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Direct Conversion of Methane Over Oxide-Type Catalysts Supported on Mesoporous Silica Under Electric Discharge

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Direct conversion of methane over oxide-type catalysts supported on mesoporous material under the dielectric barrier discharge plasma was investigated in the present study. The oxide catalysts (MgO and NiO) supported on SBA-15 was prepared by a hydrothermal and wet-impregnation method. The low-angle XRD patterns and TEM indicate that the ordered mesoporous structure was well maintained during the catalyst preparation and reaction processes. We also conducted direct conversion of methane using the catalysts under the plasma. As a result, the specific surface area of bare SBA-15 was much higher than that of the NiO/SBA-15, followed by MgO/SBA-15. Overall, the CH₄ conversion increased with increasing the specific surface area. And C₂ selectivity decreased with increasing the specific surface area.

Keywords: Mesoporous Silica, Oxide-Type Catalyst, Direct Conversion of Methane.

1. INTRODUCTION

Natural gas is discharged as a by-product of oil field or deposited in a stranded and associated gas field that is difficult in practical use due to a local restriction. Recently, a technology converting natural gas into clean petroleum fuels has received a great attention. In addition, natural gas conversion technologies are being commercialized by world major oil companies due to technical and political merits such as the use of medium and small gas resources and the countermeasure against depletion of fossil fuels. In general, methane that is a major ingredient of natural gas can be synthesized into a clean fuel through a variety of processes.^{1,2} Recently, direct conversion of methane into hydrocarbons higher than C_2 has been actively studied as an alternative to the above complex processes.

However, the direct conversion of methane is highly endothermic reaction so that the temperature higher than 600 °C is required.

When methane is thermally activated, however, the catalyst should be prevented from sintering and degradation at the high temperature.^{3,4} Most of all, non-thermal plasma has been attracted as an alternative process for the methane activation.⁵ Methane can be ionized into methyl radicals by electron-impact ionization under the plasma, and then methyl radicals can be dimerized easily into C_2H_6 as expressed in Eqs. (1) and (2).

$$CH_4 + e \to CH_3 + H + e \tag{1}$$

$$CH_3 + CH_3 + e \to C_2H_6 + e \tag{2}$$

Among non-thermal plasmas, DBD (dielectric barrier discharge) plasma is suitable to the plasma catalysis because the plasma distribution is more uniform than others.⁶ The DBD plasma has a dielectric barrier between high voltage and ground electrodes, which play a role to prevent it from being developed into the arc. In DBD, nonequilibrium discharge takes place and high-temperature electrons are formed by micro discharges. Thus, the chemical reaction can be initiated by the plasma below the temperature required for the reaction to be activated. The selection of catalyst is limited to reduce the activation energy for the reaction to be selective to desirable species. Therefore, the hybrid reaction of plasma and catalyst realizes interactive synergetic effects with high reactivity at low temperature.⁷ In the present study, the direct conversion of methane on the mesoporous silica under the plasma was carried out. Catalyst/SBA-15 was characterized by XRD, TEM, and N₂ adsorption-desorption.

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2. EXPERIMENTAL DETAILS

2.1. Preparation of Mesoporous Silica (SBA-15)

The mesoporous silica (SBA-15) was synthesized by hydrothermal method using the guideline reported in the literature regarding SBA-15 molecular sieve.⁸ In a typical synthesis, triblock-poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$, Pluronic P123) of 4 g was added to deionized water of 90 ml heated by 40 °C, and the mixture was stirred at the stirring speed of 250 rpm for 30 minutes. After 4M HCl (60 mL) and tetraethyl orthosilicate (TEOS, 9.8 mL) were added to the prepared aqueous solution, and was aged under the stirring at 300 rpm for 24 hours. After the prepared aqueous solution was separated and filter through D.I water, the aqueous solution were dried at 100 °C for 20 hours.

The powder obtained after drying was calcined in air at 550 °C for 6 hours. The calcination temperature was raised with the rate of 1.5 °C/min. Finally, the MgO and NiO catalyst was coated on the prepared SBA-15 using a wet-impregnation method. The precursor solution was prepared by dissolving Ni(NO₃)₂ and Mg(NO₃)₂ in D.I water. SBA-15 was immersed into the precursor solution. After impregnation, the catalysts were dried at 100 °C for 24 h and calcined in air condition.

2.2. Plasma System

Figure 1 shows the schematic of plasma system and DBD reactor. A quartz tube was used as the reactor, in which the catalyst/SBA-15 sample was packed. The reactor wall also plays a role as the dielectric barrier of the DBD reactor. Two electrodes were used; one was inserted in the middle of the reactor and the other was a wrapped around the outer wall of the reactor. A flange, which is not electrically conducting, was installed at the lower part of reactor to fix the catalyst pellet. The flange was also used to fix the electrode precisely at the middle of the reactor because the electric discharge can be distorted if the gap between the two electrodes was 6 mm, between which a 0.15 g catalyst pellet was packed. The discharge voltage was fixed to



Figure 1. Schematic diagram of the experimental apparatus for the direct conversion of methane under the electric discharge.

7 kV with sine waveform and the discharge frequency was fixed 1.5 kHz.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalyst/SBA-15

Figure 2 shows the low-angle and the wide-angle XRD pattern of catalyst/SBA-15. Figure 2(a) shows the three distinct peaks was observed at the Bragg angle $(2\theta) = 0.87^{\circ}$, 1.52°, and 1.74° that are associated with (1 0 0), (1 1 0) and (2 0 0) reflection planes. These peaks represent the characteristic diffraction patterns of the well-ordered 2D hexagonal structure with the P6 mm symmetry of SBA-15. And, Figure 2(b) shows the wide-angle XRD patterns of catalyst/SBA-15. A broad peak centered at 22.2° of 2θ was observed for all the samples. In the XRD pattern of NiO/SBA-15, the peak at $(2\theta) = 37^{\circ}$, 43°, 62°, 75 and 79° could be assigned to NiO (PDF#44-1159).

Also, no MgO crystallization is detected in the wideangle XRD patterns of MgO/SBA-15, implying the good dispersion of MgO/SBA-15.

The tendency similar with the XRD results could be predicted by TEM image of catalyst/SBA-15 as shown in Figure 3. The textural characteristics of catalyst/SBA-15 were characterized by the N₂ adsorption–desorption method. The specific surface area (S_{BET}), pore volume (V_{total}), mean pore diameter (d_p), pore size distribution of catalysts are summarized in Figure 4.

3.2. Catalytic Performance of Oxide/SBA-15

The effect of the presence of catalyst species on the direct conversion of methane under the plasma is investigated. As a result, the contrast tendency with the methane conversion could be predicted by C_2 selectivity



Figure 2. XRD patterns catalyst/SBA-15 samples: (a) low angle XRD pattern and (b) wide-angle XRD patterns.

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Figure 3. TEM images of catalyst/SBA-15: (a) bare/SBA-15, (b) NiO/SBA-15 and (c) MgO/SBA-15.

of SBA-15 according with the catalysts. The methane conversion of bare SBA-15 was much higher than that of the NiO/SBA-15, followed by MgO/SBA-15, as shown Figure 5. However, maximal C_2 selectivity was achieved



	$S_{BET} (m^2 \cdot g^{-1})$	$V_{total}(cm^3 \cdot g^{-1})$	$D_p(nm)$
MgO/SBA-15	139.54	0.2578	7.3889
NiO/SBA-15	280.16	0.3948	5.6371
Bare./SBA-15	515.93	0.6539	5.0696

Figure 4. Textural characteristics and pore size distributions of catalyst/SBA-15.

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Figure 5. Catalytic performance of the direct conversion of methane under the plasma at different oxide/SBA-15.

when MgO/SBA-15 was used, followed by NiO/SBA-15 and bare SBA-15. Overall, the CH_4 conversion increased with increasing the specific surface area. And C_2 selectivity decreased with increasing the specific surface area.

The formation of C_2 hydrocarbons is explained by the free-radical mechanism of CH4 precursors that precede in stepwise dehydrogenation reactions: $CH_4 \rightarrow CH_3 \rightarrow$ $C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2$. Plasma can enhance the adsorption intensity on the surface of SBA-15 by producing electrons with wide energy distribution expressed typically by the Maxwellian or Druvestyne distribution.⁹ In DBD, the mean electron energy is approximately $1 \sim 3$ eV and only a small portion of the electrons have energy strong enough to break atomic bonds. Most of the electrons with smaller energy (<1 eV) are used in vibrational excitation.¹⁰ Vibrationally-excited species are more prone to react and have lower activation energy for adsorption and reaction than that of ground state species.¹¹ This effect can enhance the overall reaction rate considerably resulting in a higher conversion.

4. CONCLUSION

The synergetic effect between plasma and catalyst/SBA-15 for the direct conversion of methane was investigated. The methane conversion of bare SBA-15 was much higher than that of the catalyst/SBA-15. In contrast, maximal C_2 selectivity was achieved when MgO/SBA-15 was used, followed by NiO/SBA-15, bare SBA-15. Overall, the CH₄ conversion increased with increasing the specific surface area. And C_2 selectivity decreased with increasing the specific surface area. Consequently, the direct conversion of methane can be more improved by the plasma catalysis on a mesoporous material.

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