Methane Oxidative Coupling in the Presence of Hydrogen Peroxide

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Methane oxidative coupling in the temperature range 400–800 °C is observed with no catalyst in the presence of hydrogen peroxide, which serves as the oxidant as well as the accelerator of the reaction of methane with oxygen.

Oxidative coupling is one of the more promising methods for the direct conversion of methane into useful products.[1] Many studies have been dedicated to this reaction, using different kinds of catalysts, and O_2 as well as N_2O as oxidant.[2,3] Here we report the gas phase oxidative coupling of methane in the presence of hydrogen peroxide with no catalyst.

The reaction was performed in a quartz reactor in the temperature range 400–800 °C with the reaction mixtures CH_4–N_2 and CH_4–air, with a total flow rate of 40–100 ml min^{-1}. In the reaction stream, hydrogen peroxide solution of either 7.6 or 23% m/m with a flow rate 0.03–0.09 ml min^{-1} was added. In the control experiments pure water was used instead of hydrogen peroxide solution.

The reaction products (ethylene, ethane, carbon oxides) were analysed by on-line GC. The results of the experiments as well as the controls are presented in Table 1.

From these results, it can be seen that addition of the hydrogen peroxide solution to the CH_4–N_2 mixture results in product formation, which starts at temperatures as low as 400 °C. A higher rate of reaction was observed when the

hydrogen peroxide solution was added to the CH_4–air mixture. However, for the control CH_4–air–pure water, there is no reaction under these conditions. Analysis of the oxygen concentration in the outlet reaction mixture (1 column 5) shows that the observed effect cannot be related to an increase in oxygen concentration in the reaction mixture, owing to partial decomposition of hydrogen peroxide. This is evident from comparison of the results of the experiments using the CH_4–air mixture and pure water, and the CH_4–N_2 mixture with hydrogen peroxide addition.

The influence of hydrogen peroxide on methane oxidative coupling might be supported by a comparison of the apparent activation energy, E_a, of the reaction with and without hydrogen peroxide:† E_a (no H_2O_2) = 208 kJ mol^{-1} $E_a(H_2O_2)$ = 65–95 kJ mol^{-1}.

Thus, the results obtained indicate that hydrogen peroxide, being stable enough (despite partial decomposition) under the reaction conditions for methane oxidative coupling, can selectively oxidize methane into C_2 products as well as serve as an accelerator of the reaction of methane with oxygen. Taking into account the possibility of formation of hydrogen peroxide *in situ* in the process of oxidative coupling[4] on solid catalysts, one can speculate that it may also be responsible for the subsequent activation of methane in the gas phase, resulting in the formation of additional amounts of C_2 products. This result may explain the recently observed[5] negative effect of reaction mixture quenching in the post-catalytic zone on the C_2 products yield.

Table 1 Influence of hydrogen peroxide on the reaction of methane oxidative coupling

Feed (10^{-3} mol/min^{-1})	$T/°C$	Conversion of CH_4 (%)	Selectivity of C_2 (%)	O_2 outlet/ 10^{-3} mol/min^{-1}
	550	0.5	100	0
CH_4 (1.56)	600	1.0	100	0
N_2 (2.90)	650	1.5	100	0.006
H_2O_2 (0.22)	700	3.2	60.0	0.006
H_2O (1.41)	750	4.3	52.7	0.031
	800	5.6	41.2	0.026
	600	4.3	30.1	0.504
CH_4 (1.56)	650	9.0	33.4	0.464
air (2.90)	700	10.5	39.9	0.482
H_2O_2 (0.22)	750	13.0	36.4	0.420
H_2O (1.41)	800	19.4	37.1	0.362
	600	0.02	100	0.607
CH_2 (1.56)	650	0.03	100	0.607
air (2.90)	700	0.1	100	0.607
H_2O (1.67)	750	0.8	51.4	0.589
	800	2.8	56.7	0.558
CH_4 (0.89)	400	2.3	14.5	0.232
air (0.89)	500	10.5	26.7	0.210
H_2O_2 (0.21)	600	15.0	18.8	0.188
H_2O (4.60)	800	18.5	18.6	0.152

Footnote

† This comparison was made according to the suggestion of a referee.

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