is much more stable than other hydrocarbons (Fig. 3). Thus, in this study, CH_4 is expected to behave as an inert molecule, such as Ar and He. In other words, results in pyrolysis of CH_4/C_2H_6 and Ar/C_2H_6 are assumed to be the same, however, their pyrolysis results were quite different. Fig. 4a shows C_3H_6 yields under CH_4/C_2H_6 and Ar/C_2H_6 conditions at different temperatures and flow rates. Interestingly, the C_3H_6 yields were greatly increased in the presence of CH_4. For example, under the condition at 1073 K and 50 mL/min, C_3H_6 yields for Ar/C_2H_6 and CH_4/C_2H_6 were 0.11 and 0.60 mmol h^{-1}, respectively, indicating the co-existing CH_4 promoted the C_3H_6 formation by more than five times. The same trend was observed for C_3H_8 formation.

Fig. 4b shows the effect of co-existing CH_4 on toluene yields. Similar to the C_3 hydrocarbons, co-existing CH_4 significantly enhanced toluene formation. For example, under the condition at 1073 K and 10 mL/min, toluene yield increased by more than four times (from 2.9 to 12.5 μmol h^{-1}).

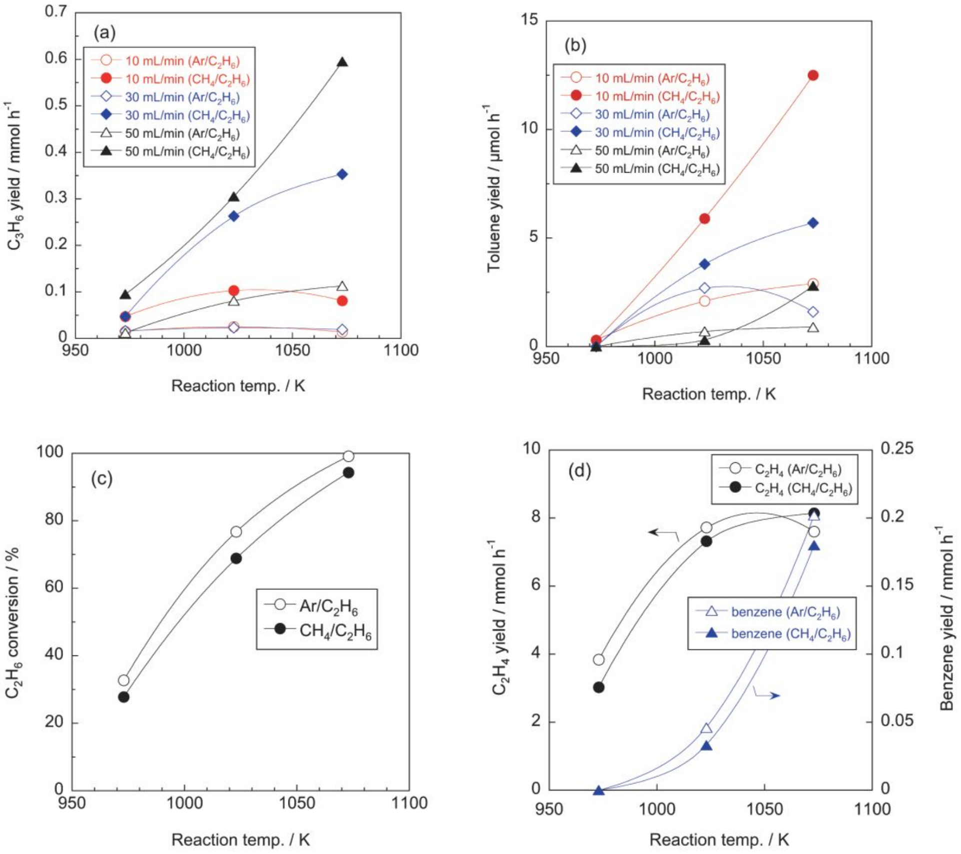

Fig. 4 (a) C_3H_6 yield, (b) toluene yield, (c) C_2H_6 conversion, and (d) C_2H_4 and benzene yields for CH_4/C_2H_6 or Ar/C_2H_6 condition at different reaction temperatures, different flow rates and C_2H_6 volume fraction of 0.17. Flow rate for (c, d): 30 mL min^{-1}.

From the perspective of the transition from petrochemical to natural gas chemistry, it is necessary to reconsider the production process of C_3H_6, which is an essential molecule in the chemical industry. In petrochemicals, C_3H_6 (and benzene, toluene, xylene) are obtained as by-products of naphtha cracking to produce C_2H_4. In contrast, C_2H_4 synthesis from C_2H_6 in natural gas produces poor by-products. In this regard, the enhancement of C_3H_6 formation by co-feed of CH_4 to C_2H_6 would be worthwhile from the viewpoint of natural gas utilization.

Fig. 4c shows C_2H_6 conversion for CH_4/C_2H_6 and Ar/C_2H_6 conditions. As described earlier, C_2H_6 conversion increases with reaction temperatures, and the co-existence of CH_4 slightly suppressed the C_2H_6 conversion. Probably, thermal cracking of C_2H_6 to form CH_4 would be inhibited by the presence of CH_4, which can be a reason why C_2H_6 conversion slightly decreased under CH_4/C_2H_6 conditions. In addition, the slight decrease in C_2H_6 conversion in the presence of CH_4 indicates that the increase in C_3 hydrocarbons and toluene is irrelevant to C_2H_6 conversion. Fig. 4d shows C_2H_4 and benzene yields for CH_4/C_2H_6 and Ar/C_2H_6 conditions. As expected from Fig. 4c, C_2H_4 and benzene were less formed under CH_4/C_2H_6 conditions because C_2H_6 conversion was suppressed in the presence of CH_4. As described later, we considered that methyl radicals were generated from CH_4 with the aid of radicals formed from C_2H_6. Fig. 4 shows that while C_2H_4 yield was hardly affected by CH_4, the formation of C_3 hydrocarbon was enhanced in the presence of CH_4. From the results, we presumed that methyl radicals derived from CH_4 promoted the recombination reaction of $C_2H_3\cdot$ (or $C_2H_5\cdot$) and $CH_3\cdot$ to form C_3 hydrocarbons.

Fig. 5 shows the effect of volume fractions of C_2H_6 on yields of lower olefins. Regardless of reaction conditions, all the product yields became higher with increasing C_2H_6 concentration. Considering that products were mainly formed from the pyrolysis of C_2H_6, it is likely that the product yields were proportional to the concentration of C_2H_6. As shown in Fig. 5a, it appeared that the C_2H_4 yields slightly decreased with the presence of CH_4. The co-existence of CH_4 contributed to the decrease in C_2H_6 conversion (Fig. 4c), thus, it is possible that the yield of the main product (i.e., C_2H_4) decreased with the presence of CH_4. On the other hand, the C_3H_6 yield was significantly increased by the co-existing CH_4 regardless of the C_2H_6 concentration. This tendency is the same as shown in Fig. 4a. Fig. 5b shows yields of aromatics at various volume fractions of C_2H_6. Like the lower olefins, aromatics yields also increased with the concentration of C_2H_6. Comparing CH_4/C_2H_6 and Ar/C_2H_6 conditions, we can see that there were no significant effects of CH_4 on the benzene, styrene and naphthalene yields, while only the toluene yield increased with the CH_4/C_2H_6 conditions, which is similar to the results shown in Fig. 4b.

Based on the above results, the effects of co-existing CH_4 on the pyrolysis reactions are summarized as follows:

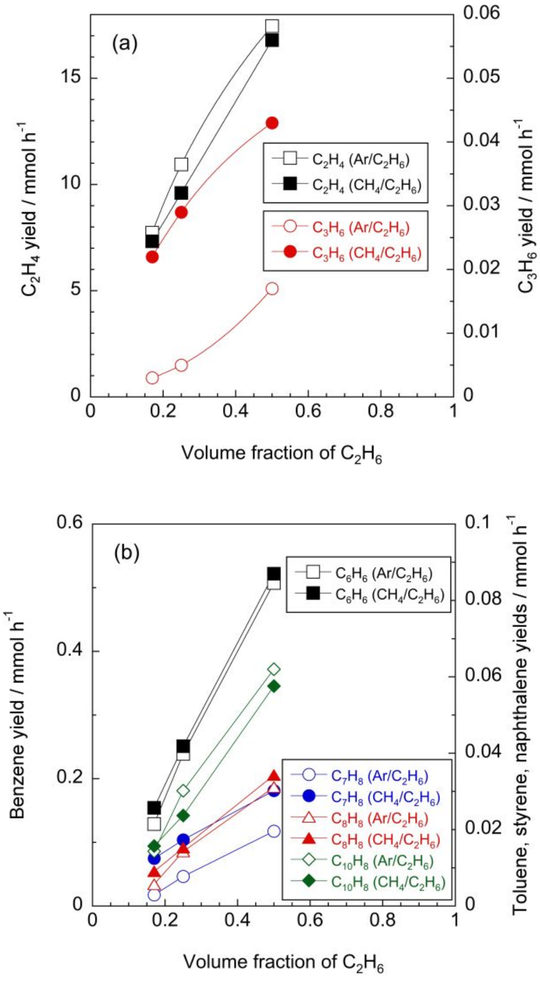

Fig. 5 Products yield for CH_4/C_2H_6 or Ar/C_2H_6 condition at different volume fractions of C_2H_6 in the mixture gases. (a) reaction temperature: 1023 K, flow rate: 30 mL min^{-1}, (b) reaction temperature: 1073 K, flow rate: 10 mL min^{-1}.

- C_3H_6, C_3H_8 and toluene yields increased significantly in the presence of CH_4.
- C_2H_6 conversion was slightly lowered in the presence of CH_4.
- The influence of co-existing CH_4 on main products (i.e., C_2H_4 and benzene) yields was small.

Mass spectrometry analysis using ^{13}C-labeled CH_4

It is well-known that CH_4 molecules are significantly stable because of both their structural symmetry and strong C-H bond.[1] Indeed, pyrolysis of CH_4 hardly took place when only CH_4 was heated to 1073 K (entry 55 in Table 1). Thus, it is not surprising that CH_4 molecules in CH_4/C_2H_6 behaved the same as an inert gas, however, CH_4/C_2H_6 showed different pyrolysis behaviour from Ar/C_2H_6. This result strongly suggests that CH_4 molecules in C_2H_6 played a role in the pyrolysis reaction. In order to understand the role of CH_4, pyrolysis using $^{13}CH_4$ was carried out. If CH_4 molecules were activated and converted into pyrolysis products, mass spectra of the pyrolysis products should be changed by incorporating ^{13}C into them.

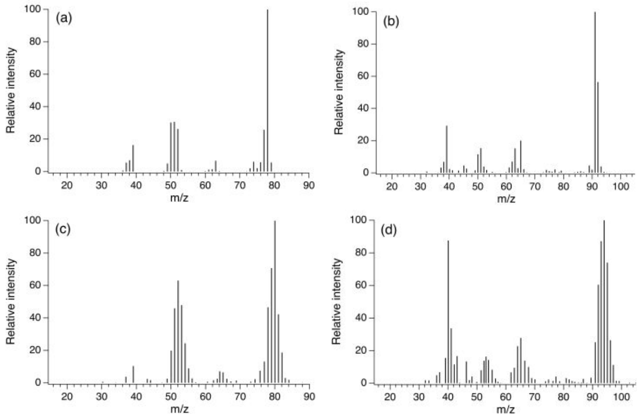

Fig. 6 Mass spectra of (a, c) benzene and (b, d) toluene formed by dehydrogenation of (a, b) He/C_2H_6 and (c, d) $^{13}CH_4/C_2H_6$ at 1073 K.

Fig. 6 shows mass spectra of the aromatic compounds formed by pyrolysis of $^{13}CH_4/C_2H_6$ or He/C_2H_6 at 1073 K (mass spectra of C_2 and C_3 hydrocarbons could not be obtained due to the limitation of separation in the GC-MS system). It was no wonder that typical mass spectra of benzene and toluene were observed under the He/C_2H_6 condition (Fig. 6a and 6b). On the other hand, it is interesting that mass spectra of benzene and toluene formed from $^{13}CH_4/C_2H_6$ (Fig. 6c and 6d) were different from those of He/CH_4; benzene and toluene from $^{13}CH_4/C_2H_6$ had higher m/z values. The m/z values at the highest peaks were 78 (benzene from He/CH_4), 80 (benzene from $^{13}CH_4/C_2H_6$), 91 (toluene from He/CH_4) and 94 (toluene from $^{13}CH_4/C_2H_6$). The increase in m/z of benzene and toluene in the presence of $^{13}CH_4$ strongly suggested that ^{13}C derived from CH_4 was incorporated into benzene and toluene during the pyrolysis reactions.

Reaction mechanism

The mass spectra shown in Fig. 6 indicated that CH_4 was incorporated into the products in the presence of C_2H_6 even though CH_4 alone did not react, which implies CH_4 molecules were activated with the aid of C_2H_6. Considering that no catalysts were used in this study, we assumed that radical species generated from C_2H_6 would play a role to activate the stable CH_4 molecules.

It is known that various radical species are formed from C_2H_6 at above 773~873 K.[29] If the radicals abstract H· from CH_4 molecules, CH_4 molecules generate radical species (mainly methyl radicals):

$$CH_4 + H\cdot \rightarrow CH_3\cdot + H_2 \qquad (10)$$

$$CH_4 + C_2H_5\cdot \rightarrow CH_3\cdot + C_2H_6 \qquad (11)$$

Consequently, the methyl radicals derived from CH_4 molecules can convert into C_3H_6 and C_3H_8 by the following radical reactions:

$$C_2H_3\cdot + CH_3\cdot \rightarrow C_3H_6 \qquad (12)$$

$$C_2H_5\cdot + CH_3\cdot \rightarrow C_3H_8 \qquad (13)$$

In the above recombination reactions, CH_4 molecules are incorporated into C_3 hydrocarbons. For example, by combining Eqs. 5, 10, and 12, we know that a CH_4 molecule is consumed to form a C_3H_6 molecule ($CH_4 + C_2H_4 + 2H\cdot \rightarrow C_3H_6 + 2H_2$)
Also, when the methyl radical reacts with a phenyl radical, toluene is formed:

$$C_6H_5\cdot + CH_3\cdot \rightarrow C_7H_8 \qquad (14)$$

The significant increases in C_3 hydrocarbons and toluene yields under CH_4/C_2H_6 conditions can be explained by the above mechanism; the increase in the concentration of methyl radicals promoted the formation of C_3 hydrocarbons and toluene. As shown in the mass spectra, CH_4-derived carbon was also incorporated into benzene, which can be explained by the recombination of propargyl radicals that is formed from $^{13}CH_3\cdot$ and C_2H_2 (Eq. 7-9).
Current strategies for CH_4 activation can roughly be categorized into (1) the development of catalysts that efficiently activate C-H bonds in CH_4 and (2) pyrolysis of CH_4, where coupling of methyl radicals proceeds with the aid of extreme high temperature (> approx. 1473 K). In this study, an alternative route for the chemical conversion of CH_4 was proposed: radicals generated from co-existing molecules (in this study, C_2H_6) activate CH_4 molecules.

Conclusions

Pyrolysis reactions of mixtures of CH_4/C_2H_6 or Ar/C_2H_6 were carried out at 973~1073 K. Even though CH_4 alone did not react in the temperature range, the pyrolysis behaviour was quite different in the presence of CH_4; the formation of C_3 hydrocarbons and toluene was enhanced. In contrast, C_2H_4 and benzene yields were not affected by the co-existing CH_4. Mass spectrometry analysis using ^{13}C-labeled CH_4 revealed that CH_4-derived carbon was incorporated into the pyrolysis products, indicating CH_4 molecules were activated and played a role in the pyrolysis reactions. Probably, radicals generated from C_2H_6 abstracted H· from CH_4 so that CH_4-derived methyl radicals would be formed. By reacting the methyl radicals with $C_2H_3\cdot$ and $C_6H_5\cdot$, C_3H_6 and toluene were formed. In other words, the increase in the concentration of methyl radicals enhanced the formation of C_3 hydrocarbons and toluene. This study clarified that CH_4 can be activated by radicals generated from co-existing molecules without the help of catalysts or extreme high temperature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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One sentence of text for table of content:

Inert CH_4 molecule can be activated and incorporated into pyrolysis products with the aid of radicals generated by pyrolysis of C_2H_6.

CH_4 Activation with Radicals