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Plasma-assisted reduction of supported metal catalyst using atmospheric dielectric-barrier discharge

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Abstract

Methane conversion was carried out in a presence of a catalyst within a dielectric-barrier discharge reactor. Temperature programmed reduction (TPR) and plasma-assisted reduction (PAR) was studied to reduce the supported metal catalysts. Prepared catalyst was successively reduced by PAR. The selectivity of C_2H_6, C_2H_4 and C_2H_2 was higher among the produced hydrocarbons when the methane conversion was carried out in the absence of a catalyst. In the presence of Pt and Co catalyst, the main products of plasma catalytic reaction were light alkanes such as C_2H_6, C_3H_8 and C_4H_{10}. The plasma catalytic reaction showed positive characteristics to produce light alkanes when Pt and Co catalyst were used after PAR. PAR was an effective method to reduce supported metal catalyst.

Keywords: Plasma-assisted reduction; Catalyst; Non-thermal plasma; Methane conversion

1. Introduction

During the last decade, intensive efforts have been devoted to the conversion of methane to liquid fuels or other chemicals. Most commercial processes convert methane to synthesis gas with steam reforming, and then synthesize methanol or gasoline from the synthesis gas. However, in recent studies, there have been lots of wide-range experiments on the direct conversion method. Oxidative coupling [1–3], thermal coupling [4] and plasma reaction [5–12] have been used for direct methane conversion, but there are a lot of difficulties in doing this because it is very difficult to breakdown the C–H bond of methane. Methane conversion with plasma has been widely studied, because it is an alternative method to avoid the difficulties of the other methods. Methane activation with plasma is very effective because methyl radicals can be easily formed and various kinds of chemical reactions can induce the high energy of plasma. For plasma chemical reactions, free radicals are believed to be much more important than any other reactive particles such as electrons, ions, photons, etc.; therefore, control and manipulation of the subsequent free-radical reactions are essential to the success of plasma application in organic syntheses [12]. The electrons within the plasma zone serve principally to excite and decompose the gas molecules at a high rate and in a non-selective fashion. To overcome this difficulty, heterogeneous catalysts can be introduced into the plasma reaction. This catalysis-assisted plasma technology does not only enhance the decomposition efficiency catalytically, but also reduces the by-products selectively. For this reason, intensive efforts have been devoted to the plasma catalytic reaction. Liu et al. [8] used corona discharge over oxidative metal catalysts at the reaction temperature of 400–600 °C to convert methane. In their work, the conversion of methane was under 30%, and the selectivity of C_2 was not over 80%. Liu et al. [9] reported non-oxidative methane conversion to acetylene over zeolite in a low temperature plasma. They presented a reaction mechanism to explain the experimental results of a 32% C_2 hydrocarbons yield. Liu et al. [11] studied comparative investigations on plasma catalytic methane conversion to higher hydrocarbons over zeolites, and they reported that the order of zeolites tested from good to poor for sustaining

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the desired streamer discharges was NaY, NaOH treated Y > HY > NaX > NaA > Linde type 5A > Na-ZSM-5. Marafee et al. [10] studied an oxidative coupling of methane in a DC corona discharge over Sr/La_2O_3 catalyst. When the DC corona discharge was applied to the catalytic reactor, the methane conversion increased five times and the selectivity for C_2 increased eight times at 853 K. Non-equilibrium plasma, which has the features of low temperature and a large amount of high-energy electron, is one of the most efficient ways of activating molecules. The applications of plasma techniques have recently been applied to prepare catalyst. Heintze et al. [13] studied methane conversion into aromatics in a direct plasma catalytic process, in their work, benzene was the main aromatic product formed in concentrations up to 0.6% with selectivities up to approximately 30%. Liu et al. [14] announced for the catalyst preparation using thermal and cold plasma. Zhang et al. [15] studied a plasma-activated $Ni/\alpha\text{-}Al_2O_3$ catalyst for the conversion of methane to syngas. From their study, the activity and stability of the plasma-activated catalyst were higher than those of conventional catalysts.

In this paper, methane conversion reaction was carried out in a dielectric-barrier discharge (DBD) reactor at atmospheric pressure. We have explored the application of plasma-assisted reduction (PAR) for Pt- and Co-based catalyst. Supported Pt and Co catalysts were prepared. Prepared catalysts were tested to reduction characteristics. PAR is used to reduce supported metal catalyst in DBD reactor. Supported metal catalyst is typically reduced by heat with hydrogen before reaction in the same reactor. It was inconvenience to reduce prepared catalyst by typical method in DBD reactor before reaction. From this idea, reduction of prepared catalyst was carried out with plasma energy at the atmosphere of hydrogen and nitrogen, and methane conversion was carried out in the same DBD reactor. The catalysts reduced by PAR and the catalysts reduced by thermal treatment were compared in this study.

2. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. The reactor was a quartz tube with an i.d. of 8 mm and the length of 270 mm. Two stainless steel wires with a diameter of 0.45 mm were installed in the quartz tube as an electrode. The outer surface of quartz tube was coated with silver as another electrode, and the length of reaction zone was 200 mm. An AC pulse power supply (ITM) with (0–10 kV, 10–40 kHz, 2–5 μs) was used in this experiment. The flowrate of methane was controlled by the mass flow controller (Bronkhorst, B-5534-FA). The reaction products of hydrocarbons were analyzed with the gas chromatograph (HP 5890 equipped with a Haysep Q packed column and FID detector). Gas chromatograph (Younglin M600D) equipped with TCD was used to analyze the produced hydrogen. The peaks were identified when the retention times compared with those of standard gases (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8 and C_4H_{10}) with a purity above 99.5%. Gamma alumina, which was used as a support, was sieved 20–42 mesh and calcined at 700 °C for 2 h. The surface area of support was 142 m^2/g, and the total pore volume was 0.36 cm^3/g. The metal oxide catalysts which contained 1–5 wt.% platinum and cobalt on the alumina were prepared by the incipient-wetness technique. All catalysts were dried at 200 °C for 2 h and then calcined between 400 and 500 °C for

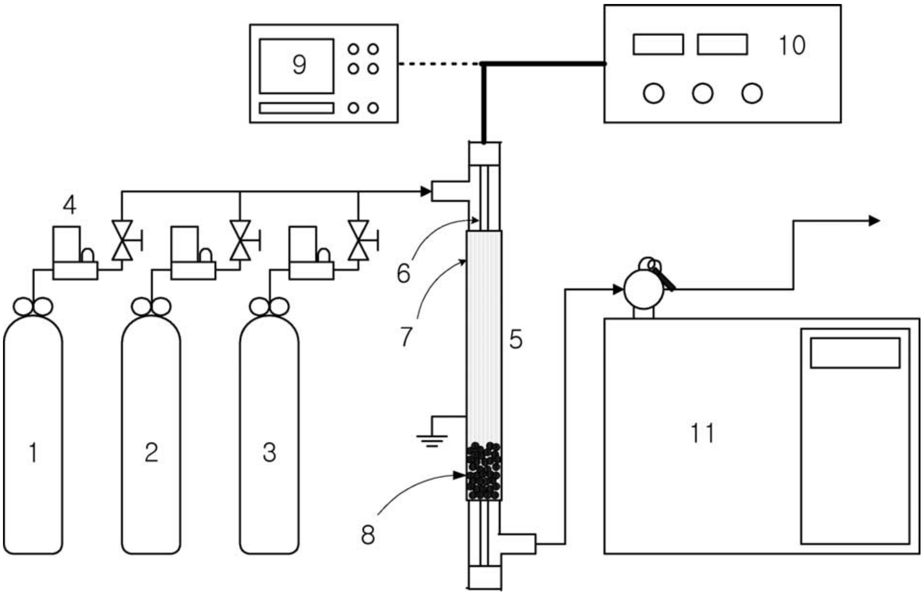

Fig. 1. Schematic diagram of the experimental apparatus: (1) methane; (2) hydrogen; (3) nitrogen; (4) mass flow controller; (5) DBD reactor; (6) inner electrode; (7) outer electrode; (8) catalyst bed; (9) oscilloscope; (10) power supply; and (11) GC.

2 h with oxygen flowrate of 100 ml/min. $H_2PtCl_6\cdot 6H_2O$ and $Co(NO_3)_2\cdot 6H_2O$ were used as the precursors. The catalyst of 1 g was packed with the lower part of DBD reactor, while the upper part remained blank. Below the catalyst-packed volume, i.e. at the lower non-plasma zone, glass beads were packed. All experiments were carried out under atmospheric pressure.

- The methane conversion is defined as

$$CH_4 \text{ conversion} = \frac{\text{moles of } CH_4 \text{ consumed}}{\text{moles of } CH_4 \text{ introduced}} \times 100.$$

- The selectivities and yields of C_2, C_3 and C_4 hydrocarbons are

$$\text{Selectivity of } C_xH_y = x\frac{C_xH_y}{\text{moles of } CH_4 \text{ consumed}} \times 100.$$

- The selectivity of hydrogen is

$$\text{Selectivity of } H_2 = 0.5 \times \frac{\text{moles of } H_2 \text{ formed}}{\text{moles of } CH_4 \text{ consumed}} \times 100.$$

- The yields of hydrocarbons are

$$\text{Yields of } C_xH_y = \text{conversion of } C_xH_y \times \text{selectivity of } C_xH_y.$$

3. Results and discussion

Temperature-programmed reduction (TPR) was performed with a Young-Lin M 600 D gas chromatograph in a quartz tube. A 10 ml/min flow of 20 vol.% H_2 in N_2 was used as the reductive gas. The rate of hydrogen consumption was monitored by a thermal conductivity detector with raising the sample temperature from 20 to 700 °C at a constant rate of 4 °C/min. As can be seen in Fig. 2, shapes of the reduction profiles were similar for Pt/γ-Al_2O_3 even the calcined temperature and the metal loading were different. The reduction profile of Pt catalyst consisted of one peak which occurred above 150 °C, and catalyst rapidly reduced below 250 °C. In the case of Co/γ-Al_2O_3, the broad hydrogen consumption peak (including several peaks) was observed in the TPR profile indicating the formation of different cobalt species during the preparation steps. A low temperature reduction peak between 120 and 390 °C and two high temperature reduction peaks above 400 °C were observed for 5 wt.% Co/γ-Al_2O_3 catalyst calcined at 400 °C. A low temperature reduction peak between 170 and 390 °C and a high temperature reduction peak between 470 and 680 °C was observed for 5 wt.% Co/γ-Al_2O_3 catalyst calcined at 500 °C. Wang and Ruchenstein [16] studied the effect of calcinations temperature (500–800 °C) on the CO_2 reforming of CH_4 over Co/MgO of various loadings (4–48 wt.%). In their study, the TPR profiles of the Co/MgO calcined at 500 °C showed a low temperature reduction peak between 260 and 300 °C and a high temperature reduction peak between 660 and 690 °C. It was a similar result to our experiments. The species reducing at slightly higher temperatures may have a somewhat stronger interaction with the gamma alumina surface. Compared with Pt/γ-Al_2O_3 and Co/γ-Al_2O_3, the peaks of Co/γ-Al_2O_3 was broad. The broad peaks indicate the existence of several species reducing at approximately the same temperature, whereas the sharp peaks indicate the existence of a single species.

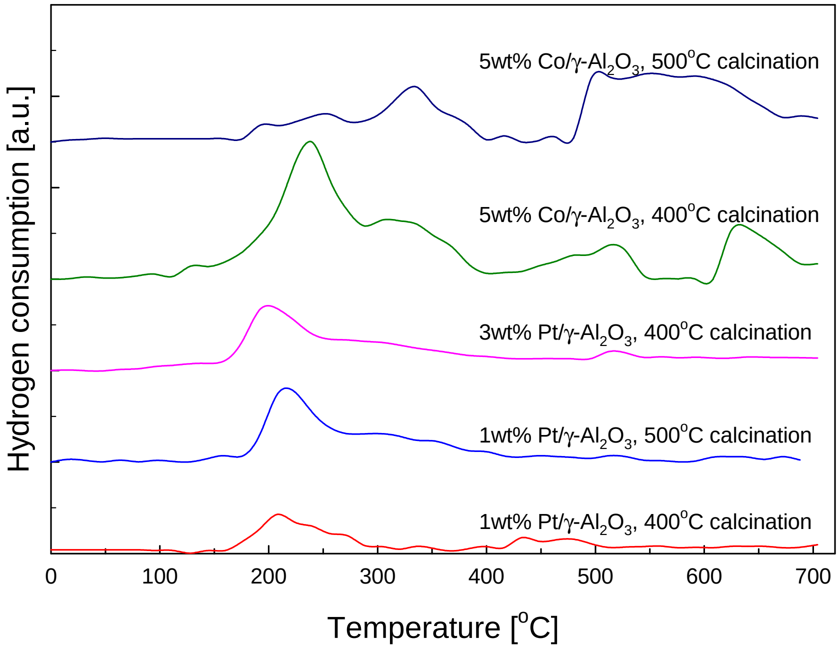

Fig. 2. TPR profile of prepared catalysts; hydrogen and nitrogen flowrate = 10 ml/min (20 vol.% H_2 in N_2).

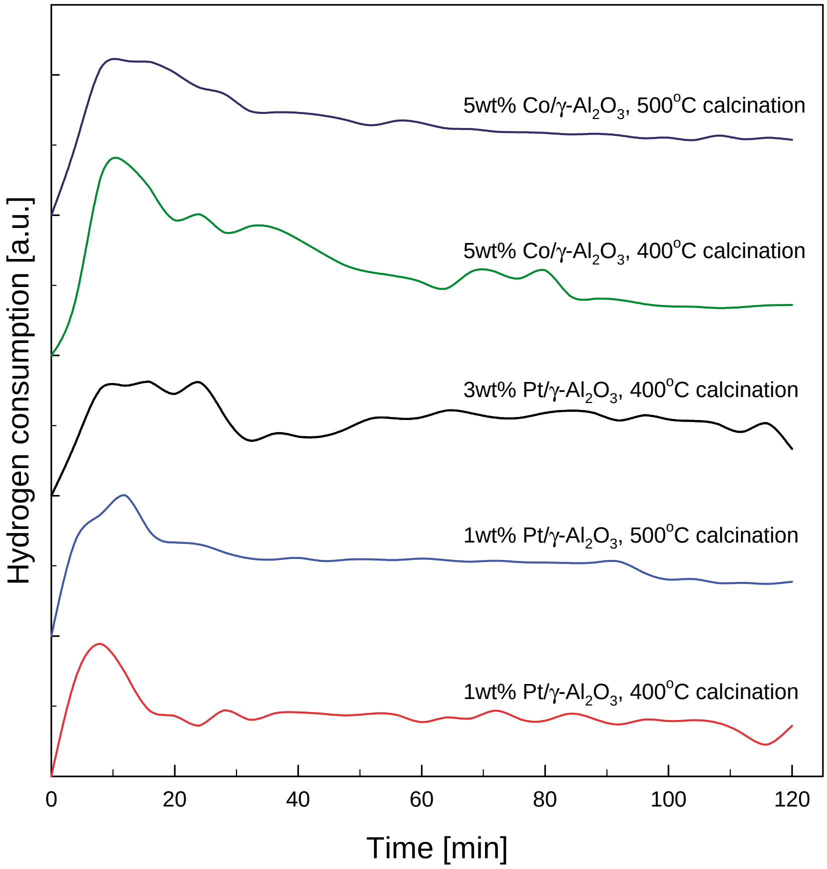

Fig. 3. PAR profile of prepared catalysts; hydrogen and nitrogen flowrate = 10 ml/min (20 vol.% H_2 in N_2).

As mentioned in Section 1, the application of plasma techniques have recently been applied to prepare catalyst [13,14]. Large amount of high-energy electron from non-thermal plasma is promising to activate hydrogen molecules. It is believed that the catalyst surface (metal oxide) in contact with the highly activated hydrogen is reduced. From this idea, non-equilibrium plasma applied to reduce metal oxide catalysts in dielectric-barrier discharge (DBD) reactor. The 1 g of sample was located at the lower part of reactor for plasma-assisted reduction (PAR), while upper the part remained blank. PAR of metal oxide catalyst was carried out 10 ml/min flow of 20 vol.% H_2 in N_2. The rate of hydrogen consumption was monitored by a thermal conductivity detector. The applied voltage was fixed at 3.0 kV, and then the power input was between 37 and 39 W with the variations of experimental condition. The voltage waveforms were sinusoidal waveforms. The power was measured by oscilloscope (Agilent, 54641A) with the integration of voltage and ampere. The results of PAR represented in Fig. 3. The reduction profile of Pt/γ-Al_2O_3 catalysts consisted of one peak during PAR. In the case of Pt/γ-Al_2O_3, shapes of the reduction profiles were similar although the calcined temperature and the metal loading were varied. Reduction of 1 wt.% Pt/γ-Al_2O_3 catalyst was mainly reduced within 20 min, whereas the reduction of 3 wt.% Pt/γ-Al_2O_3 was prolonged 30 min. It is considered that the increase of reduction time was caused by the increase of metal loading.

In PAR of 5 wt.% Co/γ-Al_2O_3, broad peak can be seen in Fig. 3. The 5 wt.% Co/γ-Al_2O_3 catalyst calcined at 400 °C was reduced for 80 min. Co/γ-Al_2O_3 catalyst calcined at 500 °C was reduced rapidly for 30 min, after then reduced smoothly. The reduction time of Co catalyst was longer than that of Pt catalyst. It was shown that Co catalyst had the

Table 1
Effect of residence time on methane conversion and selectivities; without catalyst

Methane flowrate (ml/min)	Residence time (s)	Methane conversion (%)	Selectivities (%)						
			C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	H_2
20	30.2	45.49	14.74	7.79	9.49	4.98	2.22	1.00	30.49
30	20.1	36.71	15.42	9.74	12.70	3.74	1.90	2.00	47.45

Table 2
Effect of the reduction method and the calcination temperature on methane conversion and selectivity (methane flowrate: 30 ml/min)

Reduction method	Methane conversion (%)	Selectivities (%)						
		C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	H_2
Thermal reduction (400 °C, 2 h)								
1 wt.% Pt/γ-Al_2O_3								
400 °C	30.76	30.87	0.31	–	15.23	0.14	11.21	32.76
500 °C	25.94	39.95	1.53	0.87	13.68	0.80	7.27	36.20
3 wt.% Pt/γ-Al_2O_3								
400 °C	35.92	30.47	0.79	0.18	12.37	0.34	6.90	24.90
500 °C	33.68	33.72	0.61	0.22	14.17	0.27	8.20	26.90
5 wt.% Co/γ-Al_2O_3								
400 °C	38.78	21.31	2.46	0.88	10.23	1.07	5.32	35.95
500 °C	38.69	20.01	2.29	3.19	9.03	1.35	5.40	37.74
PAR (2 h)								
1 wt.% Pt/γ-Al_2O_3								
400 °C	36.41	36.96	1.25	0.51	16.01	1.59	8.29	33.78
500 °C	33.25	37.62	1.23	0.48	15.86	2.39	8.28	36.75
3 wt.% Pt/γ-Al_2O_3								
500 °C	33.65	39.21	1.04	0.38	17.66	1.07	12.55	35.81
5 wt.% Co/γ-Al_2O_3								
400 °C	36.69	28.30	2.02	0.58	16.58	0.84	7.21	48.84
500 °C	31.52	25.69	1.99	1.53	13.51	1.31	5.32	32.49

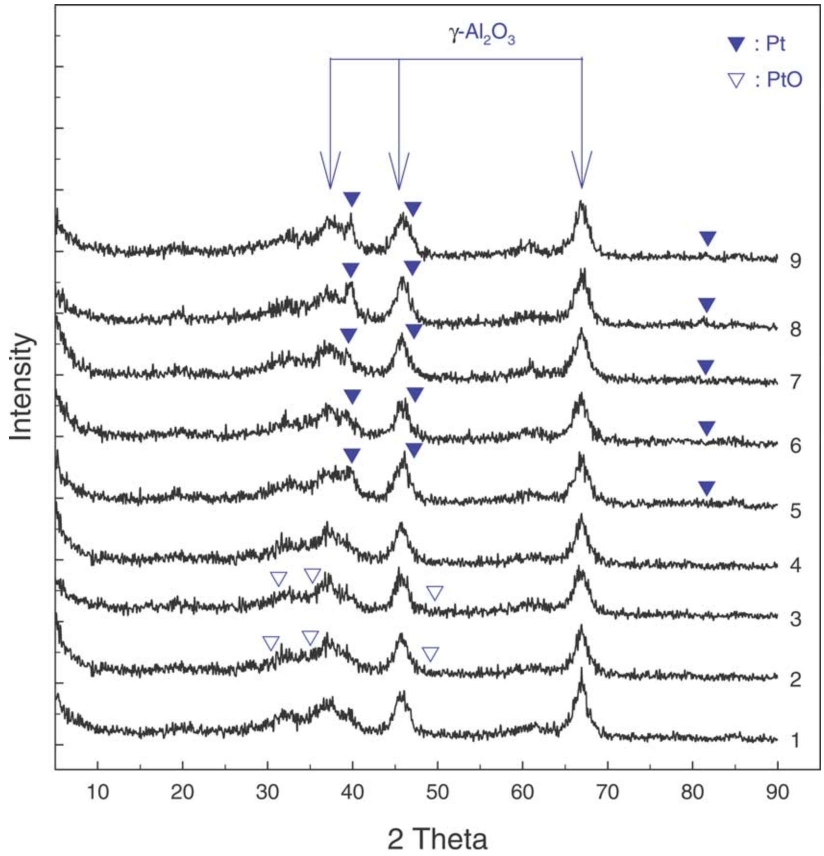

Fig. 4. XRD patterns for the catalysts of 1 wt.% Pt/γ-Al_2O_3: (1) γ-Al_2O_3; (2) 1 wt.% Pt/γ-Al_2O_3, 400 °C calcinations; (3) 1 wt.% Pt/γ-Al_2O_3, 500 °C calcinations; (4) 1 wt.% Pt/γ-Al_2O_3, 400 °C calcination, 400 °C reduction; (5) 1 wt.% Pt/γ-Al_2O_3, 400 °C calcination, PAR; (6) 1 wt.% Pt/γ-Al_2O_3, 400 °C calcination, 400 °C reduction, after reaction; (7) 1 wt.% Pt/γ-Al_2O_3, 500 °C calcination, 400 °C reduction, after reaction; (8) 1 wt.% Pt/γ-Al_2O_3, 400 °C calcination, PAR, after reaction; (9) 1 wt.% Pt/γ-Al_2O_3, 500 °C calcination, PAR, after reaction.

broad peak and a number of peaks, which indicate the existence of different cobalt species.

PAR was applied to the Pt- and Co-based catalyst. As can be seen in Fig. 3, prepared catalyst was successively reduced by PAR. It is believed that PAR is an effective method to reduce metal oxide catalyst. Hydrogen was continuously consumed during PAR in Fig. 3. It is considered that the alumina is reduced by activated hydrogen with plasma energy.

To verify the reduction effect of PAR, the experiments of methane conversion were carried out. Variation of the residence time can make a significant effect on the conversion of methane and the selectivities of hydrocarbons. The residence time was controlled by the flowrates of methane in the DBD reactor, and it was varied from 20.1 to 30.2 s. Table 2 shows the results of methane conversion and the selectivity of product as a function of residence time at the applied voltage of 3.0 kV. Experiment for the effect of residence time was carried out without catalyst. Methane conversion was increased from 36.71 to 45.49% when the residence time increased from 20.1 to 30.2 s. The selectivity of C_2H_6, C_2H_4 and C_2H_2 was higher among the produced hydrocarbons. Variation of residence time did not have a significant effect on the selectivity of product in the scope of this experiment.

The effects of the reduction method, metal loading, calcination temperature and metal species on methane conversion and selectivity were examined. Prepared catalysts were reduced by two methods. One method is the traditional method on the basis of TPR. In this case, the catalyst was reduced with reduction gases in situ 10 ml/min flow of 20 vol.% H_2 in N_2 at 400 °C for 2 h. Another method was PAR, where the catalyst was reduced in situ 10 ml/min flow of 20 vol.% H_2 in N_2 at 3.0 kV for 2 h. After reduction, the plasma catalytic reaction was carried out in a DBD reactor. All experiments were carried out with a 1 g catalyst. The effect of reduction method of the catalysts on the methane conversion was shown in Table 2. Methane conversion was between 25.94 and 38.78% as the difference of metal species, metal loading and calcinations temperatures when the catalyst reduced at 400 °C for 2 h. As shown in Tables 1 and 2, the selectivities of alkanes such as C_2H_6, C_3H_8, and C_4H_{10} in the presence of Pt and Co catalyst were higher than those of alkane selectivity in the absence of catalyst. It is believed that the catalyst with plasma energy may play an important role to generate alkane from activated methyl radicals. Methane conversions showed similar ranges independent of the difference of metal species, metal

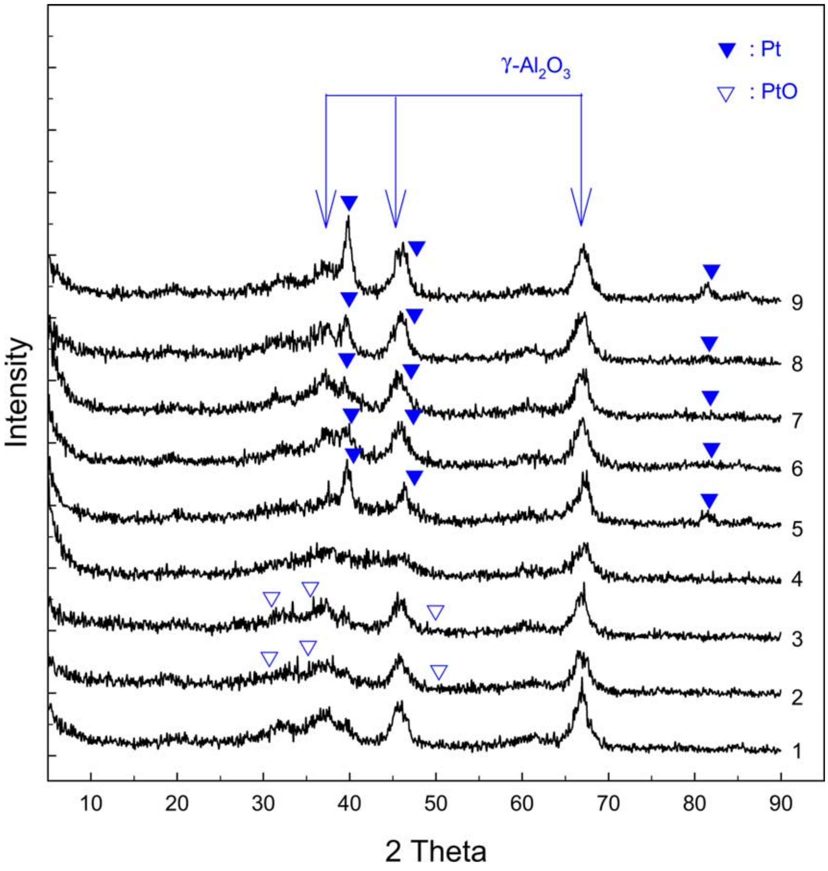

Fig. 5. XRD patterns for the catalysts of 3 wt.% Pt/γ-Al_2O_3: (1) γ-Al_2O_3; (2) 3 wt.% Pt/γ-Al_2O_3, 400 °C calcinations; (3) 3 wt.% Pt/γ-Al_2O_3, 500 °C calcinations; (4) 3 wt.% Pt/γ-Al_2O_3, 400 °C calcination, 400 °C reduction; (5) 3 wt.% Pt/γ-Al_2O_3, 400 °C calcination, PAR; (6) 3 wt.% Pt/γ-Al_2O_3, 400 °C calcination, 400 °C reduction, after reaction; (7) 3 wt.% Pt/γ-Al_2O_3, 500 °C calcination, 400 °C reduction, after reaction; (8) 3 wt.% Pt/γ-Al_2O_3, 400 °C calcination, PAR, after reaction; (9) 3 wt.% Pt/γ-Al_2O_3, 500 °C calcination, PAR, after reaction.

loading and calcinations temperatures. Overall methane conversion of plasma catalytic reaction after PAR is the similar values when the catalysts are reduced at 400 °C for 2 h.

As shown in Fig. 3, prepared catalysts were successfully reduced by PAR. In this course, extra heat was not applied, and input energy was only between 37 and 39 W. The results of plasma catalytic reaction showed similar characteristics when the catalysts were reduced by PAR and reduced at 400 °C for 2 h. The plasma catalytic reaction showed positive characteristics to produce light alkanes when Pt and Co catalyst were used after PAR in a DBD reactor. It is believed that the PAR is promising in reducing metal oxide catalyst.

The XRD analysis was carried out to investigate the structural characteristics of the catalysts reduced by PAR. The XRD patterns of 1 wt.% Pt/γ-Al_2O_3 and 3 wt.% Pt/γ-Al_2O_3 are shown in Figs. 4 and 5. Peaks with 36.72, 45.98 and 66.80 which are assigned to the 2θ values of fresh γ-Al_2O_3 phase. Peaks with 34.87, 30.05 and 50.06 are assigned to PtO phase. As can be seen in Fig. 4, XRD analysis did not show PtO peaks at different calcination temperatures. This means that Pt particles were well dispersed on γ-Al_2O_3. Peaks with 39.657, 46.260 and 81.467 are assigned to pure Pt phase. Pt peaks appeared after PAR, and higher Pt peaks appeared when the plasma catalytic reaction was carried out. It is considered that Pt particles migrated on alumina surface during the discharge, and then sintering occurred.

The XRD patterns of 5 wt.% Co/γ-Al_2O_3 are shown in Fig. 6. Peaks with 31.36, 36.88 and 65.36 are assigned to the 2θ values of Co_3O_4 phase, and peaks with 36.62, 42.66 and 61.06 are assigned to CoO phase. Co_3O_4 phase and CoO phase appeared when the Co catalyst was calcined at 400 and 500 °C. As shown in Fig. 2, a number of peaks showed in the TPR profile, and the broad peaks existed in Fig. 3. As mentioned above, a number of peaks in TPR profile and the broad peaks in PAR profile indicate the formation of different cobalt species during the calcination steps. Such a phenomenon can be identified from the analysis of XRD as shown in Fig. 6. Co catalyst showed higher CoO peaks after PAR and plasma catalytic reaction, but both of the catalysts, reduced by PAR and by thermal reduction, were showed the same pattern.

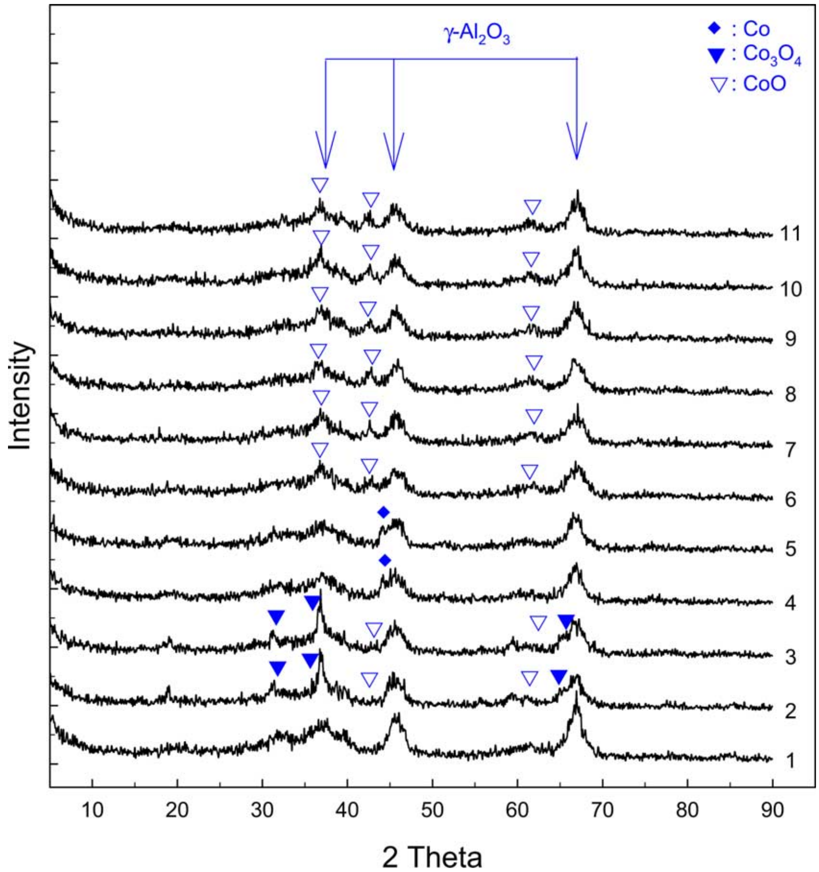

Fig. 6. XRD patterns for the catalysts of 5 wt.% Co/γ-Al_2O_3: (1) γ-Al_2O_3; (2) 5 wt.% Co/γ-Al_2O_3, 400 °C calcinations; (3) 5 wt.% Co/γ-Al_2O_3, 500 °C calcinations; (4) 5 wt.% Co/γ-Al_2O_3, 400 °C calcination, 400 °C reduction; (5) 5 wt.% Co/γ-Al_2O_3, 500 °C calcination, 500 °C reduction; (6) 5 wt.% Co/γ-Al_2O_3, 400 °C calcination, PAR; (7) 5 wt.% Co/γ-Al_2O_3, 500 °C calcination, PAR; (8) 5 wt.% Co/γ-Al_2O_3, 400 °C calcination, 400 °C reduction, after reaction; (9) 5 wt.% Co/γ-Al_2O_3, 500 °C calcination, 400 °C reduction, after reaction; (10) 5 wt.% Co/γ-Al_2O_3, 400 °C calcination, PAR, after reaction; (11) 5 wt.% Co/γ-Al_2O_3, 500 °C calcination, PAR, after reaction.

4. Conclusions

Plasma catalytic reaction was carried out in a dielectric-barrier discharge reactor. Plasma-assisted reduction (PAR) was applied to reduce Pt- and Co-based catalyst. The prepared catalyst was successively reduced by PAR. The selectivity of C_2H_6, C_2H_4 and C_2H_2 was higher among the produced hydrocarbons when the methane conversion was carried out in the absence of catalyst. In the presence of a Pt and Co catalyst, the main products of plasma catalytic reaction were the light alkanes such as C_2H_6, C_3H_8 and C_4H_{10}. Plasma catalytic reaction was carried out after PAR, and the selectivities of products showed similar to results as those reduced at 400 °C for 2 h. In the XRD analysis, metal peaks appeared after PAR and after the plasma catalytic reaction. It is assumed that metal particles migrated to the alumina surface during the dielectric-barrier discharge, and then sintering occurred. The plasma catalytic reaction showed positive characteristics to produce light alkanes when Pt and Co catalyst used after PAR. PAR was an effective method to reduce metal oxide catalyst.

Acknowledgements

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