

[Review Paper]

Methane Conversion Assisted by Plasma or Electric Field

Kazumasa OSHIMA, Tatsuya SHINAGAWA, and Yasushi SEKINE*

Dept. of Applied Chemistry, School of Advanced Science and Engineering, Waseda University,
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, JAPAN

(Received October 4, 2012)

Direct conversion of methane to other valuable products such as ethylene, methanol, benzene, carbon, hydrogen, and syngas has been widely investigated. Such conversion requires high temperatures because of the strong C–H bond in CH₄, and such high-temperature reactions present various problems: sequential reaction to decrease the selectivity to target products, need for multiple heat exchangers to use or recover high-temperature waste heat, materials that are stable at high temperatures, etc. To solve these problems, several trials have been undertaken to lower reaction temperatures using plasma, Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA), and electric fields. This review describes recent trends in methane conversion, and describes our methods to lower the reaction temperature.

Keywords

Methane conversion, Methane oxidative coupling, Methane partial oxidation, Methane steam reforming, Plasma, Electric field

1. Effective Utilization of Methane**1.1. Processes for Effective Utilization of Natural Gas**

Petroleum is widely used because of its characteristic ease of transport and storage, and easy conversion into resources that are useful for petrochemistry. However, petroleum has limited reserves, and its price depends on “geopolitics.” Therefore, much attention has been devoted to natural gas, an alternative energy source to petroleum. Although natural gas, a fossil fuel, presents similar shortcomings related to limited reserves, the regions of gas deposits are less affected by geopolitics. Methane, the main component of natural gas, contains the greatest amount of energy per carbon atom. Complete oxidation of methane emits the least amount of carbon dioxide among all hydrocarbons. Nevertheless, methane is the most stable hydrocarbon, so requires much energy for conversion. Moreover, methane exists as a gas under standard conditions, so has low energy density and presents shortcomings in terms of inefficiencies in distribution and storage.

To solve such problems for the wider use of natural gas, much effort has been devoted to transforming or converting natural gas efficiently (**Fig. 1**). Two methods of transformation to a liquid state are possible: physical transformation and chemical conversion. The

former is a process by which natural gas is cooled and transformed into liquefied natural gas (LNG) under high pressure. The latter is a process by which natural gas is converted into liquid or more valuable materials than methane. However, these processes are only economic for utilization in large gas fields, so middle or small gas fields are not sufficiently exploited. To use these gas fields, more effective utilization of methane is

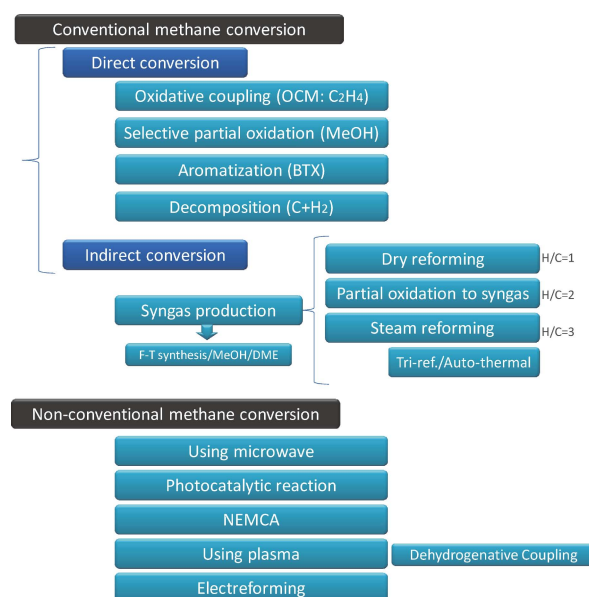


Fig. 1 Overall Scheme of Methane Conversion Processes

* To whom correspondence should be addressed.

* E-mail: ysekine@waseda.jp

desired.

1. 2. Current Circumstances Related to Natural Gas Conversion

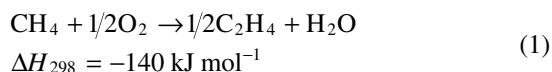
Two main processes are known for the chemical conversion of methane, as shown in **Fig. 1**. Direct conversion transforms reactants directly in one step to more valuable products. Indirect conversion involves the initial transformation of methane to synthesis gas (H_2 and CO), followed by reactions to produce liquid fuels such as methanol and FT oil.

1. 2. 1. Direct Conversion of Methane

Direct conversion is a more effective process than indirect conversion because the direct process requires fewer steps. Representative examples for direct conversion of methane include oxidative coupling of methane, direct synthesis of methanol, and methane decomposition.

(1) Oxidative Coupling of Methane

Oxidative coupling of methane is expressed as the following Eq. (1).



Much attention has been devoted to this reaction because of its advantage that ethylene can be synthesized directly in one step. Direct synthesis of ethylene, a valuable material, reduces the costs necessary for transportation and storage, so this process could contribute greatly to the expansion of natural gas utilization. Despite much research, no good catalyst has been identified with sufficiently high activity for commercial use. The main reason underlying this lack of effective catalysts is the difficulty in achieving both high conversion and high selectivity simultaneously because of the high stability of methane and the high reactivity of the product, C_2H_4 . Efforts at improving conversion result in reduced selectivity. The rate-determining step for this reaction is the formation of methyl radicals, and the high activation energy for this step requires a high-temperature environment. Consequently, a yield of ethylene higher than 30 % is rarely achieved. Evaluation of alkali metal, alkali earth, and rare earth oxides as catalysts found that a SrO -supported La_2O_3 catalyst can provide higher yields for C_2 hydrocarbons¹⁾. Subsequently, many studies were conducted to ascertain the reaction mechanism, and showed that the primary products are ethane and carbon monoxide which are converted into ethylene and carbon dioxide, respectively²⁾. Furthermore, successive elementary reactions in the gas phase were investigated³⁾. $Mn/N a_2WO_4/SiO_2$ catalyst was found to have high selectivity for C_2 ^{4,5)}. The acidity/basicity characteristic strongly affects the activity and selectivity for oxidative coupling of methane⁶⁾, and modifications such as doping of rare earths into CaO ⁷⁾ and doping of alkali into CaO ⁸⁾ enhance activity and selectivity. Moreover,

reactant mixed with a small amount of H_2O can form surface hydroxyl groups that can increase selectivity⁹⁾. Our group also investigated OCM using Ba-doped La oxide catalysts and found that $La_{0.925}Bi_{0.025}Fe_{0.05}O_{3-\delta}$ ¹⁰⁾ and $La_{0.6}Ba_{0.4}InO_{3-\delta}$ ¹¹⁾ catalysts showed high activity/selectivity for C_2 production. Great efforts have been made to enhance the activity and selectivity, but fundamental problems persist in terms of the difficulty in suppressing successive and non-selective oxidation¹²⁾.

(2) Selective Partial Oxidation of Methane

Oxidative coupling of methane proceeds *via* intermediate methyl radical, which is formed through oxidation of methane. Therefore, formation of methanol or formaldehyde has been investigated by suppressing and controlling this oxidation step¹³⁾. Ethylene, which is formed during oxidative coupling, is useful as a raw material for polymer formation, but methanol and formaldehyde are also useful materials for petrochemistry and other applications. A yield of formaldehyde higher than 60 % was achieved under conditions in which both methane and oxygen were fed at a low space velocity¹⁴⁾. However, high yield of products is unachievable at such a low space velocity. Numerous challenges are expected to continue to hinder development of this process.

(3) Aromatization of Methane

Several studies have specifically investigated direct aromatization from methane. Aromatization of carbon dioxide and methane was attempted with MFI-zeolite as a catalyst¹⁵⁾. Investigation of details of this reaction found that conversion as high as 20 % can be achieved. The reaction mechanism was presumed to involve conversion of methane into methanol first followed by oxidation of methanol to form formaldehyde and carbon dioxide, or further conversion of methanol into olefin or aromatic hydrocarbon on acid sites¹⁶⁾. In all experiments described above, dinitrogen oxide was used as the oxidant. Use of oxygen as the oxidant would make this process into a very attractive reaction scheme. $NaCl/MnO_2$ catalyst, which is known to exhibit high activity toward oxidative coupling of methane, also allowed conversion of methane as high as 13.2 %, with more than 20 % selectivity. In this case, ethylene may be formed as an intermediate and is converted into aromatic hydrocarbon¹⁷⁾.

In contrast, methane was aromatized *via* the cyclodehydration of methane with no oxidants. Mo -supported or Zn -supported H-ZSM-5 was reported to have higher activity. Especially for Mo/H -ZSM-5, 7-8 % of methane was converted into benzene at 100 % selectivity at 973 K. Furthermore, this conversion became higher as the partial pressure of methane increased¹⁸⁾. The reaction mechanism of this catalyst was investigated with Mo metal, Mo oxides, and Mo_2C . The reaction mechanism was as follows. Mo oxide, reacting with methane, formed Mo_2C which was active only for the C-H

bond in methane, so product CH_3 or CH_2 formed an intermediate to be coupled into ethane or ethylene. This product was then converted into aromatic hydrocarbon over ZSM-5 catalyst^{19)~21)}. However, the conversion of methane in this scheme was unable to reach yields higher than 30 %. Therefore, further investigation is required.

(4) Decomposition of Methane

In contrast to the oligomerization of methane, many investigations have tried to produce pure hydrogen and carbon *via* methane decomposition. The reaction is represented by the Eq. (2).



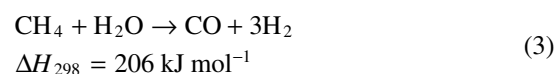
The advantage of this reaction is that no carbon monoxide or carbon dioxide is formed, so “pure” hydrogen is obtained. Pure hydrogen is a useful energy source for use in fuel cells. As fuel cells become more important, the importance of this reaction will also increase. Furthermore, the carbon formed in this reaction can be used in various materials such as carbon black, activated carbon and other carbon materials. This decomposition of methane was investigated with iron oxides, aluminum oxide, and quartz as catalysts, and found that iron oxide catalysts provided the highest yield of hydrogen²²⁾. Use of Ni-supported H-ZSM-5, H-Y, and SiO_2 catalysts found that the Ni particles of Ni/H-ZSM-5 were covered by the formed carbon and the catalytic activity was deteriorated in methane decomposition. In contrast, no deterioration was observed using H-Y and SiO_2 catalysts, and filamentous carbon was formed. These findings suggest that carbon shapes formed in this reaction affect the catalytic lifetime²³⁾. However, the formed carbon can more or less degrade catalytic activity, and regeneration of the catalytic activity must be conducted. To avoid operating this regeneration process, many investigations have assessed carbon-based catalysts. Testing of various carbon-based catalysts found that amorphous carbon such as active carbon and carbon black exhibited higher activity than ordered catalysts such as graphite and diamond powder²⁴⁾. Furthermore, conversion of methane as high as 70 % can be achieved over a wood char catalyst²⁵⁾. In the above-described systems using a carbon-based catalyst, the methane decomposition activity might be affected by the oxidized surface at the initial stage and by the pore distribution in the steady state stage before pore-plugging²⁶⁾. However, the initial activity might be affected not by the oxidized surface but by defects in the graphene layers²⁷⁾. An alternative redox system has been proposed that can produce hydrogen through two reactions, reduction of an oxide such as In_2O_3 or FeO_x by methane decomposition followed by oxidation of the catalyst using steam to produce pure hydrogen²⁸⁾.

1. 2. 2. Indirect Conversion of Methane

In contrast to the direct conversion of methane, indirect conversion has been widely investigated. Indirect processing includes synthesis gas (H_2 and CO) production and sequential conversion into methanol or FT oil. Methane can be converted into various useful materials using this scheme, but multiple processes require much energy, resulting in low energy efficiency. Therefore, current processes have low feasibility from the viewpoints of capital and operational expenses.

(1) Steam Reforming of Methane

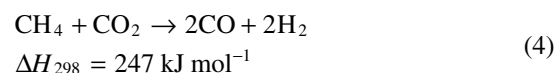
Steam reforming and partial oxidation are well-known processes for the production of synthesis gas. In the former, methane reacts with steam and is converted to synthesis gas. This endothermic reaction is expressed as the Eq. (3).



In this reaction, the hydrogen source is both methane and H_2O . Steam reforming of hydrocarbon has been frequently investigated^{29)~33)}. Nickel, an inexpensive metal, catalyzes this reaction, but the formed carbon deactivates the catalyst. To avoid this carbon deposition phenomenon, reactants with high $\text{H}_2\text{O}/\text{CH}_4$ ratios are supplied, but this requires much energy to satisfy the sensible/latent heat and lower total energy efficiency. Many investigations have tried to develop catalysts with high activity for this reaction which suppresses carbon formation. Sulfuration of the catalyst can suppress carbon deposition but also decreases the catalytic activity³¹⁾. Other approaches have controlled the structure of the metal and support³²⁾. A metal oxide such as CeO_2 , in which the lattice oxygen has mobility^{34),35)}, was used to remove the deposited carbon on the catalyst *via* its lattice oxygen. Also, a solid solution of Zr-doped CeO_2 has higher oxygen storage capacity (OSC) than only CeO_2 ^{36),37)}, and was applied to this reaction³⁸⁾. Despite these investigations, high temperatures are still necessary to achieve high activity because of the thermodynamic and kinetic limitations.

(2) Dry Reforming of Methane

The reforming reaction of methane with CO_2 , called dry reforming, is expressed as the Eq. (4).

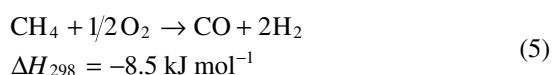


This process has received much attention for its utilization of carbon dioxide. The order of catalytic activity for Ni, Ru, Pd, Ir, and Pt is the same as that in steam reforming, but dry reforming suffers from carbon deposition on the catalyst. Ru and Rh catalysts can suppress carbon formation, so are apparently useful for this reaction³⁹⁾. The turnover frequency of this reaction depends not on the support properties but on the surface area of the supported metal, so dissociative adsorption

of methane is the rate-determining step⁴⁰⁾. To investigate this metal-support interaction, the effect of the support on the activity of Co, Ni, Ru, Rh, Ir, and Pt catalysts supported Al₂O₃ and SiO₂ were examined⁴¹⁾. Several investigations have been conducted of the metal-support effect. Another approach for increasing the catalytic activity is adding a base material such as CaO to the catalysts for suppressing carbon formation and stabilizing catalytic activity^{42),43)}. Use of MgO-CaO as a support results in higher activity and stability than that of Al₂O₃⁴²⁾. The coexistence of Ni/Al₂O₃ and CaO increases the reactivity of the coke-precursor, raising the reaction ratio and stabilizing catalytic activity⁴³⁾. Moreover, use of MgO as a catalyst support can maintain the small particle size of the metal, and thereby suppress carbon formation^{44),45)}. Another approach to enhance the catalytic activity is use of Ce_xZr_{1-x}O₂ solid solution to remove carbon deposition⁴⁶⁾. These findings are useful for this reaction, but several problems similar to those which hinder steam reforming remain unresolved.

(3) Partial Oxidation of Methane

Partial oxidation of methane is an exothermic reaction expressed as the Eq. (5).



The H₂/CO ratio of synthesis gas is 2 in this reaction, which differs from those of steam reforming (= 3) and dry reforming (= 1). In this reaction, combustion proceeds at first and the resultant heat promotes sequential steam reforming, followed by a water gas shift reaction⁴⁷⁾. Ni catalyst supported on Al₂O₃ has been widely investigated as a catalyst for this reaction. However, Ir/Al₂O₃ catalyst can show high activity for this reaction⁴⁸⁾. Furthermore, other catalysts such as Pt/Al₂O₃ and Pt/ZrO₂^{49),50)} were used for the partial oxidation reaction, but complete oxidation also occurs. To suppress complete oxidation, CeO₂-supported catalysts can achieve selective partial oxidation due to the lattice oxygen without complete oxidation⁵¹⁾. Furthermore, Pt black supported on CeO₂ promoted this reaction⁵²⁾. CeO₂ and Ce_xZr_{1-x}O₂ solid solutions were used to achieve higher activity as CeO₂ supports^{53),54)}. The high activity over these supports was apparently derived from their higher oxygen storage capacities (OSC), so that the deposited carbon in this reaction could be oxidized and removed by the lattice oxygen, thereby achieving high and stable activity^{53)~55)}.

1. 2. 3. Conventional High-performance Processes

Several trials for increasing the overall energy efficiency of the methane utilization process have been reported, such as combination of the reactions described above and efficient utilization of the external heat supply.

(1) Auto-thermal Reforming and Oxy-reforming

As explained in the previous section, both dry reforming and steam reforming are endothermic reactions, but partial oxidation is an exothermic reaction. For that reason, several trials of the internal heat supply have used simultaneous endothermic and exothermic reactions, and are designated as oxy-reforming, auto-thermal reforming, and tri-reforming⁴⁸⁾. The advantage for this combination is that selection of the ratio of CO₂/H₂O/O₂ can result in suitable H₂/CO ratio in the product gas, and H₂O and O₂ supplied as reactants can remove the formed carbon in dry reforming and steam reforming^{56),57)}.

(2) Electrically Heated Catalysis

Electrically Heated Catalysis (EHC) is a process by which the catalyst temperature is increased rapidly. Utilization of monolithic catalyst with electrodes located at the edge found that the catalyst can be heated within 1.5 min by the application of electric power and the outlet temperature reached 863 K⁵⁸⁾. Application of this system for steam reforming found that the required time for increasing the temperature can be shortened to 10 min using Ni/Al₂O₃/Alloy catalyst, compared to about 30 min for the conventional system⁵⁹⁾. The application of EHC enabled fast-start up, but the problems caused by high temperature could not be solved in this system.

The systems described above are known as conventional processes for the conversion of methane. However, the stability of the methane molecule requires much energy for its activation, which still causes several problems. In exothermic reactions such as oxidative coupling and partial oxidation of methane, the high activity of oxygen promotes gas phase reaction at high temperature, and the selectivity for the target reaction is decreased because of the non-selective and sequential oxidation of products. In endothermic reactions such as dry reforming and steam reforming of methane, the thermodynamic equilibrium allows the reaction to proceed only at high temperatures. Such high temperatures require high stability of the catalyst and apparatus at high temperatures. In addition, decreased catalytic activity resulting from carbon deposition presents a severe problem.

2. Non-conventional Systems for Methane Conversion

Various non-conventional systems have been investigated to resolve the problems described above for conventional systems. In this section, we summarize the features of non-conventional systems, such as the application of microwaves, photocatalysis, non-Faradaic reactions, and plasma.

2. 1. Microwaves

Investigations of the utilization of microwaves are

classifiable into two types: heating the gaseous reactant, and heating the catalyst directly. Several advantages can be recognized such as rapid heating and selective heating. Depending on these features, microwave heating was applied to the methane decomposition^{(60),(61)}, and showed that the activity achieved by microwave utilization was higher than that in conventional systems, which implies that hotspots were generated by the microwave heating, with much higher temperatures than provided by conventional heating. Microwave heating is expected to be more efficient than conventional heating system. However, carbon deposition in the catalyst pores will result in decreases in surface area and pore volume, followed by deactivation of the catalyst⁽⁶⁰⁾. Furthermore, examination of the input electric power and frequency on the activity found effects on the product selectivity. Methane oligomerization using a microwave system in which the input electric power was changed from 130 to 370 W showed that increased input electric power increased the selectivity for acetylene or benzene, and decreased the selectivity for ethane or ethylene⁽⁶²⁾. Furthermore, increase in the applied frequency between 2.4 to 4.6 GHz provided increased selectivity for benzene. These results suggest that optimized feedstock composition can maximize the efficiency of the process. However, to achieve high activity, high temperatures must be produced by microwave heating, and the system requires large inputs of electrical power.

2. 2. Photocatalysis

Photocatalysis requires less input energy than the conventional system, as solar irradiation is sufficient. Light irradiation activates photocatalysts, and promotes the reaction at low temperatures. Several trials have used photocatalysis for methane conversion. Methanol synthesis from methane over a photocatalyst with the application of TiO₂, Pt-WO₃ (Pt doped WO₃), La-WO₃, Cu-WO₃, and (La, Cu)-WO₃ as catalysts showed that La-WO₃ exhibited the highest activity, but greater amounts of ethane and carbon dioxide were formed as byproducts. Therefore, high selectivity to methanol was difficult to achieve in the photocatalytic system⁽⁶³⁾. Investigation of non-oxidative coupling of methane over photocatalysts over amorphous and mesoporous silica as catalysts showed that the latter exhibited higher activity, and the active site for this reaction involved dissociation of the hydroxyl group⁽⁶⁴⁾. The utilization of photocatalyst has been widely investigated. Although photocatalysis can be conducted at low (ambient) temperature, the fundamental problem is that light energy is difficult to use efficiently enough to achieve high yield of products.

2. 3. Non-Faradaic Electrochemical Modification of Catalytic Activity^{(65)~(70)}

In contrast to the photocatalytic reaction promoted by visible or UV light, reaction that is directly promoted

by electricity has been investigated to promote the electrochemical reaction over catalysts. These reactions are classifiable into two groups: Faradaic and non-Faradaic reactions. The Faradaic process is a stoichiometric electrochemical reaction in which the electron supplied as a reactant is used for stoichiometric processes. The non-Faradaic process is non-stoichiometric, in which the electron is used to enhance the reaction rate to higher than that of the Faradaic reaction. The Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) system is a non-Faradaic system, in which the number of activated molecules can reach more than ten thousand times the number of the input electrons. The mechanism of the NEMCA system uses a weak current applied on the disc catalyst to directly lower the activation energy, followed by enhancement of the reaction rate. A solid electrolyte such as YSZ (Y₂O₃ stabilized ZrO₂) is used as a main component of disc catalyst, and Ag or Pt is pasted on the surface of the disc as an electrode and a catalyst. The detailed mechanism was reported as follows; oxygen anion forms as in equation (Eq. (6)) with or without the external voltage at the boundary of the surface of supported metal and gas phase. The oxygen anion diffuses in the solid electrolyte, and reaches the three-phase interface between the metal catalyst, solid electrolyte and gas phase. On the three-phase interface boundary, the excess oxygen anions accumulate near the surface of the electrolyte. Here the oxygen anion reacts as shown in the Eq. (7).



The release/storage of the oxygen requires voltage depression, *i.e.* the external voltage contributes to the release/storage of the oxygen in the NEMCA system. The formed oxygen anion cannot release its electrical charge, and remains on the catalyst surface with diffusion on the surface. The adsorbed anion on the catalyst surface lowers the surface potential of the catalyst, which results in changed work function. This work function change weakens the bonding strength of the chemisorption of adsorbed species on the catalyst surface, with resultant lower activation energy. Therefore, the activity and selectivity on the catalyst are changed by supply of excess oxygen anion. In some cases, the λ value, the enhancement ratio of the reaction rate in the NEMCA system, was 30,000 times larger than that without the application of the external voltage. The definition of λ is expressed below.

$$\lambda = \Delta r_{(\text{catalytic})} / (i/2F) \quad (8)$$

Where F , i and Δr are the Faradaic constant, input current, and the difference between the conventional formation rate and the formation rate in the NEMCA system, respectively.

In the NEMCA system, partial heating with the application of the electric field is denied. The consumption rate of ethylene into epoxy or carbon dioxide decreased with application of the reverse potential gradient, *i.e.* the diffusion of the oxygen anion in the reverse direction. High reaction rates can be achieved in the NEMCA system, but the NEMCA system requires high temperature for the generation of the ion species which carry the electrical charge. In particular, in application of this system to methane steam reforming, the catalytic activity test was conducted at temperatures higher than about 700 K. Consequently, the NEMCA system cannot solve problems associated with the high-temperature condition.

2. 4. Plasma

Systems in which supplied electrons can activate reactants directly in the gas phase to promote the reaction rate have been widely investigated. Plasma electrons have high energy for the dissociation of the gas feed molecules into radicals. Such discharge systems are classified into two types: equilibrium discharge and non-equilibrium discharge. As an example of equilibrium discharge, decomposition and partial oxidation of methane⁷¹⁾ enabled promotion of the reaction, but much energy was consumed and the gas phase temperature was so high that fundamental problems caused by high temperatures should be considered. In contrast to equilibrium discharge, the gaseous temperature in non-equilibrium discharge is lower and that of electrons is high. As examples of non-equilibrium discharge, acetylene production from methane in a DC pulse discharge^{72),73)}, and oxidative coupling of methane in a corona discharge^{74),75)} were reported. Furthermore, partial oxidation, steam reforming, and dry reforming of methane were investigated in a grid-arc discharge⁷⁶⁾.

Our group has also investigated the utilization of non-equilibrium discharge, especially methane activation by non-equilibrium pulse discharge. The results have shown that the main product was acetylene. Using CD₄ to identify the reaction mechanism, we found that the high-density electron dissociated the CD₄ molecule into CD radical or C, which then reacted to form acetylene. High acetylene selectivity was achieved by high concentrations of CH or C₂ radical and subsequent decomposition/recombination of C, CH, C₂ or C₂H₂⁷⁷⁾. Furthermore, we compared dielectric

barrier discharge (DBD), corona discharge, and spark discharge for this reaction, and showed that catalytic activity was highest with the spark discharge. The gaseous temperature was low, around 420–460 K, which was measured by the emission spectrum. This finding suggests that the heating effect by the plasma did not promote the reaction. Consequently, the mechanism seemed to involve an electron with high energy-dissociated methane molecules⁷⁸⁾. Based on these observations described above, in the non-equilibrium discharge, the supplied electron would promote methane dissociation, and promotion of the reaction can be achieved with assistance of the discharge.

Steam reforming of methane with non-equilibrium pulsed discharge can proceed at low temperatures such as 423 K⁷⁹⁾. CO was produced *via* the reaction between H₂O and CH radical which was dissociated by the plasma. Although the system presents many advantages as described above, this system also has disadvantages such as difficulty in controlling selectivity and requirement for specific devices.

3. Catalytic Methane Conversion Assisted by Electric Field

As described above, although some non-conventional systems can provide effective conversion, these processes require high temperatures or involve low energy efficiency. The energy consumption for some of the above-described non-conventional systems is presented in **Table 1**.

We have proposed “catalytic reaction assisted by an electric field” as a novel method of methane utilization with higher energy efficiency. The schematic flow of the reaction system is shown in **Fig. 2**. We investigated steam reforming of methane (*Electreforming*) and oxidative coupling of methane (*E-OCM*) assisted by an electric field as representative reactions.

3. 1. Electreforming

Steam reforming of methane is an endothermic reaction that requires temperatures higher than 973 K because of the thermodynamic equilibrium and the rate-limiting kinetics. However, various problems occur under such high temperatures as described above. To solve these problems, we have tried to lower the reaction temperature with the assistance of an applied elec-

Table 1 Energy Demand for Non-conventional Reaction Systems

Reaction	Application	Main product	External temperature [K]	Energy demand	Reference
Decomposition	Microwave	H ₂	R.T.	83.7 MJ mol ⁻¹ -H ₂	61)
Steam reforming	NEMCA	CO, H ₂	698	39.1 J mol ⁻¹ -H ₂	70)
Oxidative coupling	Plasma	C ₂ H ₂	R.T.	8.21 MJ mol ⁻¹ -C ₂	74)
Steam reforming	Electric field	H ₂	423	256 kJ mol ⁻¹ -H ₂	82)
Oxidative coupling	Electric field	C ₂ H ₆ /C ₂ H ₄	423	7.43 MJ mol ⁻¹ -C ₂	83)

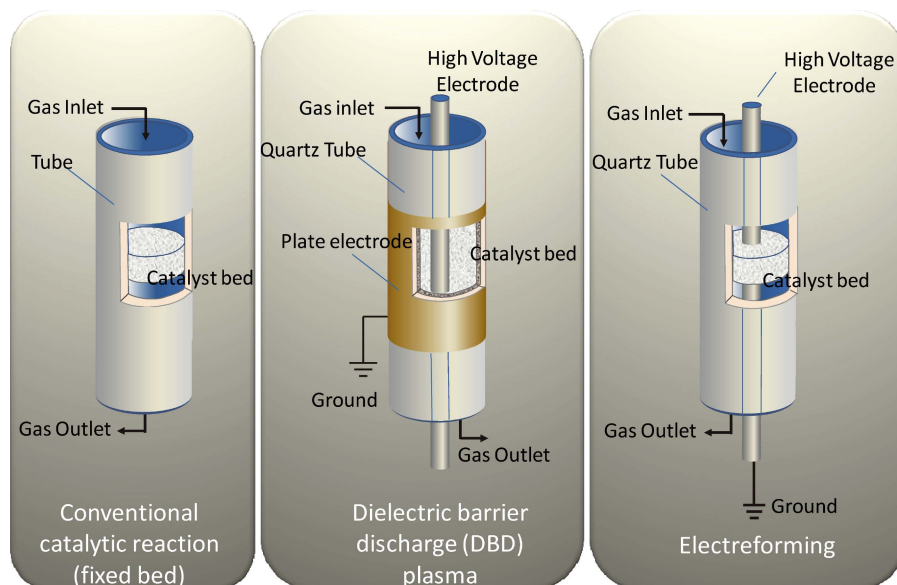


Fig. 2 Diagrams of Reactors for Conventional and Non-conventional Catalytic Systems

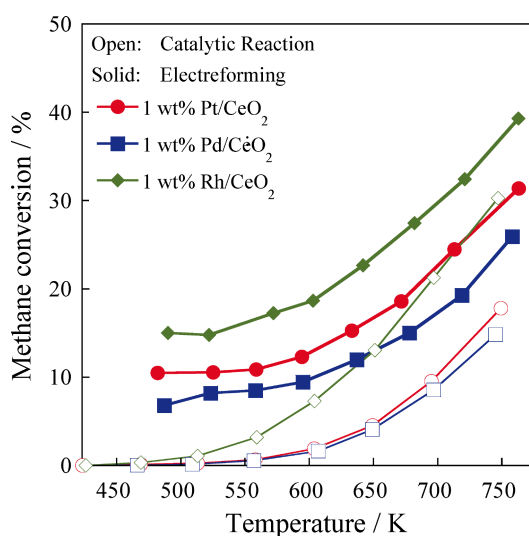


Fig. 3 Catalytic Activities for *Electreforming* over Various Catalysts Supported on CeO_2

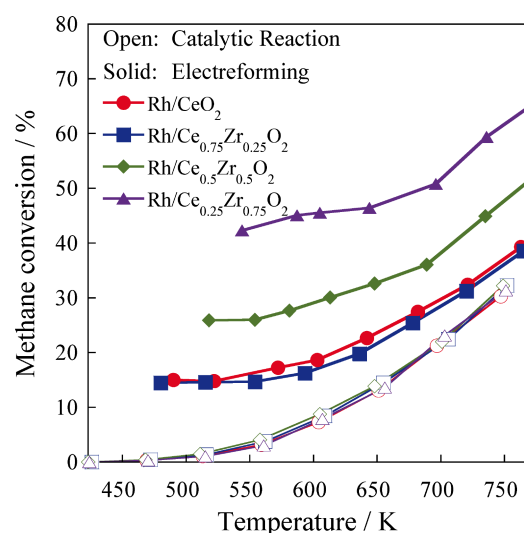


Fig. 4 Catalytic Activities for *Electreforming* over Rh Catalysts on Various $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ Catalyst-supports

tric field^{80)~82)}. We conducted *Electreforming* over noble metal catalysts such as Pt, Pd or Rh, supported on CeO_2 or $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$, which have lattice oxygen mobility. Catalytic activities over these catalysts with or without an electric field are shown in **Fig. 3**. The catalytic activity for *Electreforming* was much higher than that for the conventional reaction over each catalyst, especially at temperatures below 573 K. Screening tests revealed that the catalyst for *Electreforming* requires suitable electrical conductivity and lattice oxygen mobility. The activity for *Electreforming* over the Rh catalyst supported on $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$, which has higher lattice oxygen mobility, is shown in **Fig. 4** and **Table 2**.

The highest conversion (42 %) for *Electreforming* at low temperature was achieved over $\text{Rh/Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ catalyst. The equilibrium conversion at 542 K is *ca.* 4 %, so the activity for *Electreforming* was much higher than this theoretical value. In a conventional system, high temperatures such as 780 K are necessary to achieve the same conversion of 42 %. Consequently, the *Electreforming* method of application of an electric field can lower the temperature required for a reaction occurring at about 250 K because of the interaction between electrons, supported metal and catalyst support.

3. 2. E-OCM

We also investigated the oxidative coupling of methane

Table 2 Catalytic Activity for *Electroreforming* on Rh/Ce_{0.25}Zr_{0.75}O₂ Catalyst

Electric field	$T_{\text{thermocouple}}$ [K]	Conversion [%]	C balance [%]	Formation rate [$\mu\text{mol min}^{-1}$]			$\Sigma\Delta H_f$ [J min ⁻¹]	$\Sigma\Delta H_p$ [J min ⁻¹]	ΔE_i [J min ⁻¹]	ΔE_{ef} [J min ⁻¹]	E_{cons} [J min ⁻¹]	EPR [%]
				H ₂	CO ₂	CO						
off	424	0.0	99.7	0.0	0.0	0.0	0.0	0.0	0.0			
	470	0.3	99.6	4.5	1.5	0.0	1.3	1.3	0.0			
	515	1.1	98.8	20.3	5.4	0.0	4.8	5.8	1.0			
	561	3.0	98.4	60.2	15.0	0.0	13.3	17.2	3.9			
	607	7.9	98.7	159.6	39.2	0.2	35.1	45.7	10.6			
	656	13.6	99.5	271.6	66.6	1.4	60.5	78.0	17.5			
	703	23.1	99.6	446.5	109.7	5.7	102.8	129.2	26.4			
	751	31.3	99.3	601.4	138.1	18.4	139.4	177.1	37.7			
on	544	42.3	99.0	756.9	140.4	71.0	188.3	236.4	48.1	48.1	207.8	23.2
	587	45.1	98.5	812.6	151.6	73.6	200.6	253.1	52.5	52.6	180.6	29.1
	605	45.6	98.8	786.0	150.7	76.9	202.7	246.4	43.7	42.7	180.6	23.7
	644	46.4	99.9	848.8	163.8	68.2	206.6	261.9	55.3	51.4	195.9	26.3
	696	50.8	99.6	899.0	165.8	88.0	226.0	281.8	55.9	45.3	200.9	22.5
	736	59.4	97.0	1053.3	187.0	109.8	264.3	332.1	67.8	50.3	165.9	30.3
	774	65.6	99.2	1144.8	193.6	134.4	292.0	365.3	73.2	46.8	216.1	21.6
	812	70.1	100.7	1206.7	194.9	155.1	311.7	388.8	77.1	39.4	191.3	20.6

Table 3 Catalytic Activity for E-OCM on Various Sr–La₂O₃ Catalysts

Catalyst	Reaction	IEPD [W mm ⁻¹]	Ex. temp. [K]	CH ₄ conv. [%]	C ₂ ⁺ sel. [%]	C ₂ H ₂ sel. [%]	CO _x sel. [%]	C ₂ H ₄ /C ₂ H ₆ [-]
(1/20-Sr)–La ₂ O ₃	conventional	-	1273	7.4	45.6	0.0	54.3	0.65
	with electric field	0.33	423	8.9	49.0	0.0	50.6	0.46
(1/200-Sr)–La ₂ O ₃	with electric field	0.33	423	11.5	34.2	0.0	65.0	0.44
(1/2000-Sr)–La ₂ O ₃	plasma	1.19	423	6.7	12.0	8.8	79.1	0.48
La ₂ O ₃	plasma	1.04	423	6.4	16.1	5.8	78.2	0.46

with the assistance of an electric field (E-OCM)^{83)~85)}. The problem of the conventional OCM reaction is that non-selective and sequential oxidation in the gas phase reduces the selectivity for C₂. We tried to lower the reaction temperature with the electric field and to enhance the selectivity to C₂ by suppressing sequential oxidation. La₂O₃-based catalyst was used, which has stability and high activity for OCM. La₂O₃ is an insulator, so applying the electric field to the La₂O₃ was impossible and plasma was generated. We found that application of the electric field required suitable electrical conductivity. Therefore, we doped another cation such as SrO into La₂O₃ to increase the number of electrical conduction carriers.

The catalytic activity for E-OCM over Sr–La₂O₃ catalysts with various Sr contents is presented in **Table 3**. Spark discharge was generated over the La₂O₃ catalyst because La₂O₃ had few electrical carriers and low electrical conductivity. OCM with plasma (including spark discharge) has been widely investigated, and the mechanism has already been reported. Plasma electrons have high temperature, and can dissociate C–H bonds in methane molecules into CH radical or C. These CH radicals or C would then couple to yield C₂ compounds. Therefore, the main component of the product would be acetylene in the reaction assisted by the discharge.

We prepared Sr-doped La₂O₃ to enhance the electrical conductivity of the catalyst and to apply the electric field. The electric field was not applicable to Sr–La₂O₃ (Sr/La = 1/2000) catalyst and spark discharge was generated. However, the electric field could be applied to Sr–La₂O₃ (Sr/La = 1/200) and Sr–La₂O₃ (Sr/La = 1/20) catalysts. As shown in **Table 3**, acetylene was not detected as a product over these two catalysts, and the catalytic OCM reaction proceeded. **Table 3** also shows the comparison of the activity for E-OCM with that for the conventional OCM reaction at high temperatures over Sr–La₂O₃ (Sr/La = 1/20) catalyst, which exhibited the highest C₂ selectivity. The selectivity for C₂ was higher for the E-OCM than for the conventional OCM reaction. This observation implied that the applied electric field can suppress sequential oxidation. Based on these results, application of the electric field can lower the reaction temperature and thereby suppress sequential oxidation. Therefore, high C₂ selectivity can be achieved over the Sr–La₂O₃ catalyst. However, increased gaseous temperature caused by heat generation in the exothermic reaction was difficult to control.

The doping amount of Sr into La₂O₃ was the key parameter for successful application of the electric field in E-OCM. To elucidate the role of the doped Sr, we measured the electrical conductivity of the catalysts with the alternative current (AC) impedance method to

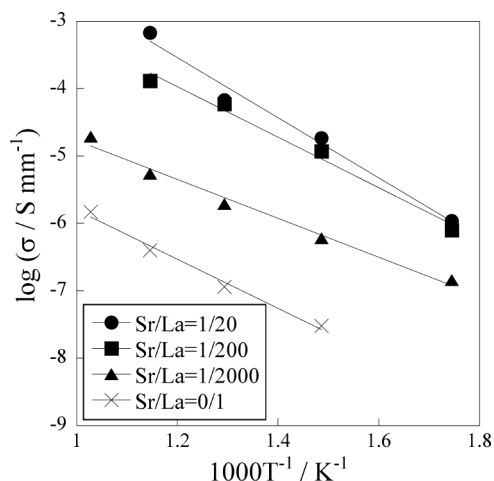
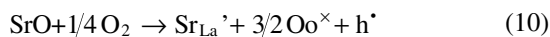


Fig. 5 Electrical Conductivities of Various Sr–La₂O₃ Catalysts Measured by the AC Impedance Method

identify the electrical conduction carrier. The results are shown in **Fig. 5**. Increased amounts of doped Sr into La₂O₃ enhanced the electrical conductivity of the catalyst, which implies that the electrical conductivity of the catalyst is an important factor for E-OCM. The mechanism for the increase in the number of the electrical conduction carriers is given by the following Kröger-Vink equations.



Based on the results described above, doping another cation into an insulator catalyst enables the formation of oxygen-ion vacancies or electron holes, which enhances the electrical conductivity sufficiently to apply the electric field to the catalyst.

These findings demonstrated the possibility of using an electrical system to achieve high activities at low temperatures for steam reforming and the oxidative coupling of methane. We compared these two reactions and evaluated the effect of the applied electric field on the methane. To elucidate factors promoting catalytic activity in the electric field, the relationship between the input electrical power density (IEPD: W mm⁻¹) and the consumption rate of methane (mmol min⁻¹ g⁻¹) is shown in **Fig. 6**. For *Electroreforming* over CeO₂ catalyst-support, increased *W/F* resulted in increases in the IEPD and the methane consumption rate. The consumption rate over Ce_xZr_{1-x}O₂ catalyst-support was higher than that over CeO₂ catalyst-support at the same IEPD. Ce_xZr_{1-x}O₂ has higher electrical conduction and oxygen mobility than CeO₂. Therefore, for Ce_xZr_{1-x}O₂, the lower energy demand for electric field formation resulted in higher energy efficiency. Furthermore, the slope for the E-OCM reaction was higher than that for *Electroreforming*, as shown in **Fig. 6**, possibly because, in addition to the reaction

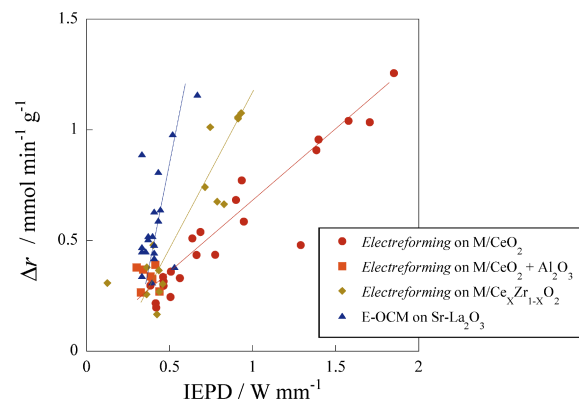


Fig. 6 Effect of IEPD on Methane Consumption Rate for Various Catalysts or Reactions

on the catalyst, non-selective oxidation in the gas phase also proceeded. Sr–La₂O₃ catalysts had lower volume density and lower electrical conductivity than CeO₂ catalyst-support, so higher voltage (*ca.* 900 V) was necessary for application of the electric field to the Sr–La₂O₃ catalyst than to the CeO₂ catalyst-support (*ca.* 300 V). Based on these factors, we found that the relationship between the IEPD and the consumption rate of methane depended on the type of reaction and the characteristics of the catalyst support.

4. Conclusion

In this review, we summarized the current issues for the conventional catalytic system, and the potential of developing a non-conventional catalytic system using plasma or an electric field (*Electroreforming* and E-OCM). Using the novel catalytic system, the reaction rate was enhanced drastically by the electric field, which enabled the reaction to proceed at low temperatures with high activity/selectivity. This high activity at lower temperature suggests that the system will be useful in some small-scale processes without a heat exchanger. Additional investigations must be conducted to reveal the detailed mechanisms related to the novel reaction. Understanding the total mechanism and factors for the achievement of high catalytic activity in the electric field will enable us to use more efficient catalytic systems. Although we have investigated the application of an electric field only for the steam reforming and oxidative coupling of methane, applications of this system to other reactions might be promising.

References

- 1) DeBoy, J. M., Hicks, R. F., *Ind. Eng. Chem. Res.*, **27**, 1577 (1988).
- 2) DeBoy, J. M., Hicks, R. F., *J. Catal.*, **113**, 517 (1988).
- 3) Shi, C., Hatano, M., Lunsford, J. H., *Catal. Today*, **13**, 191 (1992).

- 4) Wang, D., Rosynek, M. P., Lunsford, J. H., *J. Catal.*, **155**, 390 (1995).
- 5) Lunsford, J. H., *Angew. Chem., Int. Ed.*, **34**, 970 (1995).
- 6) Choudhary, V. R., Rane, V. H., *J. Catal.*, **130**, 411 (1991).
- 7) Rane, V. H., Chaudhari, S. T., Choudhary, V. R., *J. Chem. Technol. Biotechnol.*, **81**, 208 (2006).
- 8) Rane, V. H., Chaudhari, S. T., Choudhary, V. R., *J. Nat. Gas Chem.*, **17**, 313 (2008).
- 9) Takanabe, K., Iglesia, E., *Angew. Chem., Int. Ed.*, **47**, 7689 (2008).
- 10) Sekine, Y., Tanaka, K., Matsukata, M., Kikuchi, E., *Energy & Fuels*, **23**, 613 (2009).
- 11) Tanaka, K., Sekine, Y., Inoue, J., Araki, H., Matsukata, M., Kikuchi, E., *J. Jpn. Petrol. Inst.*, **55**, (1), 71 (2012).
- 12) Zavyalova, U., Holena, M., Schlogl, R., Baerns, M., *ChemCatChem*, **3**, 1935 (2011).
- 13) Bron, M. J., Parkyns, N. D., *Catal. Today*, **8**, 305 (1991).
- 14) Hargreaves, J. S. J., Hutchings, G. J., Joyner, R. W., *Nature*, **348**, 428 (1990).
- 15) Shepelev, S. S., Ione, K. G., *React. Kinet. Catal. Lett.*, **23**, 319 (1983).
- 16) Anderson, J. R., Tsai, P., *Appl. Catal.*, **19**, 141 (1985).
- 17) Claridge, J. B., Green, M. L., Tsang, S. C., York, A. P. E., *Appl. Catal. A: General*, **89**, 103 (1992).
- 18) Wang, L., Tao, L., Xie, M., Xu, G., *Catal. Lett.*, **21**, 35 (1993).
- 19) Solymosi, F., Cserenyi, J., Szoke, A., Bansagi, T., Oszko, A., *J. Catal.*, **165**, 150 (1997).
- 20) Wang, D., Lunsford, J. H., Rosynek, M. P., *J. Catal.*, **169**, 347 (1997).
- 21) Ma, D., Shu, Y., Zhang, W., Han, Z., Xu, Y., Bao, X., *Angew. Chem., Int. Ed.*, **39**, 2928 (2000).
- 22) Muradov, N. Z., *Int. J. Hydrogen Energy*, **18**, 211 (1993).
- 23) Choudhary, T. V., Sivadinarayana, C., Chusuei, C. C., Klinghoffer, A., Goodman, D. W., *J. Catal.*, **199**, 9 (2001).
- 24) Muradov, N., *Catal. Commun.*, **2**, 89 (2001).
- 25) Dufour, A., Celzard, A., Fierro, V., Martin, E., Broust, F., Zoulalian, A., *Appl. Catal. A: General*, **346**, 164 (2008).
- 26) Moliner, R., Suelves, I., Lazaro, M. J., Moreno, O., *Int. J. Hydrogen Energy*, **30**, 293 (2005).
- 27) Serrano, D. P., Botas, J. A., Fierro, J. L. G., Guil-López, R., Pizarro, P., Gomez, G., *Fuel*, **89**, 1241 (2010).
- 28) Otsuka, K., Mito, A., Takenaka, S., Yamanaka, I., *Int. J. Hydrogen Energy*, **26**, 191 (2001).
- 29) Rostrup-Nielsen, J. R., *J. Catal.*, **31**, 173 (1973).
- 30) Rostrup-Nielsen, J. R., *J. Catal.*, **85**, 31 (1984).
- 31) Bernardo, S. A., Alstrup, I., Rostrup-Nielsen, J. R., *J. Catal.*, **96**, 517 (1985).
- 32) Wei, J., Iglesia, E., *J. Phys. Chem. B*, **108**, 4094 (2004).
- 33) Urasaki, K., Sekine, Y., Kawabe, S., Kikuchi, E., Matsukata, M., *Appl. Catal. A: General*, **286**, 23 (2005).
- 34) Trovarelli, A., *Catal. Rev.: Sci. Eng.*, **38**, 4, 439 (1996).
- 35) Bevan, D. J. M., Kordis, J., *J. Inorg. Nucl. Chem.*, **26**, 1509 (1964).
- 36) Fornasiero, P., Balducci, G., Di Monte, R., Kaspar, J., Sergo, V., Gubitosa, G., Ferrero, A., Graziani, M., *J. Catal.*, **164**, 173 (1996).
- 37) Kaspar, J., Fornasiero, P., Graziani, M., *Catal. Today*, **50**, 285 (1999).
- 38) Laosiripojana, N., Assabumrungrat, S., *Appl. Catal. A: General*, **290**, 200 (2005).
- 39) Rostrup-Nielsen, J. R., Hansen, J.-H. B., *J. Catal.*, **144**, 38 (1993).
- 40) Mark, M. F., Maier, W. F., *J. Catal.*, **164**, 122 (1996).
- 41) Ferreira-Aparicio, P., Guerrero-Ruiz, A., Rodriguez-Ramos, I., *Appl. Catal. A: General*, **170**, 177 (1998).
- 42) Yamazaki, O., Nozaki, T., Omata, K., Fujimoto, K., *Chem. Lett.*, **21**, 1953 (1992).
- 43) Zhang, Z. L., Verykios, X. E., *Catal. Today*, **21**, 589 (1994).
- 44) Tomishige, K., Chen, Y., Fujimoto, K., *J. Catal.*, **181**, 91 (1999).
- 45) Matsuo, Y., Yoshinaga, Y., Sekine, Y., Tomishige, K., Fujimoto, K., *Catal. Today*, **63**, 439 (2000).
- 46) Montoya, J. A., Pascual, E. R., Gimón, C., Angel, P. D., Monzon, A., *Catal. Today*, **63**, 71 (2000).
- 47) Dissankayake, D., Rosynek, M. P., Kharas, K. C. C., Lunsford, J. H., *J. Catal.*, **132**, 117 (1991).
- 48) Ashcroft, A. T., Cheetham, A. K., Green, M. L. H., Vernon, P. D. F., *Nature*, **352**, 225 (1991).
- 49) O'Connor, A. M., Ross, J. R. H., *Catal. Today*, **46**, 203 (1998).
- 50) Hegarty, M. E. S., O'Connor, A. M., Ross, J. R. H., *Catal. Today*, **42**, 225 (1998).
- 51) Otsuka, K., Ushiyama, T., Yamanaka, I., *Chem. Lett.*, **9**, 1517 (1993).
- 52) Otsuka, K., Wang, Y., Sunada, E., Yamanaka, I., *J. Catal.*, **175**, 152 (1998).
- 53) Mattos, L. V., de Oliveira, E. R., Resende, P. D., Noronha, F. B., Passos, F. B., *Catal. Today*, **77**, 245 (2002).
- 54) Pantu, P., Gavals, G. R., *Appl. Catal. A: General*, **223**, 253 (2002).
- 55) Passos, F. B., de Oliveira, E. R., Mattos, L. V., Noronha, F. B., *Catal. Today*, **101**, 23 (2005).
- 56) Bharadwaj, S. S., Schmidt, L. D., *Fuel Proc. Tech.*, **42**, 109 (1995).
- 57) Cheekatamarla, P. K., Finnerty, C. M., *J. Power Sources*, **160**, 490 (2006).
- 58) Jung, H., Yoon, W. L., Lee, H., Park, J. S., Shin, J. S., La, H., Lee, J. D., *J. Power Sources*, **124**, 76 (2003).
- 59) Zhang, Q., Guo, Y., Zhou, L., Sakurai, M., Kameyama, H., *J. Chem. Eng. Jpn.*, **40**, 487 (2007).
- 60) Dominguez, A., Fidalgo, B., Fernandes, Y., Pis, J. J., Menendez, J. A., *Int. J. Hydrogen Energy*, **32**, 4792 (2007).
- 61) Cooney, D. O., Xi, Z., *Fuel Sci. Tech. Int.*, **14**, 1111 (1996).
- 62) Conde, L. D., Marun, C., Suib, S. L., Fathi, Z., *J. Catal.*, **204**, 324 (2001).
- 63) Taylor, C. E., *Catal. Today*, **84**, 9 (2003).
- 64) Yuliatli, L., Tsubota, M., Satsuma, A., Itoh, H., Yoshida, H., *J. Catal.*, **238**, 214 (2006).
- 65) Stoukides, M., Vayenas, C. G., *J. Catal.*, **70**, 137 (1981).
- 66) Stoukides, M., Vayenas, C. G., *J. Electrochem. Soc.*, **131**, 839 (1984).
- 67) Vayenas, C. G., Bebelis, S., Neophytides, S., *J. Phys. Chem.*, **92**, 5083 (1988).
- 68) Ladas, S., Kennou, S., Bebelis, S., Vayenas, C. G., *J. Phys. Chem.*, **97**, 8845 (1993).
- 69) Bebelis, S., Vayenas, C. G., *J. Catal.*, **118**, 125 (1989).
- 70) Yentekakis, I. V., Jiang, Y., Neophytides, S., Bebelis, S., Vayenas, C. G., *Ionics*, **1**, 491 (1995).
- 71) Bromberg, L., Cohn, D. R., Rabinovich, A., *Energy & Fuels*, **12**, 11 (1998).
- 72) Kado, S., Sekine, Y., Fujimoto, K., *Chem. Commun.*, **24**, 2485 (1999).
- 73) Kado, S., Urasaki, K., Sekine, Y., Fujimoto, K., *Fuel*, **82**, 1377 (2003).
- 74) Marafee, A., Liu, C., Xu, G., Mallinson, R., Lobban, L., *Ind. Eng. Chem. Res.*, **36**, 632 (1997).
- 75) Liu, C., Marafee, A., Mallinson, R., Lobban, L., *Appl. Catal. A: General*, **164**, 721 (1997).
- 76) Czernichowski, A., *Oil Gas Sci. Tech.*, **56**, 181 (2001).
- 77) Kado, S., Urasaki, K., Sekine, Y., Fujimoto, K., Nozaki, T., Okazaki, K., *Fuel*, **82**, 2291 (2003).
- 78) Kado, S., Sekine, Y., Nozaki, T., Okazaki, K., *Catal. Today*, **89**, 47 (2004).
- 79) Sekine, Y., Urasaki, K., Kado, S., Matsukata, M., Kikuchi, E., *Energy & Fuels*, **18**, 455 (2004).

- 80) Sekine, Y., Tomioka, M., Matsukata, M., Kikuchi, E., *Catal. Today*, **146**, 183 (2009).
- 81) Sekine, Y., Haraguchi, M., Tomioka, M., Matsukata, M., Kikuchi, E., *J. Phys. Chem. A*, **114**, (11), 3824 (2010).
- 82) Sekine, Y., Haraguchi, M., Matsukata, M., Kikuchi, E., *Catal. Today*, **171**, 116 (2011).
- 83) Tanaka, K., Sekine, Y., Oshima, K., Tanaka, Y., Matsukata, M., Kikuchi, E., *Chem. Lett.*, **41**, 351 (2012).
- 84) Oshima, K., Tanaka, K., Yabe, T., Tanaka, Y., Sekine, Y., *Int. J. Plasma Eng. Sci. Technol.*, submitted.
- 85) Oshima, K., Tanaka, K., Yabe, T., Kikuchi, E., Sekine, Y., *Fuel*, submitted.

.....

要 旨

プラズマあるいは電場によってアシストされたメタン転換

大島 一真, 品川 竜也, 関根 泰

早稲田大学先進理工学部応用化学科, 169-8555 東京都新宿区大久保3-4-1

メタンからエチレン, メタノール, ベンゼン, 炭素, 水素および合成ガスへの転換について数多くの研究が行われてきた。これら反応はメタン中の安定な C-H 結合により高温を必要とし, 逐次反応による目的生成物選択率の低下や, 多段の熱交換

や高温に耐えうる材料などが要求されるなど多くの問題がある。これを解決すべく, これまでにプラズマや NEMCA など, 低温でメタンを活性化させる試みが行われてきた。これらを総括し, 併せて我々の取組みを紹介する。

.....