Chinese Chemical Letters Vol. 13, No. 8, pp 711 – 713, 2002 711
http://www.imm.ac.cn/journal/ccl/html

Methane Coupling Using Hydrogen Plasma and Pt/γ-Al_2O_3 Catalyst

Bin DAI[1,2]*, Wei Min GONG[1], Xiu Ling ZHANG[1], Ren HE[1]

[1]Plasma Chemistry Laboratory, Dalian University of Technology, Dalian 116012
[2]Department of chemistry, Shihezi University, Shihezi 832002

Abstract: In this paper, methane coupling at ambient temperature, under atmospheric pressure and in the presence of hydrogen was firstly investigated by using pulse corona plasma and Pt/γ-Al_2O_3 catalyst. Experimental results showed that Pt/γ-Al_2O_3 catalyst has catalytic activity for methane coupling to C_2H_4. Over sixty percent of outcomes of C_2 hydrocarbons were detected to be ethylene.

Keywords: Pulse corona plasma, methane coupling, hydrogen, Pt/γ-Al_2O_3 catalyst.

Plasma technology used for methane conversion has attracted much more attention in the past ten years[1]. Such as microwave, radio frequency, pulsed, AC, and DC plasmas[2-9]. We have reported that methane coupling under pulse corona plasma in the presence of hydrogen[10]. The addition of hydrogen could improve conversion of methane and yield of C_2 hydrocarbons, moreover, increasing with increment of hydrogen. Conversion of 57.1% methane and yield of 43.4% C_2 hydrocarbons were obtained in low power, but acetylene was inevitably the main product of methane coupling.

In this paper, Pt/γ-Al_2O_3 catalyst was firstly introduced into coupling of methane in the presence of hydrogen under pulse corona plasma at room temperature and normal pressure. The experiment showed that Pt/γ-Al_2O_3 catalyst has catalytic activity for methane coupling to C_2H_4.

The experimental installation used in the present investigation was the same as that reported previously[10]. The Pt/γ-Al_2O_3 catalyst was prepared by the conventional impregnation method using aqueous of H_2PtCl_6. The support was γ-Al_2O_3, 40~80 mesh. The catalyst was dried at 383 K followed by calcination in an air stream at certain temperature for 4 h, and then reducing under hydrogen at 473 K for a few hours before reaction.

Results and Discussion

Catalytic performance of Pt/γ-Al_2O_3 on methane conversion

Table 1 showed methane reaction experiment results over Pt/γ-Al_2O_3 catalyst with

*E-mail: dbinly@263.net

various loading. From **Table 1**, it could be seen that the activity of Pt/γ-Al_2O_3 catalyst increased with Pt loading from 1.5 wt $\times 10^{-5}$ to 6 wt $\times 10^{-5}$, loading of Pt 6 wt $\times 10^{-5}$ the conversion of C_2H_4 decreased. The most active and highest selectivity for ethylene was the catalyst with the Pt loading of 6 wt $\times 10^{-5}$.

Compared with blank, the adding of medium (γ-Al_2O_3 carrier or Pt/γ-Al_2O_3 catalyst) cut down conversion of methane, the probable reason deemed to be that activation of medium consumed the part of input plasma power. The Pt/γ-Al_2O_3 catalysts also catalyzed the part of prepared C_2 hydrocarbons to C_4 products and other carbon species.

Table 1 Catalytic performance of Pt/γ-Al_2O_3 on methane conversion[a]

Catalyst ($w.t10^{-5}$)	Conv. of CH_4 (%)	Selectivity (%)			Distribution (%)		
		C_2	C_4	C^b_{unkn}	C_2H_2	C_2H_4	C_2H_6
Blank	42.2	63.3	—	36.7	6.6	8.3	85.1
γ-Al_2O_3	30.9	67.1	—	32.9	8.7	10.2	81.2
1.5Pt/γ-Al_2O_3	24.4	65.7	1.6	32.7	13.4	39.4	47.3
3 Pt/γ-Al_2O_3	27.7	66.3	1.9	31.8	17.3	50.7	32.0
6 Pt/γ-Al_2O_3	33.3	67.5	2.3	30.2	22.3	59.2	18.6
9 Pt/γ-Al_2O_3	30.9	65.2	2.8	32.0	62.5	33.3	4.2
12 Pt/γ-Al_2O_3	29.5	64.1	3.3	32.6	77.4	19.0	3.6

[a] Reaction condition: pulse voltage = 32kV, repeat frequency = 80Hz, power = 30W, CH_4:H_2 = 1:4, flow rate = 25mL/min, catalyst 1.2 mL. [b] C_{unkn} means undetermined carbon species.

Effect of applied energy on methane conversion

Table 2 showed the effect of plasma power input for activation of methane on Pt/γ-Al_2O_3 catalyst. The data from **Table 2**, showed that the conversion of methane, selectivity of C_2 hydrocarbons and the content of C_2H_4 increased gradually with increment of power input. But, hoist of applied energy also promoted the production of C_4 hydrocarbons in the system. The probably reason was that elevating of applied energy could promote catalytic activity of Pt/γ-Al_2O_3 on coupling methane to ethylene.

Table 2 Effect of applied energy on methane conversion[a]

Power/w	Conv. of CH_4 (%)	Selectivity (%)			Distribution (%)		
		C_2	C_4	C^b_{unkn}	C_2H_2	C_2H_4	C_2H_6
15	24.2	64.6	/	35.4	13.6	19.5	66.9
25	32.4	65.5	1.8	32.7	20.2	49.8	30.1
35	39.0	68.6	2.2	29.2	21.8	63.3	15.0
45	41.6	69.8	2.6	27.6	21.5	68.5	10.1

[a] Reaction condition: 6×10^{-5}w.t catalyst 1.2 mL,the other conditions were the as same in **Table 1**

References

1. B. W. Wang, G. H. Xu, C. J. Liu, *Journal of Chemical Industry and Engineering* (in Chinese), **2001**, *52* (8), 659.
2. L. T. Hsieh, W. J. Lee, C. Y. Chen, *et al.*, *Plasma Chemistry and Plasma Processing*, **1998**, *18* (2), 215.
3. L. Bromberg, D. R. Cohn, A. Rabinovich, *et al.*, *International Journal of Hydrogen Energy*,

1999, *24*, 1131.
4. A. M. Huang, G. G. Xia, J. Y. Wang, *et al.*, *Journal of Catalysis*, **2000**, *189*, 349.
5. B. Dai, X. L. Zhang, W. M. Gong, *et al.*, *Plasma Science & Technology*, **2000**, *2* (6), 577.
6. Y. Li, G. H. Xu, C. J. Liu, *et al.*, *Energy & Fuels*, **2001**, *15*, 299.
7. S. L. Yao, E. Suzuki, A. Nakayama, *Thin Solid Films*, **2001**, *390*, 165.
8. B. Dai, X. L. Zhang, W. M. Gong, *et al.*, *Plasma Science & Technology*, **2001**, *3* (1), 637.
9. S. Kado, K. Urasaki, Y. Sekine, *Chemical Communications*, **2001**, *5*, 415.
10. B. Dai, X. L. Zhang, L. Zhang, *et al.*, *Science in China (B)*, **2001**, *44* (2), 191.

Received 8 November, 2001