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Plasma catalytic methane conversion over sol–gel derived Ru/TiO_2 catalyst in a dielectric-barrier discharge reactor

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Abstract

Plasma catalytic methane conversion was carried out in the presence of sol–gel derived Ru/TiO_2 catalysts within a dielectric-barrier discharge (DBD) reactor. Plasma-assisted reduction (PAR) was applied to reduce the prepared Ru/TiO_2 catalysts in DBD reactor, and most of the catalysts were successively reduced by PAR within 15 min. The highest methane conversion was obtained when 5 wt% Ru/TiO_2 catalysts were used after calcination at 400 °C. The selectivities of light alkanes (C_2H_6, C_3H_8, C_4H_{10}) were highly increased when Ru/TiO_2 catalysts were used in DBD reactor.

Keywords: Plasma catalytic reaction; Methane conversion; Dielectric-barrier discharge; Ru/TiO_2 catalyst

1. Introduction

The conversion of methane has been widely investigated in the field of C_1 chemistry using conventional catalysis. Direct methane conversion to higher hydrocarbons needs intensive energy consumption because of the stable C–H bonds in the methane molecules [1]. Methane activation with plasma energy is a very effective method because methyl radicals can be easily formed and various kinds of chemical reactions can be induced by the high energy of electrons. In the plasma reactor, energetic electrons collide with methane molecules, resulting in activated C_1 species, which can make higher hydrocarbons. 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 have been introduced into the plasma reaction [2–10]. This catalysis-assisted plasma technology not only enhances the decomposition efficiency catalytically, but also reduces the by-products selectively. Combining plasma with a heterogeneous catalyst has been studied as an alternative method for valuable products. Liu et al. [5] reported that high catalytic activity and durability were obtained using Pd/HZSM-5 catalyst treated by glow discharge. 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 works [8–10], methane conversion over nanostructured $Pt/\gamma\text{-}Al_2O_3$ and $Ru/\gamma\text{-}Al_2O_3$ catalysts were carried out in dielectric-barrier discharge (DBD) reactor. In general, the methane conversion with catalysts was much higher compared to that obtained without catalysts. For $Pt/\gamma\text{-}Al_2O_3$ catalysts, methane conversion was increased with the increase of Pt loading on $\gamma\text{-}Al_2O_3$ and catalyst weight in DBD reactor [10]. The highest C_2H_6 selectivity was 50.3% when 3 wt% $Pt/\gamma\text{-}Al_2O_3$ catalyst was used after calcination at 300 °C.

In this work, we have investigated plasma catalytic reaction of methane with sol–gel derived Ru/TiO_2 catalysts in a DBD reactor at atmospheric pressure. Plasma-assisted

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reduction (PAR), which is a novel method to reduce metal oxide catalysts using plasma energy, was applied to reduce prepared catalysts in DBD reactor. The effects of Ru loading and calcination temperature of Ru/TiO_2 catalysts on methane conversion were studied.

2. Experimental

Sec-butanol (Yakuri pure chemicals co., LTD, 99.0%), titanium (IV) isoproxide ($Ti[O(CH_2)_3CH_3]_4$, Aldrich Chem. Co., 97.0%), acetone (J.T. Baker, 99.8%) and methanol (J.T. Baker, 99.8%) were used to prepare sol–gel derived Ru/TiO_2 catalysts. As a Ru precursor, ruthenium (III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$ Aldrich Chem. Co., 99.95%) was used. Sol–gel derived Ru/TiO_2 catalysts were prepared as shown in Fig. 1. After this process, the obtained gel was dried in the oven at 120 °C for 24 h, and then it was sieved 20–42 mesh, followed by calcination at various temperatures of 400, 500 and 600 °C for 2 h with oxygen flow at 100 ml/min in tubular furnace. The product Ru/TiO_2 catalysts as well as TiO_2 catalysts were used for methane conversion in DBD reactor.

DBD reactor for plasma catalytic reaction of methane consists of 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 inside the quartz tube as an electrode. The outer surface of quartz tube was coated with silver paste (200 mm) which served as another electrode. An AC pulse power supply with 0–10 kV of voltage (ITM), 10–40 kHz of frequency and 2 μs of pulse width was used in this experiment. The applied power was measured using an oscilloscope (Agilent, 54641A) by integrating the single period power and multiplying the frequency as shown in Eq. (1) [11,12].

$$P = \left(\int_{t_1}^{t_2} V(t)I(t)\mathrm{d}t \right) f \qquad (1)$$

where $V(t)$ is the voltage as a function of time, $I(t)$ denotes the current as a function of time, and f is the frequency. The applied power was in the range of 37–39 W according to the experimental conditions.

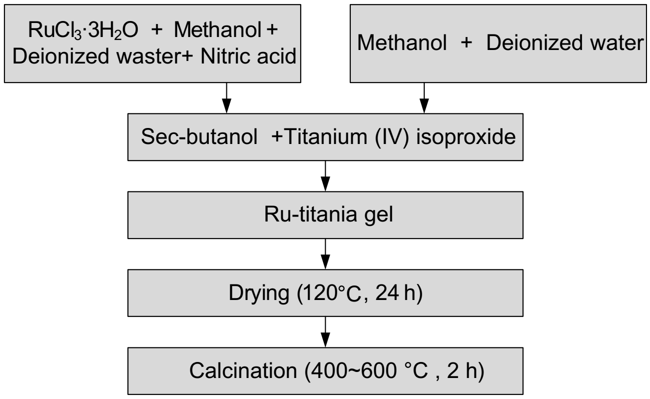

Fig. 1. Preparation procedure of sol–gel derived Ru/TiO_2 catalyst.

The flow rate of methane was controlled by the mass flow controller (Bronkhorst, B-5534-FA). The reaction products were analysed with the 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 analyse the produced hydrogen and to monitor hydrogen consumption for catalyst reduction. The peaks of the products were identified using 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}) having purities above 99.5%.

Feed gas was pure methane, and methane conversion was defined as

$$\%\ \text{conversion of } CH_4 = \frac{\text{moles of } CH_4 \text{ consumed}}{\text{moles of } CH_4 \text{ introduced}} \times 100 \qquad (2)$$

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

$$\%\ \text{selectivity of } C_xH_y = x \cdot \frac{\text{moles of } C_xH_y \text{ formed}}{\text{moles of } CH_4 \text{ consumed}} \times 100 \qquad (3)$$

The selectivity of hydrogen is

$$\%\ \text{selectivity of } H_2 = 0.5 \times \frac{\text{moles of } H_2 \text{ formed}}{\text{moles of } CH_4 \text{ consumed}} \times 100 \qquad (4)$$

The yields of hydrocarbons are

$$\%\ \text{yields of } C_xH_y = \text{Selectivity of } C_xH_y \times \text{conversion of } CH_4 \qquad (5)$$

3. Results and discussion

XRD analysis was performed to investigate the phase structures of the prepared Ru/TiO_2 catalysts. As shown in Fig. 2, the XRD patterns did not show any distinguishable peaks other than those of anatase and rutile phases at different Ru loadings. The absence of any detectable Ru

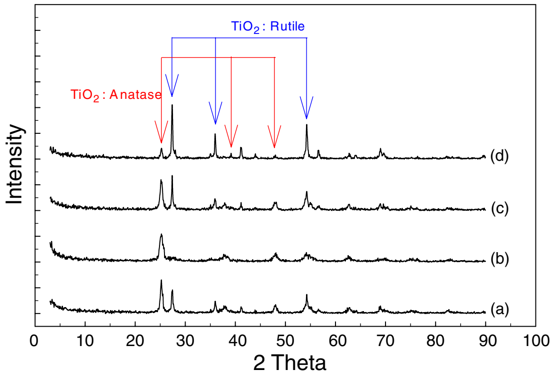

Fig. 2. XRD patterns for sol–gel derived Ru/TiO_2 catalysts: (a) 3 wt% Ru/TiO_2 (400 °C), (b) 5 wt% Ru/TiO_2 (400 °C), (c) 5 wt% Ru/TiO_2 (500 °C), and (d) 5 wt% Ru/TiO_2 (600 °C).