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Oxidative coupling of methane with microwave and RF plasma catalytic reaction over transitional metals loaded on ZSM-5

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Abstract

In the microwave and radio frequency (RF) plasma catalytic reaction at room temperature, the oxidative coupling of methane (OCM) over transitional metals loaded on ZSM-5 has been carried out. The transitional metals, Fe, Ni, Co and Cu (1B family element), loaded on ZSM-5 have been tested for the OCM using the plasma catalytic reaction. In this work, the conversion of methane to C2 products has been improved without the carbon deposition when the oxygen as a co-reactant gas was supplied. The order of the catalysts of higher conversion to C2 products in the microwave plasma reaction with plasma power of 120 W is Co–ZSM-5 > Fe–ZSM-5 ≒ Cu–ZSM-5 > Ni–ZSM-5. Selectivity to ethylene is as high as 29.8%, to ethane 10% and to acetylene 49.9% and conversion of methane was as high as about 54.9% with pressure of 5–10 Torr, total flow rate of 125 ml/min and a methane/oxygen ratio of 4:1 over Co–ZSM-5. It is suggested that the catalyst may provide an active site for combination of radicals. It was found that yield of C2 products has been enhanced in the microwave plasma catalytic reaction, as microwave plasma system of high frequency has better energy efficiency than RF plasma system of low frequency.

Keywords: Microwave plasma; RF plasma; Oxidative coupling of methane; Ion-exchanged ZSM-5; Oxygen anion; Carbon black; C2 product

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1. Introduction

Natural gas, whose main component is methane, has been imported in South Korea since 1980s when the world suffered from the oil shock two times. But now the natural gas is not only the clean alternative to the oil but feedstock transformed into more valuable resources. Recently various research efforts have been made to convert methane, which is the main component of natural gas, into high valued hydrocarbon products [1,2].

Natural gas is the third ranked resource, following coal and oil and 8.9 × 10^9 TOE of it has been confirmed to be buried all over the world. Therefore, it is not likely that natural gas will be depleted before oil. In addition, it is distributed relatively uniformly so that the scientists are interested in the remote gas technology.

Natural gas is usually liquefied for transportation. The currently used conversion processes includes the indirect processes that produce synthetic gas ($CO + H_2$) from the natural gas through its partial oxidation or steam reforming or autothermal reforming, which are utilized in manufacturing methanol, formaldehyde, low-qualified olefin and gasoline.

But these processes cause the reduced efficiency due to the high cost of energy and device. Therefore the attention is being concentrated on the direct process, which makes direct conversion of the natural gas into

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the high-qualified hydrocarbons without producing the synthetic gas [3,4].

To our knowledge, methane is directly converted into methanol or formaldehyde through partial oxidation, chloromethane through super acid or C2 hydrocarbons through coupling reaction used by oxidants.

Oxidative coupling of methane (OCM) has taken higher position on the natural gas and petrochemical industry since the oil shock because the process can directly convert methane into the valuable chemical resources such as ethane, ethylene and acetylene. However, partial activation of methane is a tricky process in that C–H bond of methane is not easily dissociated unless high temperature is applied. Therefore the desirable method is catalytic conversion of methane. Recently, many researchers have investigated technology to convert natural gas into more valuable chemical materials [5–8]. Most of previous methane activation researches are the OCM reaction with metal catalysts. The heterogeneous catalytic OCM has been the major subject of a large body of research activities. But these reactions have some problems—low conversion, low selectivity to ethylene, and high-energy cost.

To solve these problems, plasma technology has been used to convert methane recently. Several research results have presented the microwave energy for catalytic conversion of methane, i.e. using microwave and radio frequency (RF)-induced catalysis for conversion of methane to aromatic hydrocarbons, by microwave plasma catalytic reaction for higher hydrocarbons, or by oxidative/non-OCM over oxide catalysts in the ac and dc corona discharge. Recently, Lui et al. [9] have described the effects of different zeolite catalyst, the concentration of OH groups and co-oxidant (oxygen, carbon dioxide, steam and nitrogen), applied dc corona discharge and diluents gases on the conversion of methane to higher hydrocarbons.

Reactants can be converted to ethylene, ethane, acetylene, hydrogen, carbon monoxide, etc. Selectivity and conversion are depending on the power of the plasma, flow rate, methane/oxygen ratio, nature of a catalyst, incident power and pressure in the system.

In this work, we investigated that C2+ products and useful chemicals can be obtained in a microwave and RF high frequency plasma catalytic reaction of OCM over ion-exchanged ZSM-5 catalysts. Also we found the functions of oxygen in the plasma and catalytic reaction.

2. Experimental

Microwave and RF discharge is a cold (or non-equilibrium) plasma phenomenon. Both reaction systems are composed of three sections as shown in Figs. 1 and 2, respectively: reactant feed section, plasma reaction section and catalytic section.

2.1. Preparation of plasma system

In this study, we use the microwave and RF generator as a plasma source. And two types of reactors are used to activate methane. One is common single plasma reactor and the other is new plasma catalytic reactor. To evaluate the selectivity of C2 products and methane activation, transition metal-loaded ZSM-5 and Cu-loaded ZSM-5 catalyst are developed.

A variable power (maximum 250 W), low power generator, 2.45 GHz magnetron and Model ASTeX S-250 are used as a power source for the microwave discharge. This microwave power generator is generally used in plasma production applications such as homogeneous and heterogeneous chemical reaction, ion sources for ion implantation, ion-assisted deposition and plasma etching. The S-250 control unit is connected to a compact switching power supply and control electronics which operates an internal magnetron. The 1 in. quartz tube reactor constructed in the cavity is connected to coaxial cable configured to the direction of the microwave plasma.

RF plasma system is composed of the RF power supply, Model OEM-12A manufactured by ENI, operating at a frequency of 13.56 MHz and a variable power of 1200 W. The reactions are carried out in the quartz tube reactor (OD 1 in.) and the inductive coupling type, a Cu-coil connected to power supply through a matching unit is wound around a tubular reactor.

2.2. Preparation of catalyst and experimental progress

Transition metal and Cu-loaded ZSM-5 catalysts are prepared by ion-exchange method on H-form ZSM-5 (Si/Al = 30) of PQ. We use the transition metal (Fe, Co and Ni) and Cu metal, and the precursor of transition metal is of acetate form (Aldrich).

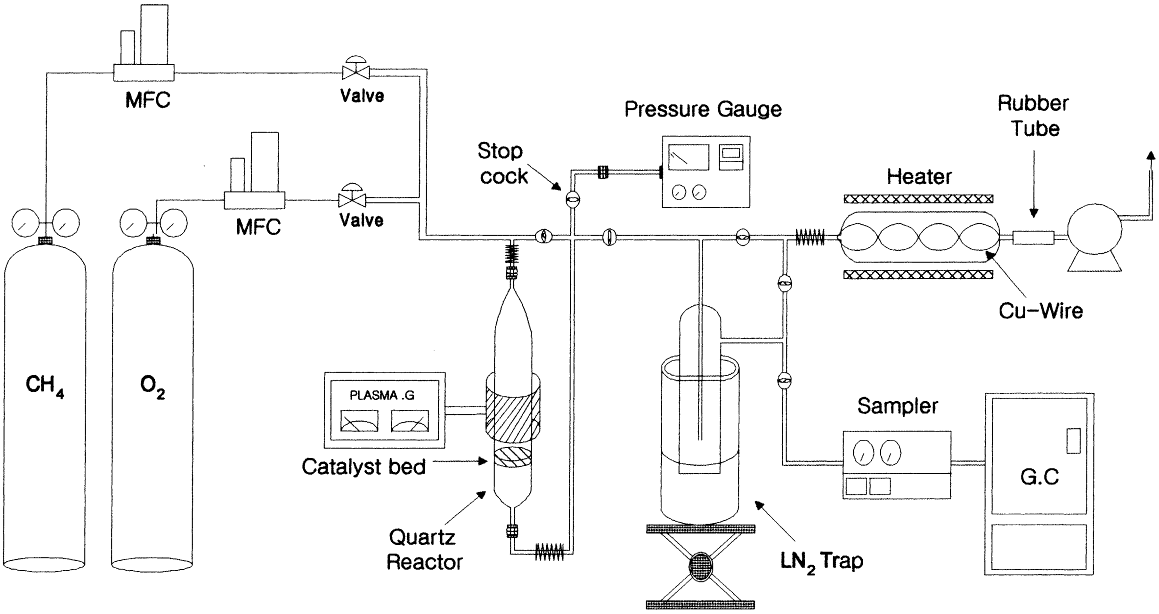


Fig. 1. Schematic diagram of the microwave plasma and catalytic reaction system with addition of oxygen.

All the catalysts, 0.02 M metal aqueous solution, are ion-exchanged on H–ZSM-5 by agitate in the reflux reaction at 90 °C for 12 h. Ion-exchanged ZSM-5 is washed by distilled water and then dried in a dry oven at 100 °C, and calcined at 450 °C for 12 h.

Combining the plasma and the conventional catalytic reaction perform the oxidation coupling of methane in this work.

The microwave discharge reactor is shown in Fig. 1. The plasma and catalytic reactor configuration was

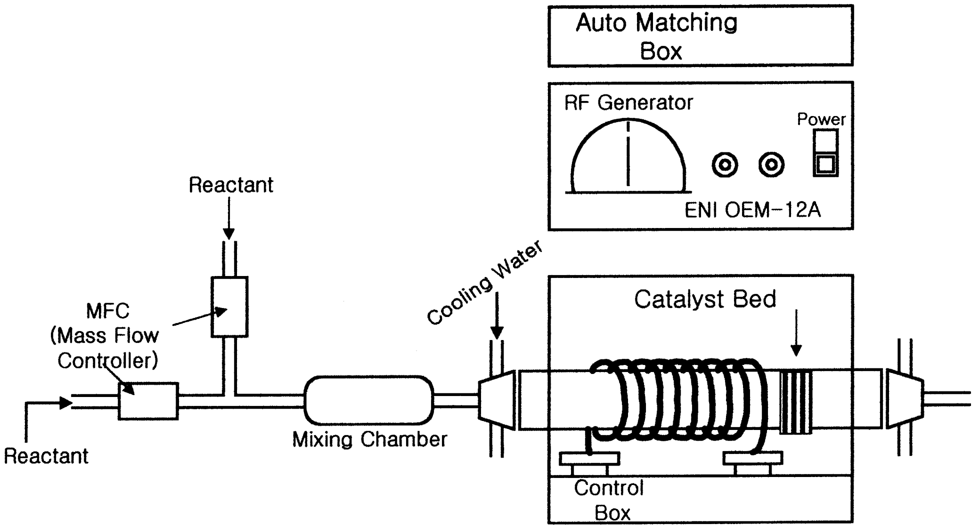


Fig. 2. Schematic diagram of the RF plasma and catalytic reaction system with addition of oxygen.

previously described [10]. The gas discharges occurs in a cavity of microwave and then reacts on catalyst at the reactor heated by a cylindrical furnace of 300 °C. The catalyst bed is placed on middle of catalytic reactor and prepared in powder form of 1.0 g. Fig. 2 shows the schematic diagram of the RF discharge reactor. All experiments are carried out on the pressure of 5–10 Torr in vacuum state. The forward and reflected power of plasma generator is monitored during the experiment to ensure the safety and protection of plasma system. Before plasma and catalytic reaction, the system is evacuated less than 10 mTorr for 2 h using a diffusion and a rotary vacuum pump, and the catalyst bed temperature is maintained at desired temperature. The flow rates of feed gases methane (99.99% pure, Metheson) and oxygen (99.9% pure, Hankook Industry Gas) are controlled by mass flow controllers (Brooks). Methane and oxygen are mixed to maintain a total flow of 125 ml/min and then let into the plasma and catalytic reactor.

The products including ethylene, ethane, acetylene, carbon monoxide, carbon dioxide and trace formaldehyde and/or methanol are analyzed by on-line gas chromatography (HP 6890, Hewlett Packard). Products are separated using Porapak N or Q columns and the detector is a thermal conductivity detector.

In case of this system, the methane and oxygen conversions are calculated as follows:

$$\mathrm{CH_4\ conversion} = \frac{\text{mole of } \mathrm{CH_4} \text{ consumed}}{\text{mole of } \mathrm{CH_4} \text{ introduced}} \times 100\%$$

$$\mathrm{O_2\ conversion} = \frac{\text{mole of } \mathrm{O_2} \text{ consumed}}{\text{mole of } \mathrm{O_2} \text{ introduced}} \times 100\%$$

The selectivities and yields of C2 hydrocarbons are

$$\text{Selectivity of } \mathrm{C_2H_6} = 2 \times \frac{\text{mole of } \mathrm{C_2H_6} \text{ produced}}{\text{mole of } \mathrm{CH_4} \text{ consumed}} \times 100\%$$

$$\text{Selectivity of } \mathrm{C_2H_4} = 2 \times \frac{\text{mole of } \mathrm{C_2H_4} \text{ produced}}{\text{mole of } \mathrm{CH_4} \text{ consumed}} \times 100\%$$

$$\text{Selectivity of } \mathrm{C_2H_2} = 2 \times \frac{\text{mole of } \mathrm{C_2H_2} \text{ produced}}{\text{mole of } \mathrm{CH_4} \text{ consumed}} \times 100\%$$

$$\text{Yield of C2 hydrocarbons} = \mathrm{CH_4} \text{ conversion} \times \sum (\text{selectivities of } \mathrm{C_2H_2}, \mathrm{C_2H_4}, \mathrm{C_2H_6})$$

3. Results and discussion

3.1. Microwave experiments

3.1.1. OCM by plasma and catalyst

To investigate the comparison of productivity, both the non-oxidative and OCM in plasma system without the catalysts are carried out. Fig. 3 illustrates the comparison of conversions (a) and selectivities (b) on the non-oxidative and OCM. The conversion of methane increases as the power rises and it is obvious that the oxygen introduced into the plasma reaction gives much higher methane conversion of above 30% and maximum conversion of 37% compared with only methane feed converted more less 30%. In terms of C2 selectivity, non-oxidative methane conversion is prior to OCM. Especially, selectivity of ethane and ethylene in the non-oxidative conversion is higher than OCM plasma reaction because of CO, CO_2-free formation. Acetylene selectivity increases more in the OCM than the non-oxidative methane conversions as the power increases, while CO_2 selectivity decreases slightly. The results of the measurements suggest that CO_2 contributes the oxidative conversion of methane by electronic dissociative attachment of CO_2 [11]

$$CO_2 + e^- \rightarrow CO + O^- \quad (1)$$

and Lui et al. [11] constantly insisted on the O^- and other oxygen species formed from these reactions may provide more active species for methane conversion.

The effect of catalyst in OCM reaction is investigated as shown in Fig. 4. The corresponding catalyst was H–ZSM-5 with 125 ml/min of flow rate (CH_4:O_2 = 4:1). The conversion of methane in the presence of catalyst increases more sharply than in the absence of catalyst and oxygen conversion maintains at ca. 10%. The catalyst has a more important role not only in formation of C2 yield but in formation of unsaturated hydrocarbon than saturated hydrocarbon. The acetylene formation increases and ethane decreases on catalyst. The selectivity of acetylene in the presence of catalyst is larger than in the absence of catalyst. The catalyst may play a role of transporting of microwave energy to generate surface

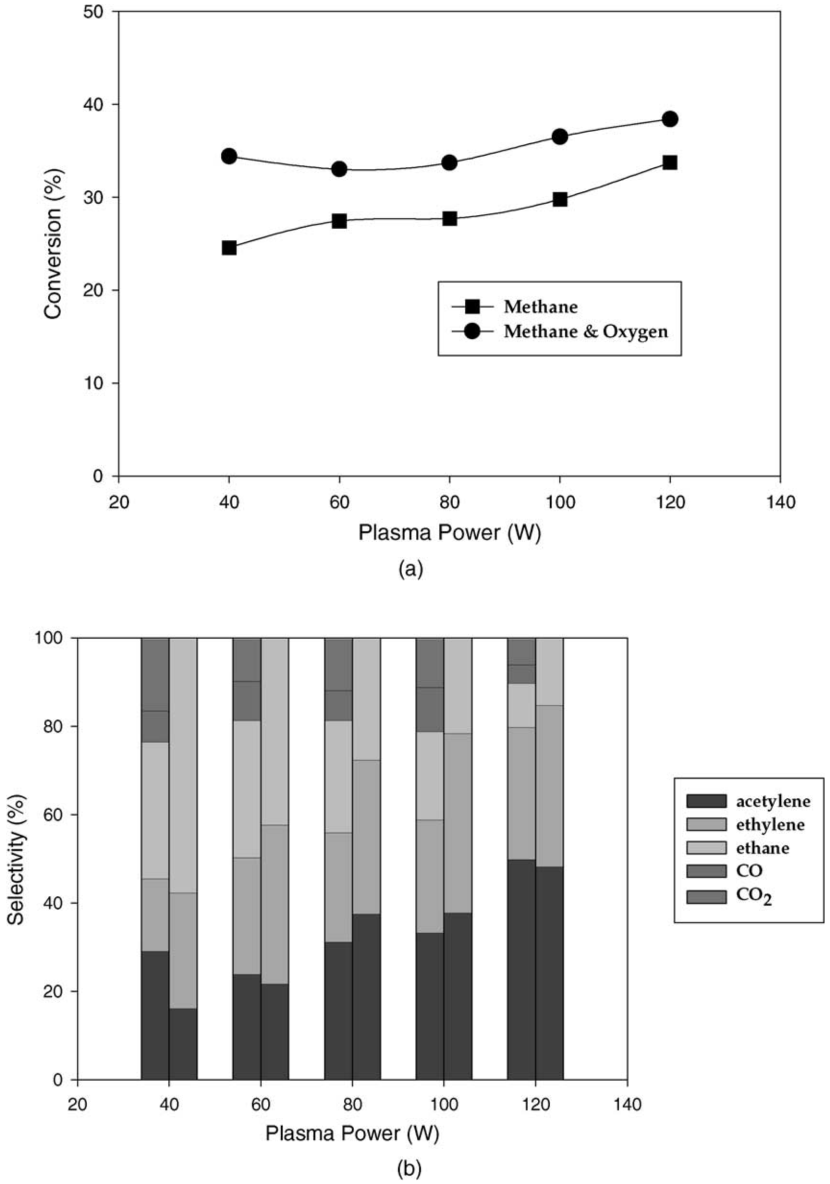


Fig. 3. Comparison of methane conversion (a) and the selectivity of C2 products (b) on addition of oxygen in the microwave plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min (the left bar shows the methane conversion in the presence of oxygen and the right side shows the one in the absence of oxygen).

electric discharge that causes the radical formation and recombination of methane [12]. Therefore it is considered that the abstraction of hydrogen from C2 manufacture to unsaturated hydrocarbons, acetylene, from saturate hydrocarbon, ethane, on the catalyst.

3.1.2. Plasma catalytic OCM over different ZSM-5

In the presence of gaseous oxygen, the cold plasma provides a source of negatively charged oxygen ion (O^- or O^{2-}) formed by electron attachment to oxygen molecules in the gas phase. The oxidizing agent

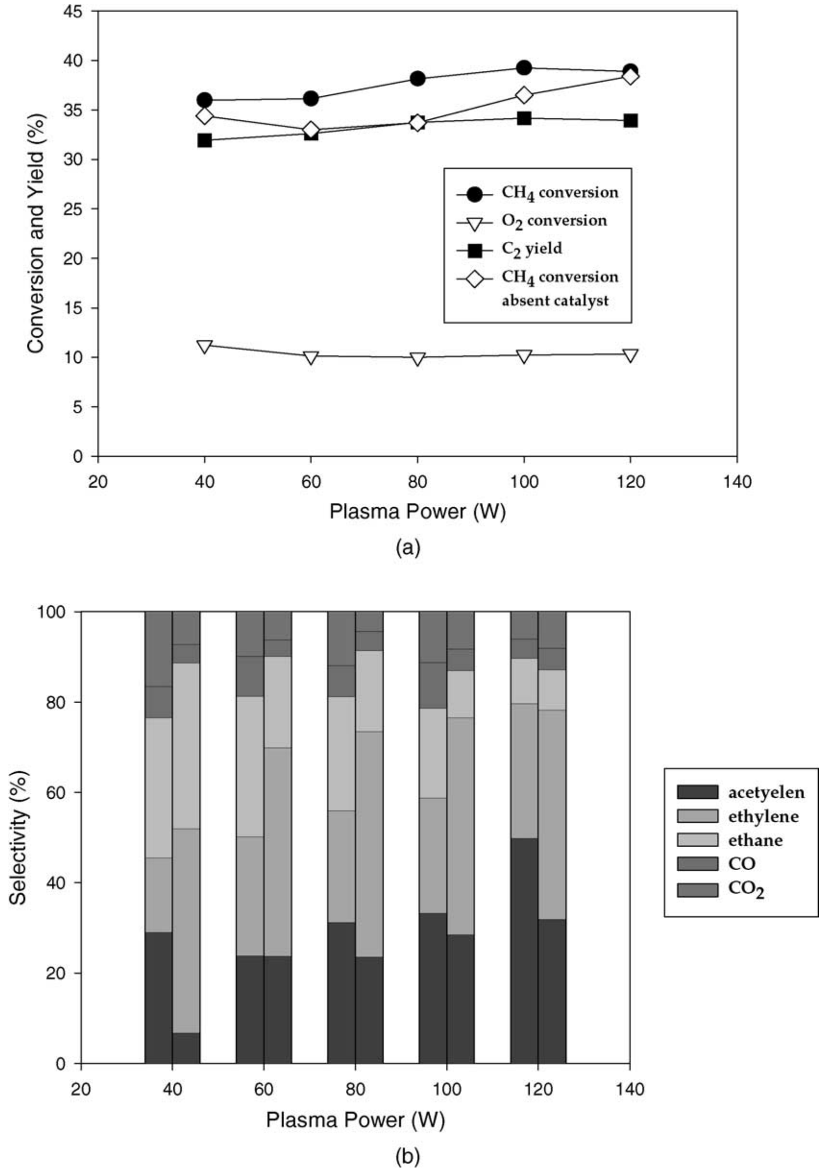


Fig. 4. Comparison of methane conversion (a) and the selectivity of C2 products (b) over H–ZSM-5 catalyst in the microwave plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min. The left side shows the results with catalyst and the right side shows the results without catalyst in (b).

may be atomic oxygen, originating from the negative oxygen ions [13].

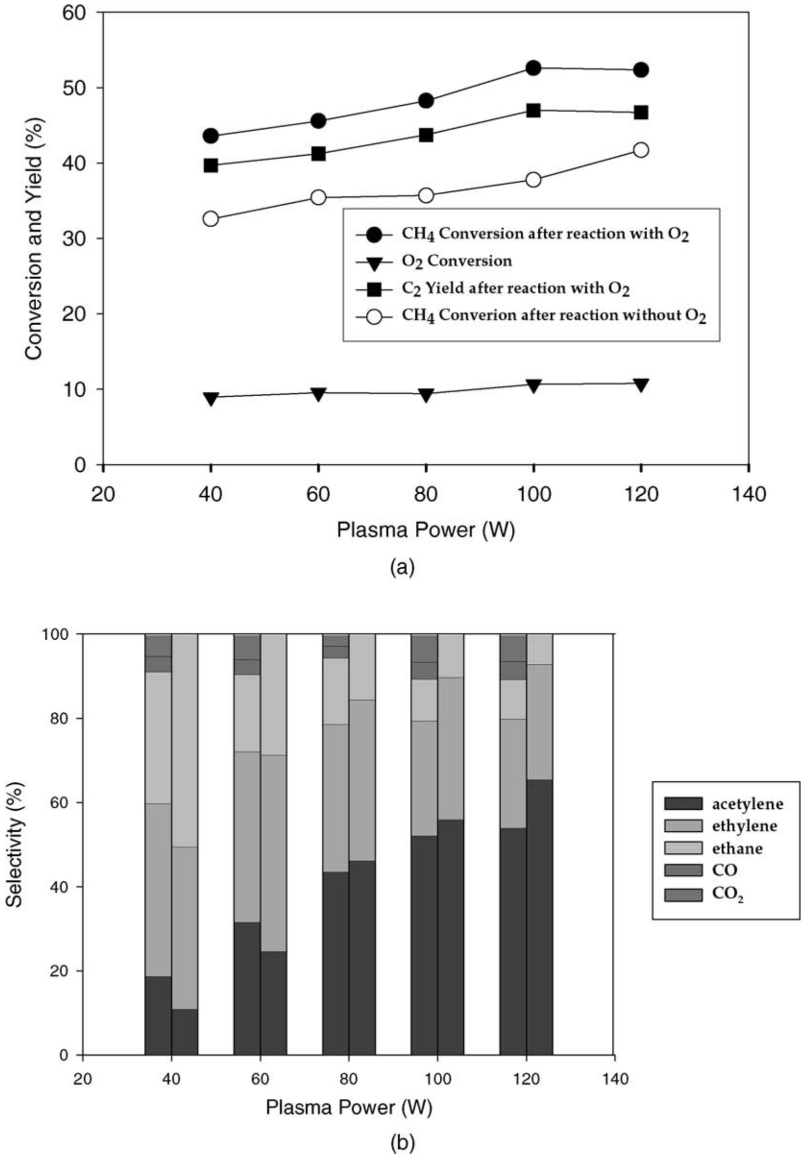
The first electronic state of atomic oxygen $O(^1D)$ and second electronic state of molecular oxygen $O_2(^1\Sigma)$ affect the radical formation of methane in gas discharge containing oxygen.

As mentioned above, the OCM over ZSM-5 is assumed to occur in a combined homogeneous and heterogeneous mechanism. It is postulated in many research results that oxygen has an important role in the supply of active species for the activation of methane and the catalyst may play a role of transportation of microwave electron energy to make the recombination of C2 to ethyl radical (C=C) or acetyl radical (C≡C).

The experimental results of OCM over transition metal and Cu-loaded ZSM-5 catalysts are shown in Figs. 5–8. The order in which ion-exchanged ZSM-5 is produced in the methane activation is as follows:

Co–ZSM-5 > Fe–ZSM-5 ≒ Cu–ZSM-5 > NiZSM-5

In case of Fe ion-exchanged ZSM-5, as shown in Fig. 5, the conversion of methane is enhanced as the power increases in the presence of oxygen. It can be seen that the C2 yield formation in the OCM plasma catalytic reaction is much more than reaction result of the H–ZSM-5. In particular, the selectivity of acetylene and ethylene increases due to formation of CO and CO_2. It is considered that the generation of CO and



(a)

(b)

Fig. 5. Comparison of methane conversion (a) and the selectivity of C2 products (b) over Fe–ZSM-5 catalyst in the microwave plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min. The left side shows the OCM reaction and the right side shows the non-OCM reaction in (b).

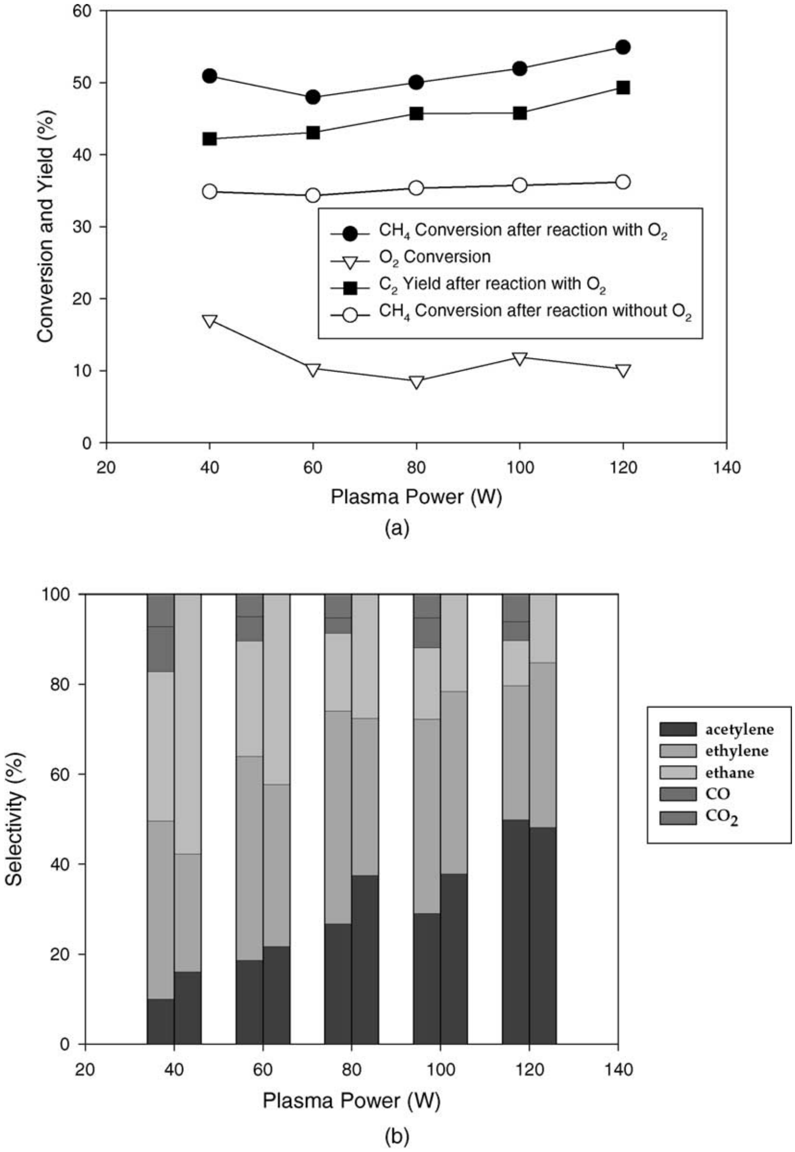


Fig. 6. Comparison of methane conversion (a) and the selectivity of C2 products (b) over Co–ZSM-5 catalyst in the microwave plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min. The left side shows the OCM reaction and the right side shows the non-OCM reaction in (b).

CO_2 affects the recombination of methyl and/or ethyl radical from methane conversion and then makes the new reaction pathway. That is oxygen as a co-reactant play the role of methane activator to produce unsaturated hydrocarbons than saturate hydrocarbon. And when it is carried out in the absence of catalyst, the ethyl and acetyl radical increase with an increase in the power so that the selectivity of acetylene may increase but ethane decrease.

Fig. 6 illustrates that methane activation is conducted to OCM by plasma and catalytic reaction over Co–ZSM-5 catalyst. Among the ion-exchanged ZSM-5 catalysts, Co–ZSM-5 catalyst is good methane conversion and yield of C2 products. The

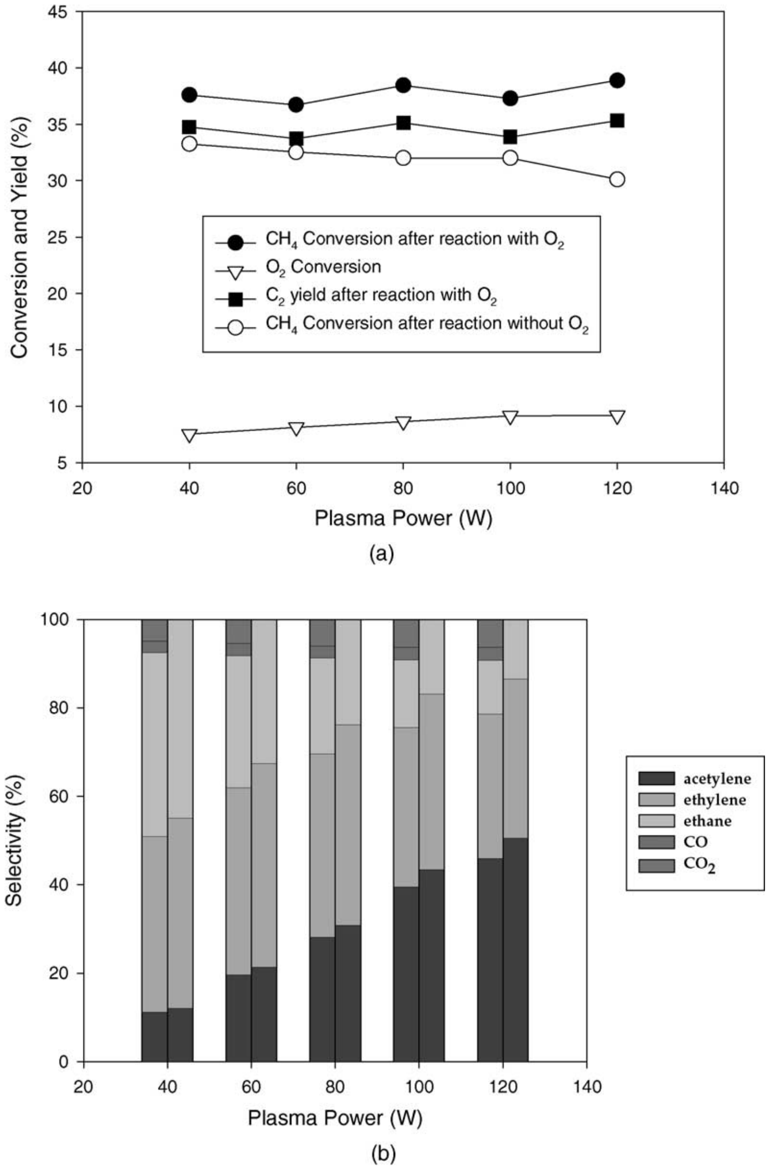
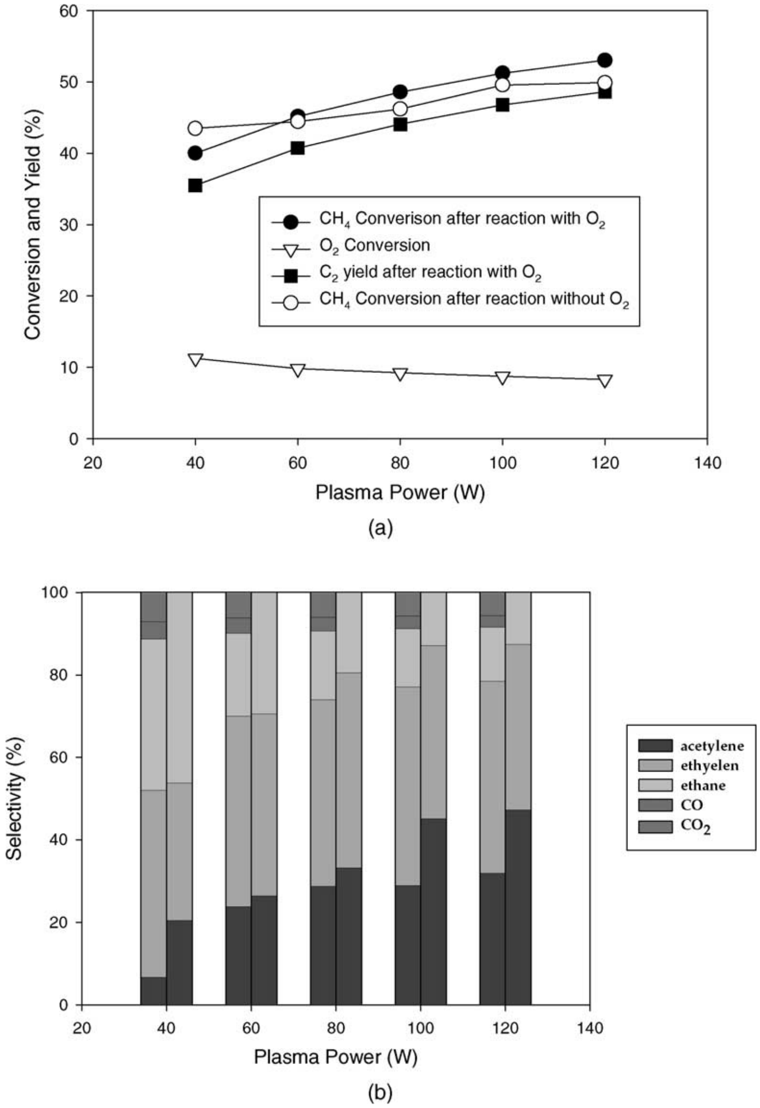


Fig. 7. Comparison of methane conversion (a) and the selectivity of C2 products (b) over Ni–ZSM-5 catalyst in the microwave plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min. The left side shows the OCM reaction and the right side shows the non-OCM reaction in (b).

highest conversion of methane is 55% at 120 W and 125 ml/min of feed and the yield of C2 product is enhanced to 45%. In this system, the conversion and yield are much more dependent on the oxygen as a co-reactant than the surface electronic discharge of catalyst. The conversion of methane in the absence of oxygen is maintained by ca. 35% (maintains at ca. 35%) through the plasma power applied.

Fig. 7 shows the result for an active catalyst, Ni, in the microwave energy system. In this case, the Ni ion-exchanged ZSM-5 expresses dramatically poor activity in the methane and oxygen reaction in the plasma catalytic system. And the conversion of



(a)

(b)

Fig. 8. Comparison of methane conversion (a) and the selectivity of C2 products (b) over Cu–ZSM-5 catalyst in the microwave plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min. The left side shows the OCM reaction and the right side shows the non-OCM reaction in (b).

oxygen is relatively low. The selectivity of ethylene or acetylene from methane on Ni–ZSM-5 has a little effect to generate C2 products compared with the other ion-exchanged ZSM-5 catalysts. Although the conversion is low in Ni–ZSM-5 system, the Ni catalyst tends to produce the C2 radicals from methane and this play a important role of reaction in the gaseous phase intermediate.

Fig. 8 shows the methane and oxygen conversion and C2 yield of OCM reaction in the Cu–ZSM-5 system and also compares them with non-oxidative methane conversion. It can be noted that the conversion of methane in this system is almost similar with and without oxygen in the Cu–ZSM-5 system. The selectivity of ethylene is also similar and the selectivity of acetylene without oxygen reaction is higher than

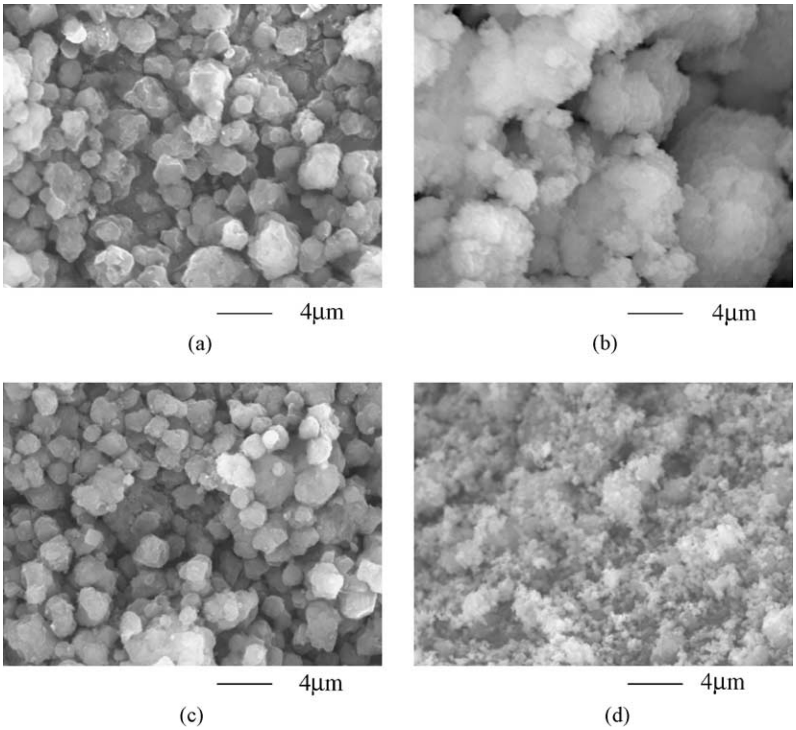


Fig. 9. Comparison of SEM image between before (a, c) and after reaction (b, d) of Co–ZSM-5 and Ni–ZSM-5, respectively.

reaction with oxygen. It is obvious that the formation of CO_2 rather than CO plays more active role in suppressing the acetyl radical on the Cu-loaded ZSM-5.

Fig. 9 presents the SEM photographs of before and after reaction of the Co–ZSM-5 and the Ni–ZSM-5 catalysts. The results shows that the morphology of Co–ZSM-5 after reaction is enlarged by the coking or surface co-polymerization of C–H radical and the morphology of Ni–ZSM-5 after reaction clearly shows the oxidation of catalyst surface. That is to say, the activity of Ni–ZSM-5 becomes more dull by oxidation of surface than the other catalysts and co-polymerization or coking, C (1s), is beneficial to the formation C2 radicals in H abstraction from methane and oxygen and in good agreement with the activity of methane conversion.

3.2. RF plasma and catalytic experiments

The OCM using RF plasma and catalytic reaction is done using Co–ZSM-5 catalyst and in microwave plasma system it showed high activity. We first conduct a consecutive plasma and catalytic reaction at the similar condition with microwave plasma catalytic reaction; i.e. 50–150 W of plasma power, 125 ml/min of feed rate with CH_4:O_2 = 4:1. As illustrated in Fig. 10, the conversion of oxygen is accelerated by RF plasma and the methane conversion is relatively low compared with oxygen conversion. The selectivity of C2 (up to 62%) is lower than in the microwave plasma catalytic reaction (almost above 75%), leading to the small amount of C2 yield (maximum 31%). It is certain that the formation of CO_x inhibits the C2 products as well as carbonaceous deposition from being formed and it generates the active species that increase activation methane and oxygen, as mentioned above.

In order to measure the activity effect at high feed rate and high RF plasma power, we prepare 250 ml/min of flow rate and the 1.2 kW of RF plasma generator. Fig. 11 shows the methane conversion both in the presence and in the absence of oxygen, when performed only in the plasma reaction without apply-

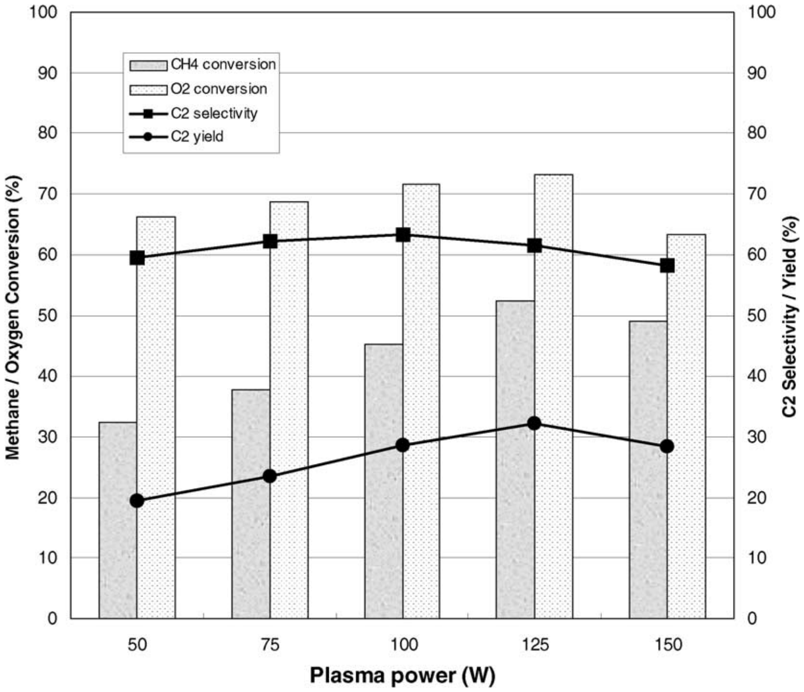


Fig. 10. Plot of the methane conversion and O_2 conversion in the RF plasma system. Also it shows the selectivity and yield of C2 product: CH_4:O_2 = 4:1, flow rate = 125 ml/min.

ing the catalytic reaction. The methane conversion of OCM is higher than the non-oxidative methane conversion and represents high oxygen conversion (above 20%) than microwave plasma and catalytic reaction (more less 10%). It is observed that the C3+ and carbon black (up to 3 wt.%) product represents according to increasing power. More than 500 W of RF plasma power leads the sharp reduction of CO_2 and increase in acetylene and production of C3+ product. More than 800 W generates carbon black, with the walls of reaction coked. Also in this experiment, the selectivity of CO and CO_2 also shows relatively low results.

Fig. 12 illustrates the RF plasma catalytic reaction in the presence of Co–ZSM-5 catalyst. In this reaction, we can get about 3–10% of formaldehyde or such liquid product as methanol, which are represented as C_{liq} in Fig. 12. It is worthy of notice that methane conversion reaches as much as 81% and oxygen conversion shows very high level, more than 24%. Especially it can be observed that the higher RF plasma power brings the remarkable increase in carbon black and C_{liq} while the selectivity of CO_x remains very low level.

Figs. 11 and 12 show that the higher flow rate and power converts methane and O_2 into the certain radical rather than into methyl radical in the presence of catalyst. As shown above, this experiment is considered to be important in that catalytic reaction outputs the liquid products, producing oxygenate compound.

3.3. Reaction mechanism

In the previous study [14], it was revealed through many research results that the OCM reaction seems to contain heterogeneous and homogeneous reaction step. It was found that the surface or lattice O^- or O^{2-} (oxygen anion) of catalyst supplied to activate methane by abstraction of hydrogen to form methyl radical and C2 products occurred in the gas phase by coupling of the methyl radicals. In the plasma and catalytic system of this work, the selectivity of CO and CO_2 decreases as the plasma power increases therefore the oxygen anion is affected by electronic discharge to activate methane, through which C2 products increase. These results suggest that oxygen anions are generated

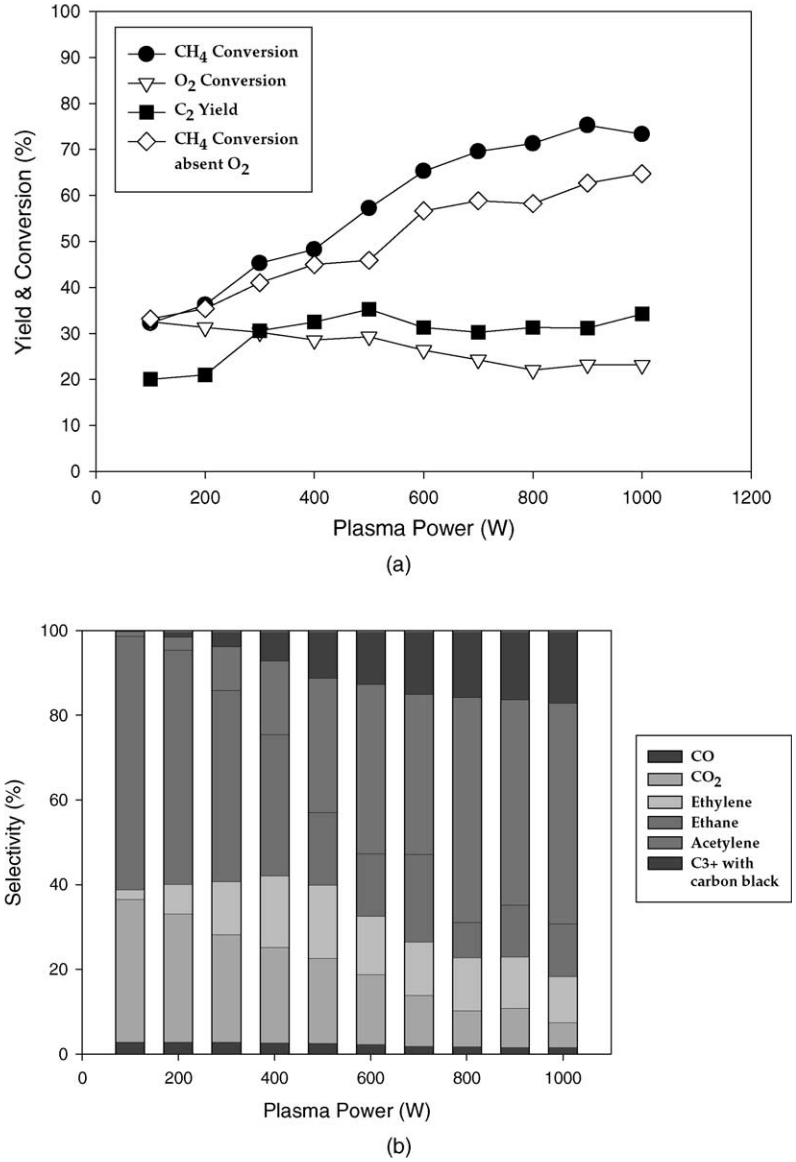


Fig. 11. Comparison of methane conversion (a) and the selectivity of the products (b) on addition of oxygen in the RF plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min.

by collision of O_2 with the electron released from microwave or RF discharge and these anions affect the activation of methane, like surface oxygen anions on the catalyst in the traditional OCM [15,16].

Tables 1 and 2 summarize the comparison of the effect with oxygen reaction on ion-exchanged ZSM-5 to activate methane into C2 products in the plasma and catalytic reaction. The larger the BET surface area becomes, the higher the activity of methane gets except on the H–ZSM-5 whose pore size is narrow. The larger specific surface area enhances total conversion and activity of methane. It was found that there is an interaction between catalyst zone and plasma reaction. It is noted that the active site in the ion-exchanged

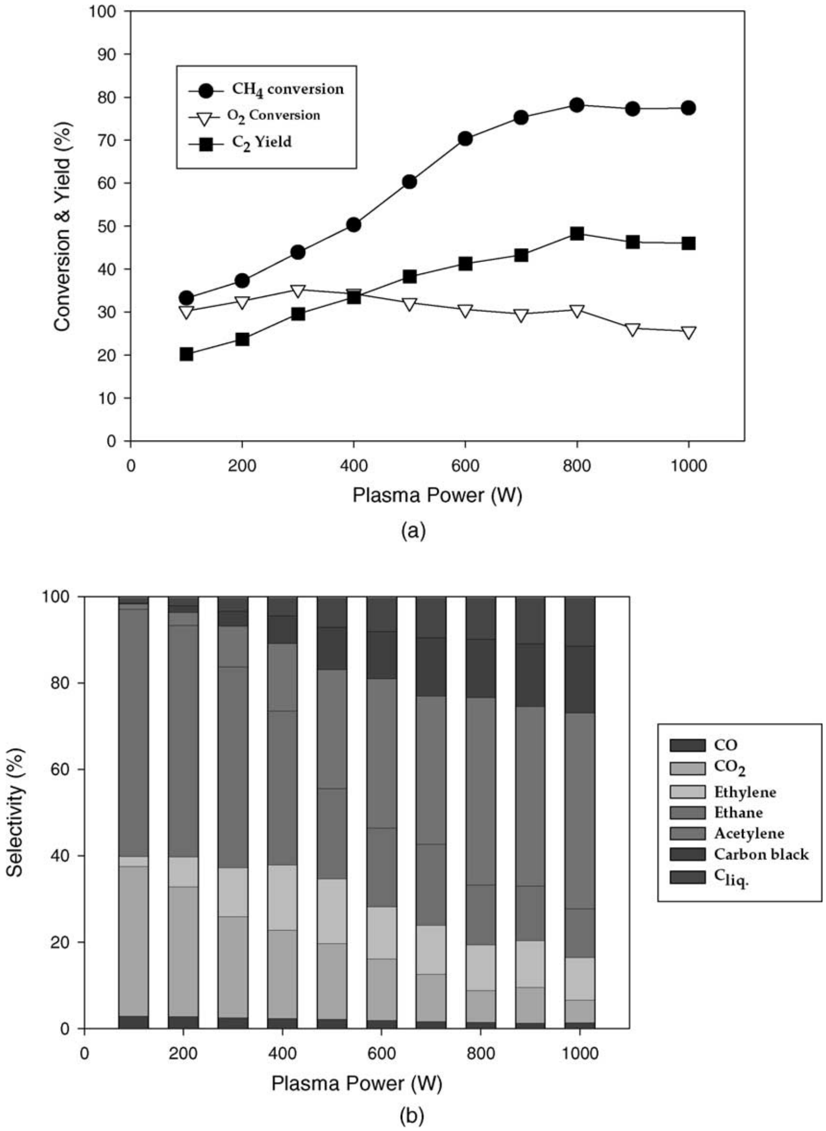


Fig. 12. Comparison of methane conversion (a) and the selectivity of the products (b) over Co–ZSM-5 catalyst in the RF plasma system: CH_4:O_2 = 4:1, flow rate = 125 ml/min.

ZSM-5 catalyst exists and it is also activated by interaction between plasma zone and catalyst.

Total conversion of methane in the microwave and RF plasma system shows 54.9 and 78.1% on the Co–ZSM-5 catalyst in the oxidative coupling reaction, respectively, and the activity is higher than the non-oxidative methane conversion. However, in the RF plasma system, the yield of desirable product (C2 product) is reduced in the high power system as shown Table 2. Thus, oxygen is very effective for cold plasma activation by the interaction between the plasma and catalyst.

The gas discharge of methane and oxygen reaction may occur as follows: OCM reaction starts as the first electron produced by the discharge of methane participates in the reaction. Oxygen dissociates to

Table 1
Experimental results of OCM in the microwave plasma and catalytic reaction over ion-exchanged ZSM-5

	Catalysts					
	No catalyst	H–ZSM-5	Fe–ZSM-5	Co–ZSM-5	Ni–ZSM-5	Cu–ZSM-5
Plasma power (W)	100	100	100	120	120	120
Product selectivity (%)						
Ethylene	48.1	25.5	27.2	29.8	32.7	46.6
Acetylene	28.6	33.4	52.2	49.9	46.0	32.0
Ethane	10.4	20.0	9.3	10.0	12.2	13.2
CO	4.7	10.0	4.3	4.2	6.3	2.8
CO_2	8.2	11.2	6.6	6.0	6.3	5.5
Methane conversion (%)	36.5	39.3	52.6	54.9	38.9	53.0
Oxygen conversion (%)	9.8	10.2	10.7	10.2	9.16	8.3
BET surface area (m^2/g)	–	425	354	349	231	335

produce in the ground state (^3P) and in metastable states (^1D) and (^1S). The reaction rates of O(^3P) and O(^1S) with methane are slow in air plasma system, however, O(^1D) is known to bring the one of the most important primary process. It was previously mentioned that the dissociation attachment or dissociation of oxygen will generate the active "oxygen anions" to enhance the conversion of methane [17–21]:

Dissociative attachment:

$$e^- + O_2 \rightarrow 2O(^3P) + e^- \rightarrow O^- + O(^1D) \qquad (2)$$

Molecular excitement:

$$O_2 + e^- \rightarrow O_2(^1\Delta_g) + e^- \qquad (3)$$

The metastable molecule $O_2(^1\Delta_g)$ mainly reacts with unsaturated compounds, and $O_2(^1\Sigma_g{}^+)$ has very low concentration so that it cannot be treated as important in this system. Also, oxygen anions are produced by gas discharge using the microwave or RF plasma and separated anions combine with one another, when the active anions species and oxygen anions attack the methane to produce the methyl radical. The methyl radical progresses consecutive to generate the C2+ products, as described in Fig. 13.

The OCM reaction by high frequency plasma and catalytic reaction provides a important information to generate C2+ production. That is to say, the oxygen anions and metastable molecule generated from electron discharge play a role of the initiation to activate

Table 2
Comparison of the results in the RF plasma and catalytic reaction according to various conditions

	Plasma reaction		Plasma catalytic reaction
Feed/catalyst	Methane	Methane:O_2 = 4:1	Methane:O_2 = 4:1/Co–ZSM-5
Plasma power (W)	1000	900	800
Product selectivity (%)			
Ethylene	9.3	12.2	10.6
Acetylene	19.6	48.5	43.3
Ethane	41.1	12.2	13.9
CO	–	1.54	1.51
CO_2	–	9.3	7.3
C3+ products (include C_{liq}, carbon black)	28.6	17.15	23.3
Methane conversion (%)	64.7	75.2	78.1
Oxygen conversion (%)	–	23.2	30.6

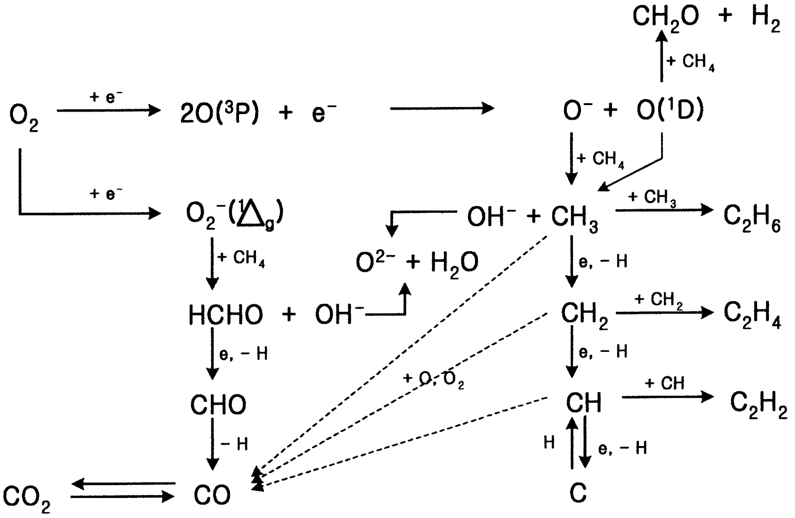


Fig. 13. Scheme diagram of the overall reaction mechanism of the OCM in the plasma and catalytic reaction.

the methane and active species as a surface anion on the catalyst.

4. Conclusion

We can summarize that the oxygen effects and ion-exchanged ZSM-5 catalysts play an important role in high frequency plasma (microwave and RF plasma). The catalytic reaction enhances catalytic conversion of methane into high value-added hydrocarbons. The combination of catalyst and microwave plasma system makes the activity and yield of C2 product more promoted under OCM than non-oxidative methane conversion. The order in which ion-exchanged ZSM-5 are tested from high activity to low one for methane conversion is Co–ZSM-5 > Fe–ZSM-5 ≒ Cu–ZSM-5 > Ni–ZSM-5. The C2 products are generated more actively in microwave plasma catalytic reaction than in the RF plasma catalytic reaction, however, the methane conversion in the OCM of RF plasma catalytic reaction is effectively higher than microwave plasma system. Also, the oxygen conversion is higher (up to 30.6%) in RF plasma catalytic reaction than microwave plasma catalytic reaction (up to 10.2%) on the Co–ZSM-5 due to high power of plasma system.

In particular, liquid hydrocarbons have been generated by high power of RF discharge system added oxygen as a co-reactant. The liquid hydrocarbons consist of methanol, formaldehyde and undetected components.

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