

Catalytic Oxidation of Methane to Methanol initiated in a Gas Mixture of Hydrogen and Oxygen

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Selective oxidation of methane to methanol at atmospheric pressure has been achieved using a gas mixture of hydrogen and oxygen over iron phosphate catalyst at >623 K.

Direct oxidation of methane into methanol would undoubtedly be highly attractive compared to the current process which consists of the conversion of methane by steam into synthesis gas, followed by the methanol synthesis over Cu-based catalysts. Many attempts have been made to oxidize methane directly into methanol.¹⁻⁴ However, this has rarely been achieved over solid state catalyst under atmospheric pressure.^{5,6} In most cases, methanol could only be produced at high pressures at which the gas phase homogeneous radical reactions are dominant, except for a few studies using N₂O as the oxidant.⁷⁻⁹ On the other hand, methane monooxygenase catalyses the oxidation of methane selectively to methanol in a biological system.¹⁰ The presence of a reductant (electron donor, usually NADH) is indispensable for the activation of dioxygen in this biological catalytic cycle. In view of this, it is expected that the presence of a reductant may also exert a favourable effect on the oxidation of methane on solid oxide catalysts. Here we report the effect of hydrogen as an activator of oxygen on the catalytic oxidation of methane with oxygen.

The experiments were carried out using a conventional flow system with a fixed-bed quartz reactor at atmospheric pressure. A large variety of catalysts including silica supported transition metal oxides (Fe₂O₃, CuO, NiO, MnO, Cr₂O₃, etc.), silica supported Pd, Pd-containing supported metal oxides, zeolites and various compound oxides have been tested. For most of these catalysts, H₂ exerted no effect or even negative effect on the conversion of methane. However, as shown in Table 1, obvious increase in methane conversion was observed in the presence of hydrogen for Fe-ZSM5, ferrisilicate (ZSM5 analogy, Si/Fe = 50), FAPO-5 (Fe : Al : P = 0.1 : 0.9 : 1) and FePO₄. FePO₄ was the most notable one among these iron containing catalysts. On this catalyst, not only methane conversion was increased with the addition of H₂, but MeOH selectivity was greatly improved as well. MeOH selectivity increased to 25.7% in the presence of H₂ under the conditions in Table 1, while only a trace amount of MeOH was observed during the oxidation of methane in the absence of H₂.

An FePO₄ catalyst performed uniquely in the presence of hydrogen. The FePO₄ used was prepared from an aqueous solution of the stoichiometric mixture of Fe(NO₃)₃ and NH₄H₂PO₄. The solution was dried at 383 K for 12 h and the

resultant powder calcined at 823 K for 5 h in an air flow. The surface area of the catalyst measured by adsorption of Kr was 8.5 m² g⁻¹. Before the methane oxidation, the catalyst bed (0.75 g) in a quartz tube (8 mm diameter) was treated in a flow of He and O₂ (8.4 kPa) at 773 K for 1 h. The reaction was started by adding methane or a mixture of methane and hydrogen carried by helium.

Regarding the mechanism for MeOH formation in the presence of H₂, it is important to make clear whether MeOH is a primary product from methane or a product *via* the reaction of the added H₂ with the CO formed from methane oxidation. Thus, the conversion of CO in a H₂-O₂ atmosphere under similar reaction conditions to those used for methane oxidation was investigated over a FePO₄ catalyst. The results showed that the predominant product was CO₂. Me was also observed as a minor product. Neither MeOH nor HCHO were detected under any of the reaction conditions. Therefore, the possibility that MeOH is formed *via* the CO-H₂ reaction could be excluded.

In order to elucidate the role of H₂, the conversion rates of methane in the presence of H₂ were compared with those in the absence of H₂ at different reaction temperatures. As shown in Fig. 1, methane conversion rates in the presence of H₂ [P(H₂) = 50 kPa] were notably higher than those in the absence of H₂ at all reaction temperatures used in this study. Moreover, in the presence of H₂, the reaction initiated at > ca. 623 K, while no reaction occurred below 673 K in the absence of H₂. The maximum oxygen conversion in Fig. 1 was 13% at 698 K in the presence of hydrogen. Under the same experimental conditions, the oxygen conversion for the

Table 1 Effect of hydrogen on the partial oxidation of methane

Catalyst	Partial pressure of H ₂ /kPa	Conversion of CH ₄ (%)	Selectivity (%)			
			MeOH	HCHO	CO	CO ₂
Fe-ZSM5	0	0.39	0	0	52.2	47.8
	8.4	0.92	0	0	54.2	45.8
Ferrisilicate	0	0.30	0	0	52.4	47.6
	8.4	1.50	0	3.2	69.0	27.8
FAPO-5	0	0.80	0	0	24.9	74.9
	8.4	1.47	1.9	0	22.7	75.3
FePO ₄	0	0.08	1.6	45.7	45.7	5.5
	8.4	0.19	20.3	48.2	25.6	5.9
	50.0	0.51	25.7	46.0	23.0	5.3

Reaction conditions: $T = 673\text{--}723\text{ K}$, $P(\text{CH}_4) = 33.7\text{ kPa}$, $P(\text{O}_2) = 8.4\text{ kPa}$, $W/F = 0.139\text{ g h dm}^{-3}$

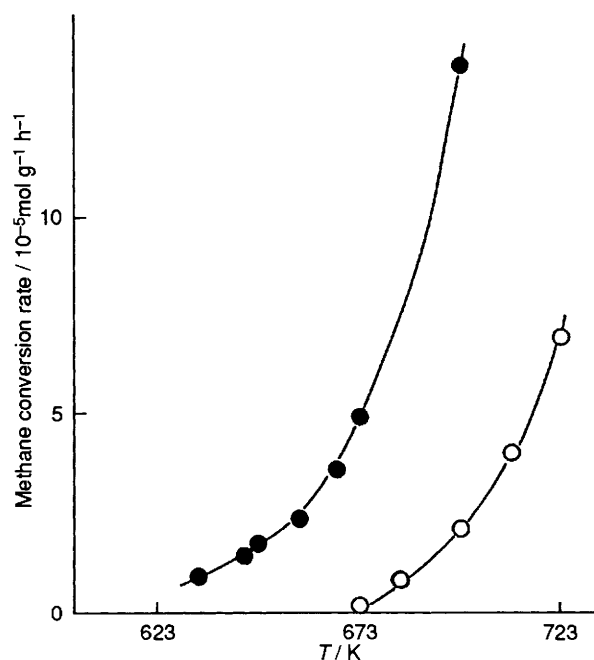


Fig. 1 Methane conversion rates in the presence and the absence of hydrogen over FePO₄ at different reaction temperatures. (○), in the absence of H₂; (●), in the presence of 50 kPa H₂.

Reaction conditions $P(\text{CH}_4) = 33.8\text{ kPa}$, $P(\text{O}_2) = 8.4\text{ kPa}$, $F(\text{total}) = 3.6\text{ dm}^3\text{ h}^{-1}$, $W = 0.75\text{ g}$.

oxidation of methane was evaluated to be 0.63% on the basis of the products (MeOH, HCHO, CO and CO₂). Thus, most of the oxygen converted was used in the oxidation of hydrogen. However, no temperature rise at the catalyst bed was observed after the addition of hydrogen under all experimental conditions in Fig. 1 because the total conversion of oxygen was less than 13%. The logarithm of the methane conversion rate plotted as a function of $1/T$ gave good straight lines both in the presence ($T \leq 673$ K) and absence of hydrogen. These observations show that the reaction at the hot spots can be neglected. The apparent activation energy for methane conversion in the presence of H₂ at ≤ 673 K was 145 kJ mol⁻¹, which is notably lower than that (205 kJ mol⁻¹) in the absence of H₂ at relatively higher reaction temperatures. The product selectivities in the presence and the absence of H₂ are shown in Fig. 2. In contrast to the fact that only a trace amount of MeOH was obtained in the absence of H₂, MeOH became predominant in the presence of H₂. At low temperatures (<653 K), the selectivity to MeOH exceeded 50% and the remaining product was HCHO. CO and CO₂ were not formed. HCHO selectivity increased with decreasing MeOH selectivity with increasing reaction temperature. This supports

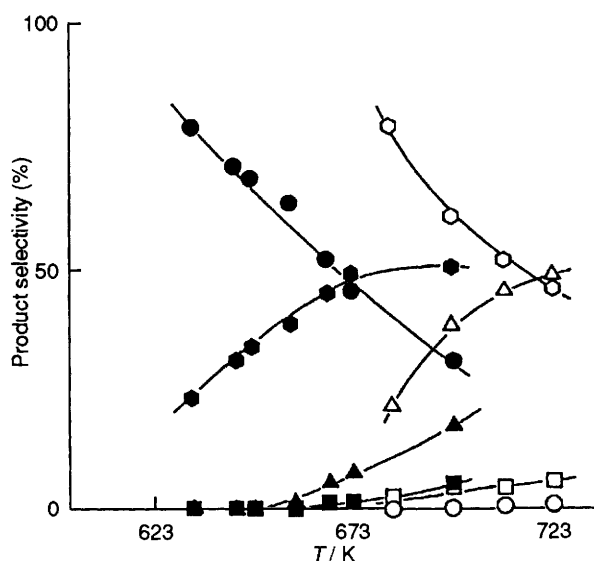


Fig. 2 Product selectivities in the presence and the absence of hydrogen at different reaction temperatures. The white symbols represent those in the absence of H₂ and the black symbols represent those in the presence of 50 kPa H₂. (○) and (●), MeOH; (◇) and (◆), HCHO; (△) and (▲), CO; (□) and (■), CO₂. Reaction conditions are the same with those in Fig. 1.

the fact that MeOH is the primary product from methane and HCHO is the secondary one. HCHO and CO were the main products in the absence of H₂. The changes in the product selectivities in Fig. 2 imply that the primary product in the absence of H₂ could be HCHO.

The results described suggest that a new kind of active centre is formed in the presence of H₂. Methane could selectively be oxidised to MeOH on such active centre at atmospheric pressure and at relatively low temperatures. Although the nature of the newly formed active centre is still unclear, this could be a very active and selective oxygen species which is reductively generated from the dioxygen on the iron site of the FePO₄ surface. In order to investigate the nature of such oxygen species, we have carried out the oxidation of methane over FePO₄ using H₂O₂. The results have shown that MeOH could also be formed with good selectivity in this case, which implies that the oxygen species formed from an O₂-H₂ mixture and that from H₂O₂ on the FePO₄ surface may be the same. Dalton and Green have suggested that an Fe^{IV} = O (from an Fe^{III}-OOH) centre is responsible for monooxygenation of methane in the methane monooxygenase catalytic cycle.¹⁰ Herron has suggested that an iron oxo species could be generated on a Pd/Fe/zeolite catalyst using either O₂-H₂ mixture or H₂O₂.¹¹ We speculate that an oxygen species such as Fe^{III}-OOH or iron oxo species might be formed on the FePO₄ surface under our reaction conditions and is responsible for the partial oxidation of methane to methanol. However, we cannot exclude the other possibility that a hydroxyl radical coupled to an iron site on FePO₄ surface activates conversion of methane into MeOH.

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