

## Formation of Methanol by the Gas Phase Partial Oxidation of Methane under Normal Pressures

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Even under normal pressures (1.5–3.0 atm), methanol is formed by the gas phase reaction of methane with oxygen in a flow quartz reactor at 425–490 °C with methanol selectivities exceeding 30% at a methane conversion of 5%.

The direct conversion of methane to methanol has been attracting growing interest not only as a target technological innovation but also as a scientific challenge.<sup>1</sup> While the gas phase radical reactions of methane with oxygen affording methanol have long been known, probably because high pressures favour methanol formation<sup>1–3</sup> and the past studies failed to detect methanol at atmospheric pressure in a flow system,<sup>4–6</sup> the previous works have been mostly conducted under high pressures.<sup>1</sup> On the other hand, the catalytic partial oxidation of methane is generally investigated in laboratories under atmospheric or low pressures.<sup>1</sup> This situation has motivated us to confirm what really happens in the gas phase reaction under normal pressures, since this will surely help us to evaluate the role of heterogeneous catalysts and to design new reactions for the partial oxidation of methane by using solid catalysts as radical generators.<sup>6</sup> Based upon knowledge of radical reactions, we expected that methanol should be formed even under atmospheric pressure. This speculation has been proven to be true. Herein, we report the details.

When a well-mixed sample of CH<sub>4</sub> and O<sub>2</sub> (CH<sub>4</sub>:O<sub>2</sub> = 4:1) was passed at 15 ml min<sup>-1</sup> (residence time = 96 s) under 3 atm pressure through a quartz glass tube (diameter = 10 mm, heating volume = 24 ml), which was kept at 437 °C by a computer-controlled electric furnace, 7.2% methane was converted and methanol was obtained with a selectivity of 28%.<sup>†‡§</sup>

Fig. 1(a) shows the conversion of methane under different pressures as a function of reaction temperature. An increase in pressure shifts the reaction curves toward lower temperatures, in agreement with the previously reported results for the high pressure reactions,<sup>1</sup> and also makes the slopes of the curves greater. Thus, to increase methane conversion from 6.7 to 14%, a temperature increase of only *ca.* 5 °C was sufficient at 3.0 atm, while an increase of more than 15 °C was needed at 1.5 atm.<sup>¶</sup>

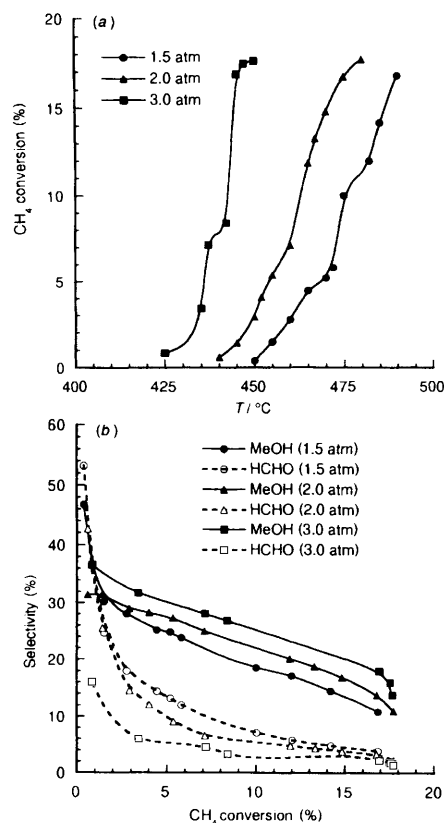
The selectivities for MeOH and HCHO plotted against CH<sub>4</sub> conversion [Fig. 1(b)] show that at the very beginning of the reaction, the selectivities for HCHO were larger than for MeOH. As the reaction progressed with an increase in reaction temperature, selectivities of HCHO markedly decreased and became smaller than those for MeOH. Since methanol and formaldehyde are easily attacked by radical species resulting in the formation of carbon oxides, an increase in methane conversion always causes a decrease in the selectivities for these partial oxidation products. At a fixed methane conversion, the selectivities for methanol are improved to a certain extent as the pressure is increased from 1.5 to 3.0 atm, whereas the selectivities for formaldehyde are reduced. As a result, the sum of the selectivities for the two partial oxidation products differs very little with change of pressure.

Since oxygen is the limiting reactant in these reactions, as shown in Fig. 2(a), increasing O<sub>2</sub> concentration appreciably decreases the reaction temperature. Fig. 2(b) shows that at low methane conversions (below 2%), the methanol selectivities are little affected by O<sub>2</sub> concentration; however, at higher methane conversions, higher O<sub>2</sub> concentrations become advantageous for methanol formation. A similar trend was also observed for HCHO. Consequently, the formation of the partially oxidized

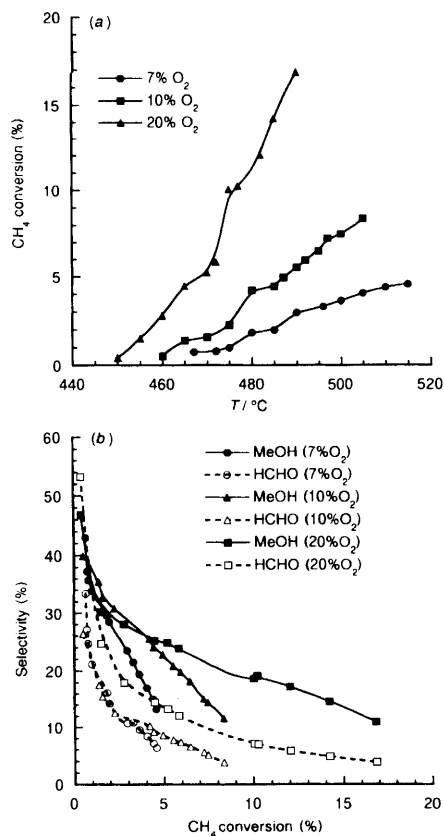
products is more favoured when a higher O<sub>2</sub> concentration is used.<sup>||</sup>

As generally expected, in order to obtain the same methane conversion, higher temperatures are needed for shorter residence times.<sup>1</sup> It was observed that to obtain a methane conversion of about 7% by the reaction of methane with oxygen at a concentration of 20% under 3 atm, the reaction temperatures required were 435, 455 and 468 °C at residence times of 96, 32 and 24 s, respectively. Within the range of the residence times investigated, however, methanol selectivities were found to be little affected.

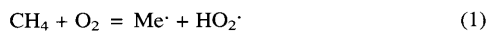
Although the mechanism for the gas phase reaction of methane with oxygen is very complicated,<sup>1</sup> the experimental results presented here may be qualitatively explained by assuming the reactions shown in Scheme 1. The formation of methanol is expected to take place from MeO· which is formed by either decomposition of MeO<sub>2</sub>H<sup>1</sup> or by the reaction of MeO<sub>2</sub>· with Me·.<sup>1,7</sup> The formation of HCHO would occur by the decomposition of MeO<sub>2</sub>· [eqn. (7)].<sup>1,8</sup> Although this reaction has a relatively high activation energy since it is a unimolecular



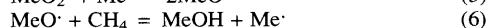
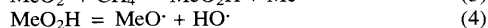
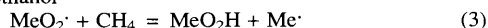
**Fig. 1** Effect of pressure on the oxidation of methane: (a) methane conversion as a function of temperature; (b) product selectivity as a function of methane conversion. Reaction conditions: quartz reactor (diameter = 10 mm), CH<sub>4</sub>:O<sub>2</sub> = 4:1 (20 vol.% O<sub>2</sub>), flow rate = 15 ml min<sup>-1</sup>, residence time = 96 s.



**Fig. 2** Effect of oxygen concentration on the oxidation of methane: (a) methane conversion as a function of temperature; (b) product selectivity as a function of methane conversion. Reaction conditions: quartz reactor (diameter = 10 mm), flow rate = 15 ml min<sup>-1</sup>, residence time = 96 s, pressure = 1.5 atm.



Formation of methanol



Formation of formaldehyde



**Scheme 1**

reaction, this self-decomposition of MeO<sub>2</sub>· may result in the formation of HCHO when the concentrations of the radical species are low. This assumption explains the fact that at the beginning of the methane oxidation HCHO prevails over methanol in the products. The results shown in Fig. 1 can also be explained by Scheme 1, since it is expected that high pressures will make eqns. (3), (5) and (6) more favourable while having little effect on eqn. (7).

Studies on the application of the above findings to the selective partial oxidation of methane, such as by combining catalysts serving as radical generators in order to lower the reaction temperatures as have been observed in reactions of higher pressures,<sup>9</sup> are under way.

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## Footnotes

† Methane conversion and product selectivity were calculated by using the following equations: CH<sub>4</sub> conversion (mol%) = 100 × [total carbon of products]/[total carbon of products + CH<sub>4</sub>(unreacted)]; and product selectivity (mol%) = 100 × (carbon of the product)/(total carbon of all products) × 100, where products refer to CO, CO<sub>2</sub>, MeOH, HCHO, HCO<sub>2</sub>H, HCO<sub>2</sub>Me, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. All reaction lines were maintained at 120 °C. After the reaction was allowed to continue at its steady state for 1 h, the produced gases were automatically analysed on-line by using three GC (two equipped with TCD, one with FID). Gas products such as H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were detected by TCD, while MeOH, HCHO, HCO<sub>2</sub>H, and HCO<sub>2</sub>Me were first converted to methane by a methanizer device and then detected by FID.

‡ Carbon oxides and formaldehyde were obtained in 67% selectivity (CO:CO<sub>2</sub> = 10:1) and 4.5% selectivities, respectively. The methanol selectivity obtained by trapping the liquid products and analysing by <sup>1</sup>H NMR was 25%, in good agreement with that obtained from GC.

§ Plotting the total selectivities for MeOH and HCHO against methane conversions from the data in Fig. 1, we realized that our results are situated in the region with those reported under higher pressures (ref. 3). Accordingly, because of the difference in pressures the space time yields (STY) of these products under normal pressures are smaller than those under higher pressures.

¶ A large CH<sub>4</sub> conversion (>5%) could also be obtained at 1 atm around 500 °C, provided that a relatively long residence time was employed. For example, when the residence times of 105 and 54 s were used, the temperatures corresponding to a 5% CH<sub>4</sub> conversion were found to be 480 and 505 °C, respectively. However, when the residence time decreased to 11 s, less than 1% methane reacted even at 550 °C. Diluting the reaction gas with N<sub>2</sub> significantly retards the reaction. For example, when a N<sub>2</sub> diluted gas (N<sub>2</sub>:CH<sub>4</sub>:O<sub>2</sub> = 5:4:1) was used, no reaction took place at 500 °C, and less than 1% CH<sub>4</sub> reacted at 550 °C at a residence time of 54 s. We have noticed that below about 600 °C, little conversions in blank reactors have been found in the methane coupling experiments carried out at 1 atm (Z. Kalennik and E. E. Wolf, *The Role of Gas-Phase Reactions during Methane Oxidative Coupling, in Methane Conversion by Oxidative Processes*, ed. E. E. Wolf, Van Nostrand Reinhold, New York, 1992, pp. 30–77). Based on our experimental results, we think the difference is very likely because of the different conditions used (residence time, O<sub>2</sub> concentration and inert gas).

|| Explosive limits of CH<sub>4</sub> at 1 atm are in the range of 5.4–59.2% by volume in O<sub>2</sub>, see: *Handbook of Chemistry and Physics*, 70th edn., ed. R. W. Weast, CRC Press, Florida, 1989.

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