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The simultaneous activation of methane and carbon dioxide to C_2 hydrocarbons under pulse corona plasma over $La_2O_3/\gamma\text{-}Al_2O_3$ catalyst

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Abstract

The pulse corona plasma has been used as an activation method for reaction of methane and carbon dioxide, the product was C_2 hydrocarbons and by-products were CO and H_2. Methane conversion and the yield of C_2 hydrocarbons were affected by the carbon dioxide concentration in the feed. The conversion of methane increased with increasing carbon dioxide concentration in the feed whereas the yield of C_2 hydrocarbons decreased. The synergism of $La_2O_3/\gamma\text{-}Al_2O_3$ and plasma gave methane conversion of 24.9% and C_2 hydrocarbons yield of 18.1% were obtained at the power input of plasma was 30 W. The distribution of C_2 hydrocarbons changed by using $Pd\text{-}La_2O_3/\gamma\text{-}Al_2O_3$ catalyst, the major C_2 product was ethylene. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pulse corona plasma; Catalyst; Methane; Carbon dioxide

1. Introduction

The oxidative coupling of methane (OCM) to C_2 hydrocarbons is a potentially attractive industrial process. A large amount of researches have been reported and a number of catalysts have been used for this reaction since the pioneer works of Keller and Bhasin [1,2]. The activation of methane by using oxygen was effective, but the yield of C_2 hydrocarbons was not high enough for the non-selective oxidation of methyl radicals with oxygen in the gas phase, [3] especially when the concentration of oxygen is high. At the same time, carbon dioxide, the main by-product of this reaction, is undesirable from the environmental point of view. If we choose less reactive carbon dioxide as an oxidant instead of oxygen for the oxidative coupling of methane, the selectivity of C_2 hydrocarbons will increase because gas phase radical reactions which result in the decrease in C_2 hydrocarbons selectivity would not occur in this case. On the other hand, carbon monoxide would be the main by-product. Only a few research papers report for using carbon dioxide as an oxidant in the oxidative coupling of methane [4–9]. Asami reported that the rare-earth oxides such as yttrium, lanthanum and samarium showed relatively high C_2 selectivity (about 30%) with stable catalytic activity by using carbon dioxide as an oxidant under the conditions of 0.1 MPa and CH_4/CO_2 molar ratio of 1 at 850 °C, but the conversion of methane was less than about 2% [4]. Wang and Chen have reported respectively that CaO/CeO_2 and La_2O_3/ZnO gave C_2 selectivity of more than 90%, the methane conversion was about 3% [7–9]. This indicates that the selectivity for C_2 hydrocarbons increases by using carbon

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dioxide as an oxidant in OCM reaction, but methane conversion does not increase. It is necessary to find a new method for active methane and improve methane conversion.

Pulse corona plasma is non-equilibrium cold plasma in a gas at atmospheric pressure, in which the electron temperature is very high, yet the ionic or molecular temperature is rather low. The advantage of this plasma technology is that less energy is consumed in heating gas and converting methane to C_2 hydrocarbons. This cold plasma has been successfully used as a new method for dehydrogenative coupling of methane into C_2 hydrocarbons in our laboratory [10,11]. Oxidative coupling and reforming of methane with carbon dioxide using streamer discharge, dielectric-barrier discharge, and high-frequency pulsed plasma have been reported [12–14]. In this paper, we report the results of synergism of catalysts and plasma for the conversion of methane-carbon dioxide mixtures to C_2 hydrocarbons.

2. Experimental

2.1. Catalyst preparation

The $La_2O_3/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnation of $\gamma\text{-}Al_2O_3$ (20–40 mesh) with lanthanum acetates in water. The paste produced was dried at 393 K and calcined in air at 1073 K for 5 h. The $Pd/\gamma\text{-}Al_2O_3$ catalyst and the $Pd\text{-}La_2O_3/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnating $\gamma\text{-}Al_2O_3$ and $La_2O_3/\gamma\text{-}Al_2O_3$ with PdCl aqueous solution, followed by drying at 393 K. The $Pd/\gamma\text{-}Al_2O_3$ and the $Pd\text{-}La_2O_3/\gamma\text{-}Al_2O_3$ catalyst should be reduced in hydrogen at plasma condition before use. For the sake of simplicity, $La_2O_3/\gamma\text{-}Al_2O_3$, $Pd/\gamma\text{-}Al_2O_3$ and $Pd\text{-}La_2O_3/\gamma\text{-}Al_2O_3$ catalysts with different La_2O_3 and Pd loading are expressed as *x*LA, *x*PA and *x*P*x*LA in this paper, where *x* denotes the nominal content of La_2O_3 and Pd in weight percent.

2.2. Experimental

The equipment used in this experiment is shown in Fig. 1. A high voltage DC pulse generator supplies the power input for the reactor, and its principal parameters were of peak value 20–32 kV tunable; pulse width 330 ns; rising time 30 ns; repetition frequency 7–70 Hz. The total power used by the generator and reactor was measured with wattmeter. The glass tube reactor with an inner diameter of 10 mm and a length of 100 mm consists of two electrodes, the top stainless electrode and the lower copper-board electrode with several 0.5-mm holes; the gap of two electrodes was 10 mm. Half gram of the catalyst sample (20–40 mesh) was placed between two electrodes. The feed gases were controlled and adjusted by a needle valve, and the effluent gases from the reactor were analyzed by a GC-14A (Shimadzu) gas chromatograph with flame ionization and thermal conductivity detectors. A PEG-20M column separated methane, ethane, ethylene and acetylene. Carbon dioxide and monoxide were analyzed with a carbon molecular serve of 601 columns. In this experiment, the methane and carbon dioxide conversions are defined as:

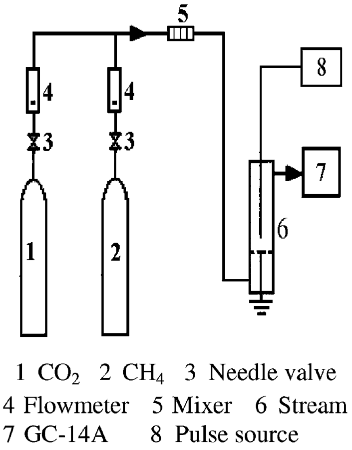

Fig. 1. Schematic diagram of the reaction system.

$$CH_4\ \text{conversion} = (\text{moles of } CH_4 \text{ consumed}/\ \text{moles of } CH_4 \text{ introduced})$$

$$CO_2\ \text{conversion} = (\text{moles of } CO_2 \text{ consumed}/\ \text{moles of } CO_2 \text{ introduced})$$

The selectivity and yield of C_2 hydrocarbons are calculated as following:

$$C_2\ \text{selectivity} = 2(\text{moles of } C_2H_6 + \text{moles of } C_2H_4 + \text{moles of } C_2H_2/\text{moles of } CH_4 \text{ reacted})$$

$$C_2\ \text{yield} = CH_4\ \text{conversion} \times C_2\ \text{selectivity}$$

3. Results and discussion

3.1. The effect of mixing ratio in pulse corona plasma

The first experiment was performed varying the mixing ratio CH_4/CO_2 in the feed. The gas pressure in the reactor was 1.013×10^5 Pa. The power input of discharge was 30 W and flow rate of feed was 25 ml/min. The conversion of CH_4 and CO_2 and the yield of C_2 hydrocarbons and CO are shown in Fig. 2 as a function of CO_2 content in the feed. Carbon dioxide conversion increased initially and then decreased slightly, however CH_4 conversion increased with an increase of CO_2 content. In the product gas, the yield of C_2 hydrocarbons decreased with increasing CO_2 content in feed. In contrast, CO production increased though CO_2 conversion decreased at high CO_2 content. This is because a part of methane is converted to CO, and C_2 selectively was relativity low at this condition. The maximum yield of C_2 hydrocarbons is 12.7% with a C_2 selectivity of 47.7% at 40% content of CO_2 in the feed. Although this value was still insufficient from a practical viewpoint, the observed yield is double of the yield reported by catalytic method [7–9].

The content of CO_2 also had an effect on the distribution of C_2 hydrocarbons, which is shown in Fig. 3. With the increase of CO_2 content, the C_2H_2 molar content in C_2 products decreased, whereas the C_2H_6 and C_2H_4 molar contents increased, though the C_2H_2 content was relatively high amounts among the C_2 compounds. For example, when the CO_2 content was increased from 20 to 80% in the feed, C_2H_2 decreased from about 88.1 to 57.4% while the C_2H_6 and C_2H_4 increased from 5.0 to 26.6% and 6.9 to 16.0%, respectively. This indicates that C_2H_2 was the main C_2 product obtained from coupling of methane under pulse corona plasma using CO_2 as oxidant.

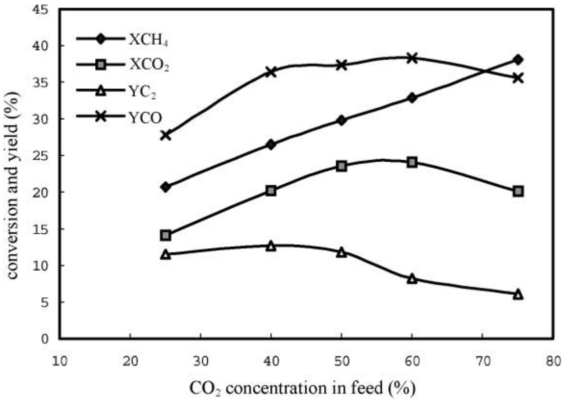

Fig. 2. The influence of the CO_2 content in the feed on the conversion of CH_4 and CO_2 and yield of C_2 and CO (power input = 30 W; flow rate = 25 ml/min).

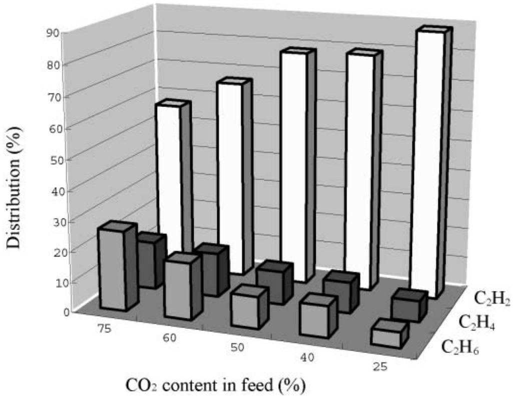

Fig. 3. The influence of the CO_2 content in the feed on the distribution of C_2 hydrocarbons (power input = 30 W; flow rate = 25 ml/min).

In the plasma, carbon dioxide is an oxidative gas which can contribute one of two oxygen atoms for methane conversion by dissociation reaction:

$$CO_2 + e \rightarrow CO + O \tag{1}$$

The active oxygen species can extract a hydrogen from the quite intre methane molecule:

$$CH_4 + O \rightarrow CH_3 + OH \tag{2}$$

The main products C_2 and CO are formed as following:

$$2CH_3 \rightarrow C_2H_6 \tag{3}$$

$$C_2H_6 + O \rightarrow C_2H_4 + H_2O \tag{4}$$

$$C_2H_6 + e \rightarrow C_2H_4 + H_2 \tag{5}$$

$$C_2H_4 + O \rightarrow C_2H_2 + H_2O \tag{6}$$

$$C_2H_4 + e \rightarrow C_2H_2 + H_2 \tag{7}$$

$$C_2H_2 + 3O \rightarrow 2CO + H_2O \tag{8}$$

So the total reactions should be:

$$2CH_4 + CO_2 \rightarrow C_2H_6 + CO + H_2O \tag{9}$$

Table 1
Catalysts activities of the CH_4/CO_2 reaction under plasma over various La_2O_3/γ-Al_2O_3 catalysts[a]

Catalysts	CO_2 conversion (%)	CH_4 conversion (%)	C_2 selectivity (%)	C_2 yield (%)	CO yield (%)	Distribution of $C_2 \sim C_3$ hydrocarbons (mol%)			
						C_2H_6	C_2H_4	C_2H_2	C_3H_8
γ-Al_2O_3	16.7	43.4	30.6	13.4	37.7	10.8	15.0	74.2	a
5LA	22.1	24.5	70.6	17.3	28.4	11.9	11.7	76.4	a
7LA	21.7	24.9	72.8	18.1	30.0	12.5	12.7	74.8	a
10LA	22.3	24.3	68.2	16.6	23.7	13.6	13.7	72.7	a
12LA	24.9	24.1	64.4	15.2	25.2	13.5	14.2	72.3	a
0.01PA	16.4	38.5	34.5	13.3	34.5	24.0	72.3	a	3.7
0.01P5LA	22.0	23.8	70.4	16.7	23.4	25.4	65.4	a	9.2

[a] Reaction conditions: atmospheric pressure, flow rate: 25 ml/min, $CH_4/CO_2 = 2$(mole ratio). The results were obtained after 15 minters of reaction; a: not determined by GC.

$$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O \quad (10)$$

$$2CH_4 + 3CO_2 \rightarrow C_2H_2 + 3CO + 3H_2O \quad (11)$$

$$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O \quad (12)$$

3.2. Catalytic activity of La_2O_3/γ-Al_2O_3 catalysts under plasma

Table 1 shows the catalysts activities of the CH_4/CO_2 reaction under plasma over various La_2O_3/γ-Al_2O_3 catalysts. The effect of various catalysts were significant, but different. When pure γ-Al_2O_3 alone was used as the catalyst under plasma, it gave a methane conversion of 43.4% and C_2 hydrocarbons selectivity of 30.6%, and the main product was CO. In contrast, all La_2O_3/γ-Al_2O_3 catalysts gave a C_2 hydrocarbon selectivity of more than 60%, and maintained the methane conversion level about 24%. It seems that the La_2O_3 and γ-Al_2O_3 interact with each other and create new active sites which catalyze the conversion of methane and carbon dioxide into C_2 hydrocarbons over La_2O_3/γ-Al_2O_3 catalysts. It should be pointed out that, the La_2O_3/γ-Al_2O_3 catalysts show no change in the distribution of C_2 products; C_2H_2 is the major C_2 product.

3.3. The role of Pd- La_2O_3/γ-Al_2O_3 catalysts under plasma

The catalytic activities of the CH_4/CO_2 reaction over La_2O_3/γ-Al_2O_3, Pd/γ-Al_2O_3 and Pd-La_2O_3/γ-Al_2O_3 catalysts under pulse corona plasma are summarized in Table 1. As discussed above the La_2O_3/γ-Al_2O_3 catalysts gave high C_2 hydrocarbons selectivity but the major C_2 product is C_2H_2. In contrast, the Pd/γ-Al_2O_3 catalyst gave high C_2H_4 content but C_2 hydrocarbon selectivity of about 40%. It is well known that C_2H_4 has more economic value than C_2H_2. If we combine La_2O_3/γ-Al_2O_3 with Pd/γ-Al_2O_3 catalysts, the new catalyst Pd-La_2O_3/γ-Al_2O_3 would not only have high C_2 hydrocarbon selectivity but also have high C_2H_4 content in the C_2 products. The results show this. The Pd-La_2O_3/γ-Al_2O_3 catalyst gave a C_2 selectivity of 70% and high C_2H_4 content about 65%. This indicated that the Pd-La_2O_3/γ-Al_2O_3 catalyst is an excellent catalyst for C_2H_2 hydrogenation under pulse corona plasma.

4. Conclusions

The oxidative coupling methane can be carried out under pulse corona plasma by using carbon dioxide as oxidant. The carbon dioxide concentration influences methane conversion and C_2 selectivity. The larger CO_2 feed concentration, the higher the CH_4 conversion. The selectivity of all the C_2 compounds decreases with increasing CO_2 content. C_2H_2 was major C_2 products in this reaction.

La_2O_3/γ-Al_2O_3 catalyst exhibits high coupling selectivity, about 72.8% of the carbon in methane was converted to C_2 hydrocarbons with the conversion of methane at 24.9%. The Pd-La_2O_3/γ-Al_2O_3 catalyst changed the distribution of C_2 products, C_2H_4 is major C_2 products. This suggests further research.

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