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Catalysis Conversion Methane into C_2 Hydrocarbons *via* Electric Field Enhanced Plasma

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Abstract: In this paper the effect of catalyst and carrier in electric field enhanced plasma on methane conversion into C_2 hydrocarbons was investigated. Methane coupling reaction was studied in the system of continuous flow reactor on Ni, MoO_3, MnO_2 catalysts and different ZSM-5 carriers. The per pass conversion of methane can be as high as 22%, the selectivity of ethylene can be as high as 23.8%, of acetylene 60.8%, of ethane 5.4% and of total C_2 hydrocarbons was more than 90%. ZSM-5-25 was the better carrier and MnO_2 was the better active component. The efficiency of energy was as high as 7.81%.

Keywords: Methane, electric field enhanced, plasma, catalysis, C_2 hydrocarbons.

The methane chemistry is interesting subject of the C_1 chemical engineering in the current world, many processes have been developed for this activation, such as oxidative coupling of methane over the convention catalysts of alkaline earth metal and other metal compounds[1], laser assisted catalytic oxidation of methane[2], electrochemical activation[3], gas discharge technology[4~7] *etc*. Above mentioned processes in activity and selectivity have not been made and still need make these processes economically viable.

Here, we present an activation method of methane conversion *via* electric field enhanced plasma catalysis into C_2 hydrocarbons, our aim is to perform electric field induced plasma catalytic reactions under the room temperature and an atmospheric gas pressure.

The catalysts were manufactured with impregnation method. The active matter was metallic catalysts or metallic oxide catalysts whose functions were dehydrogenation and coupling, for example: metallic catalysts Ni; *n*-semiconductor catalysts MnO_2, MoO_3. The metal or metallic oxide was first supported on molecular sieve carrier, then were dried and calcined, at last reduced with hydrogen (which was needed).

The experimental apparatus and flow chart have been previously described[8]. The reactor was made of a quartz tube with inside radius 10 mm. The flow rates of feed and exhaust gases were regulated by mass flow controllers D07-7A/ZMM that were calibrated with soap film flowmeter. The feed gases were mixed and then downward introduced a reactor for all experiments. The exhaust gases were used to analyze by quadrupole mass spectrograph and gas chromatograph.

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Table 1 Contrast of conversion of methane, selectivity of products and efficiency of energy

	x%	Se_1%	Se_2%	Sa %	η%
Without catalyst	6.7	89.1	7.3	0	0.73
Ni/ZSM-5-50	9.8	92.3	3.3	0	0.97
MoO_3/ZSM-5-50	9.4	77.5	7.0	8.0	1.33
MnO_2/ZSM-5-50	10.1	77.5	9.2	6.7	1.42
Ni/ZSM-5-38	22.0	95.4	0	0	2.03
MoO_3/ZSM-5-38	12.5	77.6	7.8	8.9	1.86
MnO_2/ZSM-5-38	10.6	40.2	23.5	30.6	2.98
Ni/ZSM-5-25	9.1	74.9	18.5	0	1.17
MoO_3/ZSM-5-25	14.5	59.9	21.4	10.5	2.63
MnO_2/ZSM-5-25	18.7	5.4	23.8	60.8	7.81

(flow rate of methane 80mL·min^{-1}, discharge voltage 110kV(DC)) x%: Conversion of methane %; Se_1% Selectivity of ethane; Se_2%: Selectivity of ethylene %; Sa%: Selectivity of acetylene %; S_2 % :Selectivity of C_2 hydrocarbons %; η% efficiency of energy; 25, 38 and 50: the ratio of Si/Al in ZSM-5 molecular sieve.

As for the Ni (based) catalysts, the conversion of methane was higher on Ni/ZSM-5-38 catalyst than that of Ni/ZSM-5-50, Ni/ZSM-5-25. No ethylene and acetylene was found on Ni/ZSM-5-38 catalyst. This conclusion was consistent with the XPS test results. The XPS test showed that there was $NiSiO_3$ in the Ni/ZSM-5-38 catalytic surface. The reason was that $NiSiO_3$ could not activate methane converting to ethylene and acetylene. No acetylene was found on all Ni catalyst. The reason was that the dehydrogenation performance Ni was too strong.

As for the MoO_3 catalysts, the catalytic activity of the catalyst MoO_3/ZSM-5-25 was higher than that of MoO_3/ZSM-5-38 and MoO_3/ZSM-5-50. The conversion of methane increased with decreasing the ratio of Si/Al. The selectivity of ethylene and acetylene increased with decreasing the ratio of Si/Al. The total selectivity of C_2 hydrocarbons was a bit less for MoO_3/ZSM-5-25 than that for others. The reason was methane may completely eliminated hydrogen and resulted in carbon deposition when the conversion of methane increased.

As for the MnO_2 catalysts, the conversion of methane was higher for MnO_2/ZSM-5-25 catalyst than that for MnO_2/ZSM-5-38 and MnO_2/ZSM-5-50. The selectivity of ethylene was much higher for MnO_2/ZSM-5-25 and MnO_2/ZSM-5-38 than that of MnO_2/ZSM-5-50. The selectivity of acetylene was much higher for MnO_2/ZSM-5-25 than that for MnO_2/ZSM-5-38, at the same time, the selectivity of acetylene for MnO_2/ZSM-5-38 was much higher than that for MnO_2/ZSM-5-50. The total selectivity of C_2 hydrocarbons was less for MnO_2/ZSM-5-25 than that for others.

Table 1 showed that the conversion of methane was higher with catalyst than that without catalyst. This indicated that the conversion of methane could be improved in EFEP reaction with catalysts. **Table 1** also showed that with or without catalysts the selectivity of ethylene and acetylene varied markedly. Acetylene was found after addition catalysts. This indicated that the selectivity of products could be influenced in EFEP reaction in the presence of catalysts. The efficiency of energy was higher with the catalyst than that without the catalysts. This indicated that the efficiency of energy could be improved after addition catalysts. **Table 1** also demonstrated that the Si/Al ratio of carrier influenced the conversion of methane and selectivity of products.

The yield of C_2 hydrocarbons on Ni/ZSM-5-38 was the highest among all catalysts. However, when ethane converted with Ni/ZSM-5-38 catalyst, no desired ethylene or acetylene was found. The yield of ethylene or acetylene on MnO_2/ZSM-5-25 was the highest among all catalyst. Meanwhile, the efficiency of energy on MnO_2/ZSM-5-25 was much higher than that on others. ZSM-5-25 was the better carrier and MnO_2 was the better active component.

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