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Catalytic Oxidation of Methane to Methanol with H_2–O_2 Gas Mixture at Atmospheric Pressure

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Oxidation of methane with oxygen in the presence of hydrogen has been performed at atmospheric pressure over a large variety of catalysts. Among the catalysts tested, iron phosphate showed a very unique catalytic property. The presence of hydrogen initiates the selective oxidation of methane to methanol at ≥623 K over $FePO_4$ catalyst. Formaldehyde as a secondary product is produced through methanol at higher reaction temperatures, while, in the absence of hydrogen, no reaction occurs at ≤673 K on the same $FePO_4$ catalyst. The conversion of methane is notably low at >673 K in the absence of hydrogen and only formaldehyde and carbon oxides are formed. The comparison of the kinetic results in the presence and absence of hydrogen has suggested the generation of an active oxygen species on the catalyst surface in the presence of hydrogen. The pulse reaction studies show that methanol is formed only when methane, hydrogen, and oxygen are cofed. The formation of methanol is enhanced by pretreatment of the catalyst surface with hydrogen. The lattice oxygen of the surface is suggested to be responsible for the oxidation of methane to formaldehyde in the absence of hydrogen at relatively high temperatures (>673 K), while gaseous oxygen is indispensable for the selective oxidation of methane to methanol in the presence of hydrogen. The comparison of the results for the methane oxidation using H_2O_2 and H_2–O_2 gas mixture suggests that the active species generated from H_2–O_2 gas mixture is the same as that from H_2O_2. X-ray photoelectron spectroscopy studies have indicated that Fe(II) exists on the surface after treatment in a stream of CH_4–O_2–H_2, suggesting the interconversion of Fe(III) $\rightleftarrows$ Fe(II) during the reaction. The reductive activation of dioxygen by hydrogen on an iron site must generate the active and selective oxygen species for the conversion of methane to methanol. © 1995 Academic Press, Inc.

INTRODUCTION

Catalytic partial oxidation of methane to methanol with oxygen is one of the most attractive and difficult challenges in catalysis. Although this has been intensively studied by many research groups over the past decades, only a little progress has been made. Methane can be converted to formaldehyde with high selectivity using oxygen over some solid-state catalysts if the methane conversion is limited to a low level (1–4). However, selective methanol production directly from methane has rarely been achieved over solid-state catalyst at atmospheric pressure, except for a few studies using N_2O as the oxidant (5, 6). Methanol can be produced selectively under certain conditions at high pressures (20–100 atm) (7–9). Homogenous radical reactions are dominant at such high pressure, and thus the selectivity to methanol is controlled by the factors influencing the gas phase reactions. Recently, we have revealed that methanol is the precursor of formaldehyde in the partial oxidation of methane by oxygen over $Fe_2(MoO_4)_3$ catalyst (10). However, since the reaction requires high temperature (>873 K), the methanol produced from methane is quickly transformed to formaldehyde and carbon monoxide. We believe that this is the main reason that the partial oxidation of methane to methanol using solid-state catalysts has been so difficult. Therefore, a new catalytic system working at milder conditions is worth exploring to realize the selective oxidation of methane to methanol.

It is known that methane monooxygenase (MMO) catalyzes the oxidation of methane to methanol by dioxygen in a biological system (11). The iron center in the enzyme is believed to be responsible for the catalytic oxidation of methane (12). Recently, there have been a few attempts to mimic such biological systems in the gas–solid catalytic oxidation of methane. Lyons and co-workers (13) have implanted active iron centers into the frameworks of siliceous molecular sieve matrices and examined the catalytic activity for the oxidation of methane. Although a high selectivity to methanol has been reported, their reaction conditions (~50 atm and >673 K) are close to those used for the homogeneous oxidation of methane where gas phase radial reactions rather than catalytic reactions are prevailing. Chan and Wilson (14) have suggested that porphyrin and phthalocyanine complexes encapsulated in zeolites mimic the chemistry of monooxygenase enzyme. They carried out oxidation of methane over these catalysts with molecular oxygen under the reaction conditions of 3.4 atm and 650 K. However, the main reaction product over these catalysts was carbon dioxide with a very poor selectivity to methanol (<10%). To our knowledge, there

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is no report on the selective oxidation of methane to methanol by dioxygen over solid catalysts at low pressures ($\leq$101 kPa).

Our approach is based on the fact that the presence of a reductant (electron donor, such as NADH) is indispensable for the selective oxidation of methane to methanol for the methane monooxygenase catalytic systems. As suggested by Dalton and Green (12), in the methane monooxygenase catalytic cycle, oxygen is activated on the iron centers by electrons and protons to generate a high oxidation state iron oxo species which directly oxidizes methane to methanol. Thus, over solid-state catalysts, the selective oxidation of methane to methanol by oxygen may also be realized in the presence of electron and proton donors. We have recently communicated that methane can selectively be converted to methanol at atmospheric pressure when hydrogen is used as an activator of oxygen over $FePO_4$ catalyst (15). In this paper, we report the details of this study, especially the reaction kinetics and the characterization of the catalyst and discuss the effect of hydrogen and the reaction mechanism.

EXPERIMENTAL

Catalyst

The iron phosphate ($FePO_4$) catalyst used was prepared from a mixed solution of $Fe(NO_3)_3$ and $NH_4H_2PO_4$. After the solution was dried at 363 K for 12 h, the resultant was calcined at 823 K for 5 h in air. The surface area of the $FePO_4$ powder thus prepared was measured by adsorption of Kr. The area was 8.5 m^2/g.

The preparation of the other catalysts will be described on all such occasions.

Catalytic Reactions and Kinetic Studies

The steady-state catalytic activities for each catalyst in the absence and presence of hydrogen were measured using a conventional fixed bed flow reactor (quartz tube) at atmospheric pressure. The internal diameter of the reactor at the catalyst bed was 8 mm, decreasing to 3 mm at the outlet to remove the products quickly from the hot zone of the reactor. A thermocouple was set at the center of the catalyst bed to measure the reaction temperature.

The catalyst was pretreated in the reactor at 723 K for 1 h in a flow of oxygen ($P(O_2)$ = 8.4 kPa) diluted with helium. The reactants diluted with helium were fed to the reactor. When hydrogen was cofed with methane and oxygen, a special caution should be taken to prevent explosion. The entire reaction system was barricaded with acrylic planks, and most experiments were carried out beyond the explosion limits.

The reaction products were analyzed by an on-line gas chromatography. For kinetic measurement, the conversion of O_2 was controlled to be less than 15% by changing the amount of catalyst.

Pulse Experiments

The reactions with pulse method were carried out using a quartz reactor (with the same size as the one used for the flow reactions) of which exit was connected to a gas chromatography. Helium (purity > 99.99%), after being passed through a liquid nitrogen trap to remove the traces of moisture and other impurities, was used as the carrier gas. Before the pulse reaction, the catalyst was treated at 773 K in a flow of oxygen for 30 min, then the oxygen in the line was purged out with a flow of helium at the same temperature for 30 min. The catalyst was cooled to the reaction temperature in a flow of helium before the pulse experiments, or followed by further treatments, for example, the reduction using hydrogen pulses. The pulse reaction was started by passing a CH_4-containing pulse through the catalyst bed at a fixed reaction temperature.

Catalyst Characterizations

X-ray diffraction (XRD), Mössbauer, and X-ray photoelectron spectroscopy (XPS) studies were carried out to characterize the $FePO_4$ catalyst. The XRD experiment was performed with a X-ray diffractometer (Rigaku) using Cu$K\alpha$ radiation. The Mössbauer spectra were recorded at room temperature using a ^{57}Co source and an acceleration spectrometer operated in triangular mode. The isomer shifts were calculated with respect to the position of α-Fe.

The XPS experiments were performed on a VG ESCALAB 220-I spectrometer, using Mg$K\alpha$ radiation ($h\nu$ = 1253.6 eV). The background pressure in a detect chamber was about 1×10^{-6} Pa. The electron binding energy was calibrated by referring to that of C_{1s} (284.6 eV).

RESULTS AND DISCUSSION

The Catalyst Effective for Selective Oxidation of CH_4 to CH_3OH

It has been demonstrated that Pd catalysts are effective for the hydroxylation of higher alkanes and aromatics by using O_2–H_2 gas mixture (16, 17). Because Pd would easily activate hydrogen, oxygen is reduced by this activated hydrogen, being transformed to the active oxygen species for the selective oxidation of alkanes and aromatics. We have selected such materials as the first candidate catalysts for the selective oxidation of CH_4 with oxygen in the absence and presence of H_2. The catalysts examined were Pd/SiO_2, Pd/Al_2O_3, Pd/H-ZSM5, Pd–Fe_2O_3/SiO_2 (Al_2O_3 or HZSM-5), and Pd–CuO/SiO_2 (Al_2O_3 or HZSM-5). These catalysts were prepared by impregnating the support with an aqueous solution of $PdCl_2$ or a mixed solution of $PdCl_2$ and $Fe(NO_3)_3$ or $Cu(NO_3)_2$. The cata-

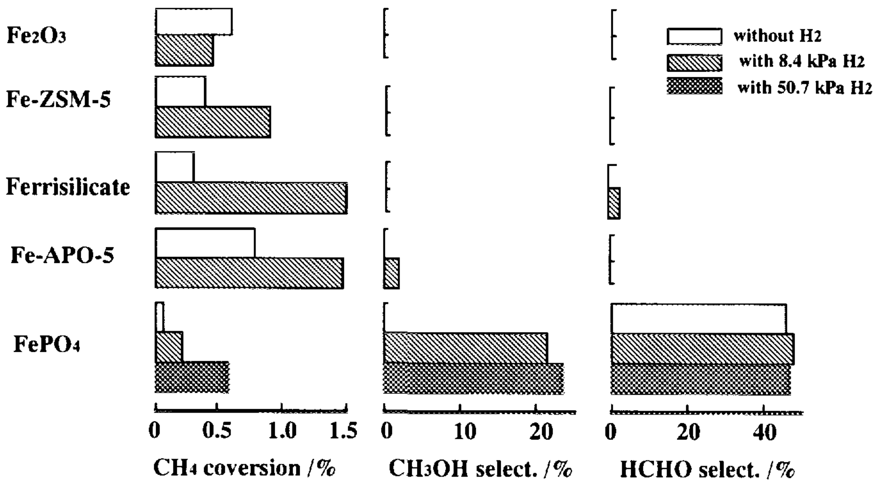


FIG. 1. Oxidation of CH_4 by O_2 in the absence and presence of H_2 for the iron containing catalysts. Reaction conditions: $P(CH_4) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $T = 673$ K, $W/F = 0.14\ g \cdot h \cdot dm^{-3}$.

lysts were calcined in air at 823 K for 5 h and reduced in the reactor with H_2 at 823 K for 2 h before the catalytic tests. The results of the catalytic tests at the temperature range of 573 K to 773 K showed that no matter whether H_2 was cofed (4.2–50.7 kPa) or not, CO and CO_2 were the only carbon oxide products. CH_3OH, HCHO, and C_2 hydrocarbons were not obtained at all. The presence of H_2 increased the O_2 conversion greatly, but decreased the CH_4 conversion. This is ascribed to the competitive reaction between H_2 and CH_4 toward O_2. These observations indicate that such catalysts are not appropriate for the partial oxidation of CH_4 in the presence of H_2.

The second group catalysts examined were a series of iron-containing compounds. The results with and without hydrogen are shown in Fig. 1. The catalysts in Fig. 1 were synthesized by the hydrothermal method except for $FePO_4$ and Fe_2O_3. As can been seen in Fig. 1, although no favorable effect of H_2 was observed for Fe_2O_3, the presence of H_2 increased the CH_4 conversion for $FePO_4$, Fe–APO-5 (Fe : Al : P; atomic ratio = 0.1 : 0.9 : 1.0), ferrisilicate (ZSM-5 analog, Fe : Si; atomic ratio = 1 : 50), and Fe–ZSM-5 (Fe content = 2 wt% and Si/Al = 50) catalysts. It is to be noted that the addition of H_2 induced the formation of CH_3OH over $FePO_4$ and Fe–APO-5. The common feature of these two catalysts is that the iron atoms in both catalysts are tetrahedrally coordinated with oxygen atoms, and FeO_4 tetrahedral units are isolated by PO_4 or AlO_4 tetrahedral units. The enhancing effects of H_2 on both the CH_4 conversion and the CH_3OH selectivity are much more notable for $FePO_4$. The best formation rate of CH_3OH observed on this catalyst was 0.16 mmol h^{-1} m^{-2} at 723 K in the presence of H_2. Although the formation rate is far from satisfactory, the production of CH_3OH has become possible at atmospheric pressure in the presence of H_2. Such favorable effects of hydrogen on the partial oxidation of CH_4 over $FePO_4$ catalyst are further ascertained under other reaction conditions as will be demonstrated later.

Other metal phosphates including V, Cr, Mn, Co, Ni, Cu, Zn, and Al, which were prepared by means of a similar method to that used for the preparation of $FePO_4$, were also tested for the oxidation of CH_4 in the presence and absence of H_2. However, no favorable effect of H_2 on the partial oxidation of CH_4 was observed for these metal phosphates under the same experimental conditions as those of Fig. 1.

Conversion of CO in H_2–O_2 Atmosphere over $FePO_4$ Catalyst

As described above, the formation of CH_3OH was notably enhanced in the presence of H_2 over $FePO_4$ catalyst. However, there is a question that the CH_3OH formed in the presence of H_2 may not be a direct product from the oxidation of CH_4 but an indirect product through the reaction of the H_2 added with the CO formed from the oxidation of CH_4. In order to make this point clear, we have investigated the conversion of CO in a H_2–O_2 atmosphere. The results are shown in Table 1. The experiments were carried out under conditions similar to those used for the CH_4 oxidation in the presence of H_2. It should be noted that the partial pressure of CO formed during CH_4 oxidation was about 0.2 kPa under the conditions of Fig. 1. From Table 1, it is clear that CO is converted mainly to CO_2 at a $P(CO)$ of 0.2 kPa. CH_4 is also produced at higher CO partial pressures. However, neither CH_3OH nor HCHO was obtained under all the reaction conditions in Table 1. Therefore, the possibility of the production of

TABLE 1

The Results of the Reaction of CO in O_2–H_2 Atmosphere

Partial pressure of CO (kPa)	Conversion of CO (%)	Product selectivities (%)	
		CO_2	CH_4
0.2	6.7	99	1
1.0	10.3	85	15
2.0	10.9	78	22

Note. Reaction conditions: $P(O_2) = P(H_2) = 8.4$ kPa, $W/F = 0.28$ g · h · dm^{-3}, $T = 723$ K.

CH_3OH through the reaction of CO with H_2 can be ruled out in this study.

Kinetic Studies for Partial Oxidation of CH_4 in the Presence and Absence of H_2 over $FePO_4$

a. Effect of reaction temperature. Figure 2 shows the rate of CH_4 conversion in the presence and absence of H_2 as functions of the reaction temperature. The results in Fig. 2 clearly show that the presence of H_2 increases the conversion rate at all the temperatures examined. Moreover, in the presence of H_2, the reaction started at >623 K, while in the absence of H_2, no product was observed at <673 K.

The O_2 conversions under the same reaction conditions of Fig. 2 were shown in Fig. 3. The O_2 conversion in the presence of H_2 can be attributed to two main reactions, namely, the CH_4 oxidation to CH_3OH, HCHO, CO, and CO_2 and the H_2 oxidation to H_2O. In the presence of H_2, the total O_2 conversion (curve a) and the O_2 conversion attributed to CH_4 oxidation (curve b), which is evaluated from the amount of the CH_3OH, HCHO, CO, and CO_2 formed, are shown in Fig. 3. The results indicate that the total conversion of oxygen in the presence of H_2 ($P(H_2) = 50.7$ kPa) is only 3–13% under the conditions used in Fig. 3. Thus, the possibility of the generation of hot spots on the catalyst due to a violent reaction of O_2 and H_2 could be excluded. In fact, at the highest oxygen conversion in Fig. 3, only a slight temperature rise (ca. 0.5 K) at the catalyst bed was observed just after the addition of hydrogen into a feed gas mixture of methane and oxygen. Therefore, the initiation of CH_4 conversion in the presence of H_2 may be ascribed to the generation of a new active species for the activation of methane. The results in Fig. 3 indicate that the proportion of the O_2 used in CH_4 conversion is only 2–5% as we expect from the reactivity difference between H_2 and CH_4.

The changes of the product selectivities for the same experiments in Fig. 2 are shown in Figs. 4A and 4B. As shown in Fig. 4A, HCHO and CO were the main products in the absence of H_2. CO_2 was also produced at higher temperatures. Only a trace of methanol was formed at ≥703 K. On the other hand, as shown in Fig. 4B, CH_3OH became one of the predominant products in the presence of H_2. CH_3OH selectivity exceeded 50% at <660 K. HCHO selectivity increased as a rise in the reaction temperature. The selectivities to CO and CO_2 were almost zero at <650 K. We have plotted the selectivities to

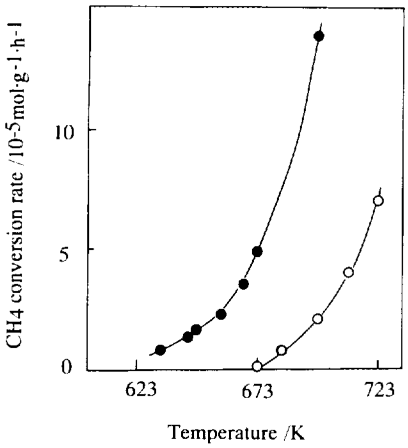


FIG. 2. Comparison of CH_4 conversion rates in the absence and presence of H_2 at different reaction temperatures. (○) In the absence of H_2, (●) in the presence of 50 kPa H_2. Reaction conditions: $P(CH_4) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $W/F = 0.208$ g · h dm^{-3}.

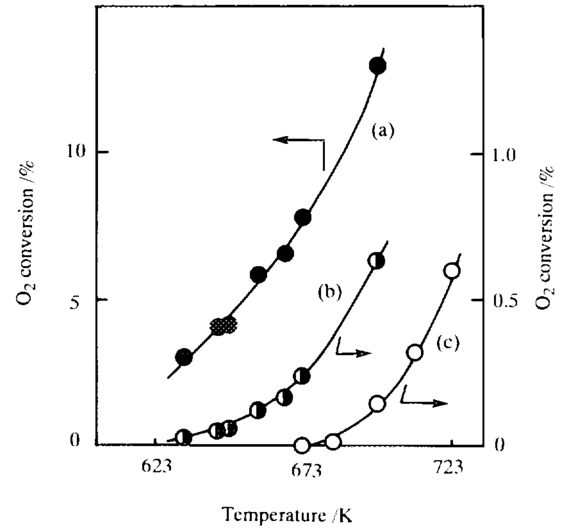


FIG. 3. Oxygen conversions in the absence and presence of H_2 at different reaction temperatures. (●) Total O_2 conversion in the presence H_2, (◑) O_2 conversion ascribed to CH_4 conversion in the presence of H_2, (○) O_2 conversion in the absence of H_2. Reaction conditions: $P(CH_4) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $W/F = 0.208$ g · h dm^{-3}.

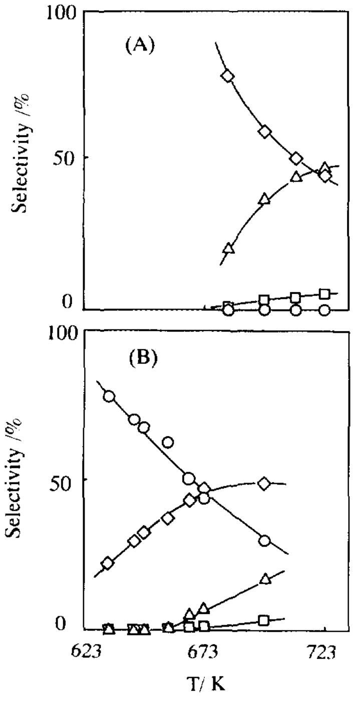


FIG. 4. Effect of reaction temperatures on the product selectivities. (○) CH_3OH, (◇) HCHO, (△) CO, (□) CO_2. (A) In the absence of H_2, (B) in the presence of 50 kPa H_2. Reaction conditions: $P(CH_4) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $W/F = 0.208$ g·h dm^{-3}.

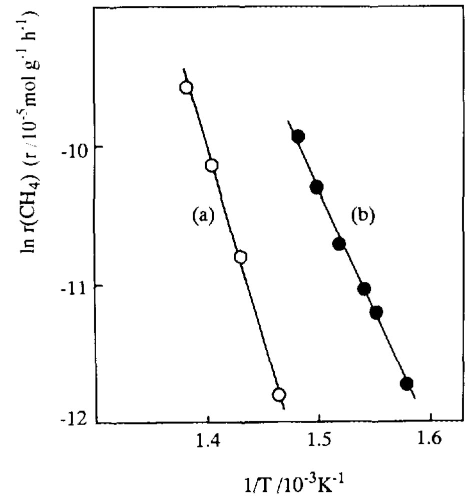


FIG. 6. Logarithm of CH_4 conversion rate vs reciprocal of the reaction temperature. (○) In the absence of H_2, (●) in the presence of 50 kPa H_2. Reaction conditions: $P(CH_4) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $W/F = 0.208$ g·h dm^{-3}.

CH_3OH and HCHO versus CH_4 conversion for the results at different temperatures in Fig. 5. As can be seen in this figure, the selectivity to CH_3OH decreases from 80 to 18% and that to HCHO increases from 20 to 45% with the increase of CH_4 conversion from 0.05 to 1.2% in the presence of H_2, while, in the absence of H_2, nearly no CH_3OH is formed and the selectivity to HCHO follows the well known decay curve (2, 18) for the HCHO selectivity with a rise in CH_4 conversion, decreasing from 55 to 15% at the same range of CH_4 conversion. The sum of the selectivities for CH_3OH and HCHO increased for three or four times at the same CH_4 conversion due to the presence of H_2. These observations strongly suggest that the reaction scheme for CH_4 oxidation in the presence of H_2 is quite different from that reported in many references for the catalytic oxidation of methane. Moreover, these results suggest that a new active center which is highly selective for the partial oxidation of CH_4 into CH_3OH is formed in the presence of H_2.

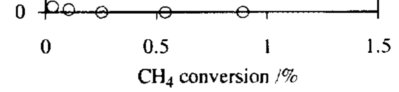


FIG. 5. Selectivity vs CH_4 conversion in the presence and absence of H_2. (●) and (○) CH_3OH selectivities in the presence and absence of H_2, respectively; (◆) and (◇) HCHO selectivites in the presence and absence of H_2, respectively. Reaction conditions: $P(CH_4) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $P(H_2) = 50$ kPa (in the presence of H2).

The logarithm of the rates of CH_4 conversion in the presence and absence of H_2 is plotted against $1/T$ in Fig. 6. In both cases, good straight lines are obtained, supporting the consideration that the reaction does not occur on the hot spots. From these two straight lines, the apparent activation energies for CH_4 activation are calculated to be 145 ± 5 and 205 ± 5 kJ/mol in the presence of H_2 at ≤ 673 K and in the absence of H_2, respectively. These observations strongly suggest again that the addition of H_2 generates a new active site for the conversion of CH_4.

b. Effect of contact time. In order to obtain a general picture of the reaction, the effect of the contact time on the CH_4 conversion was investigated both in the presence of H_2 at ≤ 673 K and in the absence of H_2 at higher temperatures. As shown in Figs. 7A and 7B, good linear relations are observed between the CH_4 conversion rates and the contact time (expressed as W/F) in both cases. These results confirm that the reactions proceed in steady state. It should be noted here that no reaction occurred (includ-

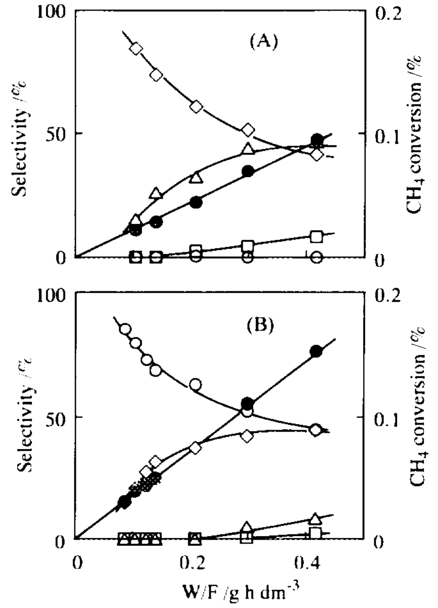


FIG. 7. Effect of contact time on the product selectivity and CH_4 conversion. (○) CH_3OH, (◇) HCHO, (△) CO, (□) CO_2, (●) CH_4 conversion. (A) In the absence of H_2, T = 698 K; (B) in the presence of 50 kPa H_2, T = 658 K. Reaction conditions: $P(CH_4)$ = 33.8 kPa, $P(O_2)$ = 8.4 kPa.

ing the reaction of H_2 with O_2) in the absence of catalyst under the reaction conditions used in this study.

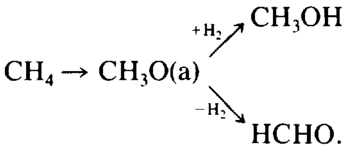
The changes of product selectivities as functions of the contact time were shown in Figs. 7A and 7B. As shown in Fig. 7A, in the absence of H_2, when the contact time approaches zero, the selectivity of HCHO approaches 100% and those of CO and CO_2 approach zero. These results suggest that HCHO is the primary product, and CO and CO_2 are formed by the further oxidation of HCHO. Thus, the reaction scheme for the oxidation of CH_4 in the absence of H_2 can be written as follows:

$$CH_4 \rightarrow HCHO \rightarrow CO \rightarrow CO_2. \qquad [1]$$

However, in the presence of H_2, the changes of the selectivity in Fig. 7B indicate that CH_3OH becomes the initial product and HCHO is formed as the secondary product through the oxidation of CH_3OH. CO must be formed by the further oxidation of HCHO. Thus, the reaction paths for the oxidation of CH_4 in the presence of H_2 can be expressed as

$$CH_4 \rightarrow CH_3OH \rightarrow HCHO \rightarrow CO. \qquad [2]$$

c. Effect of H_2 pressure. The dependence of the rate of CH_4 conversion on the partial pressure of H_2 is shown in Fig. 8A. The experiments were carried out at 648 K, 658 K, and 673 K. No reaction occurred at these reaction temperatures in the absence of H_2. Thus, the conversion of CH_4 in Fig. 8A can be ascribed to the newly formed active sites due to the presence of H_2. The rate of CH_4 conversion was increased with the increase in the partial pressure of H_2 at all the reaction temperatures and H_2 pressures examined. Figure 8B shows the variation of the product selectivity as functions of the partial pressure of H_2. The results show that the product selectivity does not depend on the pressure of H_2 at the range from 8.4 to 50.5 kPa for all the temperatures investigated. These observations exclude the possibility that hydrogen would enhance the formation of CH_3OH due to the hydrogenation of a methoxide intermediate as shown below:



$$CH_4 \rightarrow CH_3O(a) \begin{cases} \xrightarrow{+H_2} CH_3OH \\ \xrightarrow{-H_2} HCHO. \end{cases} \qquad [3]$$

Moreover, this scheme cannot explain the fact that the presence of H_2 initiates the oxidation of CH_4. Therefore, the results in Figs. 8A and 8B strongly support that the effect of H_2 is to generate a new active species which selectively activated CH_4 to CH_3OH.

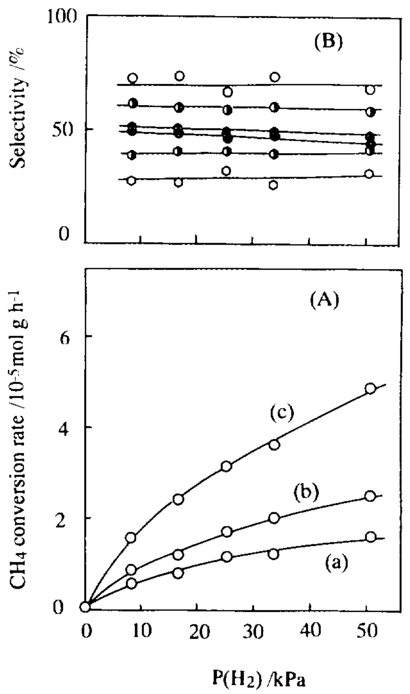


FIG. 8. Effect of H_2 partial pressure. (A) CH_4 conversion rate, (B) product selectivities. (A) a, T = 648 K; b, T = 658 K; c, T = 673 K. (B) (○), (◑), and (●) represent CH_3OH selectivities at 648 K, 658 K, and 673 K, respectively; (⬯), (◐), and (⬮) represent HCHO selectivities at 648 K, 658 K, and 673 K, respectively. Reaction conditions: $P(CH_4)$ = 33.8 kPa, $P(O_2)$ = 8.4 kPa, W/F = 0.208 g · h dm^{-3}.

As suggested in Eq. [2], HCHO is produced successively from CH_4 through CH_3OH. Here, we assume the rate constants k_1 and k_2 for each step of this successive reaction:

$$CH_4 \xrightarrow[O^*]{k_1} CH_3OH \xrightarrow{k_2} HCHO. \qquad [4]$$

Where, O* denotes the active oxygen species formed in the presence of H_2. The concentration of O* must depend on the partial pressures of H_2, O_2, and CH_4. If the conversion rate of CH_3OH to HCHO depends on the first order with regard to the concentration of CH_3OH, the formation rates of CH_3OH and HCHO can be written as

$$\frac{d[CH_3OH]}{dt} = k_1[O^*][CH_4] - k_2[CH_3OH]$$

$$\frac{d[HCHO]}{dt} = k_2[CH_3OH].$$

Assuming a steady-state concentration of O*, the low conversion of methane (<2%) under the experimental conditions in this work allows us to consider that $k_1[O^*][CH_4]$ is constant during the reaction. By solving the differential equations, we can obtain

$$[CH_3OH] = \frac{k_1[O^*][CH_4]}{k_2}(1 - e^{-k_2t}),$$

$$[HCHO] = \frac{k_1[O^*][CH_4]}{k_2}(k_2t + e^{-k_2t} - 1).$$

Therefore,

$$\frac{[CH_3OH]}{[HCHO]} = \frac{1 - e^{-k_2t}}{k_2t + e^{-k_2t} - 1}.$$

This equation shows that [CH_3OH]/[HCHO] ratio depends only on k_2 and t. It should be noted that the contact time is constant and the formations of CO and CO_2 can be neglected under the conditions of Figs. 8A and 8B. Thus, the selectivities of CH_3OH and HCHO at a fixed contact time and at a fixed temperature do not depend on the partial pressure of H_2 as shown in Fig. 8B.

d. Effects of CH_4 and O_2 pressures. The effect of the partial pressure of CH_4 on the conversion rate of CH_4 in the presence of H_2 at ≤673 K is shown in Fig. 9A. No reaction occurred in the absence of H_2 under these reaction conditions. Thus, the results in Fig. 9A reflect the reaction due to the new active species formed in the presence of H_2. Figure 9A indicates that the rate of CH_4 conversion depends on the partial pressure of CH_4 by less than first order. While, as shown in Fig. 9B, the conversion rate of CH_4 at ≥683 K in the absence of H_2 increased proportionally to the partial pressure of CH_4. Such difference suggests that the reaction mechanisms for CH_4 conversion are different from each other in the presence and absence of H_2. This will be discussed later.

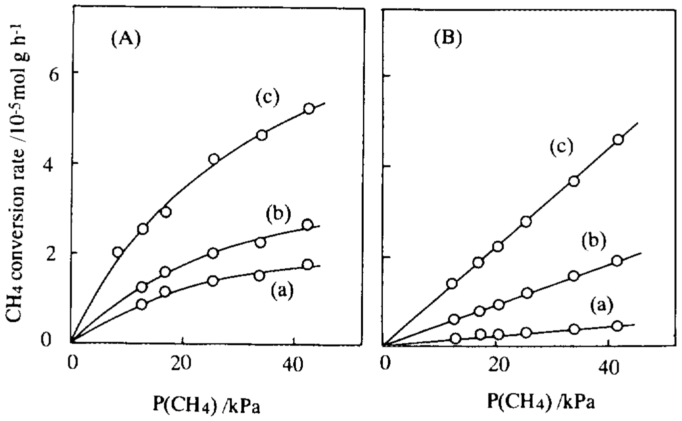


FIG. 9. Effect of CH_4 partial pressure on CH_4 conversion rate. (A) In the presence of H_2. a, T = 648 K; b, T = 658 K; c, T = 673 K. (B) In the absence of H_2. a, T = 683 K; b, T = 698 K; c, T = 713 K. Reaction conditions: $P(H_2)$ = 50.7 kPa, $P(O_2)$ = 8.4 kPa, W/F = 0.208 g · h dm^{-3}.

The influence of the partial pressure of O_2 on the rate of CH_4 conversion was investigated at the O_2 pressure region of 4.2–20 kPa both in the absence and presence of H_2. No notable change in the rate of CH_4 conversion was observed for both cases.

Pulse Reaction Studies on $FePO_4$ Catalyst

As described above, a new active species capable of converting CH_4 to CH_3OH has been postulated in the presence of H_2. In order to study the role of gaseous H_2 and O_2 in the formation of such active species, we have examined the reaction by pulse technique. Before the pulse reaction, the catalyst was pretreated in a flow of O_2 and subsequently purged with He. The effect of the further treatment of the catalyst with a H_2 or (H_2 + O_2) pulse was examined in some cases. The pulses passed through the catalyst bed were CH_4, (CH_4 + H_2), and (CH_4 + O_2 + H_2). In these pulses, CH_4 concentration was kept constant by using helium as a balance gas.

The results in Table 2 show that CH_3OH can be produced only when (CH_4 + O_2 + H_2) pulse is used irrespective of the different pretreatment of the catalyst (runs 4,

TABLE 2

Results of Pulse Experiments

Run	Pretreatment	Pulse	CH_4 conversion (%)	Selectivity (%)		
				CH_3OH	HCHO	CO
1	O_2 flow	CH_4	0.066	0	87.6	8.0
2	O_2 flow	$CH_4 + O_2$	0.067	0	85.4	8.5
3	O_2 flow	$CH_4 + H_2$	0.017	0	~100	0
4	O_2 flow	$CH_4 + O_2 + H_2$	0.15	21.0	71.4	7.6
5	$O_2 + H_2$ pulse	CH_4	0.047	0	93.1	6.9
6	$O_2 + H_2$ pulse	$CH_4 + O_2 + H_2$	0.20	26.9	67.5	5.6
7	H_2 pulse	CH_4	0.047	0	92.0	8.0
8	H_2 pulse	$CH_4 + O_2$	0.067	0	88.6	7.5
9	H_2 pulse	$CH_4 + O_2 + H_2$	0.21	26.1	67.4	6.4

Note. Conditions: $T = 698$ K, $W = 0.5$ g, He carrier (40 ml/min), pulse size 2.67 ml; in pulse: $P(CH_4) = 33.8$ kPa, $P(H_2) = 50.7$ kPa, $P(O_2) = 8.4$ kPa, and He is used as a balance gas.

6, and 9). Moreover, CH_4 conversion is notably high for these cases. This suggests that coexistence of O_2 and H_2 is necessary for the generation of the active species which is responsible for the conversion of CH_4 to CH_3OH. The fact that CH_3OH is not observed in run 5, where the catalyst has been pretreated with ($H_2 + O_2$) pulse and subsequently followed by the reaction with CH_4 pulse within 10 min, indicates that the life time of the active species formed from H_2 and O_2 is not so long at the conditions shown in Table 2. Comparison of the results of runs 4, 6, and 9 in Table 2 shows that the conversion of CH_4 and the selectivity to CH_3OH are both improved when the catalyst has been pretreated with H_2 or ($H_2 + O_2$) pulse compared to those pretreated in a flow of O_2. This observation implies that the reduction of the catalyst by H_2 or ($H_2 + O_2$) pulse is favorable for the generation of the active species.

In order to clarify the above point, we further investigated the effect of the degree of reduction of the catalyst on the reaction of ($CH_4 + O_2 + H_2$) pulse. The results are shown in Table 3. Before each run, the catalyst was firstly pretreated with an O_2 flow at 723 K followed by purging out O_2 with He and then was reduced with H_2 pulses. The number of H_2 pulse used for the reduction before each run of CH_4–O_2–H_2 pulse was shown in the first row of Table 3. The water produced by each H_2 pulse was precisely analyzed by gas chromatography. The degree of reduction of the catalyst surface was calculated from the amount of the water produced and the number of oxygen atoms of the catalyst surface. As shown in Table 3, the increase in the degree of reduction enhances both the CH_4 conversion and the CH_3OH selectivity. Therefore, the reduction of the catalyst surface is favorable for the formation of CH_3OH. These observations imply that one of the roles of H_2 in the specific conversion of CH_4 with H_2–O_2 mixture is to generate the reduction sites at the surface, namely Fe^{2+} centers. However, the Fe^{2+} itself cannot be the active species because CH_3OH is not formed from the CH_4 and ($CH_4 + O_2$) pulses as can be seen in Table 2 (runs 7 and 8).

The results of runs 1 and 2 in Table 2 suggest that the conversion of CH_4 to HCHO in the absence of H_2 does not depend on the presence of gaseous oxygen. Figure 10A shows the dependence of CH_4 conversion on the concentration of O_2 in the pulse at 698 K. The CH_4 conversion did not change with a rise in the concentration of O_2 from 0 to 8%. Furthermore, the CH_4 conversion and the HCHO yield did not change at all when gaseous oxygen was not added for the first to the eighth CH_4 pulse. These results strongly suggest that the lattice oxygen at the surface is responsible for the oxidation of CH_4 to HCHO in the absence of H_2.

The dependence of CH_4 conversion on the concentration of O_2 in the pulse in the presence of gaseous H_2 was shown in Figure 10B. The reaction temperature was lowered to 673 K at which no reaction occurred in the absence of H_2, and thus the reaction due to the surface lattice oxygen can be neglected. The results in Fig. 10B indicate that no reaction occurs without O_2 in the pulse. CH_4 conversion increases steeply with the addition of O_2 from 0 to 4% in the pulse and keeps unchanged at >4%. It should also be noted that CH_3OH is produced in Fig. 10B as well as HCHO, while only HCHO and CO are formed in Fig. 10A. These results suggest that coexistence of gaseous O_2 and H_2 is indispensable for the generation of the active oxygen species for the oxidation of CH_4 to CH_3OH.

Oxidation of CH_4 with H_2O_2 over $FePO_4$ Catalyst

In order to get information about the nature of the newly formed active oxygen species, the reactivity of H_2O_2 to-

TABLE 3

Effect of the Surface Reduction by H_2

Number of H_2 pulse (pretreatment)	Degree of reduction of the surface (%)	CH_4 conv. (%)	Selectivity (%)		
			CH_3OH	HCHO	CO
0	0	0.083	30.0	63.6	6.4
1	0.8	0.112	30.0	62.3	7.4
2	1.5	0.117	30.4	62.7	6.9
3	2.1	0.127	35.6	58.0	6.4
5	2.7	0.140	37.0	57.8	5.2
10	5.4	0.141	37.8	56.3	5.8

Note. Reaction conditions: $T = 673$ K, $W = 0.5$ g, He carrier (40 ml/min), pulse size 2.67 ml; in pulse: $P(CH_4) = 33.8$ kPa, $P(H_2) = 50.7$ kPa, $P(O_2) = 8.4$ kPa, and He is used as a balance gas.

ward the oxidation of CH_4 was examined in comparison with that of the mixture of H_2 and O_2.

The oxidation of CH_4 with H_2O_2 was performed using the flow system. H_2O_2 (30 wt% aqueous solution) was fed with a mixture of CH_4 and He to the catalyst bed by a microfeeder. The results are shown in Table 4. For comparison, the results with O_2 and (O_2 + H_2) as the oxidant are also listed in the table. Because a large amount of water was cofed for the experiments of H_2O_2, a similar amount of H_2O was also added in the case of other oxidants for a better comparison. Although the temperature was relatively high (698 K), no product was observed for the gas mixture of CH_4, O_2, and H_2O as can be seen in run 1 of Table 4 because of the presence of excess water, while the addition of H_2O_2 selectively produced CH_3OH (run 2), and this was also the case when H_2–O_2 gas mixture was used as the oxidant (run 3). When H_2O_2 was cofed with H_2–O_2 gas mixture (run 4), the conversion of CH_4 increased considerably compared to those of runs 2 and 3. Such difference may be caused by the extent of the reduction of the catalyst surface. In the case of the cofeed of H_2O_2 with H_2–O_2, the catalyst surface could be partly reduced, which was suggested in the case of the H_2–O_2 pulse experiments described earlier. Thus the reduced surface must enhance the favorable effect on the selective oxidation of CH_4 to CH_3OH with H_2O_2. The pretreatment of the catalyst in a H_2–O_2 flow (run 5) also increases the conversion of CH_4 as can be seen from the comparison of the results between runs 5 and 2. This supports the effect of the surface reduction described above. In conclusion, the results in Table 4 strongly suggest that the active oxygen species generated from H_2–O_2 gas mixture is similar to that formed from H_2O_2 on the $FePO_4$ surface.

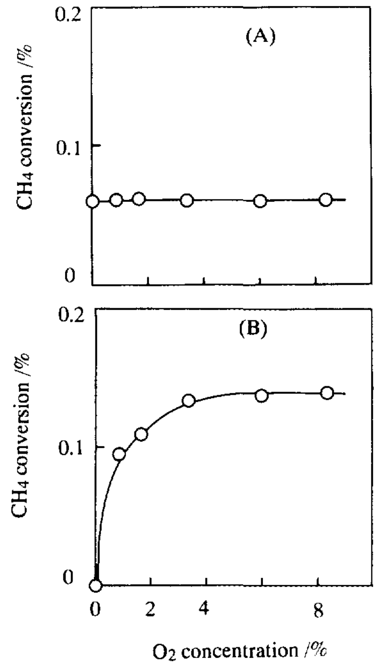


FIG. 10. Effect of O_2 concentration on CH_4 conversion in the pulse reactions. (A) in the absence of H_2. Reaction conditions: $T = 698$ K; in the pulse, $P(CH_4) = 33.8$ kPa, pulse size 2.76 cm^3, He carrier 40 cm^3/min. (B) In the presence of H_2. Reaction conditions: $T = 673$ K; in the pulse, $P(CH_4) = 33.8$ kPa, $P(H_2) = 50.7$ kPa, pulse size 2.76 cm^3, He carrier 40 cm^3/min.

Characterization of the Catalyst before and after the Reaction

The XRD studies confirmed that the iron phosphate catalyst prepared in this work consisted of $FePO_4$ compound only, i.e., other phases such as Fe_2O_3 were not observed. Moreover, no change in XRD patterns was observed after the reaction for 5 h in a stream of CH_4–H_2–O_2 gas mixture.

The oxidation state of the iron in the catalyst was studied before and after the catalytic reaction using Mössbauer spectroscopy. The spectra did not change at all after the reaction. They were fitted to a single Fe^{3+} doublet with

TABLE 4

Oxidation of CH_4 Using H_2O_2

Run	Oxidant	CH_4 conv. (%)	Selectivity (%)		
			CH_3OH	HCHO	CO
1	$O_2 + H_2O$	0	—	—	
2	$H_2O_2 + H_2O$	0.029	55.8	22.5	19.1
3	$O_2 + H_2 + H_2O$	0.128	56.0	35.9	6.8
4	$O_2 + H_2 + H_2O_2 + H_2O$	0.286	52.1	38.6	8.0
5[a]	$H_2O_2 + H_2O$	0.048	66.5	17.4	12.8

Note. Conditions: T = 698 K, $P(CH_4)$ = 33.7 kPa, $P(O_2)$ = 8.4 kPa, $P(H_2)$ = 50.7 kPa, $P(H_2O)$ = 11.8 kPa, $P(H_2O_2$ in feed gas) = 2.7 kPa, F(total) = 3.6 dm^3/h.

[a] Catalyst was pretreated in O_2–H_2 flow at 698 K.

isomer shift and quadrupole splitting of 0.35 and 0.63 mm/s, respectively. These parameters are attributed to those of the tetrahedrally coordinated Fe^{3+} with oxygen (19).

The results from XRD and Mössbauer studies suggest that the bulk of the catalyst does not change during the reaction in a stream of CH_4–H_2–O_2. However, these two methods cannot detect the changes at the catalyst surface. Thus, X-ray photoelectron spectroscopy has been used for the surface characterization. Table 5 shows the XPS data obtained for the catalyst before and after the oxidation of CH_4 with H_2–O_2 gas mixture. Obvious changes can be seen for the peaks of Fe2*p*3/2 and Fe3*p* spectra. The FWHM (full width at half maximum) for the Fe2*p*3/2 spectrum becomes larger and the binding energy shifts to a lower value after the reaction. The Fe3*p* spectrum at 57.7 eV before the reaction has split into two components at 57.8 and 56.2 eV after the reaction. The XPS data for $Fe_2P_2O_7$ are shown in the last column of Table 5. This compound containing only Fe^{2+} iron cations was prepared according to the method described by Hoggins and co-workers (20). For this compound, the binding energy of Fe3*p* is 56.2 eV, which corresponds to the low binding energy component of the spectrum observed for the $FePO_4$ after the catalytic reaction. These results undoubtedly indicate that a partial reduction of Fe^{3+} to Fe^{2+} at the surface occurs during the reaction under a gas mixture of CH_4–H_2–O_2. However, it should be noted that the FWHM of Fe3*p* spectrum for $Fe_2P_2O_7$ is much larger than that for the used $FePO_4$ catalyst, suggesting that the Fe^{2+} cations for the two cases exist under quite different configurational circumstances. It should be mentioned that the catalytic activity of the $Fe_2P_2O_7$ was notably lower compared with the $FePO_4$ catalyst for the oxidation of CH_4 with oxygen in the presence of H_2. Moreover, no CH_3OH was formed over $Fe_2P_2O_7$.

TABLE 5

XPS Results Obtained for Fe–P–O Catalyst before and after the Reaction

	Binding energy (FWHM)/eV			
	P 2*p*	O 1*s*	Fe 2*p*3/2	Fe 3*p*
$FePO_4$[a]	134.0(1.3)	532.2(2.3)	713.2(2.9)	57.7(2.65)
$FePO_4$[b]	133.8(1.5)	532.1(2.5)	712.3(3.5)	57.8(2.64), 56.2(1.8)
$Fe_2P_2O_7$	134.2(1.8)	531.8(2.8)	711.6(4.2)	56.2(5.5)

[a] Before reaction.

[b] After 5 h reaction under the following conditions: T = 698 K, $P(CH_4)$ = 33.8 kPa, $P(O_2)$ = 8.4 kPa, $P(H_2)$ = 50.7 kPa, F(total) = 3.6 dm^3/h.

Reaction Mechanism

The results obtained from the kinetic studies described earlier have revealed that the oxidation of CH_4 by oxygen in the absence of H_2 takes place at relatively higher reaction temperatures and the primary product is HCHO over $FePO_4$ catalyst. As shown in Fig. 9B, the rate of CH_4 conversion depends on the partial pressure of CH_4 by first order and by zero order with regard to the partial pressure of O_2. The results in Fig. 10A have suggested that the lattice oxygen of the surface is responsible for the activation of CH_4 in the absence of H_2. On the bases of these results, we suggest that the oxidation of CH_4 in the absence of H_2 over $FePO_4$ catalyst proceeds as follows:

$$CH_4 + O(s) \rightarrow CH_3(a) + OH(a) \qquad [5]$$

$$CH_3(a) + O(s) \rightarrow CH_3O(a) \qquad [6]$$

$$CH_3O(a) + O(s) \rightarrow HCHO + OH(a). \qquad [7]$$

The fact that the rate of CH_4 conversion does not depend on the partial pressure of O_2 implies that the replenishment

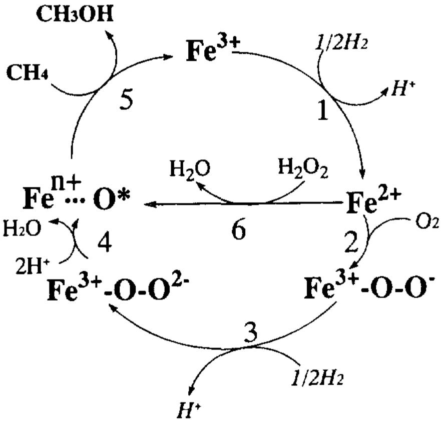


FIG. 11. Activation mechanism of oxygen for the oxidation of CH_4 with O_2–H_2 over $FePO_4$ catalyst.

of the surface oxygen by gaseous oxygen proceeds very rapidly. The conversion rate of CH_4 must be limited by reaction 5 where CH_4 is dissociated to an adsorbed methyl species. The methyl species reacts with surface oxygen giving HCHO probably through reactions 6 and 7. These reactions must be very fast because neither CH_3OH nor coupling products (C_2H_6 and C_2H_4) have been observed.

On the other hand, in the presence of H_2, the conversion rate of CH_4 was greatly enhanced and the reaction temperature required for the activation of CH_4 was lowered by about 50 K. The most characteristic feature is that CH_3OH becomes the primary and a major product. The analyses of the results obtained from the kinetic studies (Figs. 2, 4B, 5, and 6) have suggested that a newly formed oxygen species is responsible for the selective oxidation of CH_4 to CH_3OH. The pulse reaction results have indicated that the coexistence of H_2 and O_2 is necessary for the formation of this active oxygen species. Prereduction of the catalyst surface facilitated the formation of the active oxygen (Tables 2 and 3). Based on these results, we speculated a tentative mechanism for the formation of active oxygen species as shown in Fig. 11. Fe^{3+} on $FePO_4$ surface is reduced to Fe^{2+} by hydrogen in step 1, producing protons on the surface. An oxygen molecule coordinates to the reduced iron site in step 2, followed by a reductive activation of the coordinated oxygen by hydrogen in step 3. The interaction of the reduced oxygen (could be peroxide species) with protons produces water, resulting in the generation of an active oxygen species (O*) in step 4. O* might be an iron (IV) oxo species as has been speculated for the selective oxidation of CH_4 in the methane monooxygenase system (*12*). The oxidation of CH_4 to CH_3OH by O* may be written by Eq. [8], where Fe(*n*) means the iron site of valence *n*:

$$CH_4 + Fe(n)\cdots O^* \rightarrow CH_3OH + Fe(III). \qquad [8]$$

This equation does not mean a single step formation of CH_3OH from CH_4. Probably, there exist several steps from CH_4 to CH_3OH. We have not enough data to discuss about the detailed mechanism for the activation of CH_4 by O* and for the formation of CH_3OH at this moment.

If the formation of O* and its consumption by CH_4 (Eq. [8]) proceed with comparable rates, we can assume a steady state with regard to the concentration of O*. Here, let us express the formation rate of O* as

$$r_f = k_f \cdot f(P(H_2), P(O_2)) \cdot (N - [O^*]),$$

where k_f is the apparent rate constant for the formation of O*, $f(P(H_2), P(O_2))$ is a function depending on the partial pressures of H_2 and O_2, and N is the number of Fe(II) sites on the catalyst surface. Applying the steady-state assumption for the concentration of O*, the rate of CH_4 conversion ($r(CH_4)$) can be induced as

$$\frac{d[O^*]}{dt} = k_f f(P(H_2), P(O_2))(N - [O^*]) - k_8 P(CH_4)[O^*] = 0,$$

and thus,

$$[O^*] = \frac{N k_f f(P(H_2), P(O_2))}{N k_f f(P(H_2), P(O_2)) + k_8 P(CH_4)}.$$

Hence,

$$r(CH_4) = k_8 P(CH_4) \frac{N k_f f(P(H_2), P(O_2))}{N k_f f(P(H_2), P(O_2)) + k_8 P(CH_4)}.$$

This equation explains the experimental results of Fig. 9A that the rate of CH_4 conversion depends on the partial pressure of CH_4 by the order of 0–1. Further discussion for the effects of the partial pressure of H_2 (Fig. 8) and O_2 is not meaningful because we have not adequate data about the $f(P(H_2), P(O_2))$ term at this moment.

The observation that CH_3OH was produced selectively when H_2O_2 was used as the oxidant suggests that the active oxygen species (O*) described above can also be generated from H_2O_2. We speculate that such oxygen species is generated directly from H_2O_2 on iron (II) sites as shown in Fig. 11. If O* is an iron oxo species, this formation might be enhanced from H_2O_2 through iron hydroperoxide intermediate. However, we cannot exclude the possibility of OH radical as the active oxygen species which is well known in the "Fenton" chemistry (*21*, *22*). If O* is an OH radical, the formation must be enhanced by the reaction

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O, \qquad [9]$$

as has been suggested in Fenton's reagent (21, 22). The protons generated from H_2 on phosphate sites may enhance this reaction. Further investigations are definitely needed to identify the active oxygen species generated in this system.

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