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Partial Oxidation of Ethane by Reductively Activated Oxygen over Iron Phosphate Catalyst

Ye Wang and Kiyoshi Otsuka[1]

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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The catalytic oxidation of ethane was carried out at 573–773 K over iron phosphate catalyst. The oxidation of ethane by oxygen produced only ethylene and carbon oxides. The co-feed of hydrogen with oxygen remarkably accelerated the conversion of ethane. Ethanol and acetaldehyde were newly formed by co-feeding hydrogen. The partial oxidation of ethane to ethanol and acetaldehyde can also be achieved by using nitrous oxide as an oxidant. The co-feed of hydrogen with nitrous oxide increased the conversion of ethane and the yield to C_2 oxygenates. The investigation on the reaction paths suggests that ethanol is the primary product in the oxidation of ethane with hydrogen–oxygen gas mixture and with nitrous oxide. Acetaldehyde and ethylene are produced through further oxidation and dehydration of ethanol, respectively. The highest yield obtained for C_2 oxygenates was 4.4% (ethanol, 1.4%; acetaldehyde, 3.0%) at 673 K. The kinetic and mechanistic studies suggest that the oxidation of ethane proceeds by a similar reaction mechanism to the one proposed for the oxidation of methane. Oxygen is activated by the electrons and protons derived from hydrogen on the catalyst surface, generating a new oxygen species, probably adsorbed peroxide species, effective for the selective oxidation of ethane to ethanol. The same oxygen species can be generated from nitrous oxide by its reductive activation. Both kinetic results and isotopic effects on the conversion of ethane suggest that the dissociation of the C–H bond of ethane proceeds notably faster than the formation of the active oxygen species. In contrast with ethane, the rate of activation of methane was comparable to that of the generation of the active oxygen species. © 1997 Academic Press

INTRODUCTION

The direct transformation of methane and ethane to useful oxygenates has attracted much attention for the chemists and chemical engineers from the viewpoint of effective utilization of the abundant natural gas resources (1–5). Usually, a high temperature (>773 K) is required for the conversion of these light alkanes because of the low reactivity of their C–H bond. However, the useful oxygenates formed may be instantly converted into CO and CO_2 under such high temperatures. Thus, the selective partial oxidation of alkanes to oxygenates, particularly alcohols, is of great difficulty. Although many attempts have been reported for the partial oxidation of light alkanes, the viable processes and the effective catalysts have not been developed.

On the other hand, monooxygenase enzymes such as methane monooxygenase and cytochrome P-450 catalyze the selective oxidation of hydrocarbons including light alkanes to their oxygenates under ambient conditions (6, 7). It is suggested that the activation of oxygen by the electrons and protons, generating a highly active oxygen species is responsible for this biological oxidation (7, 8). The presence of a reductant (NADH or NADPH) is indispensable for these enzymatic activation of dioxygen in Eq. [1]:

$$\mathrm{RH} + \mathrm{O_2} + \mathrm{NADH} + \mathrm{H^+} \rightarrow \mathrm{ROH} + \mathrm{H_2O} + \mathrm{NAD^+}. \quad [1]$$

The concept of this type of reductive activation of dioxygen is also fundamental in several homogeneous monooxygenation systems such as Gif system (9), where iron or zinc powder and carboxylic acid are used as the electron and proton donors, respectively.

Our new approach for the selective oxidation of light alkanes by heterogeneous catalysts is also based on this concept. In this work, hydrogen is selected as the reductant instead of expensive reductant such as NADH or metal powder used in the biological monooxygenase or in the homogeneous biomimetic model systems. As shown in Eq. [2], if an appropriate catalyst is applied, hydrogen can serve as not only the electron donor but also as the proton donor, reductively activating dioxygen with these electrons and protons:

$$\mathrm{H_2} \rightarrow 2\mathrm{H^+} + 2\mathrm{e^-}. \quad [2]$$

Recently, we have reported that methane can be selectively oxidized to methanol by the oxygen co-fed with hydrogen when an iron phosphate is used as the catalyst, while methanol is not produced in the absence of hydrogen under any reaction conditions at atmospheric pressure (10, 11). Similar to methane, ethane is also one of the most difficult organic molecules to be activated. Moreover, because C_2 oxygenates, i.e., ethanol and acetaldehyde, are more reactive than methanol or formaldehyde, the selective

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[1] E-mail: kotsuka@o.cc.titech.ac.jp.

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conversion of ethane to oxygenates, particularly to ethanol, becomes more difficult. There exist many reports concerning the partial oxidation of ethane (12–25). However, most of them are concerned with the oxidative dehydrogenation of ethane to ethylene (12, 13, 16–18, 21–25). Only a few studies contribute to the direct synthesis of C_2 oxygenates. In an early communication, Iwamoto and coworkers reported that acetaldehyde could be produced with a selectivity of 6.4% at an ethane conversion of 26% over a MoO_3/SiO_2 catalyst when nitrous oxide was used as the oxidant (14). However, only a trace amount of ethanol (selectivity $\leq 0.1\%$) was obtained. The groups of Lunsford and Solymosi studied the oxidation of ethane by nitrous oxide in detail using MoO_3/SiO_2 (15) and V_2O_5/SiO_2 (19) catalysts, respectively. For both catalysts, acetaldehyde could only be obtained at a yield approaching 1%, the formation of a detectable amount of C_2H_5OH has not been observed under any reaction conditions. One of the authors has reported that a B_2O_3-containing catalyst is effective for the partial oxidation of ethane to acetaldehyde by oxygen (20). However, ethanol has not been produced.

Two possibilities may be responsible for the difficulty in producing ethanol. The one is that, although ethanol might be formed as the primary product, it would be dehydrated or oxidized quickly into ethylene and acetaldehyde under the reaction temperatures (usually ≥ 773 K) required for the activation of ethane. The other probable reason is that the reaction intermediate, such as ethyl adsorbed species or ethoxide species would be readily transformed to ethylene or acetaldehyde as compared with the formation of ethanol. Therefore, a new system capable of generating a highly reactive oxygen at low temperatures may be necessary for producing ethanol and enhancing the selectivities to C_2 oxygenates. Furthermore, in order to improve the selectivity to ethanol, the structure of the catalytic active site should be designed to prevent the intermediate such as ethoxide being further oxidized and to accelerate the protonation of the ethoxide to ethanol.

As described above, we have shown that methanol can selectively be produced from methane over iron phosphate catalyst using hydrogen-oxygen gas mixture or nitrous oxide (10, 11, 26). The previous spectroscopic studies have revealed that an adsorbed peroxide species generated from the reductive activation of oxygen by hydrogen on the active iron sites is responsible for this selective oxidation under relatively low temperatures (573–773 K) (27, 28). Whether ethanol can be synthesized from the direct oxidation of ethane using this catalytic system and what is specific for the oxidation of ethane are of great interest. Thus, the purpose of this paper is to apply this catalytic system to the oxidation of ethane. The oxidation of ethane will be carried out using iron phosphate catalyst and the effect of the presence of hydrogen and the use of nitrous oxide as the oxidant will be investigated in detail. The oxidation of ethane will be compared with that of methane to get further information about the nature of the catalytic system and the reaction mechanism.

EXPERIMENTAL

Catalyst

The iron phosphate ($FePO_4$) catalyst was prepared by mixing the aqueous solutions of $Fe(NO_3)_3$ and $NH_4H_2PO_4$. The obtained gel was then dried at 363 K for 12 h. Then, the resultant was calcined at 823 K for 5 h in air.

Catalytic Measurements and Kinetic Studies

The catalytic experiments were carried out using a conventional fixed-bed flow reactor (quartz tube) which is operated 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. The reactants used in this study were research grade C_2H_6 (99.99%), O_2 (99.5%), H_2 (99.9%), and N_2O (99.5%). These gases were used without further purification.

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. The reaction products were analyzed by an on-line gas chromatography. For kinetic measurements, the conversion of O_2 was controlled to be lower than 15%.

Kinetic Isotope Effect Measurements

The experiments were carried out using a closed-gas-circulation system made of Pyrex glass. The catalyst powder was placed in a U-shaped quartz reactor. The reactants were circulated by a circulation pump during the reaction. The total volume of this system was 310 cm^3. The system was connected through leak valves to a quadrupole mass spectrometer and a gas chromatography, respectively. C_2H_6 (Sumitomo Seika Co., 99.99%) and C_2D_6 (Cambridge Isotope Laboratories, D6, 99.9%) were used in these experiments.

RESULTS AND DISCUSSION

Oxidation of C_2H_6 by O_2 in the Absence and Presence of H_2 over $FePO_4$ Catalyst

Figure 1 shows the rates of ethane conversion at different temperatures over $FePO_4$ catalyst in the absence (a) and the presence of H_2 (b). The rate of C_2H_6 conversion was remarkably increased in the presence of H_2. The influence of H_2 on the product distribution is shown in Fig. 2. Using oxygen alone, C_2H_4, CO, and CO_2 are the only products from the oxidation of C_2H_6 as shown in Fig. 2A. C_2 oxygenates, i.e., C_2H_5OH and CH_3CHO, are not produced

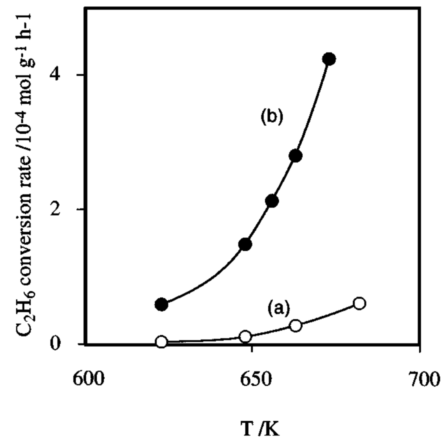


FIG. 1. The rate of C_2H_6 conversion versus the reaction temperature: (a) in the absence of H_2; (b) in the presence of 50 kPa H_2. $P(C_2H_6) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}.

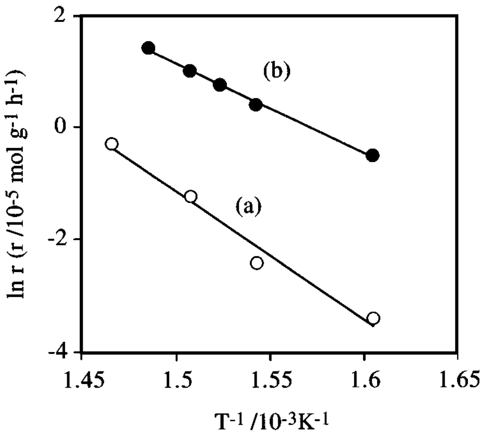


FIG. 3. Logarithm of the rates of C_2H_6 conversion against $1/T$: (a) in the absence of H_2; (b) in the presence of 50 kPa H_2. $P(C_2H_6) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}.

in the absence of H_2 at the whole temperature range. However, as shown in Fig. 2B, the product distribution is drastically changed when H_2 is co-fed with C_2H_6 and O_2. The most striking characteristic is that the oxygenates, including C_2H_5OH, CH_3CHO, and HCHO, are newly produced due to the presence of H_2. The total selectivity to these oxygenates exceeds 50% under the conditions used in Fig. 2.

The plots for the logarithm of the rates of C_2H_6 conversion against $1/T$ were shown in Fig. 3. Good straight lines are obtained both in the absence and in the presence of H_2, indicating that the increase in C_2H_6 conversion in the presence of H_2 is not due to the hot spots from the reaction of H_2 and O_2. It should be noted here that the conversion of O_2 is lower than 10% in the presence of H_2. More than 80% of the H_2 co-fed with C_2H_6 and O_2 still remains in the exit of the reactor under the reaction conditions of Fig. 1. For an example, in the presence of H_2 at 673 K, the conversion of O_2 was 8.1%. Among the O_2 reacted, the percentage of the O_2 used for the conversion of C_2H_6 into oxygenates (C_2H_5OH, CH_3CHO, HCHO) and carbon oxides (CO and CO_2) was 7.5%. The rest (92.5%) of the reacted O_2 was consumed in the oxidation of H_2 and the hydrogen of C_2H_6 into water. The apparent activation energies calculated from Fig. 3 are 190 and 134 kJ mol^{-1} in the absence and the presence of H_2, respectively. The decrease in the activation energy indicates that a new active species must be responsible for the activation of ethane in the presence of H_2.

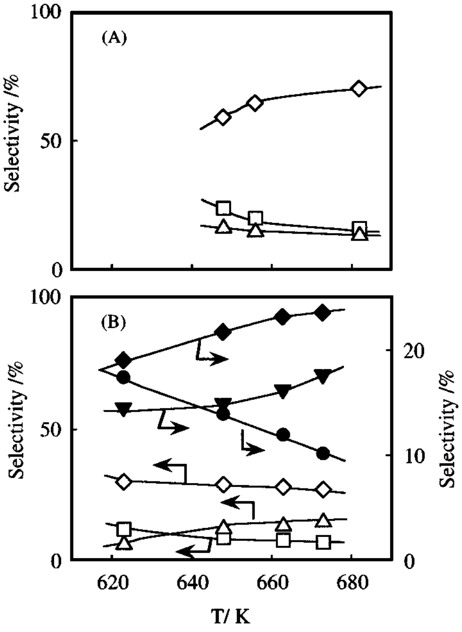


FIG. 2. Product selectivities for the oxidation of C_2H_6 by O_2 over $FePO_4$ catalyst: (A) in the absence of H_2; (B) in the presence of 50 kPa H_2. (◇), C_2H_4; (△), CO; (□), CO_2; (●), C_2H_5OH; (◆), CH_3CHO; (▼), HCHO. $P(C_2H_6) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}.

All the results obtained above resemble those reported for the oxidation of methane, where the generation of a new active oxygen species has been suggested in the presence of H_2 (11). The results of Figs. 1, 2, and 3 suggest that this oxygen species would also cause the selective oxidation of C_2H_6, producing C_2H_5OH which has so far been hardly attainable from the oxidation of C_2H_6 over solid catalysts.

Oxidation of C_2H_6 by N_2O over $FePO_4$ Catalyst

The oxidation of C_2H_6 by N_2O over $FePO_4$ catalyst was carried out at temperatures of 550–700 K. As shown in Fig. 4, the conversion of C_2H_6 started at ca 573 K. The main products are C_2H_5OH, CH_3CHO, and C_2H_4. The increase in reaction temperature decreases the selectivity to C_2H_5OH. However, the yields to C_2H_5OH and CH_3CHO increase with temperature due to the sharp increase in C_2H_6 conversion. At 673 K, the yields to C_2H_5OH and CH_3CHO are 1.5 and 2.5%, respectively.

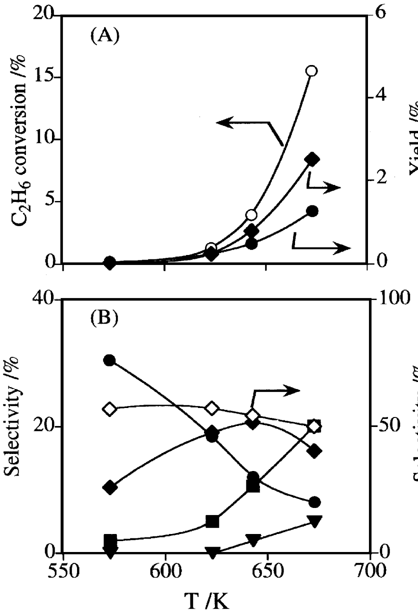


FIG. 4. Oxidation of C_2H_6 by N_2O over $FePO_4$ catalyst. (A) Conversion and yields: (○), C_2H_6 conversion; (●), C_2H_5OH yield; (◆), CH_3CHO yield. (B) Selectivities: (●), C_2H_5OH; (◆), CH_3CHO; (▼), HCHO; (■), $CO + CO_2$; (◇), C_2H_4. $P(C_2H_6) = 16.9$ kPa, $P(N_2O) = 16.9$ kPa, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}.

The effect of H_2 on the oxidation of C_2H_6 by N_2O was also investigated. The influences of H_2 on the conversion of C_2H_6 and on the yield to C_2 oxygenates ($C_2H_5OH + CH_3CHO$) are shown in Fig. 5. Notable accelerating effects of H_2 on both C_2H_6 conversion and the yield of C_2 oxygenates are seen at low temperatures ($\leq$623 K), while such an effect becomes relatively smaller at higher temperatures (673 K). Furthermore, when the temperature was increased above 673 K, a carbon deposit occurred and the conversion of C_2H_6 was remarkably inhibited due to the carbon deposit. The highest yield to C_2 oxygenates obtained in this work was 4.4% (C_2H_5OH: 1.7%; CH_3CHO: 2.7%). It should be noted here that the consumption of N_2O due to the reaction with H_2 to form H_2O in the presence of H_2 was not so serious as compared with O_2. More than 50% of the converted N_2O was used in the conversion of C_2H_6 under the conditions of Fig. 5.

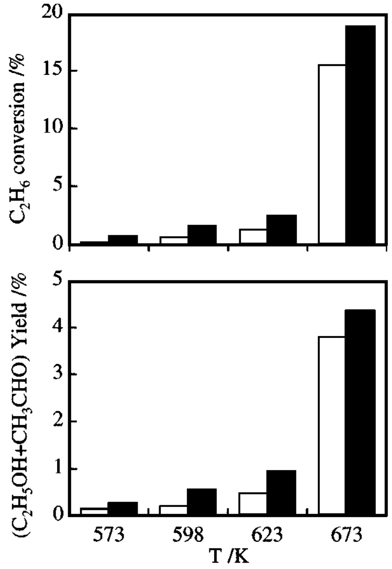


FIG. 5. The effect of H_2 on the oxidation of C_2H_6 by N_2O over $FePO_4$ catalyst: (A) C_2H_6 conversion; (B) C_2 oxygenates yield. (□), in the absence of H_2; (■), in the presence of 16.9 kPa H_2. $P(C_2H_6) = 16.9$ kPa, $P(N_2O) = 16.9$ kPa, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}.

Although CH_3OH could be obtained from the oxidation of CH_4 over MoO_3-, V_2O_5-based catalysts (29, 30) and a Cu^{2+}-exchanged Fe-ZSM-5 catalyst (31) when N_2O was used as the oxidant, the formation of C_2H_5OH from the direct oxidation of C_2H_6 by N_2O has scarcely been achieved on solid catalysts. Here, it should be noted that not only CH_3CHO but also C_2H_5OH has been produced at relatively mild conditions (573–700 K) over $FePO_4$ by using a H_2–O_2 mixture or N_2O as the oxidant. This is a very unique result. Thus, more detailed studies are subsequently carried out to elucidate the formation of C_2H_5OH over $FePO_4$ using both H_2–O_2 and N_2O.

Reaction Paths for the Oxidation of Ethane

In order to get information about the reaction schemes of the formations of C_2H_5OH and other products, the change in the product distribution with the contact time was investigated using both H_2–O_2 mixture and N_2O as the oxidant. The results are shown in Figs. 6 and 7, respectively. The oxidation of C_2H_6 using H_2–O_2 gas mixture was carried out at a temperature of 648 K where the rate of C_2H_6 conversion in the absence of H_2 could be neglected, and thus,

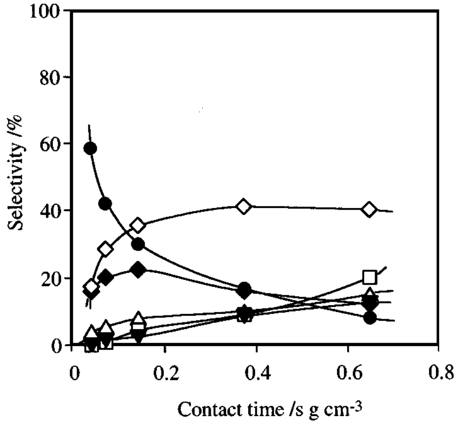


FIG. 6. Product distribution for C_2H_6 oxidation by H_2–O_2 as a function of contact time: (◇), C_2H_4; (△), CO; (□), CO_2; (●), C_2H_5OH; (◆), CH_3CHO; (▼), HCHO. $P(C_2H_6) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $P(H_2) = 50.7$ kPa, $T = 648$ K, $W = 0.5$ g (volume of catalyst bed $= 0.6$ cm^3); the contact time is varied by changing the flow rate.

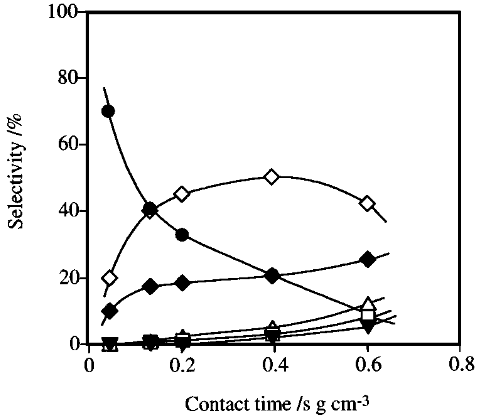
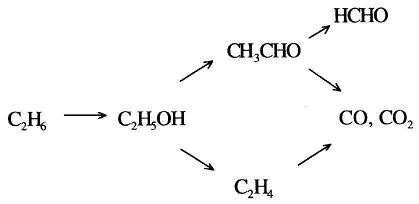


FIG. 7. Product distribution for C_2H_6 oxidation by N_2O as a function of contact time: (◇), C_2H_4; (△), CO; (□), CO_2; (●), C_2H_5OH; (◆), CH_3CHO; (▼), HCHO. $P(C_2H_6) = 33.8$ kPa, $P(N_2O) = 16.9$ kPa, $T = 623$ K, $W = 0.5$ g (volume of catalyst bed = 0.6 cm^3); the contact time is varied by changing the flow rate.

the results could reflect the reaction properties of the active oxygen species generated in H_2–O_2. Both Figs. 6 and 7 show very similar tendencies for the selectivity of each product with the contact time. The selectivity to C_2H_5OH higher than 60% can be obtained at very short contact time (≤ 0.04 s · g · cm^{-3}), and the C_2H_5OH selectivity tends to increase with further decrease of the contact time. Reversely, the increase in the contact time obviously decreases the selectivity to C_2H_5OH and increases those to C_2H_4 and CH_3CHO simultaneously. The further increase in the contact time is not beneficial to the selectivities to CH_3CHO and C_2H_4 but accelerates those to HCHO, CO, and CO_2. These results suggest that C_2H_5OH must be the primary product. CH_3CHO and C_2H_4 could be formed from the consecutive reactions of C_2H_5OH in parallel. HCHO, CO, and CO_2 may be formed by further oxidation of CH_3CHO or C_2H_4. The most rational reaction paths which we believe are as shown.



The fact that the tendencies in both Figs. 6 and 7 are similar to each other supports the speculation that the same oxygen species is responsible for the selective oxidation of C_2H_6 in the cases of using both H_2–O_2 and N_2O.

Kinetic Studies for the Oxidation of Ethane

The effects of the partial pressures of H_2 and O_2 on the rate of C_2H_6 conversion by the H_2–O_2 gas mixture are shown in Fig. 8. The rate of C_2H_6 conversion increases linearly with the partial pressure of H_2 at <10 kPa and the rate still increases considerably above this H_2 pressure. On the other hand, although the rate of C_2H_6 conversion increases with O_2 pressure under oxygen pressures lower than 5 kPa, it reaches a plateau above this O_2 pressure. This fact implies that H_2 plays a more significant role than O_2 in the activation of C_2H_6.

As reported previously (28), we have proposed that an adsorbed peroxide species is responsible for the selective oxidation of CH_4 to CH_3OH in the H_2–O_2 gas mixture. The formation of this adsorbed peroxide species was detected by FT-IR spectroscopy in H_2–O_2 gas mixtures. The intensity of the observed IR absorption at a wavenumber of 895 cm^{-1} assigned to this peroxide species measured previously (28) is plotted as functions of the partial pressures of H_2 (A) and O_2 (B) by dotted lines in Fig. 8. Similar to the curves for the rate of C_2H_6 conversion (solid lines), the concentration of the peroxide species depends linearly on the partial pressure of H_2, but it saturates at >2 kPa of O_2 pressure. The very similar dependencies on the partial pressures observed for the conversion rate of C_2H_6 and for the concentration of peroxide strongly indicate that the peroxide is responsible for the selective oxidation of ethane. Thus, we propose

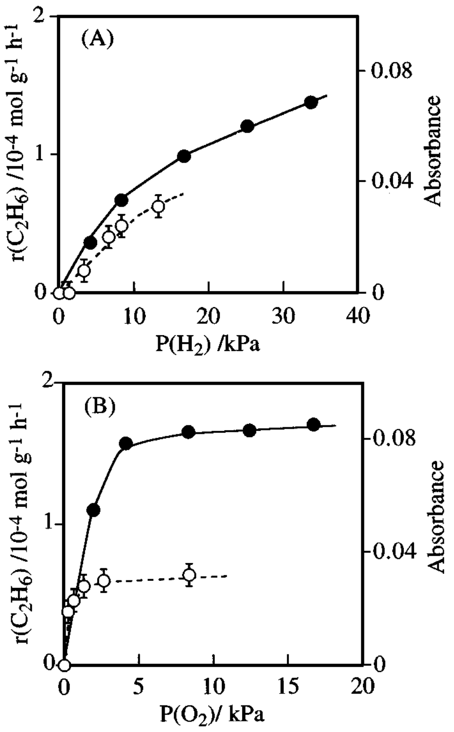


FIG. 8. The effect of the partial pressures of H_2 (A) and O_2 (B) on the rate of C_2H_6 conversion (solid lines) and the intensity of the IR absorbance ascribed to adsorbed peroxide species (dotted lines). For C_2H_6 oxidation: $P(C_2H_6) = 33.8$ kPa, $T = 648$ K, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}. (A) $P(O_2) = 8.4$ kPa; (B) $P(H_2) = 50.7$ kPa. For IR measurements: $T = 673$ K. (A) $P(O_2) = 1.3$ kPa; (B) $P(H_2) = 13.3$ kPa.

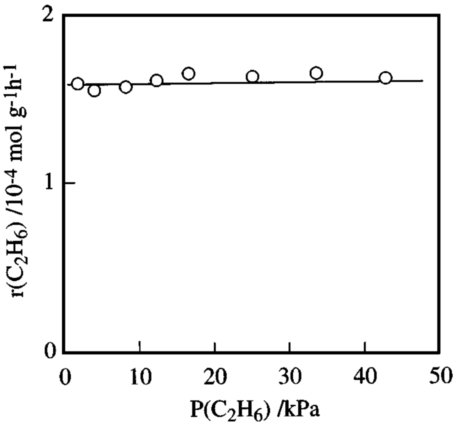


FIG. 9. Dependence of the rate of C_2H_6 conversion on the partial pressure of C_2H_6: $P(H_2) = 50.7$ kPa, $P(O_2) = 8.4$ kPa, $T = 648$ K, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}.

the following scheme for the catalytic oxidation of C_2H_6 to C_2H_5OH by the H_2–O_2 gas mixture.

$$O_2 + H_2 \rightarrow O_2^{2-}\ (a) + 2H^+\ (a) \qquad [3]$$

$$C_2H_6 + O_2^{2-}\ (a) \rightarrow C_2H_5OH + O_S^{2-}\ (\text{lattice}) \qquad [4]$$

The influence of the pressure of C_2H_6 on the rate of C_2H_6 conversion is shown in Fig. 9. The rate of C_2H_6 conversion did not change in the pressure range used in Fig. 9. This experimental fact can be explained as follows. If reaction [4] in the above scheme is fast and the overall rate is determined by reaction [3], the conversion rate of C_2H_6 should depend solely on the partial pressures of H_2 and O_2 and not depend on the partial pressure of C_2H_6 as shown in Eq. [5], where k is constant.

$$r(C_2H_6) = kf(P(H_2), P(O_2)). \qquad [5]$$

In the case of N_2O used as an oxidant, as shown in Fig. 10, the rate of C_2H_6 conversion increased linearly with the pressure of N_2O but was independent of the partial pressure of C_2H_6. These experimental results can also be explained by assuming that the overall rate of C_2H_6 conversion is determined by the formation of active oxygen species from N_2O. As reported previously (27), FT-IR spectroscopic measurements showed that the peroxide species generated from N_2O was also responsible for the conversion of CH_4 to CH_3OH. Therefore, for the oxidation of C_2H_6 by N_2O in this work, it is natural to assume that the peroxide generated from N_2O causes the selective oxidation of C_2H_6 into C_2H_5OH as demonstrated here.

$$N_2O \xrightarrow{e^-} N_2 + O^-\ (a) \qquad [6]$$

$$2O^- \rightleftarrows O_2^{2-} \qquad [7]$$

$$O_2^{2-} + C_2H_6 \rightarrow C_2H_5OH + O_S^{2-} \qquad [4]$$

Here, if the reactions of Eqs. [7] and [4] proceed very fast and the formation of O^- (a) species from N_2O is the rate-determining step, the overall rate of C_2H_6 conversion can be expressed as

$$r(C_2H_6) = k'P(N_2O). \qquad [8]$$

This equation is in accordance with the experimental results described in Fig. 10. The electron for the activation of N_2O in Eq. [6] must be supplied from the catalyst surface, i.e., surface defects or Fe(II) sites. The presence of H_2 must increase the concentration of Fe(II) on the catalyst surface and thus enhances the reaction as indicated in Fig. 5. Since N_2O is a rather weak oxidant, C_2H_6 itself could also act as a reductant for the initiation of the reaction in the absence of H_2. Once the reaction is initiated, the products, i.e., C_2H_5OH and CH_3CHO, must facilely work as the reductant to reduce Fe(III) to Fe(II) and accelerate the catalytic cycle. This may be the reason that the presence of H_2 did not show a remarkable effect on the reaction at high temperatures as described in Fig. 5. On the other hand, in the case of using O_2, the presence of H_2 is indispensable for keeping an adequate concentration of Fe(II) on the catalyst surface for the catalytic cycle because O_2 is a stronger oxidizing agent than N_2O.

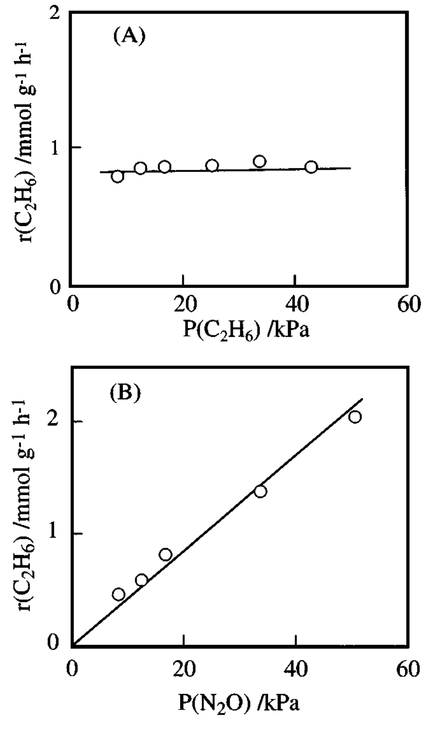


FIG. 10. Dependence of the rate of C_2H_6 conversion on the partial pressures of C_2H_6 (A) and N_2O (B). $T = 623$ K, $W = 0.5$ g, $F = 3.6$ dm^3 h^{-1}. (A) $P(N_2O) = 16.9$ kPa; (B) $P(C_2H_6) = 33.8$ kPa.

Kinetic Isotopic Effect for the Oxidation of Ethane

The results for the kinetic measurements described above suggest that the formation of the active oxygen species is the rate-determining step for the overall conversion of C_2H_6 in the cases of using both H_2–O_2 and N_2O. This implies that the activation of C_2H_6; i.e., the cleavage of C–H bond by the active oxygen is relatively fast reaction. In order to get further information on the cleavage of the C–H bond, the kinetic isotopic effect (k_H/k_D) for the oxidation of ethane was measured. The experiments were carried out using a closed-gas-circulation apparatus as described in the experimental section. Figure 11 shows the conversions of C_2H_6 and C_2D_6 with reaction time under the same reaction conditions. Good straight lines were obtained for both cases. The isotopic effect (k_H/k_D) calculated from this figure is 1.06. This value suggests that, if the experimental error (±0.1) is considered, the conversion rate of C_2H_6 and C_2D_6 could be regarded as the same. Therefore, the isotope effect measurements support the conclusion deduced from the kinetic studies; i.e., the activation of the C–H bond of C_2H_6 proceeds faster than the formation of the active oxygen species.

Comparison between the Oxidation of Ethane and Methane

(a) Reaction properties and mechanism. A very unique property for the oxidation by the active oxygen species generated on $FePO_4$ surface in H_2–O_2 or N_2O is that alcohol can be obtained as the primary product. This is common for both CH_4 and C_2H_6, *viz.*, CH_3OH and C_2H_5OH can be obtained from the oxidation of CH_4 and C_2H_6, respectively. We believe that the high activity of the oxygen species generated in H_2–O_2 or N_2O must be responsible for the initiation of the conversion of CH_4 and C_2H_6 under moderate conditions (under atmospheric pressure and at temperatures of 573–723 K). While for other reported solid catalysts, temperatures higher than 773 K are needed for the conversion of CH_4 or C_2H_6. Thus, the intermediate products, i.e., alcohols could be sustained at such a low temperature. The other factor which we believe to be more important for the selective formation of CH_3OH or C_2H_5OH is the unique structure of $FePO_4$. As reported previously (32), we have proposed that the iron site isolated by acidic groups (phosphate groups in the case of $FePO_4$) is the active site for the selective oxidation of CH_4 to CH_3OH by H_2–O_2 or N_2O. The oxidation of C_2H_6 must proceed by a similar reaction mechanism on the same active site as shown below.

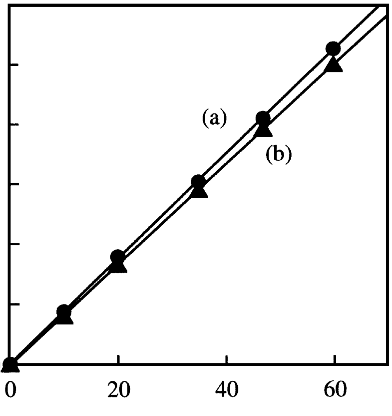
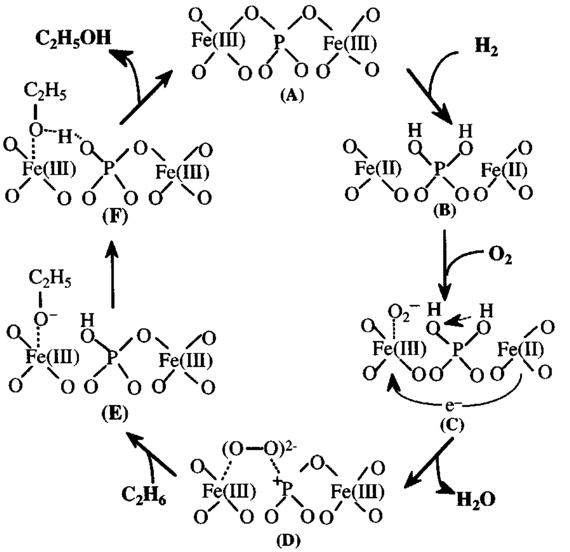


FIG. 11. Conversion of C_2H_6 and C_2D_6 versus reaction time (gas-closed circulation reaction system): (a) C_2H_6; (b) C_2D_6. $W = 0.5$ g, $T = 573$ K, $P(C_2H_6) = P(N_2O) = 2.7$ kPa; or $P(C_2D_6) = P(N_2O) = 2.7$ kPa.



In this scheme, H_2 reduces the surface, generating Fe(II) and H^+ which is adsorbed on the neighboring phosphate groups. Oxygen must be activated and transformed into adsorbed peroxide species (D) by accepting electrons from Fe(II) sites probably through the intermediate (C). The adsorbed peroxide species (D) formed in H_2–O_2 or N_2O reacts with C_2H_6, producing C_2H_5OH probably through an ethoxide intermediate (E). Here, it should be emphasized that the formation of ethanol from the ethoxide intermediate must be ensured by the unique structure of the active iron site, i.e., the iron site surrounded by the acidic phosphate groups. As shown in the scheme, the rapid protonation of the ethoxide intermediate by the acidic protons adsorbed on the neighboring phosphate groups becomes possible with such active sites. Otherwise, the ethoxide intermediate will be further oxidized into CO and CO_2, thus C_2H_5OH cannot be obtained.

The comparison between the conversion rates of CH_4 and C_2H_6 at different reaction temperatures is shown in Table 1. It can be seen that the reactivity of C_2H_6 is approximately 7–8 times higher than that of CH_4 under the same reaction conditions. However, obviously, the selectivity of the corresponding alcohols is remarkably higher in the case

TABLE 1

Comparison of the Oxidation of CH_4 and C_2H_6 by the H_2–O_2 Gas Mixture over $FePO_4$ Catalyst

	Conversion rate (mol g^{-1} h^{-1})		Selectivity (%)	
Temperature (K)	CH_4	C_2H_6	CH_3OH	C_2H_5OH
623	7.4×10^{-6}	5.9×10^{-5}	89.1	22.5
648	1.8×10^{-5}	1.5×10^{-4}	67.7	17.0
673	5.6×10^{-4}	4.2×10^{-3}	45.0	12.2
695	1.4×10^{-3}	9.8×10^{-3}	35.5	8.7

of the oxidation of CH_4. This is also the case even though the comparison is made at the same conversion level. This must be caused by the very rapid intramolecular dehydration of C_2H_5OH to C_2H_4. In fact, C_2H_4 becomes predominant among the products at a longer contact time in Figs. 6 and 7 in the oxidation of C_2H_6. Probably, the dehydration of C_2H_5OH is unfortunately catalyzed by the acidic phosphate groups on the catalyst surface. On the other hand, such an acid catalyzed dehydration is impossible for CH_3OH, thus only the consecutive oxidation of CH_3OH occurs in the case of CH_4 oxidation.

(b) Kinetic features. As described earlier, the rate of C_2H_6 conversion was independent of the partial pressure of C_2H_6 using both H_2–O_2 and N_2O, which reflects that the oxidation of C_2H_6 is rate-determined by the formation of the oxygen species. This feature obviously differs from that in the case of CH_4 oxidation where the conversion rate of CH_4 increased with the increase in the partial pressure of CH_4 as reported previously (11). As described above, the step for the activation of the C–H bond of C_2H_6 must be notably faster than the formation of the adsorbed peroxides. On the other hand, as reported previously (11), the kinetic results for the oxidation of CH_4 by H_2–O_2 can be explained by assuming that the oxidation of CH_4 proceeds in a comparable rate with the formation of the active oxygen. However, in the case of C_2H_6 in this work, since the oxidation of C_2H_6 proceeds notably faster than that of CH_4 as indicated in Table 1, the overall reaction must become to be controlled by the formation of active oxygen species.

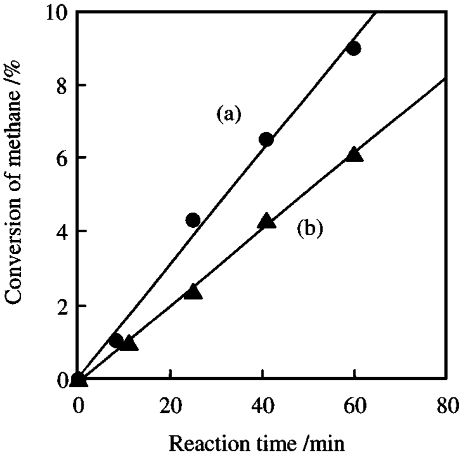


FIG. 12. Conversion of CH_4 and CD_4 versus reaction time (gas-closed circulation reaction system): (a) CH_4; (b) CD_4. $W = 0.5$ g, $T = 573$ K, $P(CH_4) = P(N_2O) = 2.7$ kPa; or $P(CD_4) = P(N_2O) = 2.7$ kPa.

As described above, the k_H/k_D for the oxidation of ethane was 1.06 at 573 K. The similar measurement was carried out for the oxidation of methane over $Fe_{0.5}Al_{0.5}PO_4$ (a model catalyst of $FePO_4$ (28)) at the same reaction conditions. The conversions of CH_4 and CD_4 versus reaction time are shown in Fig. 12. The isotopic effect (k_H/k_D) for the oxidation of methane calculated from this figure is 1.48. This value is higher than that for the oxidation of C_2H_6, but it is lower than the calculated value ($k_H/k_D = 2.6$ at 573 K), by assuming that the difference in the bond-dissociation energies for the C–H and C–D bonds wholly reflects their activation energies (33). These results are consistent with the conclusions obtained from the kinetic measurements for CH_4 and C_2H_6 oxidations as described above.

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