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Catalysis Today 89 (2004) 97–102
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Oxidative dehydrogenation of ethane with CO_2 over catalyst under pulse corona plasma

Xiuling Zhang [a,b,*], Aimin Zhu [b], Xuehui Li [a], Weimin Gong [b]

[a] *Laboratory of Plasma, Dalian University, Dalian 116622, China*
[b] *Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian 116024, China*

Abstract

The oxidative dehydrogenation of ethane to ethylene and acetylene with carbon dioxide at ambient temperature and atmospheric pressure by pulse corona plasma over various catalysts has been investigated. The products included C_2H_4, C_2H_2 and syngas (H_2 and CO). The conversion of ethane and distribution of products depend on the catalyst used, the C_2H_6/CO_2 feed ratio, the energy density of plasma, etc. The rare earth metal oxides catalyst such as La_2O_3/γ-Al_2O_3 and CeO_2/γ-Al_2O_3 enhance the conversion of ethane and the yield of ethylene and acetylene. The sequence of ethane conversion and yield of ethylene and acetylene is from CeO_2/γ-Al_2O_3 to La_2O_3/γ-Al_2O_3. The metal catalyst Pd/γ-Al_2O_3 exhibits high ethylene selectivity. The optimum C_2H_6/CO_2 ratio in the feed for oxidative dehydrogenation of ethane under plasma catalytic conditions is 1/1. The conversion of ethane and the yield of ethylene and acetylene increase with increasing of the energy density of plasma.

Keywords: Oxidative dehydrogenation; Pulse corona plasma; Ethane conversion

1. Introduction

Ethane is the main component of oil field gas or refinery tail gas. Up to date, converting the abundant ethane to ethylene at low temperature has been a challenge in chemical and petrochemical industry for many years. To find a proper method to activate ethane is essential for this conversion. Ethane dehydrogenation is a thermodynamically unfavorable reaction. High reaction temperature is required to shift the equilibrium to a state being favorable for the formation of ethylene. Coke formation becomes serious under high reaction temperature and with the absence of oxygen. To overcome the energy and coke problems associated with thermal cracking, worldwide different efforts have been tried for the oxidative dehydrogenation of ethane (ODE) [1–4]. Recently, a new process for ODE was reported by using carbon dioxide as a weaker oxidant. For this new process, some character can be listed as follows: (1) carbon dioxide as an oxidant for the ethane dehydrogenation to yield C_2H_4 and converting to CO; (2) with a lower reaction temperature and with a great decrease in coke deposit amount compared with C_2H_6 vapor-splitting dehydrogenation process [5]. Some catalysts have been proposed for oxidative dehydrogenation of ethane with carbon dioxide as oxidant, but the reaction temperature is still higher than 700 K. So, highly active method at lower temperature is required.

The pulse corona plasma is a new cold plasma. It can operate at ambient temperature and atmospheric pressure, and have been proven to be more efficient method for certain plasma chemical reactions such as oxidative coupling of methane (OCM) using O_2 or CO_2 as oxidant [6–14]. In this plasma technique, applying high voltage pulses to one electrode with fast rise time and short duration energizes a large amount of free electrons. The inelastic collisions of reactant molecules with energized electrons can create a lot of fragments, such as radicals and active species, which will be a thermodynamically initial state in the subsequent reaction [15,16]. This leads the formation of products in the plasma reactor.

Marafee et al. reported a direct conversion of CO_2 and CH_4 into higher hydrocarbons using the catalytic corona discharge. The major by-product is syngas [10]. Yao et al. suggested that a pulsed plasma with a high frequency is useful for reforming of CH_4 with CO_2. The products were C_2H_4 and syngas [9]. This indicated that the pulse corona plasma is an efficient technique for reforming low alkane with CO_2. However, few investigations have been reported regarding the ethane oxidative dehydrogenation with CO_2

* Corresponding author. Tel.: +86-411-7402726.
E-mail address: xiulingzhang2000@163.net (X. Zhang).

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doi:10.1016/j.cattod.2003.11.015

and the evaluation of the effect of catalysts on ODE under cold plasma. In this paper, we report the ethane oxidative dehydrogenation with CO_2 to ethylene and acetylene under pulsed corona plasma over various catalysts.

2. Experimental

2.1. Catalyst preparation

The rare earth metal oxide catalysts La_2O_3/γ-Al_2O_3 and CeO_2/γ-Al_2O_3 were prepared by impregnation of γ-Al_2O_3 (20–40 mesh) with lanthanum acetate and cerium nitrate solution, respectively. The produced paste was dried at 393 K and calcined in air at 1073 K for 5 h. The Pd/γ-Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 with $PdCl_2$ aqueous solution, followed by drying at 393 K. Before used the Pd/γ-Al_2O_3 catalyst should be reduced in hydrogen under the plasma condition, namely the flow of H_2 was 15 ml/min, the power of plasma 15 W and the reduced time 2 h.

The list of catalysts is reported in Table 1. The catalysts are indicated as $x La_2O_3/\gamma$-Al_2O_3, $x CeO_2/\gamma$-Al_2O_3 and $x Pd/\gamma$-Al_2O_3, where x indicates the percentage of metal oxide or metal in the catalyst.

The crystalline phases were identified by powder X-ray diffraction using D/MAX-III Model Transmission Diffractometer with Cu Kα radiation.

2.2. Experimental device

The equipment used here is similar to that reported previously [17], which consists of an electrical source of pulse high voltage, a quartz reactor of pulse corona discharge, a feed gas system and a product analysis system. A high voltage DC pulse generator supplies the power input for the reactor, and its main parameters were the peak voltage tunable from 20 to 38 kV; the pulse width 330 ns; the rising time 30 ns; repetition frequency 7–70 Hz. The total power used by generator and reactor was measured with wattmeter. Inside the glass tube reactor with an inner diameter of 10 mm and a length of 100 mm were two electrodes, the top stainless electrode and the lower copper-board electrode with several diameters 0.5 mm cylindrical hollow in it; the gap of two electrodes was 10 mm. About 0.7 ml of the catalyst sample (20–40 mesh) was placed between two electrodes. The feed gases were supplied and adjusted by a needle valve, and the effluent gases from the reactor were analyzed by a GC-14A (Shimadzu) gas chromatograph equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). Ethane, ethylene, acetylene and methane were separated using PEG-20M column and detected by FID detector, while carbon dioxide and other gases products were detected by TCD detector after their separation on carbon molecular sieve of 601 column.

In this experiment, the purity of the gases employed in the experiment was higher than 99.99%. All the experiments were operated at room temperature and atmospheric pressure. The C_2H_6 and CO_2 conversions and the product selectivity and yield are defined as

$$C_2H_6 \text{ conversion} = \frac{\text{moles of } C_2H_6 \text{ converted}}{\text{moles of } C_2H_6 \text{ introduced}} \times 100\%$$

$$CO_2 \text{ conversion} = \frac{\text{moles of } CO_2 \text{ converted}}{\text{moles of } CO_2 \text{ introduced}} \times 100\%$$

$$C_2H_4 \text{ and } C_2H_2 \text{ selectivity} = \frac{\text{moles of } C_2H_4 \text{ and } C_2H_2 \text{ produced}}{\text{moles of } C_2H_6 \text{ converted}} \times 100\%$$

$$C_2H_4 \text{ and } C_2H_2 \text{ yield} = \frac{\text{moles of } C_2H_4 \text{ and } C_2H_2 \text{ produced}}{\text{moles of } C_2H_6 \text{ introduced}} \times 100\%$$

$$\frac{C_2H_4}{C_2H_2} = \frac{\text{moles of } C_2H_4 \text{ produced}}{\text{moles of } C_2H_2 \text{ produced}}$$

$$\frac{H_2}{CO} = \frac{\text{moles of } H_2 \text{ produced}}{\text{moles of CO produced}}$$

3. Results and discussion

3.1. The activity of various catalysts on ODE under pulse corona plasma

The XRD spectrum of the bulk aluminum oxide sample shows the presence of pure γ-Al_2O_3 phases. XRD spectrum of La/Al catalysts shows the signals of γ-Al_2O_3 in addition

Table 1
The activity of catalysts on ODE under pulse corona plasma[a]

Catalysts	Conversion (%)		Selectivity (%)		Yield (%) C_2H_4 and C_2H_2	Ratio (mol)	
	C_2H_6	CO_2	C_2H_4	C_2H_2		C_2H_4/C_2H_2	H_2/CO
No catalyst	33.8	22.7	12.4	25.4	12.7	0.48	2.34
$10La_2O_3/\gamma$-Al_2O_3	37.5	18.5	20.8	32.0	19.8	0.65	2.74
$10CeO_2/\gamma$-Al_2O_3	42.4	20.6	20.4	31.3	21.8	0.65	2.64
$0.1Pd/\gamma$-Al_2O_3	30.0	24.6	46.7	6.3	15.9	7.40	1.46

[a] Reaction conditions—catalyst amount: 0.7 ml; applied power: 20 W (the peak value of pulse voltage: around 28 kV; the repetition frequency: around 44 Hz); flow rate: 25 ml/min; feed: C_2H_6 (50 vol.%), CO_2 (50 vol.%).

to very weak signals of La_2O_3 for the sample 10 La/Al. The sharper XRD peaks of CeO_2 are shown in Ce-containing samples. Only γ-Al_2O_3 signals have been detected in the XRD spectrum of Pd/Al catalyst.

All experiments have been carried out at ambient temperature and atmospheric pressure. Ethane and carbon dioxide can be continuously activated in a plasma catalytic zone. The main products are ethylene, acetylene, small amount of methane and traces of C_3–C_4. Certainly, by-products such as syngas ($CO + H_2$) and small amount of water can be obtained by using carbon dioxide as oxidant.

A comparison of ODE with and without catalysts under pulse corona plasma is shown in Table 1. From this table, it can be seen that the conversion of C_2H_6 and CO_2 was 33.8 and 22.7%, respectively, and the total yield of C_2H_4 and C_2H_2 was 12.7% without catalyst. It is apparent that the introduction of the rare earth oxide catalyst, such as La_2O_3/γ-Al_2O_3 and CeO_2/γ-Al_2O_3, into the plasma zone increased the conversion of C_2H_6, the selectivity, and the yield of C_2H_4 and C_2H_2. But CO_2 conversion reduced slightly. The total yield of C_2H_4 and C_2H_2 was 19.8 and 21.8% when La_2O_3/γ-Al_2O_3 and CeO_2/γ-Al_2O_3 were used, respectively. The selectivity of C_2H_4 increased significantly when Pd/γ-Al_2O_3 catalyst was used. The ratio of C_2H_4/C_2H_2 was as high as 7.4. This indicated that the rare earth oxide catalysts enhanced the conversion of C_2H_6 and yield of C_2H_4 and C_2H_2 while Pd/γ-Al_2O_3 catalyst favored the formation of C_2H_4. On the other hand, Table 1 showed that the rare earth oxide catalysts increased the radio of H_2/CO and that Pd/γ-Al_2O_3 catalyst decreased the radio of H_2/CO. There are two reasons resulting the increased radio of H_2/CO, the yield of CO decreased or the yield of H_2 increased. In our experiments, La_2O_3/γ-Al_2O_3 and CeO_2/γ-Al_2O_3 decreased the yield of CO. while Pd/γ-Al_2O_3 catalyst decreased the yield of H_2.

It is generally accepted that the cold plasma changes the status of reactant molecules. Instead of neutral ground state molecules, a mixture of electrons, excited molecules, ions, and radicals is full in the plasma zone. The energized electrons and excited active species will be a thermodynamically initial state in the subsequent reaction. Besides the interactions among the active species and catalyst lead to an unusual plasma catalytic reaction [14]. In our experiments, the conversion of C_2H_6 and the total selectivity of C_2H_4 and C_2H_2 increased with rare earth catalysts listing in Table 1. This indicated that active species might collide with the catalyst and activate the catalyst particles, and then the active particles of catalyst enhanced C_2H_6 conversion, and the total selectivity of C_2H_4 and C_2H_2 through chemisorptions and adsorption.

As mentioned above, the rare earth oxide catalyst, CeO_2/γ-Al_2O_3, gave higher ethane conversion and C_2H_4 and C_2H_2 yields. In the next section, we would like to discuss the activity of CeO_2/γ-Al_2O_3 on ODE under different conditions.

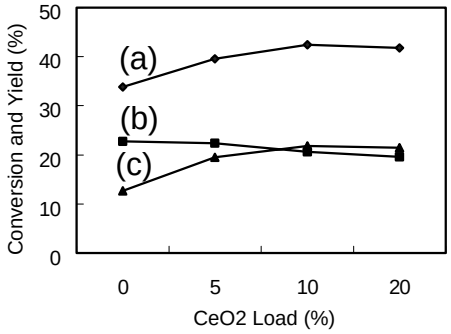

Fig. 1. Effect of CeO_2 content on the ODE: (a, ◆) C_2H_6 conversion; (b, ■) CO_2 conversion; (c, ▲) C_2H_4 and C_2H_2 yield; catalyst amount: 0.7 ml; applied power: 20 W (the peak value of pulse voltage: around 28 kV; the repetition frequency: around 44 Hz); flow rate: 25 ml/min; feed: C_2H_6 (50 vol.%), CO_2 (50 vol.%).

3.2. The effect of CeO_2 content on ODE under pulse corona plasma

The effect of CeO_2 content on the dehydrogenation of ethane in the presence of CO_2 under pulse corona plasma has been shown in Figs. 1 and 2. According to Fig. 1, the C_2H_6 conversion increased rapidly from 31.6 to 42.4% when the CeO_2 content rose from 0 to 10%. Further increasing the CeO_2 content, the conversion of C_2H_6 decreased slightly. But contrarily, the conversion of CO_2 decreased with the increasing of the CeO_2 content. The total yield of C_2H_4 and C_2H_2 increased rapidly to 21.8%, when the CeO_2 content was increased from 0 to 10%. From Fig. 2, the ratio of C_2H_4/C_2H_2 and H_2/CO increased slightly when the content of CeO_2 rose from 0 to 5%. It was no obvious influence on the ratio of C_2H_4/C_2H_2 and H_2/CO in the products with increased the content of CeO_2 further.

Fig. 3 shows the XRD spectra of various CeO_2/γ-Al_2O_3 catalysts. The XRD results indicate that the crystalline structure of CeO_2 and γ-Al_2O_3 coexists in different CeO_2 content of CeO_2/γ-Al_2O_3 catalysts. These initial crystalline forms

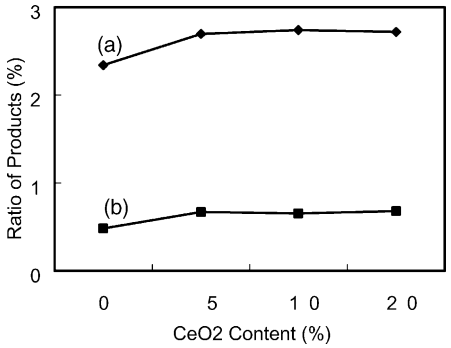

Fig. 2. Effect of CeO_2 content on the radio of products: (a, ◆) the ratio of H_2/CO; (b, ■) the ratio of C_2H_4/C_2H_2; catalyst amount: 0.7 ml; applied power: 20 W (the peak value of pulse voltage: around 28 kV; the repetition frequency: around 44 Hz); flow rate: 25 ml/min; feed: C_2H_6 (50 vol.%), CO_2 (50 vol.%).

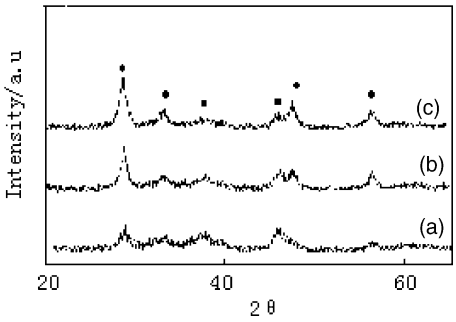

Fig. 3. XRD patterns of CeO_2/γ-Al_2O_3 catalysts: (●) CeO_2; (■) Al_2O_3; (a) $5CeO_2/\gamma$-Al_2O_3; (b) $10CeO_2/\gamma$-Al_2O_3; (c) $20CeO_2/\gamma$-Al_2O_3.

are retained in every run even after reaction and no changes can be observed.

3.3. The influence of the CO_2 concentration in the feed on ODE over $10CeO_2/\gamma$-Al_2O_3 under pulse corona plasma

Table 2 shows influence of carbon dioxide concentration in the feed on the ODE over $10CeO_2/\gamma$-Al_2O_3 under pulse corona plasma. The conversion of ethane monotonously increased with the increasing of the concentration of CO_2 in the feed, and all the conversions of C_2H_6 were higher than that without CO_2 in the feed. This suggested that the increase in conversion of C_2H_6 results from the addition of CO_2.

In this plasma catalytic reaction, C_2H_6 molecules collide with energized electrons and produce active spices, such as CH_3 and C_2H_5. This is because that the dissociation energy of CH_3–CH_3 bond is 3.8 eV, and the CH_3CH_2–H bond is 4.2 eV (the average energy of electrons produced by this cold plasma is about 6 eV), so ethane is unstable and decomposed to radicals:

$$C_2H_6 + e^* \rightarrow CH_3 + CH_3 + e \quad (1)$$

$$C_2H_6 + e^* \rightarrow C_2H_5 + H + e \quad (2)$$

In the same way, CO_2 molecules collide with energized electrons and C–O bonds are broken:

$$CO_2 + e^* \rightarrow CO + O^- \quad (3)$$

$$CO_2 + e^* \rightarrow CO + O + e \quad (4)$$

The O^- and O have been well known as active oxygen species for oxidative coupling of methane in cold plasma [8,13]. It will collide with C_2H_6 molecules and produce C_2H_4 and C_2H_2:

$$C_2H_6 + O^- \text{ or } O \rightarrow C_2H_4 + H_2O \quad (5)$$

$$C_2H_6 + 2O^- \text{ or } O \rightarrow C_2H_2 + 2H_2O \quad (6)$$

So with increasing the amount of carbon dioxide in the feed, more active oxygen species will be generated for ethane conversion, thus leading to more conversion of ethane to ethylene and acetylene.

The CO_2 conversion decreased with increasing CO_2 concentration in the feed, as shown in Table 2. All the CO_2 conversions were higher than that pure CO_2 in the feed. This indicates that C_2H_6 promoted the conversion of CO_2. According to Eqs. (3) and (4), the rates of the decomposition of CO_2 depend on the concentration of CO_2, CO, O and O^- in the plasma catalytic zone. The excited species, O and O^-, will react with the hydrocarbon radicals from C_2H_6. More O and O^- were consumed with increasing the concentration of C_2H_6 in the feed, which leads to the increase in the rate of the CO_2 decomposition reaction.

The effect of CO_2 concentration in the feed on the selectivity and the yield of C_2H_4 and C_2H_2 are also shown in Table 2. According to this table, the selectivity of C_2H_4 and C_2H_2 monotonously decreased with increasing the concentration of CO_2 in the feed, though the conversion of ethane increased. So the maximum yield of ethylene and acetylene appeared when the CO_2 concentration in the feed was 50%. On the other hand, the active oxygen species can enhance a further dissociation of the C–H bond of ethylene and acetylene and the formation of by-products such as carbon monoxide and carbon, especially when the concentration of CO_2 is high. So the yield of ethylene and acetylene decreased when the CO_2 concentration in the feed was higher than 50%.

Table 2 also shows the effect of CO_2 concentration in the feed on the ratio of C_2H_4/C_2H_2 and H_2/CO in the products. The increasing CO_2 concentration leads to an increase in the C_2H_4/C_2H_2 ratio, while the ratio of H_2/CO decreased with

Table 2
The influence of CO_2 content on ODE under pulse corona plasma over $10CeO_2/\gamma$-Al_2O_3[a]

CO_2 content (%)	Conversion (%)		Selectivity (%)		Yield (%) C_2H_4 and C_2H_2	Ratio (mol)	
	C_2H_6	CO_2	C_2H_4	C_2H_2		C_2H_4/C_2H_2	H_2/CO
0	28.9	–	18.0	38.4	16.3	0.47	–
30	31.8	25.1	20.2	34.4	17.2	0.58	3.99
40	34.1	22.1	20.0	32.8	18.0	0.61	3.21
50	42.4	20.6	20.4	31.3	21.8	0.65	2.74
60	48.8	18.8	19.8	22.6	20.7	0.88	2.46
70	57.9	16.4	14.3	15.9	17.5	0.90	2.08
100	0	11.3	–	–	–	–	–

[a] Reaction conditions—catalyst amount: 0.7 ml; applied power: 20 W (the peak value of pulse voltage: around 28 kV; the repetition frequency: around 44 Hz); flow rate: 25 ml/min.

Table 3
The effect of energy density on ODE over $10CeO_2/\gamma\text{-}Al_2O_3$ catalyst[a]

Ed (kJ/mol)	Conversion (%)		Selectivity (%)		Yield (%) C_2H_4 and C_2H_2	Ratio (mol)	
	C_2H_6	CO_2	C_2H_4	C_2H_2		C_2H_4/C_2H_2	H_2/CO
380	10.5	8.9	36.0	55.4	9.6	0.65	2.47
540	16.0	12.0	33.8	53.7	14.0	0.63	2.51
680	23.4	15.4	28.6	44.0	17.0	0.65	2.61
720	32.0	17.0	22.8	33.5	18.0	0.68	2.67
800	42.4	20.6	20.4	31.3	21.8	0.65	2.74
1030	52.6	26.3	19.1	29.0	25.3	0.66	2.91
1350	61.5	30.1	17.2	27.4	27.5	0.63	2.89
1500	72.8	41.1	16.2	24.2	29.4	0.67	2.71

[a] Reaction conditions—catalyst amount: 0.7 ml; applied power: 7–30 W (the peak value of pulse voltage: 20–38 kV; the repetition frequency: 7–70 Hz); flow rate: 5–25 ml/min; feed: C_2H_6 (50 vol.%), CO_2 (50 vol.%).

increasing CO_2 concentration. This is owing to the yield of CO increased rapidly in our experiments.

3.4. The effect of energy density on ODE over $10CeO_2/\gamma\text{-}Al_2O_3$ catalyst

Table 3 shows the effect of energy density on the ODE over $CeO_2/\gamma\text{-}Al_2O_3$ catalyst. The experiments demonstrated that the pulse corona discharge started when the energy density reaching 300 kJ/mol, and caused the change of chemical compositions in the plasma catalytic reactor. When the energy density increased further, both of the ethane and carbon dioxide conversion was promoted. The total yield of ethylene and acetylene increased until the energy density reached 1500 kJ/mol. A further increase in energy density cannot bring the increase in the total yield of ethylene and acetylene; on the contrary, it leads to the pulse corona discharge unstable and sparking. These findings are attributed to the dependence of the energy and amount of energized electrons in the plasma catalytic zone on energy density in a flow plasma catalytic reactor. By increasing the energy density of the plasma, the amount as well as the energy of electrons in the plasma increase. Which is favorable to the reactions of (1)–(4), and there have been more active species in the plasma catalytic reactor. So the higher the energy density in the reactor, the higher the conversion of ethane and carbon dioxide is. At the same time, the experiments also demonstrated that the energy density is not always advantageous to the formation of ethylene and acetylene. The selectivity of ethylene and acetylene decreased rapidly from 36.0 to 16.2%, and from 55.4 to 24.2% when the energy density in the plasma catalytic reactor increased from 380 to 1500 kJ/mol. In order to achieve an optimum result, a high energy density is not suggested. Table 3 also shows that the energy density had no obvious influence on the ratio of C_2H_4/C_2H_2 and H_2/CO in the products, instead the ratio of C_2H_4/C_2H_2 and H_2/CO remained in the range of 0.63–0.68 and 2.47–2.91 with different energy density.

4. Conclusions

At ambient temperature and atmospheric pressure, the oxidative dehydrogenation of ethane under pulse corona plasma over various catalysts using carbon dioxide as oxidant was investigated. The experiment has confirmed that the rare earth metal oxides catalyst such as $La_2O_3/\gamma\text{-}Al_2O_3$ and $CeO_2/\gamma\text{-}Al_2O_3$ enhance conversion of ethane and the yield of ethylene and acetylene. The sequence of ethane conversion and the yield of ethylene and acetylene is $CeO_2/\gamma\text{-}Al_2O_3 > La_2O_3/\gamma\text{-}Al_2O_3$. The optimum Ce content for ODE under pulse corona plasma is 10%. The metal catalyst $Pd/\gamma\text{-}Al_2O_3$ exhibits high ethylene selectivity.

Conversion of ethane increased with increasing the concentration of carbon dioxide in the feed over $CeO_2/\gamma\text{-}Al_2O_3$ under pulse corona plasma. The total yield of ethylene and acetylene had maximum value at the CO_2 content in the feed was 50%. The increasing of energy density in the plasma catalytic reactor promoted the conversion of ethane and carbon dioxide. The convenient value of energy density for the ethylene and acetylene yield was at the range of 700–1000 kJ/mol.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 29576229 and 20106003) for financial support.

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