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Selective Oxidation of Methane to Methanol over $FePO_4$ Using N_2O and H_2 at Low Temperatures

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Methane could selectively be converted to methanol with N_2O over iron phosphate ($FePO_4$) catalyst. Addition of hydrogen enhanced the conversion of methane and the yield of methanol. The formation of CH_3OH initiated at ≥ 523 K and the one-pass yield for the sum of CH_3OH and HCHO reached 5.3% at 723 K in the presence of hydrogen. A monoatomic oxygen species formed on $FePO_4$ surface was suggeted to be responsible for this active and selective oxidation of methane.

Catalytic oxidation of methane directly into methanol at atmospheric pressure is one of the most difficult subject in catalysis. Methane is a very unreactive molecule compared to methanol. Usually, a higher temperature than 873 K is required for the activation of methane over solid catalysts. However, under these circumstances, only a trace of CH_3OH is obtained because the formed CH_3OH is instantly oxidized into HCHO and CO in the presence of dioxygen as an oxidant of methane. Thus, a new catalytic system working at low temperatures is necessary for the purpose of selective oxidation of methane to methanol over solid catalysts. It is known that methane monooxygenase catalyses the oxidation of methane selectively to methanol in a biological system.1) One important step in this catalytic cycle is the reductive activation of dioxygen with a reductant (electron donor, usually NADH). In view of this, we have recently used hydrogen as the reductant to activate dioxygen for the oxidation of methane and have succeeded in converting methane selectively to methanol at atmospheric pressure over iron phosphate ($FePO_4$) catalyst.2) A newly formed oxygen species on the catalyst surface has been suggested for this selective oxidation of methane. If this oxygen species is a monoatomic type, one could anticipate that it might also be formed by using N_2O. In this communication, we wish to report the results of the oxidation of methane over $FePO_4$ by using N_2O and to examine whether hydrogen also exerts a favorable effect on the reaction as in the case of using O_2.

The experiments were carried out using a conventional flow system with a fixed-bed quartz reactor at atmospheric pressure. The steady state activity for the oxidation of CH_4 by N_2O at different reaction temperatures are shown in Table 1. As shown in Table 1, the reaction initiated at ≥ 598 K, and CH_3OH was the only product at 598 K. The selectivity to CH_3OH decreased and those of HCHO, CO and CO_2 increased with the increase of reaction temperature. These results strongly suggest that CH_3OH is the primary product, which is also the case for the oxidation of CH_4 with the O_2-H_2 gas mixture and with H_2O_2 over the same catalyst.[2] While no reaction occurred at <673 K and no CH_3OH was formed at >673 K when O_2 was used as the oxidant in the absence of H_2. These results suggest that the active oxygen species generated by using the O_2-H_2 gas mixture or H_2O_2 could also be formed by using N_2O. Lunsford et al[3] and Khan and Somorjai[4] have reported that CH_4 can be transformed to CH_3OH and HCHO by using N_2O in the presence of H_2O over MoO_3/SiO_2 catalyst. However, the reaction temperatures for our catalytic system are much lower (about 150 °C lower) than those used for MoO_3/SiO_2 catalyst. Moreover, unlike MoO_3/SiO_2 catalyst, the addition of water reduced the production of CH_3OH over $FePO_4$ catalyst. Therefore, we speculate that the nature of the active oxygen species and the reaction mechanism for our system are different from those suggested for MoO_3/SiO_2 catalyst.

Table 1. Partial oxidation of CH_4 by N_2O over $FePO_4$

Temperature /K	Conversion/%		Selectivity/%			
	N_2O	CH_4	CH_3OH	HCHO	CO	CO_2
598	0.38	0.01	100	0	0	0
623	0.82	0.08	80.0	16.4	3.7	0
648	1.70	0.24	64.5	21.4	13.2	0.9
673	5.05	0.81	40.0	27.4	28.9	3.7
698	14.9	2.15	25.1	21.9	44.6	8.4
723	41.8	6.50	14.6	11.7	58.7	15.0

Reaction conditions: $P(CH_4)= 33.8$ kPa, $P(N_2O)= 16.9$ kPa, F(total)= 3.6 dm^3/h, W= 0.5 g.

As described earlier, the reductant H_2 played an important role in generating the active oxygen species from dioxygen for the oxidation of methane to methanol. In order to examine whether H_2 also exerts a favorable effect on the formation of active oxygen species from N_2O, we have investigated the influence of the addition of H_2 on the reaction. The changes in the CH_4 conversion and CH_3OH yield as functions of H_2 partial pressure at 648 K are shown in Fig. 1. The CH_4 conversion and the CH_3OH yield increased remarkably with a rise in the H_2 partial pressure and both reached maxima at H_2 partial pressure of 16.9 kPa. The yield of CH_3OH almost increased 3 times at this partial pressure of H_2.

The results at a higher reaction temperature (723 K) and a higher N_2O/CH_4 ratio (2.0) are shown in Table 2. Although the increases in CH_4 conversion and CH_3OH yield with the addition of H_2 were not so notable, a favorable effect of H_2 similar to that observed in Fig. 1 was still sustained. The maximum yield of CH_3OH and that of the sum of CH_3OH and HCHO reached 2.8 and 5.3%, respectively, at a H_2 partial pressure of 8.4 kPa under the conditions described in Table 2. As far as we know, these are the highest values ever reported as the one-pass yields for the catalytic partial oxidation of methane.

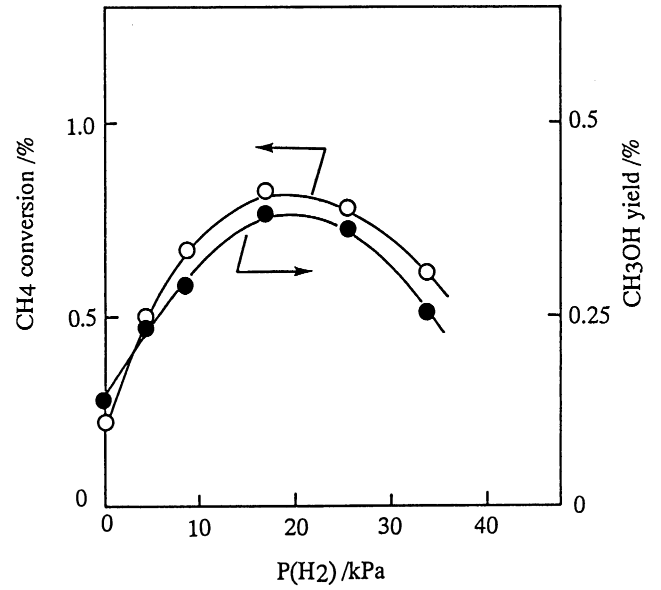

Fig. 1. Effect of hydrogen on the partial oxidation of CH_4 by N_2O over $FePO_4$ catalyst at 648 K. (○), CH_4 conversion; (●), CH_3OH yield. Reaction conditions: $P(CH_4)$= 33.8 kPa, $P(N_2O)$= 16.9 kPa, F(total)= 3.6 dm^3/h, W= 0.5 g.

Table 2. The effect of H_2 on the partial oxidation of CH_4 by N_2O over $FePO_4$

$P(H_2)$ /kPa	Conversion of CH_4/%	Selectivity/%				Yield/%		
		CH_3OH	HCHO	CO	CO_2	CH_3OH	HCHO	total
0	15.3	12.1	9.5	62.2	16.2	1.9	1.5	3.4
4.2	19.7	10.8	9.0	62.5	17.7	2.1	1.8	3.9
8.4	26.5	10.4	9.5	61.4	18.7	2.8	2.5	5.3
16.9	18.2	12.0	10.1	61.1	16.8	2.2	1.8	4.0
25.3	16.1	11.8	9.5	63.3	15.4	1.9	1.5	3.4

Reaction conditions: T= 723 K, $P(CH_4)$= 8.4 kPa, $P(N_2O)$= 16.9 kPa, F(total)= 3.6 dm^3/h, W= 0.5 g.

Further investigations have revealed that the reaction occurs at lower reaction temperatures in the presence of H_2. The formation of CH_3OH was observed even at 523 K. Figure 2 shows the specific rate of CH_4 conversion and the selectivities of the products as functions of the H_2 partial pressure at 573 K. The reaction did not occur in the absence of hydrogen under these conditions. The addition of H_2 initiated the reaction. The rates of CH_4 conversion increased with the increase of H_2 partial pressure and no decrease was observed under the H_2 pressure region examined at such a low temperature. As shown in Fig. 2, CH_3OH

was the only product at low H_2 pressures, but a small amount of HCHO was produced at higher H_2 pressures. The products of deep oxidation such as CO and CO_2 were not formed. The changes in the selectivities of CH_3OH and HCHO formations in Fig. 2 clearly indicate that HCHO is produced through the oxidation of CH_3OH.

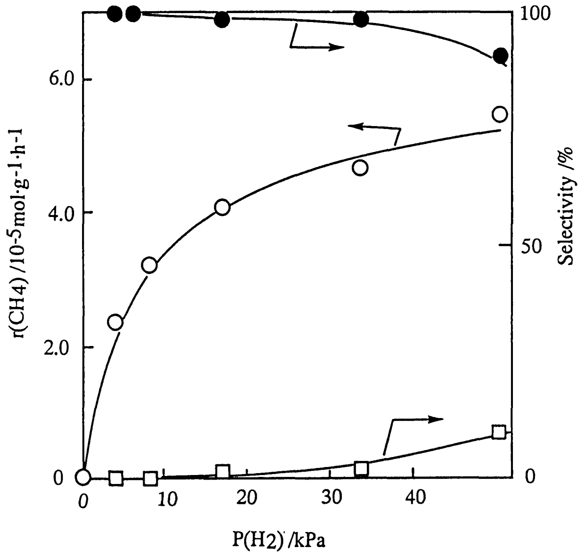

Fig. 2. Effect of hydrogen on the partial oxidation of CH_4 by N_2O over $FePO_4$ catalyst at 573 K. (○), CH_4 conversion; (●), CH_3OH selectivity; (□), HCHO selectivity. Reaction conditions: $P(CH_4)$= 33.8 kPa, $P(N_2O)$= 16.9 kPa, F(total)= 3.6 dm^3/h, W= 0.5 g.

We have demonstrated that dioxygen could be activated by using a reductant (H_2), generating an active and selective oxygen species for the oxidation of CH_4 to CH_3OH over $FePO_4$.[2] The results in this work have suggested that such oxygen species could also be formed by using N_2O alone. Thus, the active oxygen may be a monoatomic one. The addition of H_2 must accelerate the formation of this active oxygen. The active oxygen might be an iron oxo species, resembling the one suggested for methane monooxygenase catalytic cycle.[5] However, O^- or OH radical cannot be excluded at this moment. Further studies are definitely needed to clarify these arguments.

References

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