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Catalysis Today 66 (2001) 115–122

CATALYSIS TODAY

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Design of alkenes–(O_2 + NO) cell system for the selective partial oxidation of alkenes

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Abstract

Wacker type oxidations of alkenes were performed using an [alkene |Pd-black (anode)| H_3PO_4 |graphite (cathode)| O_2+NO] gas-cell at 353 K. The addition of NO to O_2 in the cathode led to a dramatic enhancement of the oxidation rate of ethylene to MeCHO more than 10 times. The kinetic experiments were studied to get information on reaction mechanisms and the optimum conditions for MeCHO synthesis. The enhancement was ascribed to the acceleration in the rate of electrochemical oxidation of Pd(0) to Pd(II) due to the formation of NO_2 at the cathode. The formation of NO_2 led to an increase in the electromotive force of the cell and the over potential at the Pd anode. The graphite without precious metals was sufficient as the cathode for the reduction of NO_2 into NO and H_2O. The electrochemical reduction of O_2 to H_2O was catalyzed by NO. In the case of propene oxidation, the formation of acrolein, the major product for the [C_3H_6–O_2] cell, was remarkably decelerated and acetone was the major product when NO had been added to O_2. These observations may be ascribed to changes in the concentrations of Pd(0) and Pd(II) which are responsible for the π-allyl and Wacker type oxidations, respectively.

Keywords: Wacker oxidation; π-Allyl oxidation; NO_x catalysis; Palladium; Fuel cell

1. Introduction

The new catalytic system using [alkene–O_2] cell systems for the selective partial oxidation of alkenes has been reported [1,2,3]. When palladium black is used as an anode-electrocatalyst for the [C_2H_4–O_2] cell, the Wacker type oxidation of C_2H_4 to MeCHO was selectively performed. This [C_2H_4–O_2] cell system has several advantages compared with the current Wacker process for the synthesis of MeCHO in the aqueous HCl with $PdCl_2$ and $CuCl_2$ as catalysts. For example: (i) products can be easily separated from the catalytic system, (ii) the cell system requires no chlorides, therefore, by-products containing chlorine are not formed, (iii) the danger of explosion is reduced because alkenes and O_2 are separated, and (iv) the cell can cogenerate electricity and MeCHO. However, the rate of oxygenate formation in this alkene–O_2 cell system was very slow (1–2 TON/Pd-atom in 1 h). Subsequently, the rate needs to be significantly enhanced for industrial application in the future.

We have very recently found that an addition of NO in a stream of O_2 in the cathode compartment leads to a dramatic enhancement of the current and the formation rate of the MeCHO [4]. In the present paper, kinetic and electrochemical investigations have been carried out to gain an understanding of favorable effect of NO on the selective synthesis of MeCHO by the [C_2H_4–(O_2 + NO)] cell.

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0920-5861/01/$ – see front matter
PII: S0920-5861(00)00611-8

2. Experimental

Fig. 1 shows the reactor and the principle of the cell system. The gases at the cathode and anode are separated with a silica–wool disk holding aqueous phosphoric acid (85 wt.%) as an electrolyte. The cell was connected to a conventional gas-flow system. The anode was prepared from Pd-black (20 mg), carbon fiber (50 mg) and PTFE powder (5 mg) by the hot-press method. The cathode was prepared by the same procedure from graphite (70 mg) and PTFE (5 mg) with and without Pt-black (20 mg). Graphite (denoted as Gr, Wako Chemical) washed with HCl aq. and distilled water and the carbon fiber (denoted as CF, Showa Denko) were used for electrode materials. The artificial area of both electrodes was 2 cm^2.

The oxidation of alkenes was performed under the following standard reaction conditions: a gas mixture of alkene (39 kPa) and water vapor (13 kPa) balanced with He at atmospheric pressure was passed through the anode compartment. A gas mixture of O_2 (51 kPa) and balanced with He or that of O_2 (51 kPa), NO (25 kPa) and balanced with He was passed through the cathode compartment. The total flow rate in both compartments was 32 ml min^{-1}. The reagents and gases with extra-pure grade were used without any purification in this work.

The reaction started by shorting the circuit at 353 K. Usually, steady state results were obtained at 40–60 min after new reaction conditions had been fixed. Therefore, unless otherwise stated, the data described in this work were obtained at a reaction time of 40–60 min after shorting the circuit. Good reproducibility was obtained within the experimental error of ±10%.

The current and the charge passed were monitored by a zero-shunt ammeter (Hokuto HM-104A) and a Coulomb meter (HokutoHF-201). The cathode and anode potentials during reactions were measured by an electrometer (Hokuto HM-103) with a standard Ag|AgCl electrode (0.196 V vs. NHE) with a capillary tube filled with H_3PO_4 aq. inserted to the silica–wool disk holding H_3PO_4 aq. (Fig. 1). The products were analyzed by GC and HPLC.

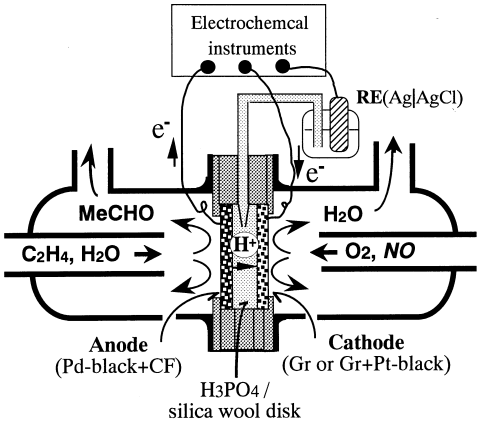


Fig. 1. Diagram of the [C_2H_4–(O_2 + NO)] cell system for the selective synthesis of MeCHO.

3. Results and discussion

3.1. Enhancing effect of the NO addition on the oxidation of C_2H_4

Fig. 2 demonstrates the time profiles of the formations of MeCHO and CO_2 and of the current

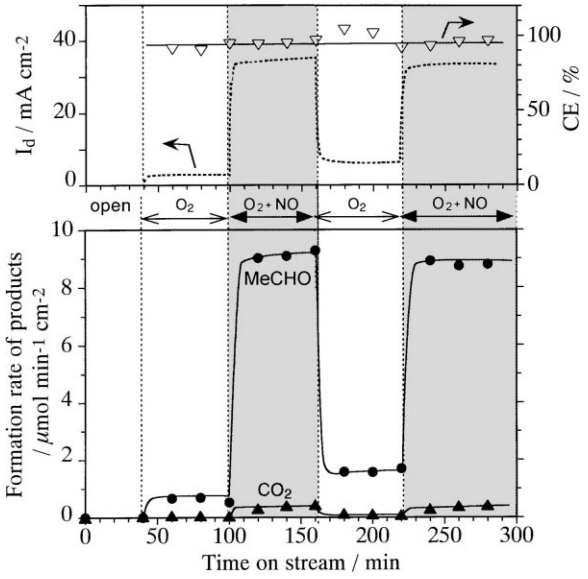


Fig. 2. Effects of NO addition to the O_2 stream at the cathode on the formation of rate of MeCHO by the [C_2H_4–O_2] cell at 353 K. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, balanced with He; cathode: Pt-black + Gr, O_2 51 kPa, or O_2 51 kPa + NO 25 kPa, balanced with He.

responding to starting and stopping of the NO addition to the stream of O_2 in the cathode compartment. When the circuit was shorted in the absence of NO at the cathode (40–100 min), a current (I_d) of 3 mA cm^{-2} flowed and MeCHO (0.5 TON in 1 h) was produced selectively (>97%). The addition of NO to the cathode compartment (100–160 min) dramatically increased the current (I_d) of 35 mA cm^{-2} and the formation rate of MeCHO (6 TON in 1 h). When the addition of NO was stopped (160–220 min), both the current and the formation rate of MeCHO immediately decreased. The starting and stopping of NO addition reversibly accelerated and decelerated both the current and the formation rate of MeCHO. Although the cofeed of NO with O_2 also accelerated the formation of CO_2, the selectivity to MeCHO was always greater than 95%. The current efficiencies (CE) indicated in this figure were those evaluated from the total amount of the products (MeCHO + CO_2) and the charge passed assuming the following electrochemical reactions at the anode (Eqs. (1) and (2)):

$$C_2H_4 + H_2O \rightarrow CH_3CHO + 2H^+ + 2e^- \quad (1)$$

$$C_2H_4 + 4H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad (2)$$

The CE were roughly 100% within the experimental error of ±10%. This was true for all the data under different conditions in this work.

3.2. Temperature dependence

The dependence of reaction temperature from 293 to 413 K on the oxidation of C_2H_4 is shown in Fig. 3. This [C_2H_4–(O_2 + NO)] cell system works even at room temperature. The formation rates of MeCHO and CO_2 as well as the current increased linearly with a rise in the reaction temperature ≤373 K. However, a decrease in the current and an increase in the formation rate of CO_2 were observed at 413 K because NO_x leaked from the cathode compartment to the anode through the diaphragm. The diaphragm, electrolyte membrane, did not work as a separator at 413 K, because of an evaporation of H_2O from H_3PO_4 aq. in the diaphragm. The CE were almost 100% within the experimental error at ≤373 K.

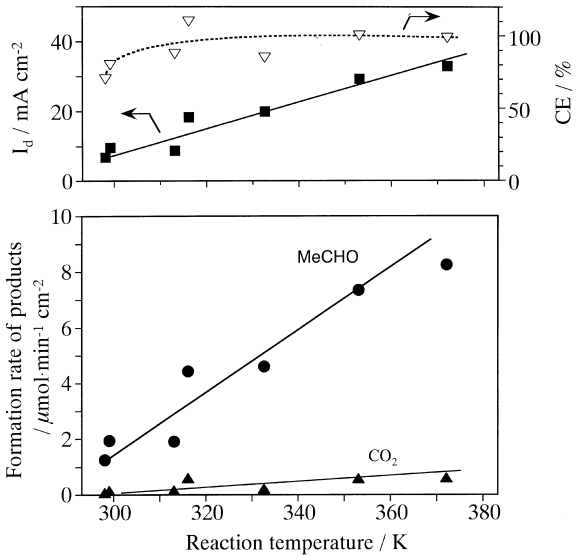


Fig. 3. Temperature dependence on the oxidation of C_2H_4 by the [C_2H_4–(O_2 + NO)] cell. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, balanced with He; cathode: Pt-black + Gr, O_2 51 kPa, NO 25 kPa, balanced with He.

3.3. Influences of Pt-black in the cathodes

A gas mixture of O_2 and NO is very active oxidant for the partial oxidation of C_2H_4 with the cell system as mentioned above. It is easy to assume that a real oxidant in a gas mixture of O_2 and NO may be NO_2 (Eq. (3)).

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \quad (3)$$

In fact, rapid formation of blown-gas was observed in the cathode compartment by the addition of NO to O_2. If NO_2 was the real oxidant, it should be confirmed that whether the Pt-black/Gr cathode used in Figs. 2 and 3 is suitable one or not for the [C_2H_4–(O_2 + NO)] cell system.

We found that the cathode prepared from Gr and PTFE powder without Pt-black showed the same good electrocatalytic performance as that of the Pt-black/Gr cathode, as shown in Table 1. Of course, the oxidation of C_2H_4 for the [C_2H_4–O_2] cell using the Gr cathode did not proceed at all. It is essential to use an active precious electrocatalyst such as Pt-black for the electrochemical reduction of O_2. However, the Gr cathode

Table 1
Effect of cathodes and oxidants on the partial oxidation of C_2H_4 by the [C_2H_4-oxidant] cell system at 353 K[a]

Cathode	Oxidant (kPa)	I_d (mA cm^{-2})	Products (μmol min^{-1} cm^{-2})		CE (%)
			MeCHO	CO_2	
Gr + Pt-black	O_2 (50) + NO (25)	33.5	9.05	0.36	97
Gr[b]	O_2 (50) + NO (25)	35.5	8.95	0.61	98
Gr	NO_2 (5)	18.3	5.00	0.11	94
Gr	O_2 (50) + NO (6)	24.9	6.05	0.27	89
Gr	NO (20)	1.6	0.31	0.05	91

[a] Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, $F = 32$ ml min^{-1}; cathode: some oxidants, balanced with He, $F = 32$ ml min^{-1}.
[b] Graphite.

is active for the electrochemical reduction of a gas mixture of O_2 and NO, maybe NO_2.

Cathodes made from carbon fiber (CF) and active carbon (AC) without Pt were examined for the oxidation in the place of the Gr cathode. Selective synthesis of MeCHO was performed for the oxidation of C_2H_4 using the CF cathode and the AC cathode but the oxidation rates of C_2H_4 were different among the cathodes. The current densities observed for each cathodes were 35.5 mA cm^{-2} (Gr cathode) ≈35 (CF cathode) >15.5 (AC cathode). The most suitable cathode was the Gr cathode. The current densities may be dependent on an electric conductivity of each cathode.

We can use a cheap Gr cathode without Pt-black when NO cofed with O_2 into the cathode compartment. Therefore, the experiments hereafter will perform by using the Gr cathode without Pt-black, unless otherwise stated.

3.4. The real oxidant and the products at the cathode

In order to identify the active oxidant at the cathode, the effects of various oxidants, NO_2 (5 kPa), a gas mixture of NO (6 kPa) and O_2 (50 kPa), and NO (20 kPa), on the current and the formation rates of MeCHO and CO_2 have been examined in Table 1. Although the partial pressure of NO_2 was low compared to the other oxidants, NO_2 gave a high current as well as a high formation rate of MeCHO. This oxidation performance is as well as that obtained using a gas mixture of NO (6 kPa) and O_2 (50 kPa). NO alone was not active oxidant for the electrochemical oxidation of C_2H_4 to MeCHO. These observations suggest that the active oxidant generated in a gas mixture of O_2 and NO is NO_2 which is responsible for the remarkable enhancement in the formation of MeCHO.

Table 2 shows the products formed by reduction of NO_x in the cathode compartment during the [C_2H_4–(O_2 + NO)] cell reactions. No formations of N_2, N_2O and NH_3 were observed in the stream of the cathode. The analysis of N-contained products dissolved in the electrolyte (H_3PO_4) membrane by using the Nessler's reagent revealed the formation of a small amount of NH_2OH or NH_3. These results suggest that NO_2 should be reduced mostly to NO and H_2O as,

$$NO_2 + 2H^+ + 2e^- \rightarrow NO + H_2O \quad \text{(cathode)} \qquad (4)$$

The NO produced here would regenerate NO_2 according to Eq. (3). Thus, NO works as a mediator (or catalyst) for the electrochemical reduction of O_2.

Table 2
Reduced products from NO_x at the cathode at 353 K[a]

Cathode	I_d (mA cm^{-2})	Products, μmol min^{-1} cm^{-2} (CE, %)			
		N_2	N_2O	NH_2OH or	NH_3
Gr + Pt-black	33.5	0 (0)	0 (0)	0.24 (1.4)	0.40 (4.0)
Gr	35.5	0 (0)	0 (0)	0.19 (1.6)	0.34 (4.7)

[a] Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, $F = 32$ ml min^{-1}; cathode: O_2 51 kPa, NO 25 kPa, balanced with He, $F = 32$ ml min^{-1}.

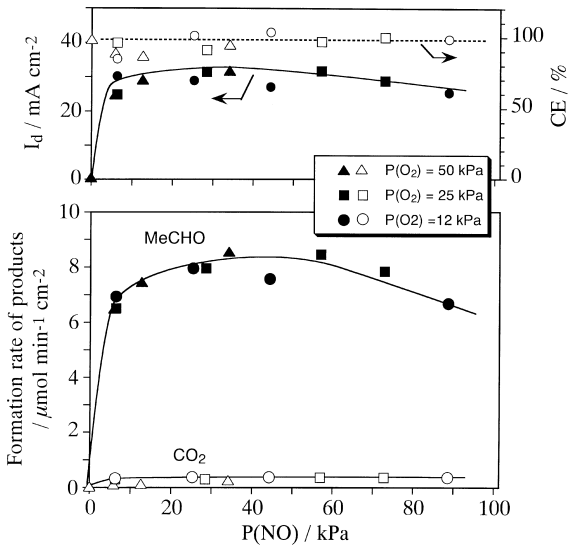


Fig. 4. Effect of the partial pressure of NO in the cathode on the oxidation of C_2H_4 by the [C_2H_4–(O_2 + NO)] cell at 353 K. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa; cathode: Gr, O_2 12, 25, or 50 kPa, NO 0–88 kPa.

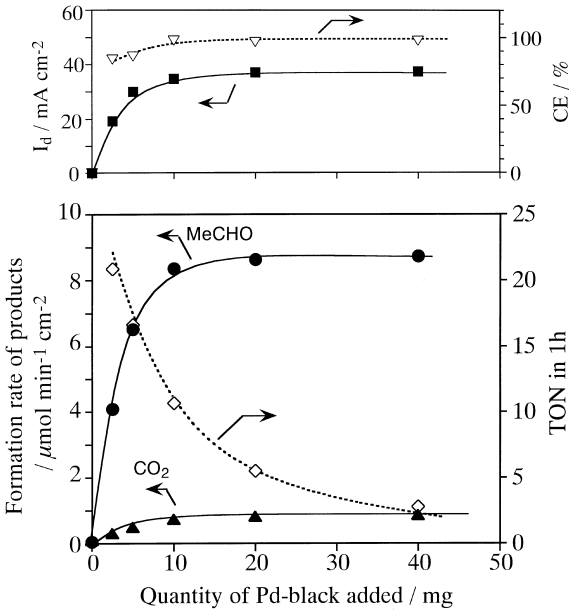


Fig. 5. Effect of Pd-black added in the anode on the oxidation of C_2H_4 by the [C_2H_4–(O_2 + NO)] cell at 353 K. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, balanced with He; cathode: Gr, O_2 25 kPa, NO 25 kPa, balanced with He.

3.5. Effects of reaction conditions at cathode

Fig. 4 shows the effect of the P(NO) with a constant $P(O_2)$ on the formation rates of products and on the current. The data obtained at different $P(O_2)$ of 51, 29, and 13 kPa are plotted all together in Fig. 4. The current and the formation rate of MeCHO may show their maximums at P(NO) of 30–40 kPa, but they depend only slightly on the P(NO). The formation rates as well as the current did not depend on $P(O_2)$ of 13, 29, and 51 kPa with a constant P(NO). This dependence of $P(O_2)$ on the oxidation was very different from that of the [C_2H_4–O_2] cell system [1,2]. These observations in Fig. 4 suggests that the concentration of the oxidant (NO_2) formed from NO and O_2 in the cathode compartment is sufficient for the oxidation of C_2H_4 or the active sites on the cathode must be saturated with NO_2 under the experimental conditions in this work.

3.6. Effects of reaction conditions at anode

Fig. 5 shows the effect of the quantity of Pd-black in the anode (CF 50 mg) on the current and the formation rates of MeCHO and CO_2. The formation rates and the current increased sharply with the quantity of Pd-black added <10 mg. A turnover number for the MeCHO formation increased with decreasing quantity of Pd-black added. However, the quantity greater than 10 mg in the wafer of the anode did neither improve the formation of MeCHO nor the current. The TON is 11 in 1 h at the anode added Pd-black of 10 mg. The highest turnover number for the production of MeCHO was 21 TON (12.8 g MeCHO/g-Pd/h) which is comparable to those of industrial catalysts.

When a Pd-balck (20 mg)/Gr (50 mg) anode was used for the oxidation instead of the Pd-black/CF anode, the selective formation of MeCHO also observed but the current density reduced to 24 mA cm^{-2}. This difference in the current density (the oxidation rate) may be due to the difference in the area of the active site on the anode.

Fig. 6 shows the influence of $P(C_2H_4)$ of 5–90 kPa in the anode compartment on the formation rates of MeCHO and CO_2 at 353 K. The change in the $P(C_2H_4)$ neither affected the formation rates of

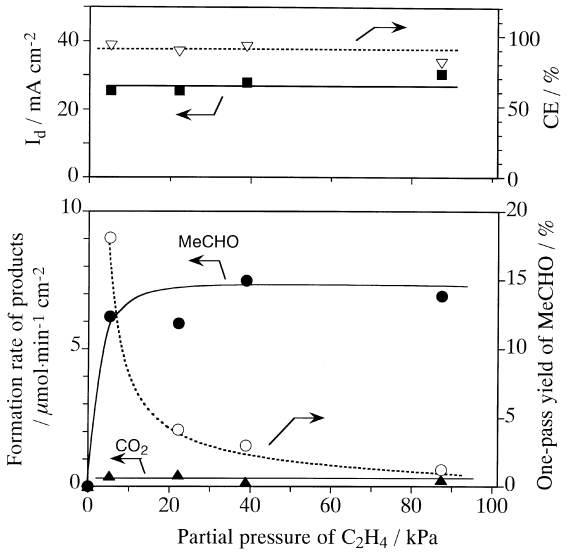


Fig. 6. Effect of $P(C_2H_4)$ on the oxidation of C_2H_4 by the $[C_2H_4–(O_2 + NO)]$ cell at 353 K. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, balanced with He; cathode: Gr, O_2 25 kPa, NO 25 kPa, balanced with He.

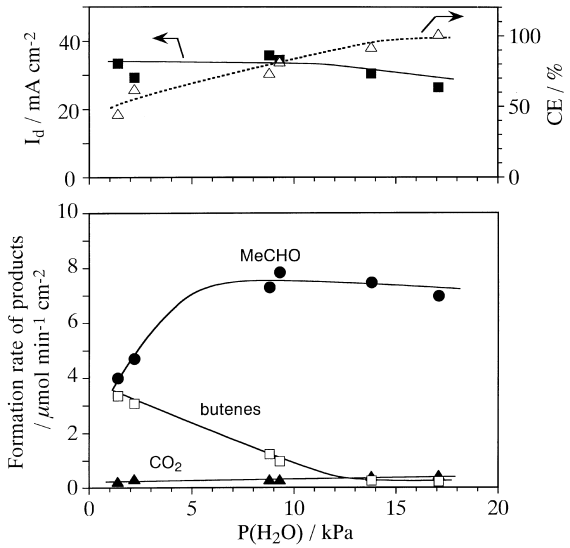


Fig. 7. Influence of $P(H_2O)$ in the anode on the oxidation of C_2H_4 by the $[C_2H_4–(O_2 + NO)]$ cell at 353 K. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 0–17 kPa, balanced with He; cathode: Gr, O_2 25 kPa, NO 25 kPa, balanced with He.

MeCHO and CO_2, product selectivities nor the current. A low $P(C_2H_4)$ of 5 kPa is enough for the oxidation with the $[C_2H_4–(O_2 + NO)]$ cell system. Therefore, the one-pass yield of MeCHO increased with decrease in $P(C_2H_4)$. The maximum yield was 18% at $P(C_2H_4) = 5$ kPa.

Fig. 7 shows the effects of $P(H_2O)$ on the oxidation of C_2H_4. The oxidation of C_2H_4 did not depend on the $P(H_2O)$ larger than 9 kPa in the anode compartment, as shown in Fig. 7. When $P(H_2O)$ was less than 9 kPa the formation rate of MeCHO and current reduced considerably, but the formation of butenes was increased through the dimerization of C_2H_4 with acid-catalysis, probably due to an increase in the acid strength of the electrolyte.

Fig. 8 shows the effects of flow rate of 3.6–69.0 ml min^{-1} in the anode compartment on the oxidation of C_2H_4 at 353 K. The flow rates did not affect the oxidation of C_2H_4, formation rates of products, product selectivities, and current efficiency. The constant selectivities suggest that the formation paths of MeCHO and CO_2 are parallel ones but not successive ones. The highest one-pass yield of MeCHO was 22.5% at the lowest flow rate of the anode gases.

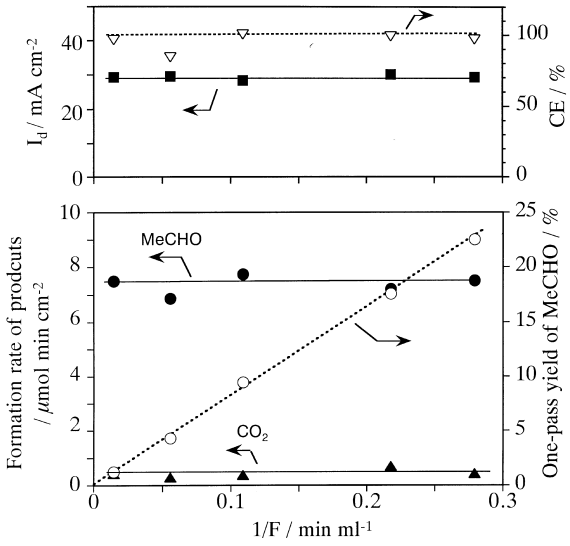


Fig. 8. Effect of the flow rate in the anode on the oxidation of C_2H_4 by the $[C_2H_4–(O_2 + NO)]$ cell at 353 K. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, balanced with He; cathode: Gr, O_2 51 kPa, NO 25 kPa, He balanced with He.

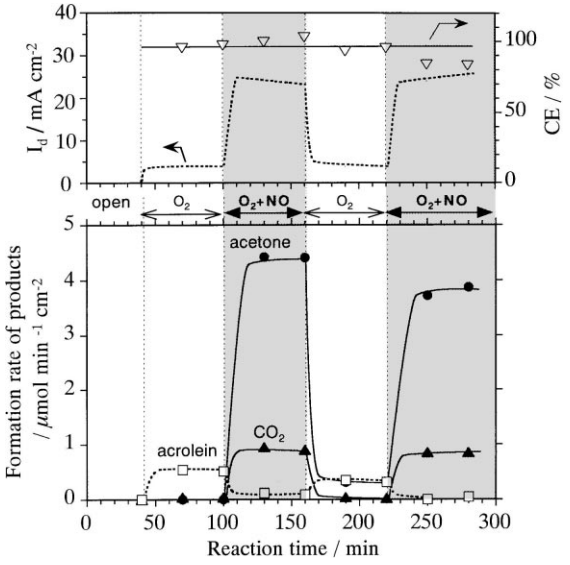


Fig. 9. Effects of NO addition to the O_2 stream in the cathode on the π-allyl and the Wacker oxidations of propene by the [C_3H_6–O_2] cell at 353 K. Anode: Pd-black+CF, C_3H_6 (39 kPa), H_2O (13 kPa), balanced with He; cathode: Pt-black + Gr, O_2 (51 kPa), or O_2 (51 kPa) + NO (25 kPa), balanced with He.

3.7. Oxidation of propene with [C_3H_6–(O_2 + NO)] cell

Effect of the NO addition to the stream of O_2 in the cathode was studied for the electrochemical oxidation of propene with the cell system, as shown in Fig. 9. The oxidation of C_3H_6 with the [C_3H_6–O_2] cell under short-circuit conditions gave acrolein as the major product [1,2]. Only a trace of acrylic acid, acetone and CO_2 were observed. The addition of NO to O_2 dramatically changed the product selectivities and the oxidation rate of C_3H_6. The shorting of the [C_3H_6–O_2] cell (40–100 min) enhanced the formation of acrolein very selectively (>90%). The addition of NO to O_2 enhanced the current and dramatically accelerated the formation of acetone (100–160 min). In contrast, the formation of acrolein dramatically reduced. The stopping of the NO addition (160–220 min) drastically decreased the acetone formation but increased the acrolein formation. These responses to the starting and stopping of the NO addition were reversibly observed.

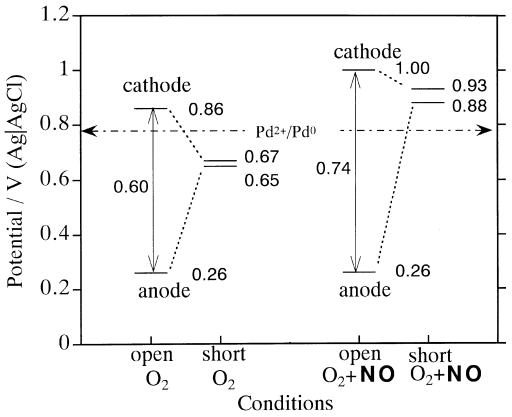


Fig. 10. Effects of oxidations on the cathode and the anode potentials under open and short-circuit conditions at 353 K. Anode: Pd-black + CF, C_2H_4 39 kPa, H_2O 13 kPa, balanced with He; cathode: Gr, O_2 51 kPa, NO 25 kPa, balanced with He.

3.8. Electrochemical potentials of the cell

Electrochemical potentials at cathode and anode for the [C_2H_4–O_2] and the [C_2H_4–(O_2 + NO)] cells were plotted in Fig. 10. The cathode potential for the [C_2H_4–(NO + O_2)] cell under open-circuit conditions was 1.00 V (vs. Ag|AgCl), which was considerably higher than the value (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–(NO + O_2)] cell must be due to the formation of NO_2 (Eq. (3)) which is a stronger oxidant than O_2 and NO. 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 over-potentials 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 over-potential of 0.07 V was considerably smaller than that for the [C_2H_4–O_2] cell (0.19 V), suggesting the easier electrochemical 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, respectively. The higher anode potential for the former explains 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(II)/Pd(0) = 0.79 V (vs. Ag|AgCl), we can expect an easy formation of Pd(II) at the anode for the [alkene–(O_2 + NO)]

cell under short-circuit condition. In contrast, the oxidation of Pd(0) to Pd(II) for the [C_2H_4–O_2] cell must be difficult under short-circuit conditions. Therefore, the presence of NO with O_2 enhanced the formation of MeCHO due to the accelerated formation of Pd(II).

3.9. Reaction scheme for the oxidation of C_3H_6

It is well known that two types of catalytic oxidation of alkenes can proceed over palladium, i.e., the oxidation via π-allyl complexes of alkenes on palladium metal surface [5,6] and the Wacker type oxidation catalyzed by Pd(II) [7,8]. It is reasonable to assume that the two types of oxidation of propene proceed also on the Pd-anode of our [C_3H_6–(O_2 or $O_2 + NO$)] cells.

Let us assume that the Wacker type oxidation proceeds on Pd(II) at the three phase boundary, Pd-black (s), H_3PO_4 aq. (l) and C_3H_6 (g);

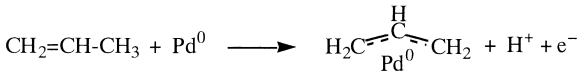
$$Pd(0) \rightarrow Pd(II) + 2e^- \quad (5)$$

$$Pd(II) + C_3H_6 \rightarrow Pd(II)\,(C_3H_6) \quad (6)$$

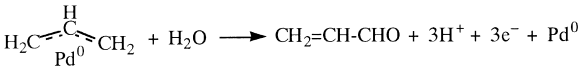
$$Pd(II)\,(C_3H_6) + H_2O \rightarrow Pd(I)\,(CH_2CH(OH)CH_3) + H^+ \quad (7)$$

$$Pd(I)\,(CH_2CH(OH)CH_3) \rightarrow CH_3COCH_3 + H^+ + Pd(0) \quad (8)$$

On the other hand, π-allyl oxidation of C_3H_6 occurs on Pd(0) in the anode.



(9)



(10)

The anode potential for the [C_2H_4–($O_2 + NO$)] cell at short-circuit conditions was higher than the standard redox potentials of $Pd^{2+}/Pd^0 = 0.79$ V (vs. Ag|AgCl) by ca. 0.24 V. The higher anode potential would enhance the oxidation of Pd(0) to Pd(II) (Eq. (5)), which accelerates the Wacker type oxidation of C_2H_4 to MeCHO. The situation was the same in the case of oxidation of C_3H_6. In other words, the higher anode potential due to the formation of NO_2 at the cathode (Eq. (3)) enhances the Wacker type oxidation of C_3H_6 to acetone according to Eqs. (5)–(8). While, the anode potential of the [C_2H_4–O_2] cell at short-circuit conditions was lower than the standard potential of Pd^{2+}/Pd^0. Pd^0 was stable under the conditions of the [C_2H_4–O_2] cell system and π-allyl oxidation of C_3H_6 was favorable. The removal of NO and NO_2 from the cathode compartment reduces the electrochemical oxidation of Pd(0) to Pd(II), which increases the steady state concentration of Pd(0) at the three phase boundary. This inevitably accelerates the π-allyl type oxidation of C_3H_6 according to Eqs. (9) and (10).

4. Conclusion

The [alkene–($O_2 + NO$)] cell system performed the selective Wacker oxidation of alkene with a high formation rate of product and a high TON. NO added in the stream of O_2 works as the mediator for electrochemical reduction of O_2–H_2O over the Gr cathode without addition of precious metals. The selectivities to the Wacker and the π-ally oxidations of propene could be controlled with and without addition of NO to O_2 due to changing oxidation state between Pd(II) and Pd(0). The enhancing effect of the NO addition would be able to apply for other fuel cell systems [9].

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