CHEMISTRY LETTERS, pp. 1955-1958, 1986.

Conversion of Methane to Aromatic Hydrocarbons by Combination of Catalysts

Kiyoshi OTSUKA* and Takayuki KOMATSU
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

Aromatic hydrocarbons were synthesized by passing CH_4 and O_2 through the two catalyst beds, i.e., the catalyst active for oxidative coupling of CH_4 and that for converting light hydrocarbons to aromatics.

Partial oxidation of methane into higher hydrocarbons attracted much attention since pioneering work reported by Keller and Bhasin.1-7) More and more groups are beginning to work in this area and there is increasing industrial activity.8) However, a challenging work to convert methane into aromatic hydrocarbons by partial oxidation of methane has not been succeeded yet, except the works using N_2O as an oxidant.9)

Recent work in our laboratory has demonstrated that alkali carbonates-added Sm_2O_3 and alkali halides-added transition metal oxides show high catalytic activities for oxidative coupling of CH_4 by O_2 giving C_2H_6 and C_2H_4 (C_2-compounds). On the other hand, it has been reported that light paraffinic hydrocarbons such as C_2H_6, C_3H_8,and C_4H_{10} can be converted to aromatic hydrocarbons using H-ZSM-5 zeolites and Ga and Al ions-exchanged ZSM-5.10,11) Ono et al. suggested that the role of the metal cations are for the efficient transformation of the intermediate olefins into aromatic hydrocarbons.12) Thus, we expect that the combination of these two types of catalysts can produce aromatic hydrocarbons directly from CH_4 by passing reactants through the catalyst beds. In this report, we describe the catalysts which give aromatic hydrocarbons directly from methane.

The nickel oxides and manganese oxides containing alkali salts were prepared by immersing NiO and MnO_2 in aqueous solutions of alkali salts. The content of the alkali metals in the oxides was 20 mol% for each catalyst. The catalysts were calcined in air at 973 K for 2 h before the experiments. ZSM-5 zeolites were synthesized according to the method described in a patent.13) The silicalite used was prepared by the similar method. The ZSM-5 zeolites were exchanged with H^+, Ga^{3+}, or Al^{3+} in aqueous solutions of the nitrates of the cations. The contents of Ga^{3+} and Al^{3+} were adjusted to be 2.0 wt.%.

The test of the catalysts were carried out using a fixed-bed reactor with a conventional gas-flow system at atmospheric pressure. The catalysts were packed in a reactor of porcelain(Al_2O_3) tube (11 mm i.d.) placed in a conventional furnace. The reaction products at time on stream of 25 min were analyzed by gas chromatography using column packings of Gaskuropack 54 and active carbon. The conversion of CH_4, the selectivities and the yields of the products were calculated on the basis of carbon number of CH_4 reacted.

C_2H_4 and C_2H_6 are the main hydrocarbon products in partial oxidation of CH_4 over alkali halides-added transition metal oxides.[4] However, a detailed analysis of the products for higher hydrocarbons indicated that we could not neglect the formations of higher hydrocarbons. Table 1 shows the conversions of CH_4 and O_2, the selectivity to hydrocarbons ($\geq C_2$), and the yields of hydrocarbons observed for LiCl-added nickel oxide (denoted as LiCl/Ni-oxide) and NaCl/Mn-oxide. The latter catalysts were mechanically mixed with quartz sand (denoted as QS) (6.0 g), silica gel (6.0 g), or silicalite (3.0 g) as a diluent before being packed in the reactor (third, fourth, and fifth column, respectively) because the dispersion of the catalyst increased the total yields of hydrocarbons as well as the yields of aromatic compounds. The carbon containing products other than the hydrocarbons in Table 1 were CO_2 and CO. The experimental conditions are given in a margin of the table. As can be seen in Table 1, the formation of benzene was clearly observed for the catalysts LiCl/Ni-oxide and NaCl/Mn-oxide. As far as we know, the results in Table 1 are the first demonstration of the synthesis of aromatics by partial oxidation of CH_4 in the presence of oxygen in the gas phase, although the yield is still small.

Table 1. The catalysts active for oligomerization and aromatization of CH_4

Catalyst	LiCl/Ni-oxide	NaCl/Mn-oxide + QS	NaCl/Mn-oxide + silica gel	NaCl/Mn-oxide + silicalite
CH_4 conversion(%)	39.1	39.8	36.6	37.4
O_2 conversion(%)	99.0	99.3	97.0	99.2
Selectivity(%) to hydrocarbons ($\geq C_2$)	65.2	67.1	58.3	60.3
Yields(%)				
C_2H_4	20.0	20.7	15.6	17.1
C_2H_6	2.9	2.5	2.0	2.8
C_3H_6	1.3	1.0	0.8	0.8
C_4H_8	1.1	2.1	2.6	1.3
Benzene+Toluene	0.2	0.4	0.4	0.6
Total hydrocarbons	25.5	26.7	21.4	22.6

Reaction conditions: T=1023 K; weight of catalysts without diluent=2.0 g; Partial pressures at the entrance of the reactor= CH_4(0.16 atm), O_2(0.07), He(0.77); Total flow rate=61 ml min^{-1}.

As described earlier we can expect that combination of the two types of catalysts, one of which is effective to oxidative coupling of CH_4 (coupling catalyst) and the other to oligomerization of the C_2-compounds and subsequent cyclization and dehydrogenation to give aromatic hydrocarbons (aromatization catalyst), may increase the yields of aromatics from CH_4. Table 2 shows the results for Li_2CO_3/Sm_2O_3 (a coupling catalyst), Ga-ZSM-5 zeolite, and the combinations of the Li_2CO_3/Sm_2O_3 (denoted as Li/Sm_2O_3 hereafter) with various cation exchanged ZSM-5 zeolites (aromatization catalysts). The Li/Sm_2O_3 (2.0 g) and the ZSM-5 zeolite (1.0 g) were packed in series in the reactor at intervals of 6 cm between the two catalysts. The temperatures at the centers of the catalyst beds were 1023 and 973 K for Li/Sm_2O_3 and ZSM-5 zeolites, respectively. The reactants were fed first through the former catalyst bed and subsequently through the latter. Li/Sm_2O_3 alone (second column in Table 2) or Ga-ZSM-5 alone (third column) did not produce aromatics at all. When Ga-ZSM-5 was used alone, CH_4 was oxidized to CO and CO_2 and not to higher hydrocarbons. However, as can be seen in Table 2, the combination of Li/Sm_2O_3 and ZSM-5 zeolites produced aromatics as we expected. The combination of Li/Sm_2O_3 and Ga-ZSM-5 gave the best yield of aromatics 2.2%. The selectivity to aromatics was 6.8% in the total products. Thus, Ga-ZSM-5 zeolite is the most effective catalyst to give aromatic hydrocarbons under the experimental conditions described earlier.

Table 2. Conversion of CH_4 over Li/Sm_2O_3 and various ZSM-5(Si/Al=45) zeolites packed in series in the reactor

Catalysts	Li/Sm_2O_3 only	Ga-ZSM-5 only	Li/Sm_2O_3 H-ZSM-5	Li/Sm_2O_3 Ga-ZSM-5	Li/Sm_2O_3 Al-ZSM-5
CH_4 conv.(%)	34.5	9.1	31.3	32.8	33.3
O_2 conv.(%)	99.0	24.4	99.4	95.4	98.6
Selectivity to hydrocarbons(%)	56.0	2.2	49.1	38.7	53.0
Yields (%)					
C_2H_4	11.5	0.0	9.5	3.7	9.0
C_2H_6	6.8	0.2	4.3	6.2	7.3
C_3H_6	1.1	0.0	0.9	0.6	2.1
C_4H_8	trace	0.0	0.0	0.0	trace
Benzene+Toluene	0.0	0.0	0.6	2.2	0.6
Total	19.4	0.2	15.3	12.7	19.0

Partial pressures=CH_4(0.21 atm), O_2(0.09), He(0.70); Flow rate=28.5 ml min^{-1}.

Table 3 shows the results of reactions using Ga-ZSM-5 zeolite with the active catalysts for oxidative coupling of CH_4. The experimental conditions were same as those described for Table 2 except the weight of the ZSM-5 catalysts (2.0 g) and partial pressures and flow rates of reactants. For every catalyst combinations in Table 3, selectivity to aromatics are greater than 6%. The yield of aromatics was also improved compared to the results in Table 2. LiCl/Ni-oxide and NaCl/Mn-oxide in combination with Ga-ZSM-5(Si/Al=25) gave fairly high selectivities (>16.3%) and yields (>5.5%) of aromatics. It is noted that considerable amounts of light paraffins and olefins produced through the coupling catalysts still remain unreacted in effluent gas. Therefore, the yield of aromatics must be improved if we could find better catalysts having higher catalytic activities in the conversion of light hydrocarbons to aromatics. It is also to be noted that the yield of total hydrocarbons decreased considerably when the aromatization catalyst was combined with the coupling catalyst. This result can be ascribed to the deep oxidation of olefins and the coke formation on aromatization catalysts. Therefore, the better aromatization catalyst mentioned above must be the one which also improves these points.

Table 3. Conversion of CH_4 over various coupling catalysts and Ga-ZSM-5 packed in series in the reactor

Coupling catalyst	LiCl/Ni-oxide a)	NaCl/Mn-oxide + QS a)	Li/Sm_2O_3 a)	LiCl/Ni-oxide b)	NaCl/Mn-oxide + QS b)
CH_4 conv.(%)	36.4	35.7	35.2	33.7	34.2
O_2 conv.(%)	98.1	98.9	98.8	98.8	97.2
Selectivity to hydrocarbons(%)	47.3	44.8	40.5	42.1	42.1
Yields(%)					
C_2H_4	9.7	8.5	4.1	6.0	5.1
C_2H_6	1.5	2.7	5.5	1.6	2.9
C_3H_6	2.3	0.5	2.4	0.7	0.4
C_4H_8	0.0	0.0	0.0	0.4	0.3
Benzene+Toluene	3.8	4.3	2.2	5.5	5.6
Total	17.3	16.0	14.2	14.2	14.3

Partial pressures=CH_4(0.16 atm), O_2(0.07), He(0.77); Flow rate=64 ml/min. a) Si/Al ratio of Ga-ZSM-5 used was 45. b) Si/Al ratio of Ga-ZSM-5 used was 25.

References

1) G.E. Keller and M.M. Bhasin, J. Catal., 73, 9(1982).
2) W. Hinsen, W. Bytyn, and M. Baerns, Proc.8th Int.Congr.Catal.,3, 581(1984).
3) T. Ito, Ji-Xiang Wang, Chiu-Hsun Lin, and J.H. Lunsford, J. Am. Chem. Soc., 107, 5062(1985).
4) K. Otsuka, K. Jinno, and A. Morikawa, Chem. Lett., 1985, 499; K. Otsuka, Qin Liu, M. Hatano, and A. Morikawa, ibid., 1986, 903; K. Otsuka, Qin Liu, and A. Morikawa, Inorg. Chim. Acta, 118, L01(1986); K. Otsuka, K. Jinno, and A. Morikawa, J. Catal., 100, 353(1986).
5) H. Imai and T. Tagawa, J. Chem. Soc., Chem. Commun., 1986, 52.
6) T. Moriyama, N. Takasaki, E. Iwamatsu, and K. Aika, Chem. Lett., 1986, 1165.
7) K. Asami, S. Hashimoto, T. Shikada, K. Fujimoto, and H. Tominaga, Chem. Lett., 1986, 1233.
8) US Pat. 4499322(1985), 4499323(1985); WO 85/04821, WO 85/04867.
9) S.S. Shepelev and K.G. Ione, React. Kinet. Catal. Lett., 23, 319(1983); J.R. Anderson and P. Tsai, Appl. Catal., 19, 141(1985).
10) J.R.Anderson, K.Foger, T.Mole, R.A.Rajadhyaksha, and J.V.Sanders,58,14(1979).
11) P.Chu, US Pat.,4120910(1978); A.W.Chester and Y.F.Chu, US Pat.,4350835(1982).
12) G. Sirokman, Y. Sendoda, and Y. Ono, Zeolite, 6, 299(1986).
13) C.J. Plank, E.J. Rosinsky, A.B. Schwarts, DE 2 405 909 (1974).

(Received August 27, 1986)