STUDIES ON NON-INITIATOR METHANE OXIDATION
TO FORMALDEHYDE IN NON-EQUILIBRIUM PLASMA

Liu Wanying, Huang Dairong, Zhang Jiren, Zhang Jiaqi
Chengdu Institute of Organic Chemistry, Academia Sinica

ABSTRACT — In the absence of any initiator, methane may be oxidized to formaldehyde directly under mild conditions of non-equilibrium plasma. The reaction selectivity can be achieved up to 80% at the best condition. In this paper, the relation of formaldehyde yield, reaction selectivity, mole ratios of starting materials and the plasma power can be empirical formulas. The mechanism of the reaction was discussed.

INTRODUCTION

Methane oxidation to formaldehyde has been studied widely since 1960's. In general, previous works were carried out in the presence of initiator or at high temperature or at high pressure, and formaldehyde selectivity is low. The aim of this work is exploration for a possible new path on methane oxidation to formaldehyde under mild condition in the absence of any initiator.

Almost all molecules can be changed to excited states, ions and free radical by non-equilibrium plasma, and they can achieve up to very high activated states. While chemical reaction is beginning, high energy electron and other activated species losing their energy, the chemical reaction is stopped. This shows that realization of high selectivity and yield is entirely possible, if the products were disengaged from plasma region or were captured rapidly at the instant when reaction begins. In fact, some chemical reactions have been carried out in non-equilibrium plasma, but they can not be carried out in classical chemistry. 

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EXPERIMENTAL

Starting materials and apparatus were from commercial source. The purity of methane and oxygen are 99.9%. The model Gp300-6 rf plasmagenerator was obtained from Jilin Mongan factory of electron equipments. The model 715 spectrophotometer and model 103 gas chromatograph were obtained from Shanghai factory of analytical equipments. The formaldehyde was analyzed by colorimetric method based on the Hantzsch reaction\(^4\). Other components were analyzed by gas chromatography.

The methane oxidation were performed with a reactor as shown in Fig.1. The products were colleted in a cold trap. The discharge pressure, frequency and input power were controlled at 0.8 to 1.5 Torr, 13.6 MHz and 140 to 290 W respectively. While mole ratios of methane to oxygen were changed, the pressure, frequency and input power remained constant. While input power was changed, other conditions remained constant during the course of the experiments.

![Diagram of reactor and products collector]

Fig.1 The reactor and products collector
1.discharge region, 2.reaction region
3.rf power source, 4.coupling capacitance
5.products collector, 6.cold trap

RESULTS AND DISCUSSION

In the absence of any initiator, the direct oxidation of methane to formaldehyde was carried out in non-equilibrium plasma. The formaldehyde obtained was the chief product, whatever the experimental conditions were changed. The reaction selectivity can be achieved up to 80% at the best condition of mole ratios. The methanol, ethanol, acetaldehyde, carbon monoxide and water were obtained as by-products.
We have investigated the effect of the mole ratio of methane to oxygen and the plasma power on formaldehyde formation. The results are plotted in Fig. 2 to Fig. 5.

**Fig. 2** The relation between yield and mole ratios

**Fig. 3** The relation between selectivity and mole ratios

**Fig. 4** The relation between yield and plasma power

**Fig. 5** The relation between selectivity and plasma power

The formaldehyde yield was decreased with the increase in the mole ratios at constant pressure, frequency and plasma power as shown in Fig. 2. The curve of the selectivity has a maxi-
mum under the same controlled conditions as shown in Fig. 3.

Fig. 4 and 5 show that both of formaldehyde yield and selectivity are increased with the increase in the plasma power at constant pressure, frequency and mole ratios.

After having been treated by means of mathematical method the relations of formaldehyde yield or selectivity to mole ratios and plasma power can be expressed in the empirical formulas as follows:

\[
Y = ax^b \tag{1}
\]
\[
Y_1 = \frac{1}{a + bx + cx^2} \tag{2}
\]
\[
Y = ae^{bX_1} \tag{3}
\]
\[
Y_1 = \frac{1}{a + bx_1} \tag{4}
\]

where \(Y\) is formaldehyde yield; \(Y_1\) is selectivity; \(X\) is mole ratio; \(X_1\) is ratio of plasma power to flow. This formulas are applicable to Fig. 2 to Fig. 5 in proper order.

In Fig. 2 to Fig. 5, the values denoted by circlet are fitted to the values calculated from formula (1) to formula (4). It is clear that the calculated values are consistent with the experimental ones. The coefficient of the formula (1) to formula (4) are:

- for the formula (1), \(a=0.894\) \(b=0.733\)
- for the formula (2), \(a=41.68\) \(b=-56.22\) \(c=19.47\)
- for the formula (3), \(a=0.228\) \(b=-1.4\times 10^{-3}\)
- for the formula (4), \(a=0.868\) \(b=9.44\times 10^{-3}\)

In the chemical reaction of plasma, electron energy and electron densities, i.e. the electron energy function \(f(\xi)\) are responsible for the reaction rate and products distribution. The electron energy function \(f(\xi)\) is related to pressure, frequency and plasma power. When pressure, frequency and power remained constant, \(f(\xi)\) may be considered constant. The reaction rate and the products distribution depend on the mole ratios of starting materials. Conversely, when pressure and mole ratios remained constant, \(f(\xi)\) is changed with the plasma power. It is clear that the results agree well with this analysis.

Because formaldehyde is situated in the branch stage of
chain reaction of methane oxidation and the plasma has a high ability of the excitation, no formaldehyde was isolated from oxygen and methane mixture discharge in previous works. In Fig. 1, it shows the products can be disengaged from the plasma region, easily, and the products may be captured rapidly, in the cold trap. Therefore, high selectivity has been obtained.

The mechanism of the plasma reaction is quite complex. In general, plasma reaction are discussed on basis of the properties of starting materials and products. Based upon the discharge theory and the knowledge of methane oxidation, the mechanism of this reaction could be proposed. In non-equilibrium plasma, the atomic oxygen, excited state oxygen and the ozone can be produced from oxygen; methyl, methylene and atomic hydrogen etc. can be produced from methane. The formaldehyde ams formed by the interaction of methyl and atomic oxygen, and hydroxyl radical was formed by the interaction of atomic oxygen and atomic hydrogen under the reaction conditions. On the one hand, methanol was formed from hydroxyl and and methyl; on the other hand, new methyl was formed from hydroxyl and unionized methane. Thus formaldehyde was formed again from methanol and atomic oxygen. The alkane and alkene with two carbon atoms can be formed from methyl and methylene in non-equilibrium plasma. According to reference, they can form formaldehyde, methanol and acetone.

We think that the reaction is stopped basically at the stage of formaldehyde formation in this experiments. Therefore, the formaldehyde is always the main product. This mechanism is different from that of the references, so the regularity of the curve in Fig. 2 and 3 is also different from that of the selectivity.

It should be noted that the mole ratios for best selectivity were inconsistent with the mole ratios for the best methane conversion. Further study is required for this problem.

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