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Partial oxidation of alkenes by a membrane catalyst utilizing fuel cell reactions

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Abstract

Partial oxidation of ethylene with a gas-cell system were studied at 353 K. The gas-cell structure was [C_2H_4, H_2O|(Pd-black + VGCF)-anode|H_3PO_4/silica–wool|cathode|O_2] (VGCF: vapor growing carbon fiber). Addition of NO to O_2 stream at the cathode dramatically enhanced the oxidation rate of ethylene to MeCHO more than 10 times with high selectivities >95%. The enhancement of the formation rate of MeCHO was due to the acceleration of the electrochemical oxidation rate of Pd^0 to Pd^{2+} at the anode by a strong oxidant of NO_2 produced from O_2 and NO. NO_2 was electrochemically reduced to H_2O and NO that functioned as a mediator over the graphite-cathode. When a membrane of carbon matrix holding H_3PO_4 was chosen instead of H_3PO_4/silica–wool, both H^+ and e^- could conduct from anode to cathode side through the H_3PO_4/carbon matrix, self-short circuiting condition. The oxidation of C_2H_4 could perform with the self-shorted cell reactor excluded electric parts. Several carbon matrices were tested for the oxidation by the self-shorted cell and the suitable one was a sheet of (VGCF + AC + PTFE) (AC: active carbon) prepared by the hot-press method. This self-shorted gas-cell was more active than the cell system. In the case of propene oxidation, acetone was selectively produced with the self-shorted cell. Kinetic studies were carried out to get information for reaction mechanism of the alkene oxidation. The self-shorted cell works as a new type of membrane catalytic system for the oxidation of alkene [alkene|oxidation catalyst|mixed conductor of H^+ and e^-|reduction catalyst|oxidant]. This membrane catalyst also functioned as a hydrogen permeation membrane.

Keywords: Membrane catalyst; Wacker oxidation; Fuel cell; NO_x

1. Introduction

Selective partial oxidation of alkenes in the gas phase using alkene–O_2 cell systems has been previously reported, as shown in Fig. 1 [1–3]. When C_2H_4 was supplied to the gas-cell system, C_2H_4 was electrochemically oxidized with H_2O to MeCHO over the Pd-anode. Protons and electrons were, respectively, conducting through a lead wire and electrolyte to the cathode, and reduced O_2 (oxidant). The gas-cell system has several advantages compared with the current Wacker process in the aqueous HCl with $PdCl_2$ and $CuCl_2$ as catalysts. These are as follows: (a) the separation of MeCHO from the reaction system is very easy because of the heterogeneous system in the gas phase; (b) the cell system requires no chlorides, and so, the formation of chlorine containing by-products can be avoided; (c) the danger of explosion is reduced because C_2H_4 and O_2 are separated by the membrane; (d) the cell cogenerates electricity and valuable oxygenates (MeCHO) when a load is put in the outer circuit. However, the rate of oxygenate formation in this cell system was very low (1–2 turnover

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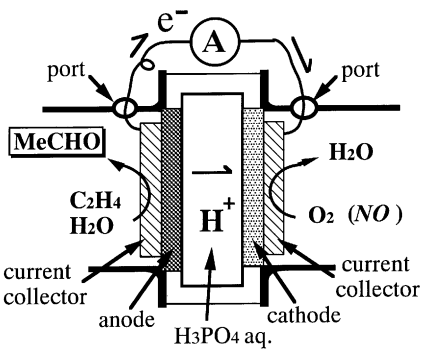

Fig. 1. Diagram of C_2H_4–O_2 cell system for the synthesis of MeCHO.

number of Pd-atom for MeCHO formation in 1 h). We have recently found that an addition of NO into the stream of O_2 dramatically enhanced the current and the formation rate of MeCHO more than 10 times [4].

As described above, the cell system for the partial oxidation of C_2H_4 has advantages compared with the current Wacker process. However, the complicated cell structure was a big disadvantage for industrial application. The cell reactor needs current collectors, lead wires and their ports. If the center part in Fig. 1 could conduct both H^+ and e^-, as shown in Fig. 2, we could exclude the electric parts from the reactor and a self-shorted cell system would be developed. This self-shorted cell is as a new type of membrane catalyst |catalyst for oxidation|mixed conductor of H^+ and e^-|catalyst for reduction|. In addition, this membrane catalyst is expected as a hydrogen permeation membrane.

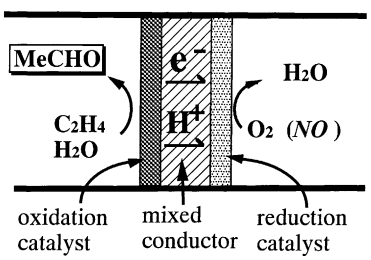

Fig. 2. Conception of a new type of membrane catalyst, self-shorted cell system.

2. Experimental

2.1. The cell system

The reactor and the principle of the cell system were already mentioned in Fig. 1. The gases at the cathode and anode are separated with a silica–wool disk (thickness 1 mm) holding aqueous H_3PO_4 (85 wt.%) as an electrolyte. The anode (thickness 0.2 mm) was prepared from Pd-black (20 mg), vapor growing carbon fiber (VGCF, 50 mg) and PTFE powder (5 mg) by the hot-press method [1,2]. The cathode (thickness 0.2 mm) was prepared by the same procedure from graphite (70 mg) and PTFE (5 mg) with and without Pt-black (20 mg). The geometric area of both the electrodes was 2 cm^2. The two electrodes were attached on both the sides of H_3PO_4/silica–wool disk. The cell was connected to a conventional gas flow system. The oxidation started by shorting the circuit at 353 K. Current and charge passed were monitored by a zero-shunt ammeter (Hokuto HM-104A) and a coulomb meter (Hokuto HF-201). The cathode and anode potentials during reactions were measured by an electrometer (Hokuto HE-106) with a standard Ag|AgCl electrode (0.196 V vs. NHE) with a capillary bridge inserted to the H_3PO_4/silica–wool disk.

2.2. Membrane catalyst

The membrane catalyst (Fig. 2) was assembled as below. First, the H^+ and e^- mixed conduction sheet (thickness 0.5 mm) was prepared by impregnating H_3PO_4 (aq.) (85 wt.%) into a carbon matrix. This carbon matrix was prepared from a mixture of carbon materials (70 mg) and PTFE powder (5 mg) by the hot-press method [1,2]. The carbon matrix was soaked in H_3PO_4 (85 wt.%) for 1 day. Conduction of H^+ was expected through the channel of H_3PO_4 and e^- conduction was through carbon matrix. Thus, this sheet would function as the hydrogen (H^+ and e^-) permeation material. Second, a porous sheet catalyst (thickness 0.2 mm) for alkene oxidation was the same as the porous Pd-anode, as described above. Another porous sheet catalyst (thickness 0.2 mm) for reduction of a gas mixture of O_2 and NO was the same as graphite-cathode. The two sheet catalysts were attached on both the sides of the carbon sheet holding H_3PO_4. The assembled membrane catalyst from the

three different sheets was attached at the center of the reactor, as shown in Fig. 2.

2.3. Reaction conditions

A gas mixture of alkene (39 kPa) and water vapor (13 kPa) balanced with He to atmospheric pressure was passed through the anode or the oxidation side. A gas mixture of O_2 (51 kPa) and He or that of O_2 (51 kPa), NO (25 kPa) and He was passed through the cathode or the reduction side. The total flow rate in both the compartments was 32 ml min^{-1}. Oxidation of alkene was carried out for several hours for both the reaction system at 353 K. Products were analyzed by a GC (ShimazuGC-8A with TCD detector and Porapack-Q and active carbon (AC) columns) and a HPLC (Shimazu VP-10 with UV detector and ODS-3 column) at every 30 min. Product selectivities were calculated on the basis of carbon number.

3. Results and discussions

3.1. Effect of NO addition to the gas-cell

The oxidation of C_2H_4 using the gas-cell was performed at 353 K. Fig. 3 demonstrates the time profiles of the formations of MeCHO and CO_2 and of the current responding to the addition and removal of NO into the O_2 stream. Under open-circuit conditions, no products were obtained. When the circuit was shorted, a current density of 3 mA cm^{-2} flowed and MeCHO was produced selectively (>97%). The addition of NO to the stream of O_2 increased the current density, remarkably, to 35 mA cm^{-2} and the formation rates of MeCHO and CO_2. When the addition of NO was stopped, both the current and the formation rates immediately decreased. The addition and removal of NO reversibly increased and decreased the current and the formation rates of MeCHO and CO_2. The selectivity to MeCHO was always greater than 95%. The current efficiencies were evaluated from the formation rates of MeCHO as a $2e^-$ reaction and CO_2 as a $6e^-$ reaction. The current efficiencies were roughly 100% within the experimental error of ±10%.

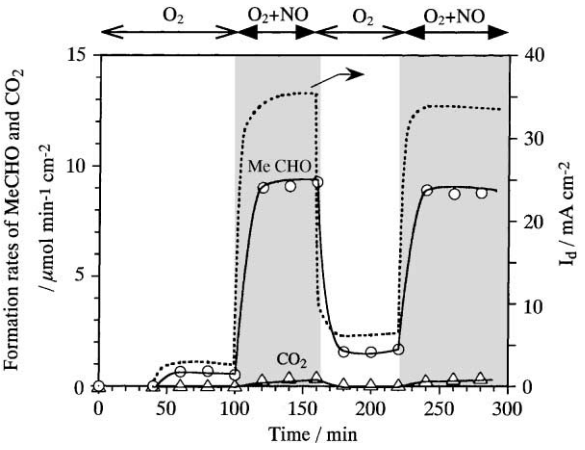

Fig. 3. Effect of NO addition to O_2 stream at the cathode on the oxidation of C_2H_4 at the anode with the C_2H_4–O_2 cell at 353 K. The anode: Pd-black + VGCF, C_2H_4 39 kPa, H_2O 13 kPa, balanced with He, total flow rate 32 ml min^{-1}. The cathode: Pt-black + Gr, O_2 51 kPa, or O_2 51 kPa + NO 25 kPa, balanced with He, total flow rate 32 ml min^{-1}.

We have already proposed the reaction scheme for the oxidation of C_2H_4 by the C_2H_4–O_2 cell [3,5,6]. The oxidation of C_2H_4 into MeCHO is caused by Pd^{2+} electrochemically generated. The rate of MeCHO formation under short-circuit conditions depends on the Pd^{2+} formation. Thus, the rate of MeCHO formation or that of Pd^{2+} formation should depend strongly on the anode potential under short-circuit conditions.

3.2. Electrochemical potential

The cathode potential for the C_2H_4–(O_2 + NO) cell under open-circuit conditions was 1.00 V (vs. Ag|AgCl), which was considerably higher than the values (0.86 V) observed for the C_2H_4–O_2 cell and the C_2H_4–NO cell (0.85 V). The increase in the cathode potential for the C_2H_4–(O_2 + NO) cell must be due to the formation of NO_2 (Eq. (1)), a stronger oxidant than O_2 and NO. The addition of NO to O_2 in the cathode compartment colored the anode gas into brown, obviously indicating the generation of NO_2:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \quad (1)$$

The open cell voltage for the C_2H_4–(O_2 + NO) cell was 0.74 V which was larger than the value (0.60 V) for the C_2H_4–O_2 cell. Under short-circuit conditions, the polarizations at the anode and the cathode for the C_2H_4–(O_2 + NO) cell were 0.62 and 0.07 V, respectively. The cathode polarization of 0.07 V was considerably smaller than that for the C_2H_4–O_2 cell

(0.19 V), suggesting the easier reduction of NO_2 than O_2. The anode potentials under short-circuit conditions for the C_2H_4–(O_2 + NO) and C_2H_4–O_2 cells were 0.88 and 0.65 V (vs. Ag|AgCl), respectively. The higher anode potential for the former under short-circuit conditions may explain the remarkable enhancement in the current and the formation rate of MeCHO when NO was cofed with O_2. Considering the redox potential of $Pd^0/Pd^{2+} = 0.79$ V (vs. Ag|AgCl), we can expect an easy formation of Pd^{2+} at the anode for the C_2H_4–(O_2 + NO) cell under short-circuit condition, which inevitably increases the current and the formation rate of MeCHO. Therefore, the addition of NO to the O_2 stream enhanced the formation of MeCHO due to the accelerated formation of Pd^{2+}.

3.3. Cathode reactions

The oxidation of C_2H_4 for the C_2H_4–O_2 cell did not proceed using the graphite-cathode without Pt-black. An active precious electrocatalyst such as Pt-black was essential for the reduction of O_2. In the case of the C_2H_4–(O_2 + NO) cell, the same good electrocatalytic performance for the formation of MeCHO was obtained by using the graphite-cathode. When a low pressure of NO_2 (5 kPa) was supplied to the graphite-cathode, a good performance for the oxidation of C_2H_4 was obtained, a current density of 18.5 mA cm^{-2} and a MeCHO formation rate of 5.0 μmol min^{-1} cm^{-2}. The reduction of NO_2 should occur quite easily over the graphite-cathode. The maximum formation rate of MeCHO of 8.6 μmol min^{-1} cm^{-2} was obtained using the graphite-cathode under the following conditions: $P(C_2H_4)$ 39 kPa, $P(H_2O)$ 13 kPa, $P(O_2)$ 50 kPa, P(NO) 25 kPa, T 353 K.

The analyses of the effluent gases from the cathode compartment indicated no formation of N_2, N_2O and NH_3. The analysis of the products (NH_2OH and NH_3) dissolved in the H_3PO_4 electrolyte in a silica–wool by using a Nessler's reagent revealed the formation of a small amount of NH_2OH or NH_3 (14–24 μmol h^{-1}, 2–4% current efficiency). These results suggest that NO_2 should be reduced mostly to NO at the cathode [4]:

$$NO_2 + 2H^+ + 2e^- \rightarrow NO + H_2O \quad (2)$$

The NO produced here would regenerate NO_2 according to Eq. (1). Thus, NO works as a mediator (or catalyst) for the electrochemical reduction of O_2.

3.4. Oxidation of C_2H_4 by a self-shorted cell system

As described so far, the C_2H_4–(O_2 + NO) cell system showed a very good performance for the synthesis of MeCHO. However, the complicated cell structure was a big disadvantage for industrial application. The cell reactor needs current collectors, lead wires and their ports. If the center part of the membrane (H_3PO_4/silica–wool) could conduct both H^+ and e^- (Fig. 2), we could exclude the electric parts from the reactor and develop a self-shorted cell system. Based on this idea, several carbon matrices holding H_3PO_4 (aq.) of 85 wt.% (H_3PO_4/carbon matrix) were tested for oxidation. If we chose a suitable H_3PO_4/carbon matrix, conduction of e^- was expected through carbon matrix and conduction of H^+ was through the channel of H_3PO_4.

Several H_3PO_4/carbon matrices were tested for C_2H_4 oxidation, as shown in Fig. 4. The (Pd-black + VGCF)-anode in the cell system works as an oxidation catalyst at the reaction system in Fig. 2 and the graphite-cathode works as a reduction catalyst. These catalysts were the same components for the experiments in Fig. 4. When we chose H_3PO_4/(AC + VGCF), H_3PO_4/carbon-felt, H_3PO_4/(VGCF + celite), and H_3PO_4/(VGCF + hydrophilic-PTFE) for the matrix holding H_3PO_4 (AC, VGCF), significant oxidation of C_2H_4 was observed producing MeCHO and CO_2. The VGCF material cannot hold H_3PO_4 (aq.), but has a good electric conductivity (0.012 Ω m). On the other hand, AC, carbon-felt, celite, and hydrophilic-PTFE materials have hydrophilic property. These materials could hold H_3PO_4 (aq.). The selectivities to MeCHO were greater than 95% for the four systems. In addition, no oxygenates were observed in the reduction side. The H_3PO_4/carbon matrix also worked as a separator.

When a gas mixture of O_2 and NO removed with He, the formations of MeCHO and CO_2 immediately stopped. When a gas mixture of C_2H_4, H_2O, O_2, and NO was passed over the oxidation catalyst (Pd-black + VGCF) in a separate experiment, formation of CO_2 was observed as a major product [4]. These results strongly suggested that the H_3PO_4/(VGCF + AC)

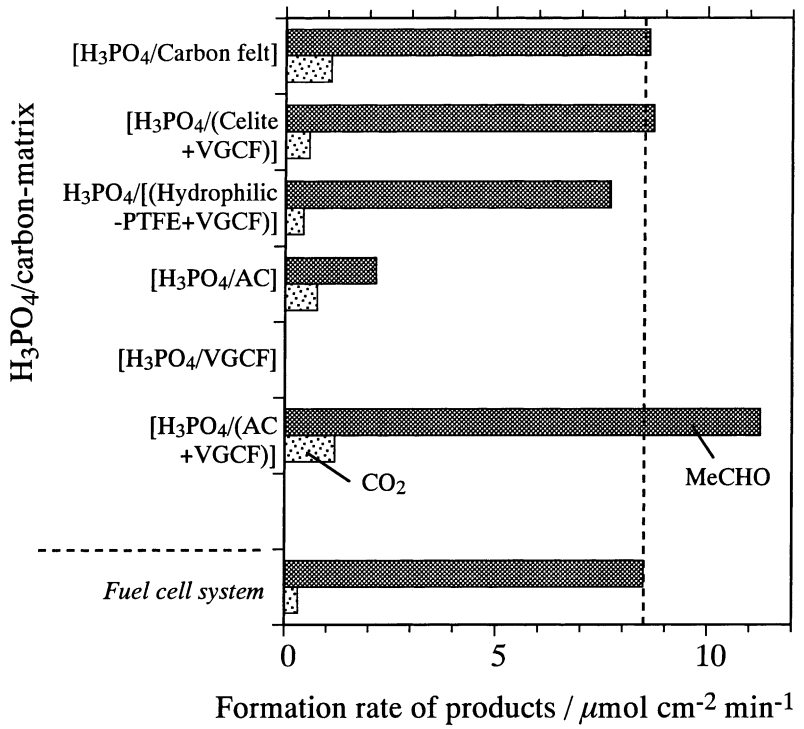

Fig. 4. Effect of various carbon matrices holding H_3PO_4 as a H^+ and e^- mixed conductor on the oxidation of C_2H_4 to MeCHO by the self-shorted cell (the membrane catalyst) at 353 K. Reaction system: [C_2H_4, H_2O|(Pd-black + VGCF) catalyst|H^+ and e^- mixed conductor|graphite catalyst|O_2, NO]. Oxidation side: C_2H_4 37 kPa, H_2O 16 kPa, balanced with He, total flow rate 32 ml min^{-1}. Reduction side: O_2 76 kPa, NO 25 kPa, total flow rate 32 ml min^{-1}.

functioned as the mixed conductor of H^+ and e^- and the oxidation of C_2H_4 should proceed through the reaction scheme as in Fig. 2, self-shorted cell. This self-shorted cell seems to be a new type of membrane catalyst.

3.5. Optimum conditions for the MeCHO formation by the membrane catalyst

As mentioned above, the most effective H_3PO_4/matrix was H_3PO_4/(VGCF + AC). The formation rate of MeCHO of 11.3 μmol min^{-1} cm^{-2} was larger than that of 8.6 μmol min^{-1} cm^{-2} observed in the gas-cell system. Fig. 5 shows the effect of the amount of AC in the carbon matrix (VGCF + AC + PTFE (5 mg)) on the oxidation of C_2H_4. Sum of VGCF and AC was constant of 70 mg. The catalytic activities for the oxidation of C_2H_4 strongly depended on the content of the carbon matrix. The formation rate of MeCHO

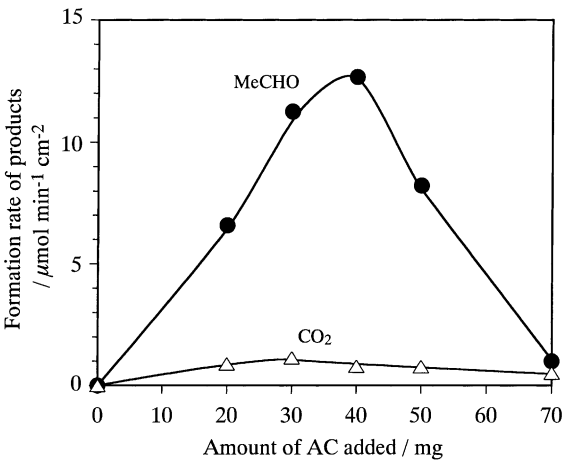

Fig. 5. Effect of amount of AC added to the (VGCF + AC) matrix holding H_3PO_4 on the oxidation of C_2H_4 with the membrane catalyst at 353 K. Total amount of VGCF and AC was 70 mg, other conditions were the same as Fig. 4.

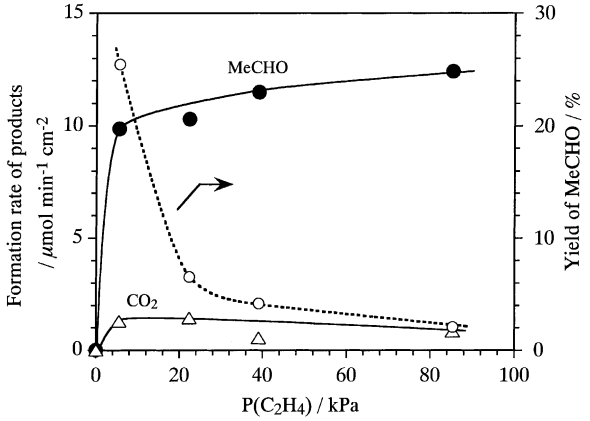

Fig. 6. Effect of $P(C_2H_4)$ on the oxidation of C_2H_4 with the membrane catalyst at 353 K. Reaction conditions were the same as Fig. 4, except for $P(C_2H_4)$.

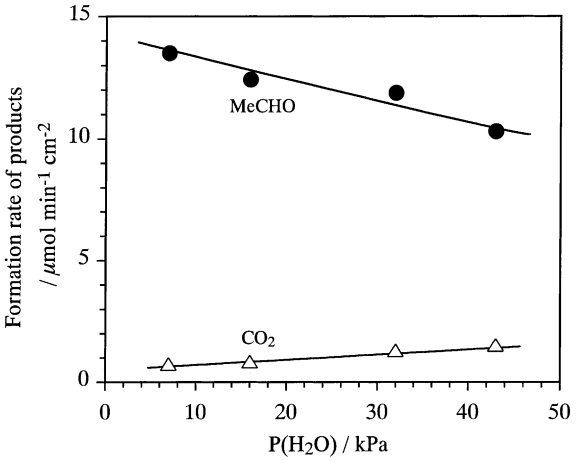

Fig. 7. Effect of $P(H_2O)$ on the oxidation of C_2H_4 with the membrane catalyst at 353 K. Reaction conditions were the same as Fig. 4, except for $P(H_2O)$.

increased with increase in the amount of AC added. This increase in the oxidation activity may be due to an increase in H^+ conductivity through H^+ channel (H_3PO_4/AC). The maximum formation rate of MeCHO (12.7 μmol min^{-1} cm^{-2}) was obtained at 40 mg of AC. Excess addition of AC to the carbon matrix decreased the catalytic activity. This unfavorable effect may be due to an increase in electric resistance because of a high electric resistance of AC. Balance of H^+ conduction (H_3PO_4/AC) and e^- conduction (VGCF) is important for the oxidation by the membrane catalyst.

Fig. 6 shows the effect of partial pressure of C_2H_4 on the oxidation by the membrane catalyst at 353 K. The formation rate of MeCHO slightly depended on the $P(C_2H_4)$. A low $P(C_2H_4)$ of 5 kPa was enough for the oxidation. Therefore, one-pass yield of MeCHO increased with decreasing $P(C_2H_4)$, 15% yield at $P(C_2H_4) = 5$ kPa. This result suggested that adsorption of C_2H_4 was enough to the (Pd-black + VGCF) catalyst at lower pressure of C_2H_4.

Fig. 7 shows the effect of partial pressure of water vapor on the oxidation by the membrane catalyst at 353 K. When water vapor was not supplied to the reaction system, the membrane catalyst did not function as a separator. $P(H_2O) > 7$ kPa was enough for the membrane catalyst to perform the oxidation of C_2H_4. The formation rate of MeCHO slightly decreased with increasing $P(H_2O)$. This decrease in the MeCHO formation may be due to the competitive adsorption between C_2H_4 and H_2O on the oxidation catalyst.

3.6. Propene oxidation by the membrane catalyst

The membrane catalyst was applied for the oxidation of propene to get some mechanistic information for the oxidation because some different types of oxidations of propene were expected, epoxidation (propene oxide), allyl oxidation (acrolein), and Wacker oxidation (acetone) [1–7]. Oxidation of propene was carried out with supplying propene (39 kPa) instead of C_2H_4 to the same membrane catalyst [C_3H_6, H_2O|(Pd-black + VGCF) catalyst|H_3PO_4/(VGCF + AC)|graphite-catalyst|O_2, NO].

Fig. 8 shows the temperature dependence of the oxidation of C_3H_6 by the membrane catalyst. Products were acetone as the major one, CO_2 and a trace amount of acrolein, but there was no formation of propene oxide. Even at 313 K, the formation of acetone and CO_2 were observed. The formation rate of acetone considerably increased with rising temperature. The maximum formation rate of acetone was obtained at 353 K. On the other hand, increases in the formation rate of CO_2 were small at all temperatures. The experiment at >372 K was not favorable because

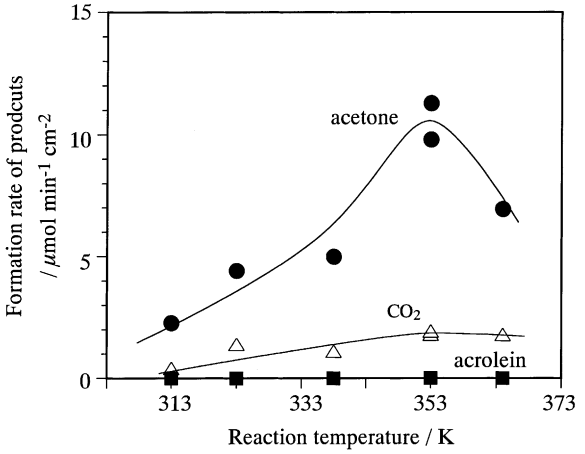

Fig. 8. Temperature dependence on the oxidation of propylene with the membrane catalyst at 353 K. Oxidation side: (Pd-black + VGCF) catalyst, C_3H_6 37 kPa, H_2O 90% of saturated vapor pressure, balanced with He, total flow rate 32 ml min^{-1}. Reduction side: graphite catalyst, O_2 76 kPa, NO 25 kPa, total flow rate 32 ml min^{-1}.

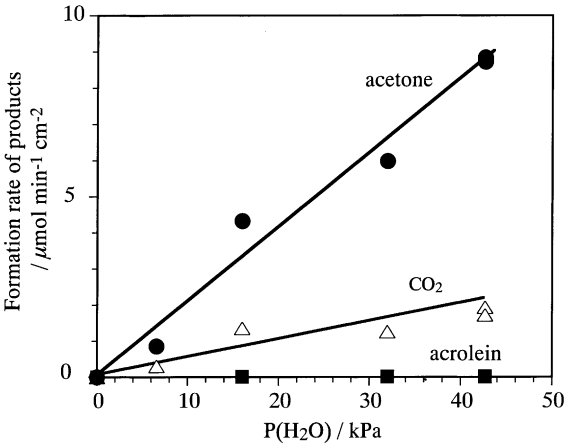

Fig. 9. Effect of $P(H_2O)$ on the oxidation of propylene with the membrane catalyst at 353 K. Reaction conditions were the same as Fig. 8, except for $P(H_2O)$.

of an evaporation of H_3PO_4 from the (VGCF + AC) matrix.

The highest formation rate of acetone was 11.3 μmol min^{-1} cm^{-2} with a high selectivity of 95%. These results clearly proved that the Wacker type oxidation of alkene proceeded over the membrane catalyst, with no allyl oxidation and no epoxidation.

Fig. 9 shows the effect of partial pressure of water vapor on the oxidation by the membrane catalyst. The formation rate of acetone linearly increased with increase in $P(H_2O)$. The formation rate of CO_2 also increased with $P(H_2O)$. In the case of C_2H_4 oxidation in Fig. 7, a low pressure of H_2O was enough for the formations of MeCHO and CO_2. Dependence of $P(H_2O)$ on the oxidation of C_3H_6 was very different from that observed for the C_2H_4 oxidation.

Therefore, effect of $P(C_3H_6)$ on the oxidation was studied in Fig. 10. The formation rate of acetone slightly increased with decreasing $P(C_3H_6)$. This dependence of $P(C_3H_6)$ on the oxidation was contrary for that observed for the C_2H_4 oxidation (Fig. 6). A low partial pressure of C_3H_6 of 5 kPa was suitable for the oxidation by the membrane catalyst.

The results of Figs. 9 and 10 suggested that the adsorption of C_3H_6 on the oxidation catalyst (Pd-black + VGCF) was strong enough to compare with the adsorption of C_2H_4. In other words, C_3H_6 should cover the surface of the oxidation catalyst even at lower pressure of C_3H_6. Higher pressure of C_3H_6 did not enhance the formation of acetone, but seemed to slightly inhibit the oxidation. The adsorptions of alkene and H_2O should be a competitive process on the oxidation catalyst.

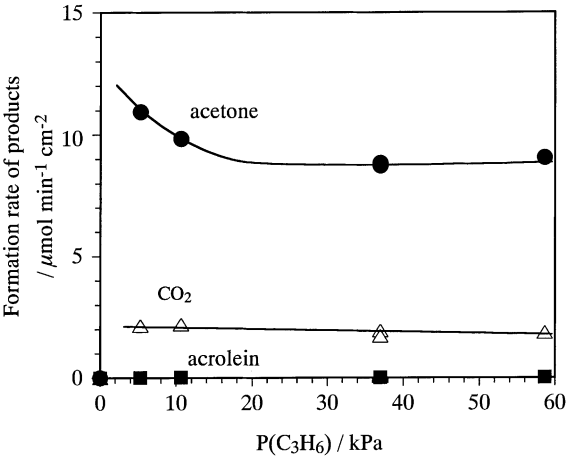

Fig. 10. Effect of $P(C_3H_6)$ on the oxidation of propylene with the membrane catalyst at 353 K. Reaction conditions were the same as Fig. 8, except for $P(C_3H_6)$.

3.7. Hydrogen permeation property

In order to prove the mixed conduction of H^+ and e^- through the membrane, hydrogen permeation experiments were carried out using the [(Pd-black + VGCF)|H_3PO_4/(VGCF + AC)|(Pt-black + graphite)] membrane. A gas mixture of H_2 (0–101 kPa) and N_2 (0–101 kPa) was introduced to the oxidation side instead of C_2H_4, and pure Ar gas was introduced to the reduction side instead of O_2 and NO. Fig. 11 shows the effect of the partial pressure of H_2 on the permeation rates of H_2 and N_2 from the oxidation side to the reduction side. The permeation rate of H_2 was considerably larger than that of N_2. The permeation rate of H_2 increased with increasing $P(H_2)$. The ratio of the permeation rate of H_2 and N_2 (a separation factor) at $P(H_2) = P(N_2) = 50.5$ kPa was more than 150, which was far larger than the factor of 3.75 estimated by Knudsen diffusion mechanism [8]. When the similar permeation experiment was carried out by using a mixture of H_2 and He ($P(H_2) = P(He) = 50.5$ kPa), the separation factor of H_2 and He was 40 which was larger than the separation factor of 1.41 (Knudsen diffusion). These results clearly proved that the permeation of H_2 was not due to the Knudsen diffusion mechanism. The hydrogen permeation would proceed through the mixed conduction of H^+ and e^-, as we expected.

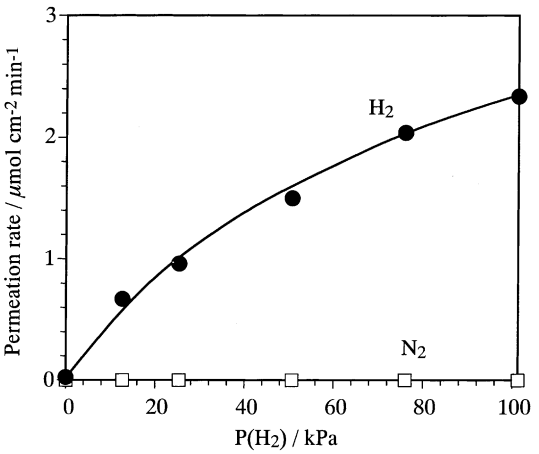

Fig. 11. Permeation rate of H_2 and N_2 as functions of $P(H_2)$ (or $P(N_2)$) through the three-layered membrane catalyst at 353 K. Reaction system: [$H_2 + N_2$|(Pd-black + VGCF) catalyst|H_3PO_4/(VGCF + AC) sheet|(Pt-black + VGCF) catalyst|Ar + H_2O]. $P(H_2) + P(N_2) = 1$ atm.

3.8. Reaction scheme

The experimental results in this work propose that the oxidation of C_2H_4 to MeCHO and C_3H_6 to acetone by the membrane catalyst proceeded through Wacker type oxidation catalyzed by Pd^{2+}, as shown in Fig. 12.

First, Pd^0 in the oxidation catalyst oxidized to Pd^{2+} by the strong oxidant of NO_2 produced from O_2 and NO at the opposite side. A strong oxidation potential of NO_2 was propagated through the mixed conductor of H^+ and e^- (H_3PO_4/(VGCF+AC)) to the oxidation catalyst. A concentration of Pd^{2+} on oxidation catalyst should be saturated. Pd^{2+} oxidized C_2H_4 with H_2O to MeCHO and H^+ [3,5,6]. Both H^+ and e^- conducted into the mixed conductor to the opposite side and reduced NO_2 to H_2O and NO over the graphite-catalyst. Adsorptions of C_2H_4 and H_2O on the catalyst were easy at lower pressures. The steady-state concentration of Pd^{2+} should be enough. Therefore, the formation rate of MeCHO would be determined by the chemical reaction rate between Pd^{2+}, C_2H_4 and H_2O. To enhance the formation rate of MeCHO, the chemical reaction rate between Pd^{2+}, C_2H_4 and H_2O must be improved by modification of Pd^{2+} species on the oxidation catalyst. In the case of C_3H_6 oxidation, adsorption of C_3H_6 on the oxidation catalyst should be strong and inhibited the adsorption of H_2O. Thus, a

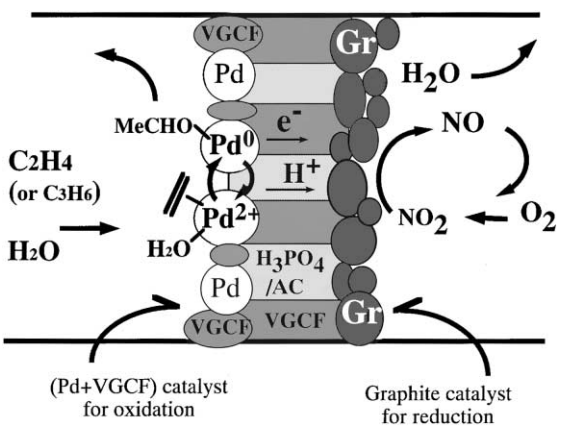

Fig. 12. Model of the reaction mechanism of the oxidations of C_2H_4 and C_3H_6 by the membrane catalyst.

higher pressure of H_2O was suitable for the oxidation. The formation rate of acetone should increase at higher pressure of $H_2O > 50$ kPa. To perform a drastic acceleration of the acetone formation, an improvement of catalysis of Pd species is essential as similar to the C_2H_4 oxidation.

4. Conclusion

As described so far, the new type of the membrane catalyst system, [alkene, H_2O|(Pd-black + VGCF)|H_3PO_4/(VGCF + AC)|graphite|O_2, NO], was active for the Wacker oxidation of C_2H_4 and C_3H_6 at 353 K. The turnover number of Pd for MeCHO formation was over 10 in 1 h. This catalytic activity was as good as that of the industrial catalyst. This new type of the membrane catalyst can be applied to other catalytic reactions, oxidative dehydrogenation of alcohol, selective hydrogenation of unsaturated compound, hydroformylation of alkene, etc. [9].

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