Direct Conversion of Methane to Higher Hydrocarbons

Kiyoshi OTSUKA

Department of Chemical Engineering, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

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Recent works in our laboratory on the direct, catalytic conversion of methane into higher hydrocarbons have been reviewed. The topics reviewed are the oxidative coupling of methane to C_2 compounds ($C_2H_6 + C_2H_4$), the selective synthesis of C_2H_4 , and the synthesis of aromatic hydrocarbons. Among the metal oxides tested, rare earth metal oxides showed high stability, high C_2 -selectivity, and high catalytic activities for oxidative coupling of CH_4 . Kinetic studies on oxidative coupling of CH_4 over Sm_2O_3 suggest that the reaction be initiated by diatomic oxygen species, probably by peroxide ions O_2^{2-} . A comparison of the results on the reactions using O_2 and N_2O as oxidants showed that O_2 was a better oxidant for catalytic conversion of CH_4 into C_2 compounds. Alkali halides, especially LiCl, enhanced the selective synthesis of C_2H_4 in partial oxidation of CH_4 over metal oxides. The effect of LiCl was most marked for the oxides of the first series transition elements. The role of alkali metals of the alkali halides is to create active compound oxides of the alkali metals and the host metal oxides. The role of halides is to supply halogen atoms which catalyze dehydrogenation of C_2H_6 to C_2H_4 in the gas phase. The NaCl/Mn-oxide/silicalite catalyzed the synthesis of higher olefins and aromatics directly from CH_4 . The combination of a coupling catalyst and an aromatization catalyst improved the synthesis of aromatics with relatively high selectivity (>16.3%) and yield (>5.5%).

1. Introduction

Predicted shortage in the supply of crude oil has given natural gas an important position as an alternative source of hydrocarbons. Prospects are good for maintaining secure, reliable and adequate supplies of natural gas at competitive prices well into the future. Currently natural gas is used principally as a fuel in residential, commercial, and industrial services. Industries are now searching for new or novel ways to enhance the use and value of this methane-containing natural resources.

Natural gas generally occurs in remote areas of Siberia, Western Canada, Australia and Asia; thus, its location and transportation pose a major obstacle in its efficient exploitation. It would be extremely valuable if methane, usually comprising over 90 mole% of the hydrocarbon fraction of natural gas, could be converted into more easily handleable or transportable products such as olefins, aromatics, and higher order hydrocarbons that are used as precursor materials in chemical processing.

Besides its major use as an energy source,

methane is also used, to some extent, as a chemical raw material. One of the largest nonfuel uses of methane is the production of methanol. An innovative process for producing gasoline and light olefins from methanol was developed by Mobil Corp.^{1),2)} In the Mobil process, methane (or coal) is first converted into synthesis gas which then is converted into methanol by a catalytic process and subsequently into light olefins and higher hydrocarbons using a shape-selective zeolite catalyst (ZSM-5). Using methane as a starting carbon source, it is converted into synthesis gas by steam reforming over a nickel catalyst. The steam reforming of methane is a highly endothermic reaction.

The process, methane to methanol then to light olefins and higher hydrocarbons, suffers from large energy requirements, from complicated engineering steps, and also from inefficiency in oxidation of methane to carbon monoxide and in subsequent reduction of carbon monoxide to methanol and to higher hydrocarbons.

Obviously a direct conversion of methane into

light olefins and higher hydrocarbons is preferred because it then can yield desired products in one step. However, the conversion of methane into higher hydrocarbons via dehydrogenative coupling and oligomerization is limited due to the following two difficulties: the strength of the carbon-hydrogen (C-H) bond and thermodynamics. Temperatures higher than 1,073 K are required to effect practical conversion. The combined process consisting of oxidative coupling and oligomerization of methane can surmount these difficulties.

Under the oxidation conditions that can activate methane in the presence of oxygen, the intermediate products such as light olefins and higher hydrocarbons are quickly oxidized deeply to carbon dioxide and water because both the free energy changes and heats of reaction are favorable for the formation of these final stable products. Only within the last several years, researchers have succeeded in breaking the C-H bond and converting methane into useful chemicals by using specially designed catalysts. Detailed information about the past and recent developments in functionalization of methane is available in monographs and reviews.^{3)~8)}

This paper selects and reviews our current research activities on the following three topics dealing with partial catalytic oxidation of methane (1) to C₂ compounds (ethane and ethylene), (2) to ethylene selectively, and (3) to aromatic hydrocarbons.

2. Oxidative Coupling

2.1 Active and Selective Catalysts

Since Keller and Bhasin⁹⁾ reported the possibility of synthesizing C₂ compounds (C₂H₆ + C₂H₄) by oxidative coupling of methane over metal oxides, many groups^{10)~25)} have begun to work in this area, and there have been increasing industrial activities²⁶⁾ thereon. Keller and Bhasin⁹⁾ tested large numbers of metal oxides to catalyze methane coupling. To minimize the accompanying gas-phase noncatalytic reactions, they carried out the reaction by periodic feeding of air and methane. Oxides of Pb, Sb, Tl, Cd, and Mn were found to be the most active catalysts for the formation of C₂ compounds with selectivity of < 50%. However, in the normal, concurrent feeding mode of reactants, none were found to give good selectivity to the desired products.

Hinsen et al.¹⁰⁾ reported that catalytic conversion of methane could also be carried out in a con-

Reaction conditions : T=973 K, P(O₂) = 0.4 kPa,
P(CH₄) = 18.2 kPa, catalyst weight = 0.50 g.

Fig. 1 Catalytic Activities of Metal Oxides in Oxidative Coupling of CH₄

tinuously operated catalytic flow reactor when a suitable catalyst and suitable reaction conditions were chosen. They found that catalyst PbO/Al₂O₃ was the most active. PbO on SiO₂ carrier was most effective for C₂-selectivity approaching 72%, but its catalytic activity was low.¹⁰⁾

Recent work in our laboratory^{11),18)} has demonstrated that rare earth metal oxides exhibited better catalytic activity and selectivity in the oxidative coupling of methane. **Fig. 1** shows catalytic activities (rate per surface area of catalyst) for the formations of C₂ compounds (C₂H₄ + C₂H₆) examined for various rare earth metal oxides, PbO, Bi₂O₃, SnO₂, Ga₂O₃, GeO₂, In₂O₃, ZnO, CdO, CaO, and MgO (all in powder form) under the experimental conditions shown in the figure caption. All experiments were performed using a fixed-bed reactor with a conventional gas-flow system. Activities of the metal oxides, which have already been reported to be good catalysts for the reaction,^{9),10)} are shown on the right side in **Fig. 1**. The products were C₂H₆, C₂H₄, CO, CO₂, and H₂O. The results in **Fig. 1** show that the specific activity for the formation of C₂ compounds is the highest for Sm₂O₃. The selectivity to C₂H₆ and C₂H₄ calculated on the basis of carbon number of the CH₄ reacted for the same experiments in **Fig. 1** are plotted in **Fig. 2**. **Fig. 2** indicates that the oxides giving higher than 70% selectivity to C₂ compounds (C₂H₄ + C₂H₆ denoted by C₂) are the rare

Fig. 2 Selectivities to C_2H_6 , C_2H_4 , and the Sum of the C_2 Compounds

earth metal oxides (except for Ce, Pr, and Tb), Bi_2O_3 , and CaO . In general, lanthanide oxides, including lanthanum itself, showed particularly high C_2 -selectivity ($>80\%$). The selectivity observed for Sm_2O_3 and for Dy_2O_3 reached to 93%.

The catalytic tests performed under the same conditions have been extended to all the stable oxides of the metals in the periodic table. Many metal oxides showed higher catalytic activity than that of Sm_2O_3 and PbO as far as the conversion of methane was concerned, but they gave mostly deep oxidation products with low C_2 -selectivity of less than 3%. The oxides in **Fig. 2** are believed to have basic or amphoteric properties. Generally, basic oxides showed high selectivity to the formation of C_2 -hydrocarbons.^{9)~21)}

As mentioned above, Sm_2O_3 was the most active and selective catalyst among the metal oxides examined under the experimental conditions shown in **Fig. 1**. However, conditions such as low oxygen pressure (0.4 kPa), high $P(CH_4):P(O_2)$ ratio (45), and low reactant flow rate ($4.5 \text{ ml} \cdot \text{min}^{-1}$) used for the catalyst tests were not suitable for evaluating the true catalytic activity of Sm_2O_3 because the oxygen conversion exceeded 95%. Therefore, the catalytic test of Sm_2O_3 was performed under higher $P(O_2)$, lower $P(CH_4):P(O_2)$, and higher flow rate than those conditions shown in **Fig. 1**. **Fig. 3** shows the effect of W/F (weight of catalyst/flow rate of reactants) on C_2 -STY (space time yield of C_2 compounds), on C_2 -yield, on selectivity to

Reaction conditions : $T=1,023 \text{ K}$, $P(CH_4)/P(O_2)=6$, $W=0.010-0.150 \text{ g}$, $F=1.68-45.0 \text{ l} \cdot \text{h}^{-1}$.

Fig. 3 The Effect of W/F on the Reaction over Sm_2O_3

higher hydrocarbons, on CH_4 -conversion, and on O_2 -conversion. The O_2 -conversion decreased at W/F lower than $0.01 \text{ g} \cdot \text{h} \cdot \text{l}^{-1}$. The C_2 -STY increased remarkably by lowering W/F . The C_2 -STY reached $2.98 \text{ mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at $W/F 0.000223 \text{ g} \cdot \text{h} \cdot \text{l}^{-1}$. The selectivity to the coupling products (mostly C_2 compounds) at this W/F was fairly high (64%).

The C_2 -STYs and C_2 -selectivities reported recently for different catalysts are summarized in **Table 1**.²⁷⁾ Since the experimental conditions used for testing C_2 -STYs are so different from each other as can be seen in the table, we cannot compare the true catalytic activity of the catalysts. The C_2 -STYs listed in **Table 1** for the catalysts examined by other researchers must increase greatly when W/F is lowered than the values indicated in column seven. However, at this moment, the C_2 -STY observed for Sm_2O_3 is from one to three orders of magnitude greater than the values reported previously.

No appreciable decreases in activity and selectivity were observed for Sm_2O_3 after 180 h of operation at 973 K. Sm_2O_3 was a very stable catalyst for oxidative conversion of methane. High stability, high C_2 -selectivity, and high catalytic activity observed for Sm_2O_3 suggest that this oxide be one of the most promising catalysts for converting natural gas into ethane and ethylene. The catalytic tests performed at low W/F s for other rare earth

Table 1 Comparison of the Activities of Catalysts for Oxidative Coupling of CH₄

Catalyst	C ₂ -STY mmol·g ⁻¹ ·h ⁻¹	C ₂ -select. %	Temp. °C	P(CH ₄) kPa	P(CH ₄)/P(O ₂)	W/F g·h·l ⁻¹	Ref. No.
PbO/SiO ₂	1.2	71.4	740	70	10	0.43	10
Li/MgO	0.9	46.5	720	29	1.9	1.3	13
PbO/MgO	11.1	85.3	750	61	37.8	0.045	22
LaAlO ₃	62.3	78	710	88	33.3	0.017	20
Li/Mn-oxide	13.5	43	750	57	2.0	0.167	15
K/BaCO ₃	0.21	42	800	2.8	2.0	22.2	21
Li/ZnO	3.31	61	740	55	2.1	0.67	23
K/Bi/Al ₂ O ₃	90	30	700	51	10	0.0029	24
BaO/CaO	20.9	61	800	40	5.0	3.39	25
Sm ₂ O ₃	527	61	750	87	6.0	0.0033	27
Sm ₂ O ₃	2,980	60	750	87	6.0	0.000223	27

P(CH₄) = 18.2 kPa, P(O₂) = 0.98 kPa, and catalyst weight = 3.3 mg.

Fig. 4 Temperature Effects on the Rates of Formations of the Products over Sm₂O₃

metal oxides such as La₂O₃, Nd₂O₃, Dy₂O₃, and Eu₂O₃ showed that catalytic activities of these oxides were also very high and comparable to the activity of Sm₂O₃. In general the rare earth metal oxides were stable at high temperatures. Thus, the use of cheaper oxides La₂O₃ or Nd₂O₃ should be of practical advantage in converting methane into C₂ compounds.

2.2 Kinetic Studies

Kinetic studies on the reaction over Sm₂O₃ were carried out to see the general features of oxidative coupling of methane catalyzed by metal oxides.^{18),19)}

(1) Temperature Effects

Temperature effects on the rates of formation of

Fig. 5 Overall Reaction Scheme

products are shown in Fig. 4.¹⁸⁾ The O₂-conversion was controlled less than 5% at ≤973 K. The apparent activation energies calculated from the straight lines for the C₂ compounds (C₂H₆ + C₂H₄), ethylene, and carbon oxides (CO + CO₂)¹⁸⁾ were 135, 173, and 66 kJ mol⁻¹, respectively. The higher activation energy for the synthesis of C₂ compounds than that for carbon oxides shows that the higher the temperature the better is the selectivity to and the yield of C₂ compounds. The highest activation energy for the formation of ethylene indicates that the selectivity to ethylene becomes favorable as temperature increases. Experiments using different hydrocarbons, i.e., CH₄, C₂H₆, and C₂H₄ as the starting reactants showed that the overall reaction scheme for oxidation of methane at low conversion levels could be as shown in Fig. 5. The direct synthesis of ethylene (the dotted arrow) was negative. The unexpected observation that the selectivity to C₂ compounds became favorable with increasing temperature was also confirmed for all of the rare earth metal oxides in Fig. 1, for Li/MgO¹²⁾, for PbO/MgO²²⁾, and for K/Bi/Al₂O₃²⁴⁾. This fact implies that a common reaction mechanism is involved in the reactions over these basic metal oxides.

(2) Pressure Effects

The effects of oxygen pressure on the rates of products over Sm_2O_3 at 973 K are shown in **Fig. 6**.^{18),19)} The C_2 -selectivity decreases steadily with increasing oxygen pressure. However, the selectivity which is quite high at low $P(\text{O}_2)$ attains 100% at $P(\text{O}_2)$ 0.3 kPa. **Fig. 7** shows the effect of CH_4 pressure. Both the rate and C_2 -selectivity increased with increasing CH_4 pressure.

Pressure effects were also examined at 873, 923, and 1,023 K. At each temperature, the following

$P(\text{CH}_4) = 18.2 \text{ kPa}$ and $T = 973 \text{ K}$

Fig. 6 $P(\text{O}_2)$ Effects on the Rate and C_2 -selectivity

$P(\text{O}_2) = 0.98 \text{ kPa}$ and $T = 973 \text{ K}$

Fig. 7 $P(\text{CH}_4)$ Effects on the Rate and C_2 -selectivity

rate equation fitted the rate of methane conversion (r_c):¹⁹⁾

$$r_c = k \frac{K_m P(\text{CH}_4)}{1 + K_m P(\text{CH}_4)} \cdot \frac{K_o P(\text{O}_2)}{1 + K_o P(\text{O}_2)} \quad (4)$$

where, k , K_m , and K_o are the constants at fixed temperatures.

(3) Reaction Mechanism

The above rate equation was well explained by assuming the following reaction mechanism:¹⁹⁾

where, the superscript (*) means excited molecules (vibrational, electronical, or charged) generated on the surface or generated by collision with the surface. The C-H bond breaking (iii) is the rate-determining step in the overall reaction. Here, it is to be noted that initiation (step iii) is caused not by a monoatomic oxygen but by a diatomic oxygen. The coupling of two CH_3 radicals (or alternatively CH_3 -groups adsorbed) produces ethane (step iv). Deep oxidation takes place through the oxidation of CH_3 radicals (or groups) (step v). Reactions iv and v may occur either on the surface of Sm_2O_3 or in the gas phase near the surface.^{19),28)} Oxidative dehydrogenation of the C_2H_6 formed gives C_2H_4 as described in **Fig. 5**.

The C_2 -selectivity is determined by the competition between reactions iv and v. The decrease in the C_2 -selectivity with increasing $P(\text{O}_2)$ (**Fig. 6**) can be ascribed to the increase in the rate of reaction v compared to the rate of reaction iv.

The temperature effect on the selectivity of the products (**Fig. 4**) indicated that the higher the temperature the better was the selectivity to C_2 compounds. Since the abstraction of H from CH_4 (reaction iii) requires a large activation energy (149 kJ mol^{-1}),¹⁹⁾ the concentration of CH_3 radicals (or methyl groups) must increase sharply with the rise in temperature. Note that the rate of reaction iv depends on the square of CH_3 concentrations, but the rate of deep oxidation (reaction v) is proportional to CH_3 concentration. Thus, acceleration in the rate of C_2 -formation with temperature is greater than that of deep oxidation. This observation explains the higher C_2 -selectivity at higher temperatures.

2.3 Oxidative Coupling of Methane using N₂O

With certain catalysts and under certain reaction conditions, partial oxidation of methane can be achieved successfully when nitrous oxide is used as the oxygen source.^{29)~32)} Therefore, we have compared the results of oxidative coupling of methane using O₂ and N₂O over rare earth metal oxides.^{33),34)} The results at relatively high pressures of the oxidants (P(O₂) = P(N₂O) = 10.5 kPa, P(CH₄) = 48.8 kPa) are shown in Figs. 8 and 9. The conversions of the oxidants in Fig. 8 show

that the reactivity of O₂ is greater than that of N₂O for most of the oxides tested.

As can be seen in Fig. 9, the selectivity to the coupling products is higher when N₂O is used for all the rare earth metal oxides tested. In general, temperatures higher than 873 K are required for producing higher hydrocarbons (≥C₂) when O₂ is used as an oxidant. However, when N₂O is used, the temperature effect on the selectivity to higher hydrocarbons is not so apparent especially for Pr₆O₁₁, Nd₂O₃, Sm₂O₃, and Dy₂O₃ (Fig. 9). Thus, N₂O is a peculiar oxidant causing a selective

Fig. 8 Conversions of CH₄ and Oxidants in Partial Oxidation of CH₄ over Rare Earth Metal Oxides at 823, 873 and 923 K

Fig. 9 Product Distributions (Selectivities) in Partial Oxidation of CH₄

coupling of methane at temperatures lower than 873 K. The effects of pressure of the oxidants on the rate and selectivity to the products were examined for Sm_2O_3 at temperature as low as 823 K.³⁴⁾ Although only a trace of ethane was formed at O_2 -pressure greater than 2 kPa, the C_2 -yield increased sharply when O_2 pressure decreased below 0.6 kPa. On the other hand, the rate of formation of C_2 compounds was not affected by change in N_2O pressure. The maximum yield of C_2H_6 observed when O_2 was used as the oxidant was much greater than when N_2O was used. These results indicate that O_2 is a better oxidant for the catalytic conversion of methane into C_2 compounds.

Detailed kinetic studies on the reaction using N_2O as the oxidant suggested that the reaction mechanism be quite different from the case in which O_2 was used as the oxidant.³⁴⁾ Decomposition of N_2O over Sm_2O_3 was proposed to be rate-determining.

2.4 Oxygen Species Responsible for Activating Methane

Only a few reports on the fundamental work concerning the oxygen species responsible for activating methane over metal oxides are available. Liu et al.³⁰⁾ have demonstrated that surface O^- ions are the active oxygen for initiating partial oxidation of methane over $\text{MoO}_3/\text{Cab-O-Sil}$ using N_2O as an oxidant. Ito et al.¹³⁾ have suggested the $[\text{Li}^+\text{O}^-]$ centers were responsible for abstracting H from CH_4 over Li-promoted MgO . As mentioned earlier, the kinetic studies on oxidative coupling of methane suggest that a diatomic oxygen be responsible for the activation of methane (reaction iii). The idea that the oxidation of methane is initiated by diatomic oxygens is generally accepted for gas phase reactions.^{35),36)} The kinetic studies described earlier, however, cannot specify the kind of diatomic oxygen species responsible for the reaction over Sm_2O_3 . The species may perhaps be O_2^- , O_2^{2-} , or a chemically adsorbed O_2 on the surface.

Lunsford and coworkers^{37),38)} have implied that the active oxygen species over La_2O_3 may be a superoxide ions O_2^- . Recently we have demonstrated that the reactions of CH_4 with Na_2O_2 , BaO_2 , and SrO_2 proceed smoothly, yielding C_2 compounds with high selectivity at <673 K.³⁹⁾ This observation indicates that the peroxide ions O_2^{2-} on the surface are very reactive for C-H bond breaking. ESR spectra for the Na_2O_2 sam-

ple used in the experiments showed that the sample contained superoxide O_2^- ions. However, no correlation between the O_2^- and activation of methane was observed.³⁹⁾ Therefore, we suggested that the dioxygen species responsible for initiating the abstraction of H from CH_4 over Sm_2O_3 could be O_2^{2-} .

3. Direct Conversion of Methane to Ethylene

3.1 Alkali Halides/Transition Metal Oxides

Ethylene is one of the major raw materials in chemical industry. As described earlier (Fig. 5), ethylene is formed stepwise from methane to ethane and finally to ethylene ($\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4$). Usually, in oxidative coupling of methane, the selectivity to ethylene is relatively low compared to the selectivity to ethane because the ethane is mainly oxidized to CO and CO_2 with low selectivity to ethylene. The high $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio in the C_2 -products is of great advantage since no further process to convert ethane to ethylene is required. Therefore, catalysts converting methane into ethylene with higher selectivity and yield are strongly desired. Thus, we have looked for catalysts which give ethylene directly from methane with high one-pass conversion and yield.^{15),16),17)}

Enhancing effects of alkali metals on oxidative coupling of methane have been first reported by Hinsien et al.¹⁰⁾ for $\text{PbO}/\text{Al}_2\text{O}_3$. The promoting effects of alkali metals have also been observed for MgO ,^{12),13),21)} Sm_2O_3 ,¹⁴⁾ ZnO ,²³⁾ and $\text{Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$.²⁴⁾ Among the alkali salt additives tested, we found lithium chloride exerted the most favorable effect on the reaction over Sm_2O_3 , since it increased not only the yields of C_2 compounds but also the ratio of $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$. This favorable effect of LiCl was observed for many other metal oxides (Eu_2O_3 , La_2O_3 , CeO_2 , MgO , CaO , SiO_2 , Al_2O_3 , ZrO_2 , Nb_2O_5 , Ga_2O_3 , GeO_2 , In_2O_3 , SnO_2 , PbO , Bi_2O_3 , TiO_2 , V_2O_5 , Cr_2O_3 , MnO_2 , Fe_2O_3 , Co_3O_4 , NiO , CuO , and ZnO). Among the oxides tested, however, the enhancing effect of LiCl on the yield of ethylene was most marked for the oxides of the first series transition elements.^{15),17)}

Table 2 shows the results observed for the transition metal oxides¹⁵⁾ when the reactants were on stream for 20 min. The metal oxides without LiCl catalyzed only deep oxidation of methane. However, as can be seen in Table 2, high C_2 -yields were observed for the oxides of Ti, Mn, Co, Ni, Cu, and Zn in the presence of LiCl. The C_2 -yield observed for LiCl/Mn-oxide has been the highest

Table 2 Synthesis of C₂H₄ from CH₄ over LiCl/Transition Metal Oxides

Catalyst	% CH ₄ conversion	% O ₂ conversion	% C ₂ H ₄ selectivity	% C ₂ H ₆ selectivity	% C ₂ yield	% C ₂ H ₄ yield
LiCl/Ti-oxide	17.6	40	77.1	5.7	14.6	13.6
LiCl/Cr-oxide	26.1	85	0	0	0	0
LiCl/Mn-oxide	47.3	95	59.4	5.3	30.6	28.1
LiCl/Fe-oxide	22.2	92	0	0	0	0
LiCl/Co-oxide	48.0	91	32.1	3.4	17.0	15.4
LiCl/Ni-oxide	25.9	57	56.2	15.6	18.6	14.5
LiCl/Cu-oxide	49.5	80	20.6	0	10.2	10.2
LiCl/Zn-oxide	22.0	49	42.6	26.3	15.2	9.4

Reaction conditions: T=1,023 K, P(CH₄)/P(O₂)=2, P(CH₄)=5.1 kPa, and W/F=0.167 g·h⁻¹·l⁻¹.

Table 3 Synthesis of Ethylene over NaCl/Mn-oxides at Different Pressures of Reactants

P(CH ₄) + P(O ₂), atm	0.09	0.19	0.34	0.64	0.83	1.00
Catalyst weight, g	0.40	0.40	0.40	0.40	0.40	0.25
CH ₄ conversion, %	46.8	46.1	41.5	38.9	36.1	32.0
O ₂ conversion, %	99.4	98.8	99.5	92.9	97.4	97.6
Selectivity to hydrocarbons (≥C ₂), %	65.2	56.0	51.4	45.5	53.1	48.9
Yields, %						
C ₂ H ₄	25.7	19.8	16.8	14.2	14.9	11.9
C ₂ H ₆	1.7	2.2	2.6	1.9	2.2	2.0
C ₃ H ₆	0.5	0.6	0.7	0.9	1.1	0.9
C ₄ H ₈	1.9	2.8	0.9	0.4	0.7	0.5
Benzene + Toluene	0.8	0.4	0.4	0.2	0.3	0.2
Total H. C.	30.6	25.8	21.3	17.6	19.2	15.7
STY (mmol·g-cat ⁻¹ ·hr ⁻¹)						
C ₂ H ₄ + C ₂ H ₆	9.2	14.7	23.4	36.7	50.4	64.0
Total H. C.	10.2	17.3	25.7	40.1	56.6	72.3

Reaction conditions: T=1,023 K; P(CH₄) : P(O₂)=2 : 1, and total gas flow rate=100 ml·min⁻¹.

(30.6%) ever reported. The C₂-yield for LiCl/Ni-oxide increased to 28.9% when W/F was increased to 0.34 g·h⁻¹·l⁻¹. The striking effect of LiCl on the C₂H₄-selectivity is shown in the last column of **Table 2**. The percentage of ethylene in the C₂ compounds produced was greater than 90% for the LiCl-added oxides of Ti, Mn, Co, Ni, and Cu. NaCl and LiBr also exerted similar favorable effects on the C₂H₄/C₂H₆ ratio. **Table 3** shows the results of ethylene synthesis over the NaCl-added (20 mol%) Mn-oxides at different pressures of the reactant.⁴⁰⁾ As can be seen in the table, the main product was ethylene under all conditions tested. It is noteworthy that propylene, butene, benzene, and toluene were also produced. The yield of total hydrocarbons (≥C₂) was quite high (30.6%) when the pressure of the reactant was 0.09 atm. STYs of C₂ compounds and total hydrocarbons (≥C₂) increased linearly with increasing pressure of the reactant.

As demonstrated above, alkali halide-added transition metal oxides showed high catalytic activity for converting methane directly into ethylene. However, deactivation of the catalysts was a serious problem. NaCl/Mn-oxide in **Table 3** was superior to LiCl/Ni-oxide because the lifetime of the former was much longer than that of the latter.

Regeneration of the used catalyst can easily be performed by adding a new alkali halide.

Fig. 10 shows the change in the C₂H₄/C₂H₆ ratio with time on stream for the reaction over LiCl (20 mol%)/Ni-oxide. Analysis of the effluent gas indicated the formation of CH₃Cl during the reaction. Relative concentration of CH₃Cl are also plotted in **Fig. 10**. Similar trends observed for the two curves strongly suggest that the CH₃Cl plays an important role in the selective synthesis of ethylene.

3.2 Role of Alkali Halides

Weissman and Benson⁴¹⁾ reported that chlorine radicals catalyzed the formation of ethylene from methane at high temperatures in the gas phase. The observation that only alkali halides can enhance selective conversion of methane to ethylene suggests that halogen radicals supplied from the alkali halides play a significant role in the reaction. The results in **Fig. 10** suggest the important role of CH₃Cl for selective synthesis of ethylene. We have observed that CH₃Cl catalyzed dehydrogenation of ethane to ethylene at temperatures above 923 K.⁴²⁾

A tentative reaction mechanism explaining the action of chlorine atom is as follows:⁴²⁾

Reaction conditions : T=1,023 K, P(CH₄) : P(O₂) = 5 : 2, P(CH₄) = 10.1 kPa, W/F=0.167 g·h⁻¹.
Fig. 10 Changes in the C₂H₄/C₂H₆ Ratio and Relative Concentration of CH₃Cl with Time on Stream of Reactants

Eq.(a) indicates the catalytic conversion of methane into ethane over alkali metal-added transition metal oxides. The role of alkali metals is to create compounded oxides of the alkali metal and the host transition metal oxides.⁴³⁾ The compounded oxides catalyze the formation of ethane very selectively.⁴³⁾ The CH₃Cl generated in reaction (b) liberates a chlorine atom in reaction (c). The C₂H₆ formed in reaction (a) would be converted quickly into C₂H₄ in reactions (d) and (e). Chlorine atoms are regenerated by reactions (f) and (g). Thus, the chlorine atoms supplied from alkali chlorides catalyze the synthesis of C₂H₄ from C₂H₆ during the stay of the flowing gases in the hot reactor zone.

4. Methane to Aromatics

Conversion of methane into aromatic hydrocarbons would open a new route for synthesizing highly functionalized chemicals directly from natural gas. However, the challenging work to convert methane directly into aromatics by partial oxidation has not yet been successful, except the cases in which N₂O as a mild oxidizing agent was used.^{31),32)} We can readily recognize that this difficulty arises from the large difference in the reactivities of methane and aromatic hydrocarbons. Under severe oxidation conditions that can activate methane in the presence of O₂, there may be but a

Table 4 Synthesis of Higher Hydrocarbons over NaCl/Mn-oxide/Silicalites

P(CH ₄)/P(O ₂)	2.5	1.7
CH ₄ conversion, %	43.9	52.7
Hydrocarbon selectivity, %	63.4	46.4
Yields, %		
C ₂ H ₄	22.8	19.2
C ₂ H ₆	1.7	0.9
C ₃ H ₆ +C ₄ H ₈	2.4	2.8
Benzene + toluene	1.0	1.6
Total H. C.	27.8	24.5

Reaction conditions: T = 1,023 K, P(CH₄) + P(O₂) = 23 kPa, Flow rate=61 ml·min⁻¹, and catalyst weight=3.0 g

slight chance of getting aromatics without converting them wholly into CO₂.

As demonstrated earlier (Table 3), the NaCl-added Mn-oxide formed aromatics though in small yields (≤0.8%) during partial oxidation of methane in the presence of oxygen. The yields were improved when the NaCl/Mn-oxide was supported on silicalites as shown in Table 4. This observation implies that ZSM-5 type structure might exert a favorable effect on the synthesis of aromatics.

It is reported that light paraffinic hydrocarbons can be converted into aromatics in the absence of oxygen using the ZSM-5 zeolites ion-exchanged with H⁺, Ga³⁺ and Al³⁺.^{44),45)} Thus, we can expect that the combination of two types of catalysts, one for oxidative coupling of methane (coupling catalyst) and the other for oligomerization of the coupled products and for subsequent cyclization to aromatic hydrocarbons (aromatization catalyst), may increase the yields of aromatics directly from methane by passing the mixture of methane and oxygen through the respective catalyst beds.

Deep oxidation of CH₄ occurred exclusively

when the aromatization catalyst was used alone in the presence of O_2 . The coupling catalyst mixed with the aromatic catalyst did not give any aromatics either. Therefore, experiments were carried out with the reactant (CH_4 and O_2) passing through the two catalysts, coupling and aromatization, packed in series in the reactor with some space between the each catalyst bed.⁴⁶⁾ The results obtained are shown in **Fig. 11**. The combinations of Li_2CO_3/Sm_2O_3 , $LiCl/Ni$ -oxide, and $NaCl/Mn$ -oxide (coupling catalysts) with Ga-ZSM-5 (aromatization catalyst) in such series produced significant amounts of aromatics as had been expected. For all catalyst combinations in **Fig. 11**, the selectivity to aromatics was greater than 6%. $LiCl/Ni$ -oxide and $NaCl/Mn$ -oxide with Ga-ZSM-5 (Si/Al = 25) gave fairly high selectivities (>16.3%) to and yields (>5.5%) of aromatics. Considerable amounts of light hydrocarbons produced by these coupling catalysts remained unreacted in the effluent gas. Therefore, yields of aromatics can be improved if catalysts having higher catalytic activities for conversion of light hydrocarbons to aromatics could be developed. Moreover, better reactor design and better reaction conditions such as $P(CH_4)/P(O_2)$ ratio, temperature control of and distance between the each

catalyst bed, and flow rate of reactant should also enhance aromatics yields.

5. Some Concluding Remarks

This paper has covered only one of the approaches by which methane is partially oxidized to higher hydrocarbons. Other important products synthesized directly from methane are methanol and formaldehyde. Detailed information about the past and recent works on this subject is available.^{5),6),8)} Other topics of methane activation and functionalization are also receiving serious considerations.^{3),4),7)} Methane chemistry, based on its ubiquitous and secure supplies, presents great opportunities and challenges for heterogeneous and homogeneous catalysis.

The catalysts described in this paper may provide a new route to the production of ethylene and higher hydrocarbons from methane. However, the results to date, while encouraging, are still short of commercial realization. However, if progress on catalysts of greater conversion, selectivity, and lifetime continues, the new route can achieve commercial realization.

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Fig. 11 Synthesis of Aromatic Hydrocarbons from CH_4 by Combination of Coupling and Aromatization Catalysts in Series

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要 旨

メタンから炭化水素 ($\geq C_2$) の直接合成

大塚 潔

東京工業大学化学工学科, 152 東京都目黒区大岡山 2-12-1

近年, 化学工業原料としてのメタンの新しい利用法について関心が高まっている。水蒸気改質により合成ガスとすることなしに, メタンを部分酸化で直接目的化合物に転換することができれば, エネルギーの節約とプロセスの簡略化から, その工業的意義は大きい。本稿では, メタンから直接 C_2 以上の炭化水素への接触的転換反応について著者らの研究を紹介した。取上げた反応は, メタンの酸化カップリング反応による C_2 炭化水素 ($C_2H_6 + C_2H_4$) の合成, メタンからエチレンの選択的合成, および芳香族炭化水素の合成である。

酸化カップリング反応に有効な触媒を探索した結果, 希土類酸化物, 中でも Sm_2O_3 が活性, C_2 選択性, および触媒寿命の点で最も優れた触媒であることがわかった (Figs. 1, 2, 3, Table 1)。速度論的研究 (Figs. 4, 6, 7) から, Sm_2O_3 触媒上では, メタンの活性化は分子状活性酸素種 (たぶん O_2^{2-}) によって引き起こされることを示唆した。酸化剤として N_2O を用いてメタンのカップリング反応を行い, O_2 を酸化剤として用いた結果と比較した (Figs. 8, 9)。メタンの酸化カップリン

グ反応用酸化剤としては, O_2 が優れていることがわかった。

エチレンの選択的合成には, 金属酸化物触媒にハロゲン化アルカリを添加すると良いことがわかった。特に $LiCl$ や $NaCl$ を第一遷移金属酸化物に添加した触媒は, 高い収率 (9~28%) でエチレンを合成することがわかった (Tables 2, 3)。アルカリ金属は遷移金属酸化物との間に, エタンの生成に高活性な複合酸化物を形成する。ハロゲン化アルカリから生成したハロゲン原子は, エタンの脱水素反応を気相で触媒しエチレンを生成する。ハロゲン化アルカリの以上の二つの働きにより, メタンからエチレンの選択的合成が可能となる。

メタンからベンゼンとトルエンの合成には, $NaCl/Mn$ -酸化物/シリカライト触媒が有効である (Table 4)。メタンの酸化カップリング用触媒と C_2 炭化水素の芳香族化用触媒である $Ga-ZSM-5$ ゼオライトを二段に組合せると, 比較的高い選択率 (>16.3%) と収率 (>5.5%) で芳香族炭化水素が合成できることを示した (Fig. 11)。

Keywords

Aromatization, Conversion, Methane, Oxidative coupling, Oxide catalyst, Partial oxidation