Effect of La_2O_3/ -Al_2O_3 Catalyst on the Activation of CH_4 and CO_2 to C_2 Hydrocarbons under Non-equilibrium Plasma

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Abstract: In the reaction of methane and carbon dioxide to C_2 hydrocarbons under non-equilibrium plasma, methane conversion was decreased, but selectivity of C_2 hydrocarbons was increased when using La_2O_3/ -Al_2O_3 as catalyst. So the yield of C_2 hydrocarbons was higher than using plasma alone. The synergism of La_2O_3/ -Al_2O_3 and plasma gave methane conversion of 24.9% and C_2 yield of 18.1%. The distribution of C_2 hydrocarbons changed when Pd- La_2O_3/ -Al_2O_3 was used as catalyst, the major C_2 product was ethylene.

Keywords: Non-equilibrium plasma, catalyst, methane, carbon dioxide.

The oxidative coupling of methane (OCM) to C_2 hydrocarbons using carbon dioxide as oxidant is an attractive process from environmental point of view. Only a few research papers reported for it[1-3]. In general, the yield of C_2 hydrocarbons was about 6%. This indicated that the method of catalytic activation was unfavorable to the reaction. It is necessary for us to find a new method in order to activate reaction and improve C_2 hydrocarbon yield. Non-equilibrium plasma is a 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 was consumed in heating gas and more conversion of methane to C_2 hydrocarbons was achieved. There are hardly papers to report the results of synergism of catalysts and plasma which using in conversion of methane-carbon dioxide to C_2 hydrocarbon reaction.

In this paper, the La_2O_3/ -Al_2O_3 catalyst was prepared by impregnation of -Al_2O_3 (20 ~ 40 mesh) with lanthanum acetate in water. The catalysts of Pd/ -Al_2O_3 and Pd-La_2O_3/ -Al_2O_3 were prepared by impregnating -Al_2O_3 and La_2O_3/ -Al_2O_3 with PdCl aqueous solution. The evaluation of catalysts was carried out using a plasma reactor with gas chromatograph equipped with flame ionization and thermal conductivity detectors. CH_4 and CO_2 space velocity was 7500 h^{-1}. The power input of plasma was 30 W.

Results and Discussion

1 Effect of La_2O_3/ -Al_2O_3 catalysts under plasma

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From the results of **Table 1**, it is found that the roles of various catalysts were obvious, but different. When pure -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%, the main product was CO. In contrast, all La_2O_3/ -Al_2O_3 catalysts gave a C_2 hydrocarbon selectivity of more than 60%, and maintain the methane conversion level about 24%. It seems that the molecular of La_2O_3 and -Al_2O_3 interacted each other at the interfacial area and created new active site which offer the active and selective performance of the conversion of methane and carbon dioxide into C_2 hydrocarbons over La_2O_3/ -Al_2O_3 catalysts. It should be pointed out that, the La_2O_3/ -Al_2O_3 catalysts had no change the distribution of C_2 products, C_2H_2 is the major C_2 product.

Table 1 Effect of La_2O_3/ -Al_2O_3 catalysts under plasma

Catalysts	X_{CO_2} (%)	X_{CH_4} (%)	S_{C_2} (%)	Y_{C_2} (%)	Y_{CO} (%)	Distribution of C_2~C_3 /mol%			
						C_2H_6	C_2H_4	C_2H_2	C_3H_8
-Al_2O_3	16.7	43.4	30.6	13.4	37.7	10.8	15.0	74.2	—
5% La_2O_3/ -Al_2O_3	22.1	24.5	70.6	17.3	28.4	11.9	11.7	76.4	—
7% La_2O_3/ -Al_2O_3	21.7	24.9	72.8	18.1	30.0	12.5	12.7	74.8	—
10% La_2O_3/ -Al_2O_3	22.3	24.3	68.2	16.6	23.7	13.6	13.7	72.7	—
12% La_2O_3/ -Al_2O_3	24.9	24.1	64.4	15.2	25.2	13.6	14.2	72.3	—

2 The role of Pd- La_2O_3/ -Al_2O_3 catalysts under plasma

The La_2O_3/ -Al_2O_3 catalysts gave high C_2 hydrocarbons selectivity but the major C_2 product was C_2H_2. In contrast, the Pd/ -Al_2O_3 catalyst has high C_2H_4 content but C_2 hydrocarbon selectivity was about 40%. It is well known that C_2H_4 has more economic value than C_2H_2, if we combine La_2O_3/ -Al_2O_3 with Pd/ -Al_2O_3 catalyst to prepare the new catalyst Pd-La_2O_3/ -Al_2O_3, it would not only have high C_2 hydrocarbon selectivity but also have high C_2H_4 content in the C_2 products. The result of experiment in **Table 2** just proved this. The Pd- La_2O_3/ -Al_2O_3 catalyst gave a C_2 selectivity of 70% and C_2H_4 content about 65%. This indicated that the Pd- La_2O_3/ -Al_2O_3 catalyst is an excellent catalyst for C_2H_2 hydrogenation under non-equilibrium plasma.

Table 2 Effect of Pd/ -Al_2O_3 and Pd-La_2O_3/ -Al_2O_3/catalysts under plasma

Catalysts	X_{CO_2} (%)	X_{CH_4} (%)	S_{C_2} (%)	Y_{C_2} (%)	Y_{CO} (%)	Distribution of C_2~C_3 /mol%			
						C_2H_6	C_2H_4	C_2H_2	C_3H_8
0.01% Pd/ -Al_2O_3	16.4	38.5	34.5	13.3	34.5	24.0	72.3	—	3.7
0.05% Pd/ -Al_2O_3	27.0	34.7	39.5	13.7	33.3	26.0	64.2	—	9.8
0.1% Pd/ -Al_2O_3	28.0	34.6	40.5	14.0	34.2	34.6	43.4	—	15.0
0.01% Pd/5% La_2O_3/ -Al_2O_3	22.0	23.8	70.4	16.7	23.4	25.4	65.4	—	9.2

Reference

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