Oxidative Coupling of Methane in the Homogeneous Gas Phase under Pressure

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Non-catalytic oxidative coupling of methane to give ethane and ethylene is considerably enhanced under pressures of up to 1.6 MPa in the temperature range 650—800 °C.

Recently attention has been directed to oxidative coupling reactions of methane, in the hope of developing new uses of natural gas. A number of studies on the catalytic reaction have been published.[1—6] We have reported that a lead oxide catalyst supported on MgO exhibits high activity and selectivity for the reaction.[7] It has also been reported that a trace of C_2 hydrocarbon is obtained without catalyst at 750 °C (ref. 6) and that C_2H_2 and C_2H_4 are obtained from methane at high temperature (in flame) above 1000 °C under atmospheric pressure.[8] On the other hand, partial oxidation of methane to form CH_3OH and HCHO has been studied extensively at low temperature (less than 600 °C).[9,10] In some cases, C_2 hydrocarbons were formed with quite low selectivity.

In the present work, the oxidative coupling of methane has been studied in the gas phase under pressure at temperatures as low as 750 °C. The effect of temperature under pressure has also been examined.

Oxidation of methane was conducted in a flow-type tubular reactor made of Incolloy H. Quartz tubes were inserted into the reactor to minimize direct contact of reactant gases with the metal surface. The volume of the reacting zone was 3.5 ml. The standard reaction conditions were: T 750 °C, $CH_4 : O_2 : N_2$ 14 : 1.6 : 84.4, flow rate 350 ml min^{-1}. All reactants and products were analysed by gas chromatography.

Figure 1 shows the effect of pressure under the standard conditions. No reaction was observed without catalyst under atmospheric pressure, but conversions of methane and oxygen increased as the pressure was raised and the formation both of C_2+ hydrocarbon and CO_x (mostly carbon monoxide) proceeded without formation of methanol or formaldehyde. Conversions of CH_4 and O_2 reached 10.2 and 78.7%, respectively, at 1.6 MPa. With the increase in the pressure, the selectively for C_2+ hydrocarbons decreased from 60 (0.35 MPa) to 45% (1.6 MPa), as a result of a marked increase in CO formation. The ratio of C_2H_4 to C_2H_6 increased with increasing pressure, and at 1.1 MPa and above the selectivity for ethylene was higher than that for ethane. The major part of

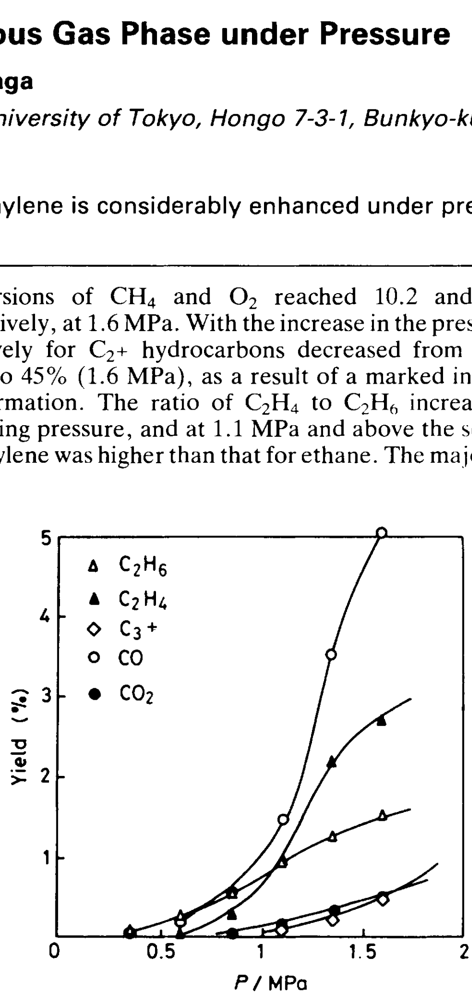

Figure 1. Effect of pressure; T 750 °C, $CH_4 : O_2 : N_2$ 14 : 1.6 : 84.4, flow rate 350 ml min^{-1}.

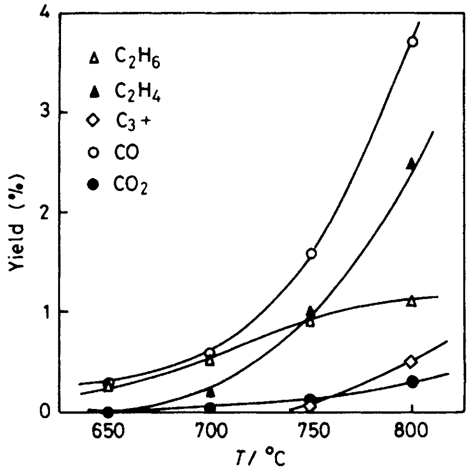

Figure 2. Effect of temperature; *P* 1.1 MPa, $CH_4:O_2:N_2$ 14:1.6:84.4, flow rate 350 ml min^{-1}.

the C_3+ hydrocarbon was propene; the remaining components were propane, butenes, butanes, and butadiene. Carbon dioxide selectivity was almost constant (4—8%) irrespective of the pressure. This value was much lower than that for the catalytic reaction under atmospheric pressure.

Figure 2 demonstrates the effect of temperature. The yield of each product increased with temperature. Although C_2+ selectivity increased between 650 and 750 °C (50—54%), it decreased at 800 °C (47%). High temperature favoured ethylene formation.

It is thought that the formation of C_2 hydrocarbons from methane on a PbO/MgO catalyst proceeds exclusively through coupling of methyl radicals formed by the abstraction of hydrogen by lattice oxygen of the PbO catalyst.[11] Here, the non-catalytic oxidation of methane at high temperature is inferred to proceed by a radical chain mechanism initiated by hydrogen abstraction from methane by O_2. The fact that oxidative coupling of methane proceeds under pressure may be explained in terms of two effects (Scheme 1). One is promotion of methyl radical formation (bimolecular initiation of the chain); the other is the third body effect, which stabilizes the vibrationally excited molecules. If the stabilization of excited ethane does not proceed effectively, the excited ethane should decompose to methyl radicals quickly because of its excess energy, which is enough to dissociate the carbon–carbon bond. In fact reaction at 1.1 MPa gave a much higher yield of C_2 hydrocarbons than that at 0.6 MPa, even when the residence time of reactant gas in the reaction zone was kept at the same level for the two cases.

$$CH_3\cdot + CH_3\cdot \rightleftharpoons CH_3\text{–}CH_3^*$$

$$CH_3\text{–}CH_3^* + M \longrightarrow CH_3\text{–}CH_3 + M^*$$

In summary, oxidation of methane to C_2+ hydrocarbons and carbon monoxide proceeds significantly without catalyst in the gas phase under pressure.

Received, 9th April 1987; Com. 468

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