Chinese Chemical Letters Vol. 15, No. 7, pp 779-780, 2004
http://www.imm.ac.cn/journal/ccl.html

Direct Synthesis of Oxygenates from Water and Methane *via* Dielectric-barrier Discharge

Bao Wei WANG*, Gen Hui XU

State Key Laboratory of C_1 Chemical Technology, Tianjin University, Tianjin 300072

Abstract: In this investigation, a clean, atomic economic and direct synthesis of oxygenates (methanol, ethanol) form water and methane *via* dielectric-barrier discharge was developed at room temperature and under atmospheric pressure. The effect of discharge voltage on this process was studied. The results showed that the conversion of water can be as high as 7%, the selectivity of methanol and ethanol can be as high as 100%.

Keywords: Oxygenates, methane, water, dielectric-barrier discharge.

Direct conversion of water and methane into useful chemicals and clean energy remains to be a big challenge in catalysis in the 21st century. Although a large number of studies have contributed to the direct decomposition of water and conversion of methane in the past decade and many new methods and catalysts have been developed for the direct activation and conversion of water and methane, there is still no direct process with commercial viability at this moment[1]. In this investigation, a clean and direct conversion of methane to oxygenates (methanol, ethanol) from water and methane in low-power non-equilibrium plasma reaction was developed at room temperature and under atmospheric pressure.

The experimental apparatus and flow chart have been depicted in the previous papers [2,3]. The reactor was made of a quartz tube with inside diameter of 6 mm. All the experiments were carried out under atmospheric pressure and at room temperature. The feed methane is regulated by mass flow controllers D07-7A/ZMM and D08-4C/ZM mass flow display devices, which has been calibrated with soap film flowmeter, then mix with vapor and downward were introduced into the reactor for all experiments. A quadrupole mass spectrograph (Balzers MSC200) was used for the detection of oxygenates produced. After reaction, the exhaust gases were cooled with ice in order to gain oxygenates. The liquid products were analyzed by gas chromatograph with a thermal conductivity detector (TCD) and H_2 carrier gas.

The effect of the discharge voltage on concentration and weight of liquid product was shown in **Table 1**. We can see that the weight of liquid product and the concentration of methanol and ethanol increased with the increase of voltage, the concentration of water

---

* E-mail:wangbw@tju.edu.cn

decreased with the increase of voltage, when the inlet flow rate of water and methane was constant.

Table 1 Effect of discharge voltage on water conversion and product distribution

voltage/kV	product weight /g	methanol concentration/%	ethanol concentration/%	water concentration /%
20	1.47	2.15	1.14	96.71
30	1.51	7.24	2.14	90.62
40	1.54	10.12	2.55	87.33

flow rate of methane was 40 mL/min, flow rate of vapor 30 mL/min, product was weighted after 60 minutes

The effect of the discharge voltage on the conversion of water and the selectivity of methanol and ethanol was shown in **Table 2**. **Table 2** indicated that the conversion of water and the selectivity of methanol increased with the increase of voltage, the selectivity of ethanol decreased with the increased of voltage, when the inlet flow rate of water and methane was constant.

Table 2 Effect of discharge voltage on water conversion and product selectivity

voltage/kV	water conversion /%	methanol selectivity/%	ethanol selectivity /%
20	1.68	73.05	26.95
30	5.14	82.94	17.06
40	7.12	85.09	14.91

The reason was that the acceptant energy of water and methane increased when the voltage increased. The amount of dissociation water and methane increased. Thus, the conversion of water and the weight of liquid product increased when the voltage increased. The concentration of methanol increased more than that of ethanol when the discharge voltage increased. The reason was that methanol can be produced through $OH^{\bullet}+CH_3^{\bullet}\rightarrow CH_3OH$ (1). However, ethanol can be produced through $OH^{\bullet}+CH_2^{\bullet}+CH_3^{\bullet}\rightarrow CH_3CH_2OH$ (2) or $OH^{\bullet}+C_2H_5^{\bullet}\rightarrow CH_3CH_2OH$ (3). The reaction (1) was two radicals reaction and only needed one step. Nevertheless, the reaction (2) was three radicals reaction that reaction probability was not easy as two radicals reaction. The reaction (3) needed two steps. Also the reason is that the selectivity of methanol was much significant than that of ethanol.

References

1. K. Otsuka, Y. Wang, *Appl. Catal. A*, **2001**, *222* (1-2), 145.
2. B.W. Wang, G. H. Xu, *Science in China (B)*, **2002**, *45*(3), 299.
3. B.W. Wang, G. H. Xu, *J. of Fuel Chem. & Tech.*, **2002**,*30*(2), 97.

Received 18 June, 2003