Methane Conversion over Nanostructured Pt/γ-Al₂O₃ Catalysts in Dielectric-Barrier Discharge

Seung-Soo Kim†, Jinsoo Kim*, Hwaung Lee**, Byung-Ki Na*** and Hyung Keun Song**

Department of Environmental Engineering, Donghae University, 119, Jiheung-dong, Donghae, Gangwon-do 240-713, Korea
*College of Environment & Applied Chemistry, Kyung Hee University, Yongin-si, Kyunggi-do 449-701, Korea
**Clean Technology Center, Korea Institute of Science and Technology, P.O. BOX 131, Cheongryang, Seoul 136-650, Korea
***School of Chemical Engineering, ChungBuk National University,
San 48, Gaeshin-dong, Heungduk-gu, Cheongju, Chungbuk 371-763, Korea
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Abstract−Spherical nanostructured γ-Al₂O₃ granules were prepared by combining the modified Yoldas process and oil-drop method, followed by the Pt impregnation inside mesopores of the granules by incipient wetness method. Prepared Pt/γ-Al₂O₃ catalysts were reduced by novel method using plasma, which was named plasma assisted reduction (PAR), and then used for methane conversion in dielectric-barrier discharge (DBD). The effect of Pt loading, calcination temperature on methane conversion, and selectivities and yields of products were investigated. Prepared Pt/γ-Al₂O₃ catalysts were successfully reduced by PAR. The main products of methane conversion were the light alkanes such as C_2H_6, C_3H_8 and C_4H_{10} when the catalytic plasma reaction was carried out with Pt/γ-Al₂O₃ catalyst. Methane conversion was in the range of 38-40% depending on Pt loading and calcination temperature. The highest yield of C_2H_6 was 12.7% with 1 wt% Pt/γ-Al₂O₃ catalysts after calcinations at 500 °C.

Key words: Plasma-assisted Reduction, Dielectric-barrier Discharge, Pt Catalyst, Methane Conversion, Non-thermal Plasma, Boehmite Sols

INTRODUCTION

As fossil fuels such as oil and coal are depleted, the value of natural gas as an alternative fuel is becoming greater and greater [Liu et al., 1996, 2001; Larkin et al., 2001]. This is the reason why many researchers have been trying to convert methane, the main component of natural gas, to liquid fuels or more useful chemicals. But, there are numerous difficulties in doing so because of the stability of methane. Natural gas can be indirectly converted to liquid fuels or other chemicals by way of synthesis gas, or directly transformed to C_2 hydrocarbon or methanol. Most commercial natural gas converting processes convert methane to synthesis gas by steam reforming, and then synthesize methanol or gasoline by using this synthesis gas as an intermediate. Since the process producing synthesis gas by steam reforming of natural gas requires much endothermic heat, it needs considerable energies and high temperature over 800 °C. To overcome these problems, there have been many studies on the direct conversion method. Oxidative coupling [Safrank et al., 1987; Zhang et al., 1988, 2002; Lin et al., 1988, 1997; Inui et al., 1997], thermal coupling [Holmen et al., 1995], steam reforming [Nam et al., 2000], plasma [March et al., 1983; Chang et al., 1991; Liu et al., 1996, 1997; Marafee et al., 1997; Savinov et al., 1999; Jeong et al., 2001; Savinov et al., 2004] and so on have been tried for direct methane conversion.

Methane conversion with plasma has been widely studied as an alternative method. Especially, methane conversion and methane reforming with CO_2 have been extensively studied [Liu et al., 1996,

1997, 1998, 1999a, 2001; Larkin et al., 2001; Zhang et al., 2002; Eliasson et al., 2000; Thanyachotpaiboon et al., 1998]. Methane activation with non-thermal plasma is very effective not only in that methyl radicals could be easily made by the high energy of plasma, but also in that various kinds of chemical reactions could be induced through the high energy [Liu et al., 1998, 1999b; Eliasson et al., 2000; Thanyachotpaiboon et al., 1998]. The methyl radicals produced from plasma make C_2, C_3 and C_4 hydrocarbons by coupling with other methyl radicals [Liu et al., 1996, 1998]. However, the conversion was limited by the plasma power and the plasma reaction produced various kinds of by-product. Recently, to solve these problems, heterogeneous catalysts were introduced into the plasma reaction.

Liu et al. [1998, 1999] investigated the effect of zeolite on the plasma methane conversion. Also, metal oxide catalysts were widely used for producing high value-added compounds from methane [Jeong et al., 2001; Chen et al., 2001; Kim et al., 2004a, b]. Moreover, preparation of catalyst and surface treatment of catalyst have been attempted by using plasma energy [Li et al., 2004; Liu et al., 2002, 2004; Wang et al., 2004; Zhang et al., 2000; Heintze et al., 2002]. Li et al. [2003] reported that conversion of methane was increased by 5-10% by plasma treatment of Ni catalyst, maintaining the same selectivity of synthesis gas. Liu et al. [2004] also reported that Pd/HZSM-5 catalyst treated by glow discharge showed high catalytic activity and durability. In their work, the conversion of methane was almost 100% at 450 °C while the conversion was 50% without plasma treatment at the same conditions. In our previous work [Kim et al., 2004], the plasma-assisted reduction of novel metal catalyst was proposed by using dielectric-barrier discharge. The reduction of catalyst was completed rapidly in the plasma, and the selec-

†To whom correspondence should be addressed.
E-mail: ks7070@dreamwiz.com

tivity of alkane such as ethane and propane was highly increased.

Although the above mentioned plasma-catalytic reactions showed improved results, the catalysts used are in powder forms. For practical applications in large scale, spherical catalysts having the desired pore structures are preferred. In this study, spherical nanostructured Pt/γ-Al$_2$O$_3$ catalysts were prepared by combining the sol-gel granulation process and the incipient wetness method. Then, methane conversion on Pt/γ-Al$_2$O$_3$ catalysts using dielectric-barrier discharge was investigated. The effect of catalyst on methane conversion and product selectivities was studied.

EXPERIMENTAL

Spherical nanostructured Pt/γ-Al$_2$O$_3$ catalysts were prepared by Pt impregnation inside γ-Al$_2$O$_3$ granules. First, spherical γ-Al$_2$O$_3$ granules were prepared by combining the Yoldas process and oil drop method, modifying the recipe of Lin and co-workers [Deng and Lin, 1997; Buelna and Link, 1997]. Briefly, 2 M stable boehmite sols were synthesized from hydrolysis and condensation of aluminium isopropoxide (Aldrich, Mw=204.25, 98% purity; ALISOP), followed by peptization with 1 M HNO$_3$ at the molar ratio of [HNO$_3$]/ [AlOOH]=0.07. Stable 2 M boehmite sol was aged by adding 1 M HNO$_3$ to the volume ratio of acid/sol=0.2, followed by stirring at 75 °C until the mixture became so viscous that it could not be stirred even with magnetic stirring at maximum power. This partially gelled sol was transferred to droppers for the generation of sol droplets of about 5 mm in size. The sol droplets fell through a liquid bath consisting of a paraffin oil layer (30 cm height) and a 10 wt% ammonia solution layer (10 cm height). After aging 1 h in the ammonia solution, the granules were then collected with a sieve and washed several times with alcohol and distilled water. Spherical γ-Al$_2$O$_3$ granules were obtained after these wet particles were dried in air at 40 °C for 48 h and calcined in air at 450 °C for 3 h.

For the Pt impregnation, Pt solution was prepared by dissolving H$_2$PtCl$_6$·6H$_2$O in distilled water. Then, this solution was impreg-nated into prepared spherical γ-Al$_2$O$_3$ granules. Impregnated alumina granules were calcined at 400 °C, 500 °C or 600 °C for 2 h with oxygen flow rate of 100 ml/min.

Fig. 1 shows the experimental apparatus for catalytic plasma reactions. A quartz tube with an i.d. of 8 mm and length of 270 mm was used for Dielectric-Barrier Discharge reactor. An inner electrode (two stainless steel wires) was installed in the quartz tube, and the diameter of the electrode was 0.45 mm. The outer surface of the quartz tube was coated (200 mm) with silver paste as another electrode. In this work, an AC pulse power supply (ITM) with [0-10 kV, 10-40 kHz, 2-5 μs] was used. The flow rate of methane was controlled by the mass flow controller (Bronkhorst, B-5534-FA). The reaction products of hydrocarbons were analyzed with a gas chromatograph (HP 5890 equipped with a Haysep Q packed column and FID detector). A gas chromatograph (Younglin M600D) equipped with TCD was used to analyze the produced hydrogen and to run plasma assisted reduction (PAR). The peaks of product were identified with the standard gases (CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_4$, C$_3$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$) which had purity above 99.5%.

Catalyst of 0.3 g packed the lower part of the DBD reactor for catalytic plasma reaction, 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:

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

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:

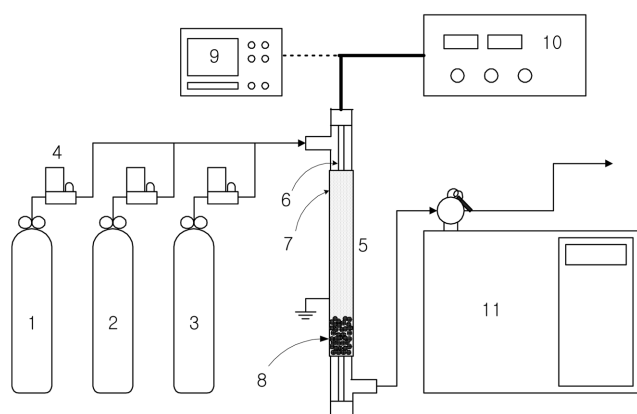$$\text{Yields of } C_xH_y = \text{Conversion of } CH_4 \times \text{Selectivity of } C_xH_y.$$

Fig. 1. Schematic diagram of experimental apparatus.

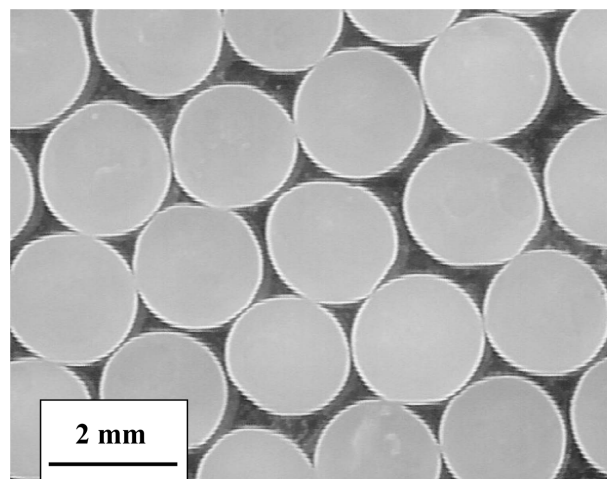|	
1. Methane	7. Outer electrode
2. Hydrogen	8. Catalyst bed
3. Nitrogen	9. Oscilloscope
4. Mass flow controller	10. Power supply
5. DBD reactor	11. GC
6. Inner electrode	

Fig. 2. Appearance of spherical nanostructured γ-Al$_2$O$_3$ granules.

RESULTS AND DISCUSSION

Fig. 2 shows the appearance of the spherical γ-Al$_2$O$_3$ granules prepared by the sol-gel/oil-drop method. When the sol droplets fell through the liquid bath, the paraffin oil layer facilitated the droplets into spherical wet-gel granules by surface tension and the ammonia layer strengthened the structure of the wet-gel particles by aging. The granule diameter was about 2 mm, which is ideal for use in the moving or fluidized bed reactors for large scale applications. The granules are made of nanoscale γ-Al$_2$O$_3$ crystallites, which are bound together during the calcination step which causes coarsening and sintering. Such a unique microstructure gives rise to a strong bonding between the primary particles and provides excellent mechanical strength. The Pt loading inside mesopores of the granules could be precisely controlled by the incipient wetness method. Because of the nanoscale primary crystallite size, the Pt/γ-Al$_2$O$_3$ granules offer very narrow pore size distribution in the range of 2-6 nm as shown in Fig. 3.

Plasma treatment is one of novel methods for preparation and reduction of catalysts. Non-thermal plasma makes large amounts of free electrons which have high energy. The produced high energy electrons are used to activate other molecules. In a plasma state, hydrogen can be easily activated by high energy electrons, which can lead to reducing metal oxide catalyst. Generally, metal oxide catalysts are reduced at high temperature in a hydrogen atmosphere. A catalyst surface (metal oxide) in contact with highly activated hydrogen can be reduced. In this work, plasma was applied to reduce prepared Pt/γ-Al$_2$O$_3$ catalysts in a dielectric-barrier discharge reactor.

Plasma-assisted reduction of metal oxide catalyst was carried out at a flow rate of 10 ml/min 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 in the range of 37-39 W with the variation of experimental conditions. The power was measured by oscilloscope (Agilent, 54641A) with integration of voltage and current.

The results of PAR for Pt/γ-Al$_2$O$_3$ catalysts are shown in Fig. 4. The reduction profile of Pt/γ-Al$_2$O$_3$ catalysts consists of one peak during PAR. Most of hydrogen consumption for 1 wt% Pt/γ-Al$_2$O$_3$
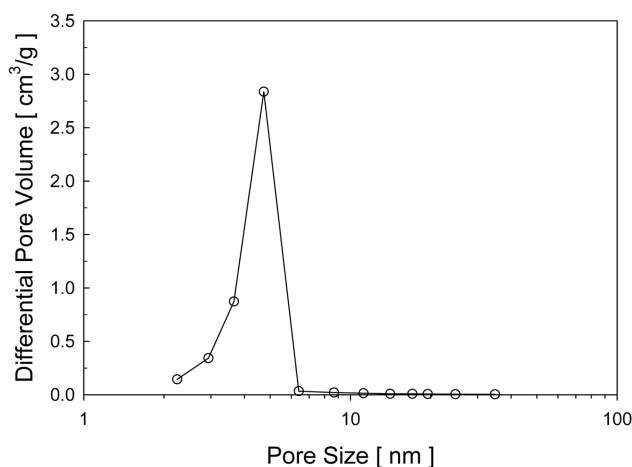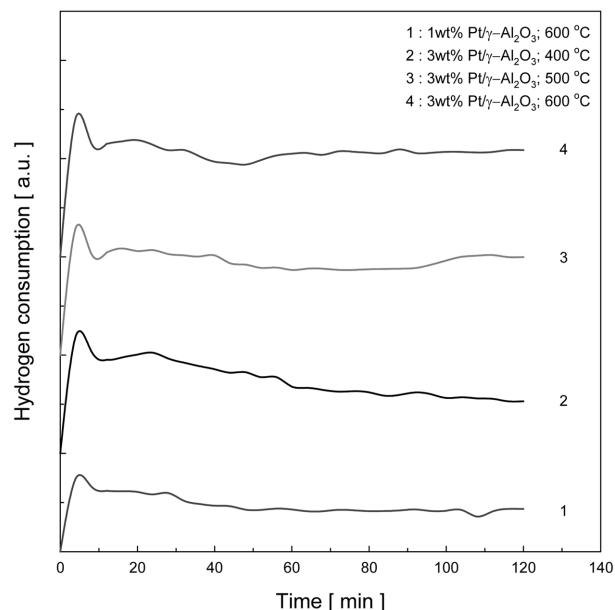

Fig. 4. **Plasma-assisted reduction profile of prepared catalysts (Pt/ γ-Al₂O₃); hydrogen and nitrogen flow rate=10 ml/min (20 vol% H₂ in N₂).**

catalysts occurred within 10 min, and it was prolonged 30 min. The reduction of 3 wt% Pt/γ-Al$_2$O$_3$ catalysts calcined at 400 °C was prolonged for 60 min. In contrast, the catalysts calcined at 500 °C and 600 °C reduced quickly compared to those calcined at 400 °C. In the case of Pt/γ-Al$_2$O$_3$ catalysts, most of the hydrogen was consumed within 40 min and the shape of reduction profiles was similar although the calcination temperature and the metal loading were varied. In our previous work, γ-alumina, which was used as a support, was sieved 20-42 mesh and calcined at 700 °C for 2 h [Kim et al., 2004]. 1 wt% Pt/γ-Al$_2$O$_3$ catalyst was mainly reduced within 20 min, and 3 wt% Pt/γ-Al$_2$O$_3$ was reduced within 30 min.

The effects of metal loading and calcination temperature on methane conversion and product selectivity were examined. The experimental results are showed in Table 1. Prepared catalysts were reduced by PAR at 3.0 kV for 2 h with reduction gases. After reduction, the plasma catalytic reaction of methane was carried out *in situ* with a flow rate of 30 ml/min at the applied voltage of 3.0 kV. All experiments were carried out with 0.3 g catalyst. To verify the effect of catalysts, a blank experiment was carried out without catalysts. Methane conversion was 36.7% when the catalyst was absent. The selectivity of C$_2$H$_6$, C$_2$H$_4$ and C$_2$H$_2$ was higher among the produced hydrocarbons, which were 15.4%, 9.7% and 12.7%, respectively. Also, the selectivity of hydrogen showed a high value of 47.5%.
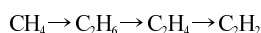
The methane conversions were 32.7%, 33.0% and 31.9%, when 1 wt% Pt/γ-Al$_2$O$_3$ catalysts were calcined at 400 °C, 500 °C and 600 °C, respectively. The methane conversion for 3 wt% Pt/γ-Al$_2$O$_3$ catalysts showed very similar values according to calcination temperature. This indicates that the methane conversion was not affected much by the calcination temperature of Pt/γ-Al$_2$O$_3$ catalysts. However, methane conversion for 3 wt Pt/γ-Al$_2$O$_3$ catalysts was slightly increased compared to that for 1 wt% Pt/γ-Al$_2$O$_3$ catalysts. It is attributed to the increase of Pt loading, since Pt is an active site for methane conversion. The main products in the dielectric-barrier dis-

Fig. 3. **Pore size distribution of Pt/γ-Al₂O₃ catalysts prepared by sol-gel granulation process.**

Table 1. Effect of Pt loading and calcination temperatures on methane conversion and selectivity (methane flowrate: 30 ml/min)

	Pt loading (wt%)	Calcination temperature (°C)	Methane conversion (%)	Selectivities (%)						
				C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	H_2
	Without catalyst		36.7	15.4	9.7	12.7	3.7	1.9	2.0	47.5
Spherical γ-Al$_2$O$_3$ granule	1 wt% Pt/γ-Al$_2$O$_3$	400	32.7	32.9	0.6	-	15.4	1.0	14.1	15.5
		500	33.0	39.5	0.78	-	11.0	0.4	7.1	15.0
		600	31.9	34.5	0.5	-	15.3	0.3	7.1	15.7
	3 wt% Pt/γ-Al$_2$O$_3$	400	35.2	30.3	0.4	-	13.4	0.3	9.6	15.2
		500	36.4	27.6	0.4	-	13.1	0.3	9.6	15.3
		600	36.0	30.2	0.5	-	12.9	0.3	9.7	14.9
20-42 mesh γ-Al$_2$O$_3$[a]	3 wt% Pt/γ-Al$_2$O$_3$	500	33.7	39.2	1.0	0.4	17.7	1.1	12.6	35.8

[a]Catalysis Today 89 (2004) 193-200.

charge were C_2 hydrocarbons without catalyst. In previous works, we have investigated the reaction pathways and kinetics of methane decomposition in a dielectric-barrier discharge. We suggested a simplified reaction pathway as follows [Kim et al., 2003a, b]:

$$CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2$$

Meanwhile, reaction pathways seemed to be changed when Pt/γ-Al$_2$O$_3$ catalysts were used in a DBD reactor. Acetylene (C_2H_2) was not produced among the reaction products, and main products were light alkane such as C_2H_6, C_3H_8 and C_4H_{10}. The highest selectivity of C_2H_6 was 39.5% when 1 wt% Pt/γ-Al$_2$O$_3$ catalyst calcined at 500 °C were used. This value was 2.56 times higher compared to that without catalyst. The selectivity of C_3H_8 was 6.2%, which was 2.94 times higher compared to that measured without catalyst. In the previous work, 1 wt% Pt/γ-Al$_2$O$_3$ catalysts were prepared by incipient wetness method with 20-40 mesh ground alumina [Kim et al., 2004]. The main products were also light alkane when the prepared catalyst was used after calcination at 500 °C.

Fig. 5 depicts the yield of main products from catalytic plasma reaction. The data plotted in the figure have been extracted from those given in Table 1. The highest C_2H_6 yield was 13.0% when 1 wt% Pt/γ-Al$_2$O$_3$ catalysts were used after calcination at 500 °C. It showed that the yields of products were not much affected by calcination temperatures for 3 wt% Pt/γ-Al$_2$O$_3$ catalysts.
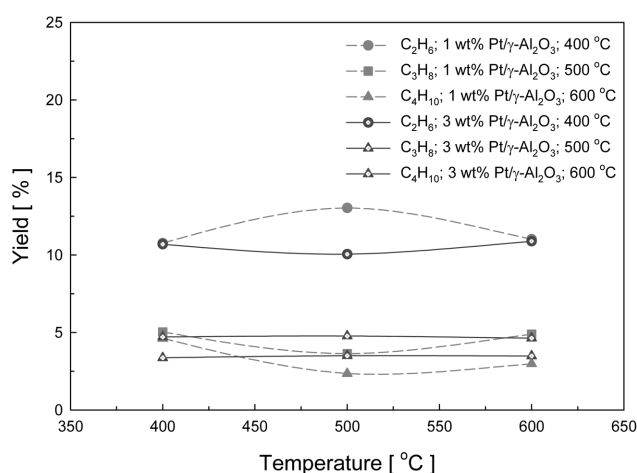

Fig. 5. Effects of the Pt loading and calcination temperature on the yield of ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}); methane flow rate=30 ml/min; after PAR.

Table 2 represents surface area, pore volume and pore size of the Pt/γ-Al$_2$O$_3$ catalysts after calcination at various temperatures. Surface area decreased with increasing calcination temperatures, and the surface area did not much change after PAR. The pore struc-

Table 2. Physical characteristics of prepared Pt/γ-Al$_2$O$_3$ catalyst

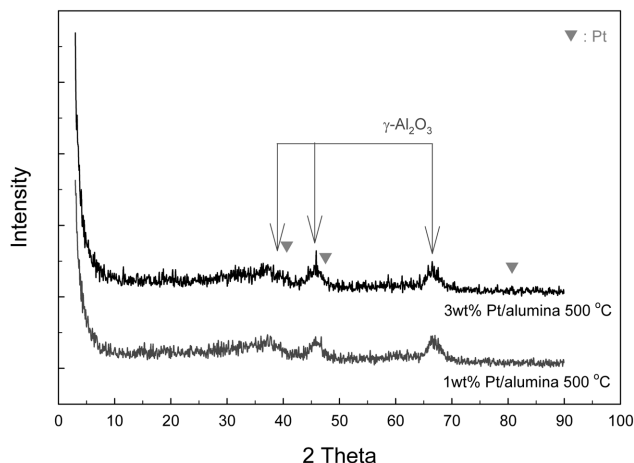|	Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Before PAR	1 wt% Pt/γ-Al$_2$O$_3$, 400 °C	369	0.54	5.9
	1 wt% Pt/γ-Al$_2$O$_3$, 500 °C	315	0.50	6.4
	1 wt% Pt/γ-Al$_2$O$_3$, 600 °C	280	0.50	7.2
After PAR	1 wt% Pt/γ-Al$_2$O$_3$, 400 °C	345	0.50	5.8
	1 wt% Pt/γ-Al$_2$O$_3$, 500 °C	312	0.50	6.4
	1 wt% Pt/γ-Al$_2$O$_3$, 600 °C	273	0.49	7.2
Before PAR	3 wt% Pt/γ-Al$_2$O$_3$, 400 °C	337	0.47	5.5
	3 wt% Pt/γ-Al$_2$O$_3$, 500 °C	319	0.48	5.9
	3 wt% Pt/γ-Al$_2$O$_3$, 600 °C	285	0.47	6.6
After PAR	3 wt% Pt/γ-Al$_2$O$_3$, 400 °C	336	0.47	5.6
	3 wt% Pt/γ-Al$_2$O$_3$, 500 °C	321	0.48	5.9
	3 wt% Pt/γ-Al$_2$O$_3$, 600 °C	282	0.48	6.8

Fig. 6. XRD patterns for the Pt/γ-Al₂O₃ catalysts prepared by sol-gel granulation process.

ture of Pt/γ-Al$_2$O$_3$ catalysts was mainly affected by calcination temperature and slightly by Pt loading. With increasing calcination temperatures, the crystallite size of the catalysts grew, resulting in a decrease of surface area. Also, the pore size increased during calcination of catalysts because of micro-pore enlargement and collapse. In Table 2, pore size was increased according to the increase of calcination temperature. In contrast, pore volume of catalysts was hardly affected with Pt loading and calcination temperature. It is believed that micro-pores of catalyst were enlarged because of increasing calcination temperature. From Table 1, the highest selectivity of C$_2$H$_6$ obtained when 1 wt% Pt/γ-Al$_2$O$_3$ catalysts were used after calcinations at 500 °C. However, the physical properties of the catalysts were very similar with other catalysts, as shown in Table 2.

The XRD analysis was carried out to investigate the phase structure of the prepared catalysts. The XRD patterns of 1 wt% and 3 wt% Pt/γ-Al$_2$O$_3$ catalysts are shown in Fig. 6. Both catalysts were calcined at 500 °C and reduced by PAR. Peaks with 36.7, 46.0 and 66.8 are assigned to the 2θ values of fresh γ-Al$_2$O$_3$ phase. Peaks with 30.1, 34.9 and 50.1 are assigned to PtO phase, and peaks with 39.7, 46.3 and 81.5 are assigned to pure Pt phase. As can be seen in Fig. 6, XRD analysis did not show PtO and Pt peaks at different Pt loading. This means that not only were Pt particles well dispersed on γ-Al$_2$O$_3$ but also Pt/γ-Al$_2$O$_3$ catalysts were reduced well by PAR.

CONCLUSIONS

Plasma catalytic reaction was carried out on spherical nanostructured Pt/γ-Al$_2$O$_3$ catalysts in a dielectric-barrier discharge reactor. Nanostructured Pt/γ-Al$_2$O$_3$ catalysts with 2 mm diameter were prepared by combining the sol-gel granulation process and the incipient wetness method. Plasma-assisted reduction was applied to reduce Pt/γ-Al$_2$O$_3$ catalysts, and prepared catalysts were successively reduced by PAR in a dielectric-barrier discharge reactor.

The selectivities of C$_2$H$_6$, C$_2$H$_4$ and C$_2$H$_2$ were higher among the produced hydrocarbons when the methane conversion was carried out in the absence of catalyst. In the presence of Pt/γ-Al$_2$O$_3$ catalysts, however, the main products were the light alkanes such as C$_2$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$. The highest yield of C$_2$H$_6$ was 13.0% when

1 wt% Pt/γ-Al$_2$O$_3$ catalysts were used after calcination at 500 °C.

Pore structures of the catalysts were mainly affected by calcination temperature, and slightly by Pt loading. The surface area decreased with increasing calcination temperature due to the crystallite growth. However, the pore volume showed similar values under investigated conditions. XRD analysis showed qualitative results that Pt particles were well dispersed on γ-Al$_2$O$_3$, and prepared Pt/γ-Al$_2$O$_3$ reduced well by PAR.

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