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Electrochemical cells as reactors for selective oxygenation of hydrocarbons at low temperature

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Abstract

New oxidation methods for the partial oxidation of alkenes at low temperatures (<373 K) using gaseous alkene–O_2 fuel cell systems and for hydroxylation of alkanes and aromatics applying H_2–O_2 fuel cell reactions are shown. Catalytic oxidation systems can be converted into electrochemical cells which control the reaction rate and selectivity by a variable resister or potentiostat in the outer circuit, as shown for the Wacker type and π-allyl type oxidations. The hydroxylation of benzene to phenol and of light alkanes could be realized at room temperature by applying H_2–O_2 fuel systems. The reverse H_2–O_2 cell reaction enables the epoxidation of propylene into porpylene oxides. It is also possible to combine the two reactions for the cogeneration of phenol and epoxide. Some problems to develop these processes on a commercial scale are also discussed.

Keywords: Fuel cell; Oxidation; Alkenes; Benzene; Light alkanes

1. Introduction

An important subject for the selective oxidation of hydrocarbons is to find and explore a simple method for controlling the rate of conversion and the product selectivities because, in general, it is not easy to control the rate and the selectivity by conventional methods of catalytic oxidations. Other subjects expected in the oxidation processes are the selective and one-step oxygenations of aromatics and alkanes under mild conditions. For example, a new oxidation process replacing the current Wacker process, new methods for direct hydroxylation of benzene to phenol and those for direct oxidation of light alkanes such as methane, ethane and propane into their oxygenates using oxygen at low temperatures are desired for the chemical industry of the next century. In order to realize these difficult oxygenations and to develop a technique for controlling the oxidation of hydrocarbons, a catalytic method based on new concept should be proposed. The new catalytic oxidation method to be presented in this short review is based on electrochemical cell reactions under mild conditions (<373 K) at atmospheric pressure.

Fuel cell is a device for converting the change in the free energy of a chemical reaction to electricity through electrochemical cell reactions. In the case of an H_2–O_2 fuel cell, we can get electricity through the formation of water from O_2 and H_2. When an acidic electrolyte is used, the electrochemical oxidation of H_2 to e^- and H^+ occurs at the anode Eq. (1) and the reduction of O_2 with e^- and H^+ to H_2O takes place at the cathode Eq. (2). The net reaction is the forma-

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tion of water from H_2 and O_2 Eq. (3). Conversely, when the oxidation of H_2 with O_2 Eq. (3) occurs catalytically, we can decompose the reaction into two electrochemical cell reactions, i.e., the anode Eq. (1) and the cathode Eq. (2) reactions.

$$\text{Anode}: H_2 \rightarrow 2H^+ + 2e^- \quad (1)$$

$$\text{Cathode}: 1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (2)$$

$$\text{Overall } H_2 + 1/2O_2 \rightarrow H_2O \quad (3)$$

This idea suggests that a catalytic oxidation of hydrocarbons with O_2 can be also decomposed into two reactions, i.e., the oxygenate formation at the anode and the reduction of O_2 into water at the cathode. Under these circumstances, we can design a hydrocarbon-O_2 fuel cell by using an acid electrolyte held in a membrane as a separator.

If the oxidation of hydrocarbons can be performed by using a fuel cell system described above, several advantages are expected as follows [1–9]. i) The reaction rate can be controlled easily by controlling the current with a variable resistor in the outer circuit. For example, when the circuit is opened, the oxidation of hydrocarbons is immediately stopped. If the product selectivities depend on the current or the anode potential, the optimum conditions for the selectivities can be easily adjusted. ii) One can get useful oxygenates as well as electric power output at the same time. iii) Since the hydrocarbon and O_2 are separated by a diaphragm holding an electrolyte, the danger of explosion can be diminished compared with a conventional catalytic system using a mixture of substrates and oxidant.

The selective oxidation of hydrocarbons using solid oxide fuel cell systems (SOFC) have been demonstrated and investigated in detail by the groups of Vayenas [1,2], Stoukides [3], Otsuka [4], Steele [5], Takehira [6] and other groups [2,3]. Especially, Vayenas et al. [2] proposed an interesting concept of non-faradic electrochemical modification of catalytic activity (NEMCA) for catalytic oxidations and studied the electrochemical modification of catalysts in detail. However, the cell systems using solid oxide electrolytes such as yttria, calcium-, or strontia-stabilized zirconia or perovskite type compound oxides required a higher temperature than 873 K to get a sufficient conductivities of O^{2-} or H^+. Thus, the application of SOFC at high temperatures was restricted to only a few selective oxidations of hydrocarbons. Therefore, the fuel cell systems introduced in this work are specifically restricted to those with H^+-conducting electrolytes working at low temperatures (<373 K). It should be noted that the application of an electrochemical cell reactor with H^+-conducting electrolyte in a membrane was first applied by Langer et al. at low temperatures for hydrogenation of NO into NH_2OH and the concept of cogeneration of chemicals and electricity was already proposed [10].

The hydroxylation of aromatics and saturated hydrocarbons can be performed at ambient temperature with enzymes such as cytochrome P-450 [11] or methane monooxygenase [12]. Although there still remains some ambiguity about the nature of the active oxygen species for the hydroxylation of substrates, it is generally believed that a molecular oxygen adsorbed on the iron site (Fe^{III}) is activated through the reduction by an electron donor such as NADH with the aide of electron-transfer system in cytochrome P-450 [11]. Here, the activation of dioxygen could be expressed as whole as follows,

$$O_2 + \text{Por} - Fe^{III} + 2H^+ + 2e^- \rightarrow \text{Por}^+ - Fe^{IV}{=}O + H_2O \quad (4)$$

where the active oxygen species is the high-valent iron-oxo species on porphyrin cation radical (Por^+–$Fe^{IV}{=}O$). In the light of these reductive activation of O_2 in monooxygenase systems, if we introduce a special electrocatalyst in the cathode of H_2–O_2 fuel cell, we can expect the generation of an active oxygen species which might hydroxylate aromatics and saturated hydrocarbons at the cathode during H_2–O_2 fuel cell reactions at ambient temperature.

The purpose of this paper is to demonstrate new oxidation methods for the partial oxidation of alkenes at low temperatures (<373 K) using gaseous alkene–O_2 fuel cell systems and for hydroxylation of alkanes and aromatics applying H_2–O_2 fuel cell reactions.

2. Anode oxidation of hydrocarbons in a fuel cell reactor

2.1. *Wacker oxidation of ethylene*

As described earlier, a catalytic oxidation of hydrocarbons with O_2 might be decompose into the anode (oxygenates formation) and the cathode reactions (water formation). We apply this idea to the partial oxidation of ethylene into acetaldehyde (Wacker oxidation [13]) as an example. Wacker oxidation of ethylene to acetaldehyde is one of the most important oxidation processes in the current chemical industry. It is well known that this oxidation is catalyzed through the redox couple of Pd^{2+}/Pd^0 and Cu^{2+}/Cu^+ in HCl solutions, as schematically shown in Fig. 1. This catalytic oxidation Eq. (5) must be decomposed into the anode and cathode reactions, Eq. (6) and Eq. (7), respectively.

$$\text{Overall } C_2H_4 + H_2O + 1/2O_2 \rightarrow \text{MeCHO} + H_2O \quad (5)$$

$$\text{Anode } C_2H_4 + H_2O \rightarrow \text{MeCHO} + 2H^+ + 2e^- \quad (6)$$

$$\text{Cathode } 1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (7)$$

It is reasonable to assume that the selective oxidation of ethylene at the anode Eq. (6) is catalyzed by Pd-electrode and the electrochemical reduction of O_2 Eq. (7) can be catalyzed by noble metals such as Pt-electrode. The electrolyte to be used as a proton conductor held in a separator between the anode and the cathode compartments should work and be stable at temperatures above 373 K. For this reason an aqueous solution of H_3PO_4 was used as the electrolyte. Thus, we designed a fuel cell for the partial oxidation of ethylene as demonstrated in Fig. 2 [9,14].

Details of the experimental procedure and preparation of electrodes were already reported elsewhere [14]. The Pd-anode and Pt-cathode were prepared by the hot-press method from their metal blacks mixed with graphite and PTFE powder. The wafers (0.1 mm×20 ϕ) of these electrodes were attached on a silica-wool disk (2 mm×26 ϕ) impregnated with H_3PO_4 aq. (85 wt%, 0.7 ml). A gas mixture of C_2H_4, H_2O and He (4:2:3, total pressure=101 kPa) was introduced to the anode compartment and O_2 (101 kPa) was introduced to the cathode compartment at 373 K. The open circuit voltage of this cell was ca. 0.65 V.

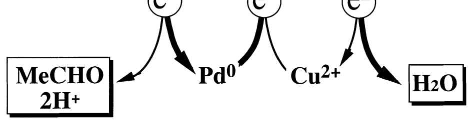

Fig. 1. Reaction scheme for the Wacker oxidation of ethylene.

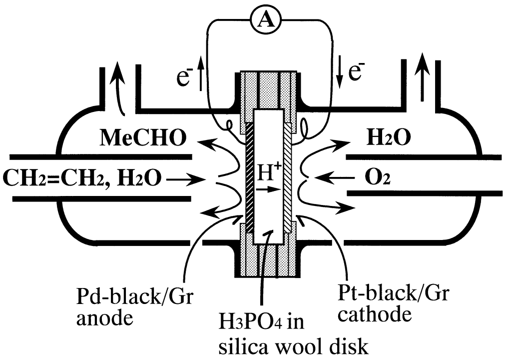

Fig. 2. Schematic diagram of the fuel cell for the partial oxidation of ethylene to acetaldehyde.

No products were observed under open-circuit conditions. When the circuit was closed (shorted), MeCHO and a trace of CO_2 were formed with a current density of 10 mA cm^{-2}. The selective oxidation of C_2H_4 to MeCHO proceeded with a selectivity >97%, current efficiency >87%, and a yield of 7% by using a Pd-anode of 3 cm^2 superficial area. The reaction did not require electricity input from the outer circuit. We could easily control the formation rate of MeCHO. For example, the oxidation of C_2H_4 was immediately stopped when the circuit was opened. If the potential between the anode and the cathode was decreased by using a potentiostat or a variable resistance, the formation rate of MeCHO was decreased accordingly. If the potential was increased by using a variable power supplier, the formation rate was accelerated exponentially.

When a mixture of acetic acid and ethylene was introduced into the anode compartment, vinylacetate (<10%) and MeCHO (>85%) were produced by using the same technique [15].

$$\text{Anode}: C_2H_4 + MeCO_2H \rightarrow C_2H_3OCOMe + 2H^+ + 2e^- \quad (8)$$

This was not selective acetoxylation but the result suggested the possibility of other oxidations of alkenes by using the same cell reactor demonstrated in Fig. 2.

The advantages of this fuel cell system for the synthesis of MeCHO compared with the current Wacker oxidation process with a mixture of C_2H_4 and O_2 in the liquid phase are followings: i) The fuel cell work used in this system is chlorine free. ii) Since the oxidation of ethylene occurs heterogeneously at the gas–solid interface, no separation processes for products and catalysts are required. iii) It is quite easy to control the reaction rate or the current by variable resistance. iv) The danger of explosion is reduced because C_2H_4 and O_2 are separated by a membrane holding aqueous solution of H_3PO_4.

2.2. *Control of selectivities to π-allyl and Wacker oxidations of alkenes*

The same reactor (Fig. 2) was applied for the oxidation of propylene at 365 K [15,16]. The open-circuit voltage under standard reaction conditions (anode: $C_3H_6/H_2O/He=2/1/2$, cathode: O_2, total pressure for both sides=101 kPa, T=365 K) was about 0.70 V. When the circuit was closed, the formation of acrolein (selectivity 77%), acrylic acid (7%), acetone (15%) and CO_2 (6%) were observed. It is reasonable to assume that acrolein and acrylic acid are the products in π-allyl type oxidation Eq. (9) and Eq. (10) and acetone is the one in Wacker oxidation Eq. (11).

$$\text{Anode}: C_3H_6 + H_2O \rightarrow CH_2CH_2CHO + 2H^+ + 2e^- \tag{9}$$

$$CH_2CH_2CHO + H_2O \rightarrow CH_2CH_2CO_2H + 2H^+ + 2e^- \tag{10}$$

$$C_3H_6 + H_2O \rightarrow CH_3COCH_3 + 2H^+ + 2e^- \tag{11}$$

$$C_3H_6 + 6H_2O \rightarrow 3CO_2 + 18H^+ + 18e^- \tag{12}$$

Fig. 3 shows the effects of applied voltage to the anode (with reference to the cathode) on the rates of formation of products and on the current. The formation rate of acrylic acid was not plotted here because of difficulty in simultaneous determination of the quantity of the acid. Zero voltage means the short-circuit conditions without any applied voltage. When a positive voltage was applied between the two electrodes, the current and the formation rate of acetone increased remarkably with increasing the voltage. The increase in the formation of CO_2 was not so appreciable. In contrast with acetone and CO_2, the formation rate of acrolein and acrylic acid were decreased markedly with increasing the voltage. The selectivity to acetone increased to ca. 90% at an applied voltage larger than +0.15 V. Thus, the π-allyl oxidation was inhibited and the Wacker oxidation was accelerated dramatically by a positive applied voltage. On the other hand, application of a negative voltage (or of an external load in the outer circuit) decreased the rates of formations of acetone and CO_2 sharply with the voltage, while that of acrolein decreased gradually. Therefore, the selectivity to acrolein increased when the negative voltage or the external load was applied across the cell. The selectivity to the sum of acrolein and acrylic acid (measured in separate experiments) was 96% at −0.2 V and the current efficiency of the sum of the products based on the stoichiometric anode oxidations of Eqs. (9)–(12) was 100% within the experimental

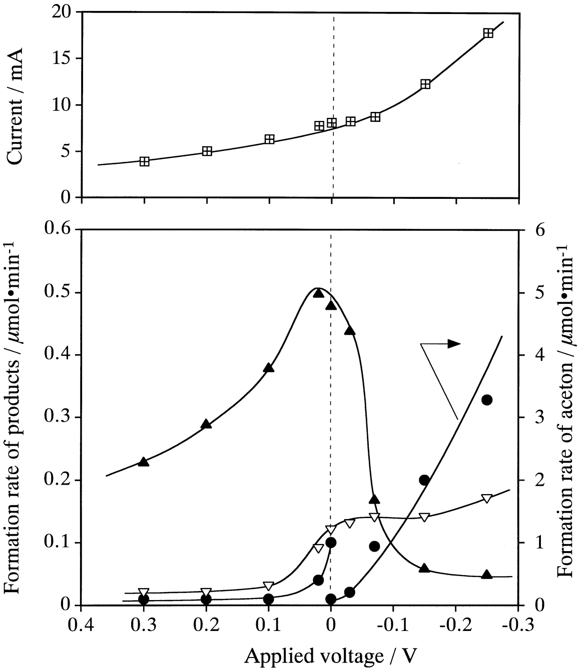

Fig. 3. Effects of the applied voltage on the rates of Wacker and π-allyl oxidations of propylene. T=365 K, the cell reactor as [O_2 (101 kPa), Pt-black-cathode | H_3PO_4 aq. (85 wt%) in silica wool disk | Pd-black-anode, C_3H_6 (40 kPa), H_2O (20 kPa)], total flow rates 20 ml min^{-1}. Anode: Pd-black (20 mg)+Gr powder (50 mg)+PTFE powder (5 mg), cathode: Pt-black (20 mg)+Gr powder (50 mg)+PTFE powder (5 mg). Acrolein (▲), acetone (●), CO_2 (▽), current (⊞).

error of ±2%. These results indicate that the Wacker oxidation is strongly inhibited by the negative voltage. Moreover, the results confirmed the electrochemical stoichiometric reactions of Eqs. (9)–(12). Under the reaction conditions at the left hand side in Fig. 3, we can get useful chemicals (acrolein and acrylic acid) as well as electric power output at the same time.

As described above, we can control the selectivity to the Wacker oxidation and the π-allyl oxidation from the outer circuit by controlling the applied voltage. This change in the product selectivities can be explained on the basis of the oxidation state of Pd. According to the Wacker type reaction mechanism suggested in the reference [13], let us assume that the oxidation proceeds on Pd^{2+} cations;

$$Pd^{2+} + CH_2{=}CH - CH_3 + H_2O \rightarrow (Pd^+ - OH)(CH_2{=}CH - CH_3) + H^+ \quad (13)$$

$$Pd^+ - OH(CH_2{=}CH - CH_3) \rightarrow Pd^+ - CH_2CH(OH)CH_3 \quad (14)$$

$$Pd^+ - CH_2CH(OH)CH_3 \rightarrow Pd^0 + CH_3COCH_3 + H^+ \quad (15)$$

$$Pd^0 \rightarrow Pd^{2+} + 2e^- \quad (16)$$

On the other hand, the π-allyl type oxidation takes place on Pd^0 [17];

$$Pd^0 + CH_2{=}CH - CH_3 \rightarrow Pd^0(CH_2 \overset{\cdot\cdot}{-} CH \overset{\cdot\cdot}{-} CH_2) + H^+ + e^- \quad (17)$$

$$Pd^0(CH_2 \overset{\cdot\cdot}{-} CH \overset{\cdot\cdot}{-} CH_2) + H_2O \rightarrow Pd^0 + CH_2 = CH - CHO + 3H^+ + 3e^- \quad (18)$$

When the positive voltage was applied between the two electrodes, the potential of the Pd-black anode must be more positive than that under the short-circuit conditions. This positive potential should increase the concentration of Pd^{2+} and decrease that of Pd^0 in the active zone of the three boundary phase, i.e., electrode (solid), H_3PO_4 aq. (liquid), and propylene (gas). Therefore, the formation rate of acetone in Wacker oxidation was accelerated with increasing the positive voltage and that of the π-allyl oxidation was dramatically decreased. When a negative voltage (or a load in the outer circuit) was applied, the anode potential should be more negative than that under the short circuit conditions. This negative potential inevitably decreases the concentration of Pd^{2+} and increases that of Pd^0. Consequently, the rate of Wacker oxidation decreased sharply and that of the π-allyl oxidation decreased gradually due to the decrease in the current.

Table 1
Effects of some additives to Pd-black anode on the formation rates of acetone and acrolein

Additives [a]	Current (mA)	Formation rate (μmol min^{-1})	
		Acetone	Acrolein
None	6.5	0.02	0.33
HCl	6.2	1.83	0.03
NaCl	10.2	0.22	0.54
H_2SO_4	6.6	0.34	0.29
H_2PdCl_4	4.1	1.29	0.00

[a] additives 25 μmol. T=365 K, the cell reactor as [O_2 (101 kPa), Pt-black-cathode/H_3PO_4 aq. (85 wt%) in silica wool disk/Pd-black-anode, C_3H_6 (40 kPa), H_2O (20 kPa), superficial area of electrodes=2 cm^{-2}. Anode: Pd-black (20 mg)/Gr (50 mg), cathode: Pt-black (20 mg)/Gr (50 mg).

If the above explanation is true, the selectivity to acetone should be increased by addition of Cl^- to the Pd-anode because the redox potential of Pd^{2+}/Pd^0 is known to be decreased in the presence of Cl^-. Table 1 shows the effects of some additives to the Pd-anode on the oxidation of propylene under short circuit conditions. The selectivity to acetone increased to almost 100% with addition of HCl. The addition of NaCl also increased the selectivity to acetone. Thus, the presence of Cl^- enhanced the formation of acetone, the Wacker oxidation product. The effect of H_2PdCl_4 was a dramatic enhancement of the selectivity of acetone to 100%. These results strongly support that the formation of acetone is catalyzed by Pd^{2+} through Wacker oxidation during the fuel cell reaction.

The method of selectivity control described above was also applicable to the oxidation of butenes. The results for the oxidation of 1-butene performed by using the same fuel cell reactor as Fig. 2 are demonstrated in Fig. 4. The formation rate of the product in Wacker oxidation, 2-butanone, was enhanced but those in π-allyl oxidation, methyl–vinyl–ketone and crotonaldehyde, were reduced with positive applied voltage. The Wacker oxidation product was not produced at all when negative voltage was applied (left side in Fig. 4). These results can be explained by the same mechanism described for the oxidation of propylene.

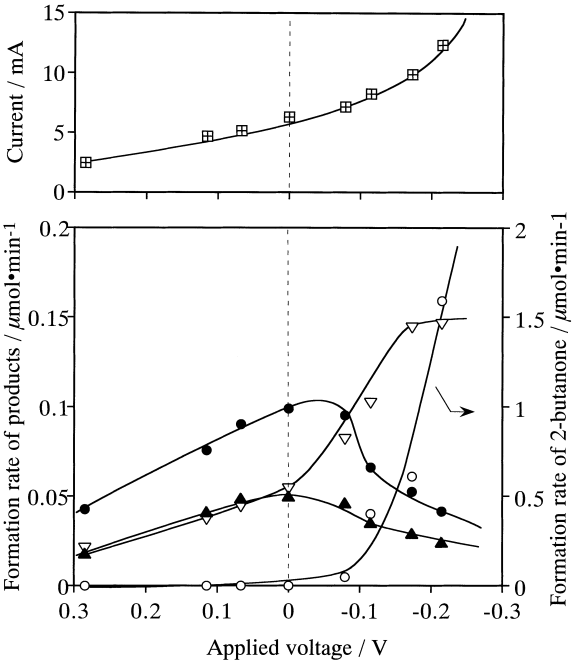

Fig. 4. Effects of the applied voltage on the rates of Wacker and π-allyl oxidations of 1-butene. T=366 K, the cell reactor as [O_2 (101 kPa), Pt-black-cathode | H_3PO_4 aq. (85 wt%) in silica wool disk | Pd-black-anode, 1-C_4H_8 (40 kPa), H_2O (20 kPa)]. Methyl–vinyl–ketone (●), crotonaldehyde (▲), 2-butanone (○), CO_2 (▽), current (⊞).

We believe that the technique described above can generally be applied to various Wacker type and π-allyl type oxidations [18].

3. Cathode oxidation of hydrocarbons applying H_2–O_2 fuel cells

As described above, the oxidations of alkenes could be performed at the anode applying electrochemical cell reactions under mild conditions. However, although a great number of different electrocatalysts had been tested, the hydroxylation of aromatics and oxidation of alkanes did not take place when these hydrocarbons were passed through the anode compartment under short-circuit and applied-voltage conditions. We found that these difficult oxidations occurred when the hydrocarbons had been passed through the cathode compartment during H_2–O_2 cell reactions. In this section, oxidations of alkanes and aromatics at the cathode of H_2–O_2 fuel cell are described.

3.1. *Benzene to phenol by continuous generation of Fenton reagent*

It is well known that the Fenton's reagent (Fe^{2+}+H_2O_2+H^+) can hydroxylate aromatics at mild conditions [19]. In our early studies, we confirmed the accumulation of H_2O_2 Eq. (19) in aqueous solution of HCl during H_2–O_2 fuel cell reaction at room temperature by using an Au-cathode attached to a Nafion-H membrane as a protonic electrolyte [20]. If Fe(III)-salts is added to an aqueous solution of HCl in the cathode compartment, both of the following reactions at the cathode can be expected under short-circuit conditions.

$$\text{Cathode}: O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (19)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (20)$$

The Fenton reagent prepared through these reactions generates hydroxyl radical in Eq. (21)[19]. Under these circumstances, we can expect the hydroxylation of benzene to phenol by Fenton chemistry Eq. (22).

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow HO^{\bullet} + H_2O + Fe^{3+} \qquad (21)$$

$$PhH + HO^{\bullet} + Fe^{3+} \rightarrow PhOH + Fe^{2+} + H^+ \qquad (22)$$

In fact, when Fe^{3+} and benzene had been coadded into the aqueous solution of HCl in the cathode compartment of H_2–O_2 fuel cell, the continuous formation of phenol was observed. However, oxidation of cyclohexane did not occur in this system [21], because the concentration of cyclohexane dissolved in aqueous solution of HCl was very low. Moreover, the reactivity of $HO^{\cdot}$ in aqueous solution must be decreased compared with that in hydrophobic conditions [22]. Therefore, if hydrophobic conditions and a suitable electrocatalyst are selected, a powerful active oxygen species may be directly produced on the cathode. This active oxygen may realized the oxygenation of alkanes at the cathode.

3.2. *Oxidation of cyclohexane and benzene over $SmCl_3$/graphite cathode*

On the basis of the hypothesis described above, the H_2–O_2 fuel cell system for the oxidation of alkanes

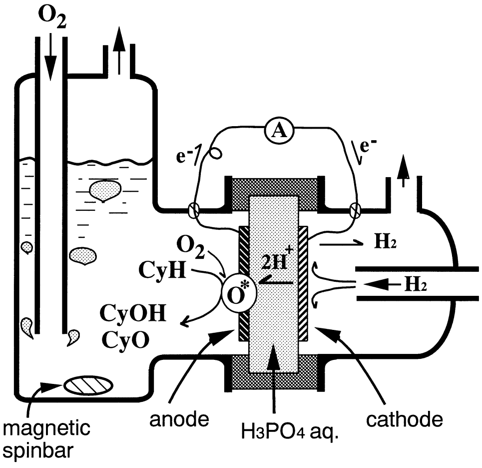

Fig. 5. Diagram of the H_2–O_2 fuel cell for the partial oxidations of cyclohexane and benzene at room temperature.

was designed as indicated in Fig. 5. The system was composed of [O_2(g), alkane(l), cathode catalyst | H_3PO_4 aq. (1 M) in silica wool disk | Pt-black/graphite, H_2(g)]. The H_3PO_4 works as an electrolyte of H^+ conductor in the presence of hydrophobic substrates. This oxidation system was operated by batch type procedure. Many electrocatalysts impregnated in graphite were tested for oxygenation of cyclohexane as shown in Fig. 6 [23–25]. No formation of products was observed over all the cathodes tested in Fig. 6 under open circuit conditions. The graphite with rare earth chlorides, especially with $NdCl_3$ and $SmCl_3$, were active for oxygenations of cyclohexane to cyclohexanol and cyclohexanone [23,24]. Constant current (ca. 5 mA) and constant formation rate of the products continued over $SmCl_3$/graphite cathode for 20 h. The current efficiency estimated as 2 e^- reaction for formation of the products was about 5%. The yield of the products was low (0.012%) because a volume of the cathode compartment was large (40 ml, cyclohexane 0.37 mol) to compare with a superficial area of the cathode (2.5 cm^2). The $SmCl_3$/graphite cathodes was also active for hydroxylation of benzene and toluene. It is very rare case that rare earth element works as a catalyst for oxygenation of alkanes and aromatics under mild conditions.

Fig. 7 shows the effects of cathode potential on the partial oxidation of cyclohexane over $SmCl_3$/graphite and $FeCl_3$/graphite. The reactivity of $FeCl_3$/graphite for the oxidation of cyclohexane was lower than that of $SmCl_3$/graphite [24,25]. However, it is interesting to compare the reactivities of both cathodes because Fe cation is known to be the most typical active center of the monooxygenase or monooxygenase mimic systems [11,12,19] for the oxidation of hydrocarbons. The potentials for both cathodes were -0.24 V (vs. Ag|AgCl) under short-circuit conditions. The maxima formation rates of the sum of products were obtained for both cathodes at short-circuit conditions. In the case of $SmCl_3$/graphite, the sum of the formation rates of oxygenates decreased with increasing the cathode potentials. The selectivities of cyclohexanol and cyclohexanone were roughly constant at all the potentials examined. In the case of $FeCl_3$/graphite, the sum of the formation rates of oxygenates also decreased with increasing the potential, but the selectivity to cyclohexanol increased from 30% under short circuit condition (-0.24 V vs. Ag | AgCl) to 100% ($+0.20$ V) with increasing the potential. This observation suggests that the redox of Fe^{3+}/Fe^{2+} may affect the reaction path for the formation of cyclohexanol and cyclohexanone [24]. However, the redox of Sm^{3+}/Sm^{2+} cannot be expected under the reaction conditions in Fig. 7. The reaction mechanisms or the active oxygen species for the two systems must be quite different.

In order to get information about the nature of the active oxygen species, the reactivities of different hydrocarbons (*n*-hexane, adamantane, benzene, toluene, dimethylsulfate) and their product selectivities were compared between the two electrodes. Furthermore, the experimental results in the presence of radical trap reagent (CCl_4) and kinetic isotope effects for the oxidation of cyclohexane were compared between the two cathodes. It was concluded that the active oxygen species on $FeCl_3$/graphite was $HO^\bullet$ but that on $SmCl_3$/graphite could not be $HO^\bullet$ [24,25]. Although the real form of the active oxygen species on the latter cathode is not known at the moment, the results of cyclic voltammetry studies suggested that the active oxygen species could be produced from the adduct of Sm^{3+} and $HO_2^\bullet$, generating an electrophilic oxygen species of $Sm^{(3-\delta)+}(HO_2^{\delta+})$ [24]. The model of the active center of this $SmCl_3$/graphite cathode is shown in Fig. 8. The Sm^{3+} coordinated to carboxylic groups (or other functional groups) on graphite surface may work as the active center for the reductive

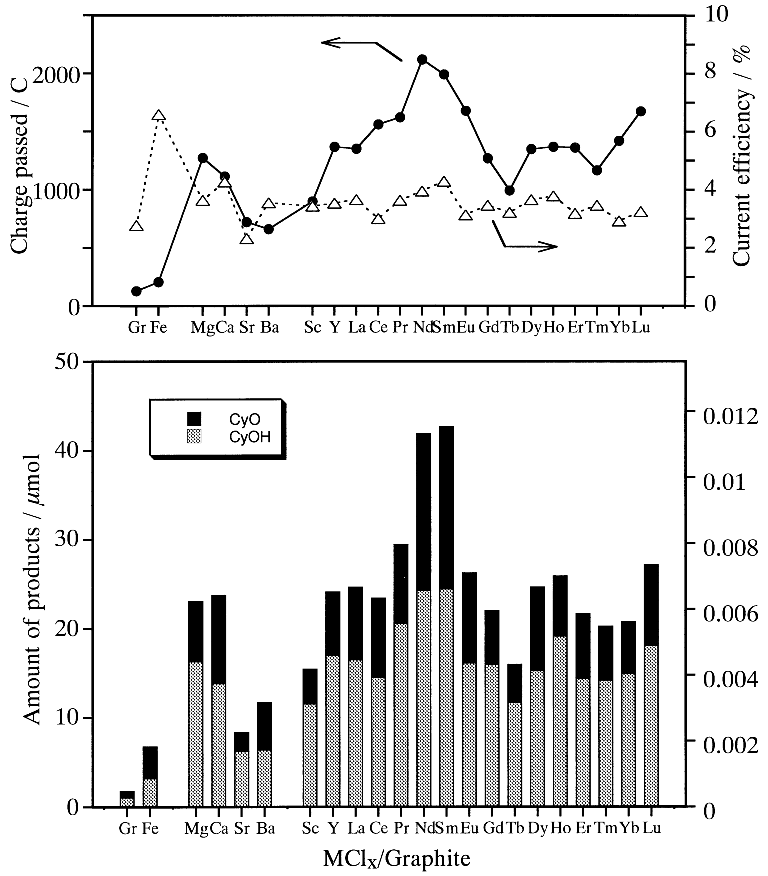

Fig. 6. Partial oxidation of cyclohexane to cyclohexanone and cyclohexanol over the cathodes containing various metal chlorides during H_2–O_2 fuel cell reactions. T=298 K, reaction time 20 h, superficial area of the cathode=2.5 cm^2, the fuel cell as [O_2 (101 kPa), cyclohexane (40 ml), cathode | H_3PO_4 aq. (1 mol l^{-1}) in silica wool disk | anode, H_2 (98 kPa), H_2O (3.3 kPa)]. Cathode: metal chloride (0.5 mol%)/graphite (70 mg), anode: Pt-black (20 mg)/graphite (50 mg). (▨) Cyclohexanol, (■) cyclohexanone, (●) charge passed, (△) current efficiency.

activation of O_2 by e^- and H^+ and for the partial oxidation of various hydrocarbons.

3.3. Hydroxylation of benzene over the cathode based on carbon whisker

The active site model in Fig. 8 suggests that the functional groups on graphite might play an important role for oxidations of benzene and cyclohexane. Therefore, the cathodes based on other carbon materials, such as carbon whisker (CW), carbon black, and active carbon were tested for the hydroxylation of benzene. The carbon whisker pretreated by a hot aqueous solution of HNO_3 was the most active carbon cathode for the hydroxylation of benzene into phenol and hydroquinone among the carbon materials tested [26]. The carbon whisker without oxidation pretreatment was not active for the reaction. This result suggests that some functional groups, such as carboxyl-groups and quinone–hydroquinone-groups, formed on the surface of carbon whisker by the oxidation treatment with HNO_3 would work as the sites for reductive activation of O_2 even in the absence of metal cation additives in the cathode.

The addition of Pd-black to the carbon whisker cathode enhanced the current remarkably. On the other hand, the addition of Fe_2O_3 improved the oxidation efficiency for the formation of phenol and hydroqui-

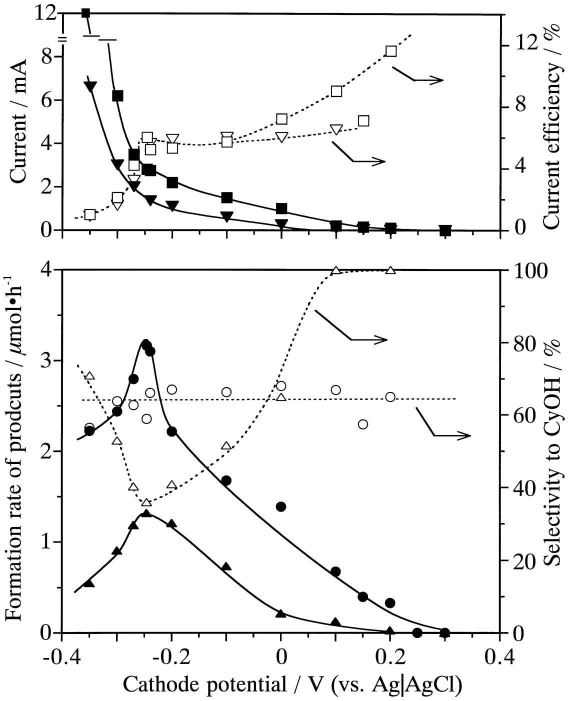

Fig. 7. Effects of the cathode potentials on the partial oxidation of cyclohexane over $SmCl_3$/graphite and $FeCl_3$/graphite cathodes during H_2–O_2 fuel cell reactions. Total formation rate of CyOH and CyO at $SmCl_3$/graphite) (●), and at $FeCl_3$/graphite (▲), selectivity to CyOH for $SmCl_3$/graphite (○), and for $FeCl_3$/graphite (△), current for $SmCl_3$/graphite (■), and for $FeCl_3$/graphite (▼), current efficiency for $SmCl_3$/graphite (□), and for $FeCl_3$/graphite (▽).

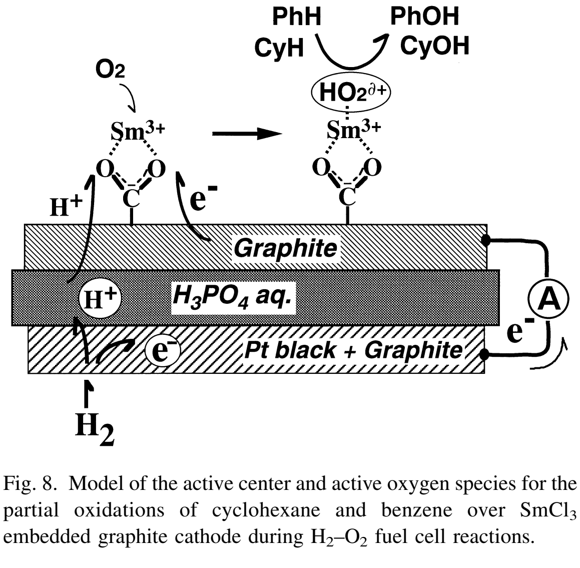

Fig. 8. Model of the active center and active oxygen species for the partial oxidations of cyclohexane and benzene over $SmCl_3$ embedded graphite cathode during H_2–O_2 fuel cell reactions.

none. Coaddition of Pd-black and Fe_2O_3 showed the synergistic effect on the hydroxylation of benzene to phenol and hydroquinone [26]. The active oxygen species over the carbon whisker cathodes with and without additives of Pd and Fe_2O_3 was assumed to be $HO^{\bullet}$. The hydroxylation of benzene must proceed through the Fenton Chemistry. The synergism of Pd black and Fe_2O_3 can be explained in terms of the cooperative actions of the additives as indicated in Fig. 9. It is well known that Pd^0 catalyzes the formation of H_2O_2 from H_2 and O_2. In this system, Pd-black would be accelerated by the electrochemical reduction of O_2 (current) and formation of H_2O_2 (step 1). The redox of Fe^{3+}/Fe^{2+} on Fe_2O_3 enhances the generation of $HO^{\bullet}$ from H_2O_2 (step 2) that attacks benzene (step 3) producing PhOH and HQ through the Fenton Chemistry. Therefore, the synergistic effect on the hydroxylation of benzene was due to the increases in the formation rates of H_2O_2 by Pd-black and $HO^{\bullet}$ by Fe_2O_3.

3.4. *Cogeneration of phenol and electricity*

The H_2–O_2 fuel cell system described above can cogenerate electricity and oxygenates if we put a load in the outer circuit. The advantages of this cogeneration have already been discussed by many researchers [1,4,7,10]. However, for every chemical cogeneration systems reported so far, including our systems described above, when a load was put in the outer circuit to obtain electric power output, the production of chemicals was always reduced because of the decrease in the current compared to the short-circuit conditions.

In contrast with these circumstances, we found that the carbon whisker (CW) cathode added with copper compounds ($CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$ and CuO) showed quite specific results [27]. A typical example observed for the $CuSO_4$-added cathode is demonstrated in Fig. 10. This figure indicates the amount of products (phenol and hydroquinone), the charge passed in 3 h (batch procedure) and the electric power output as functions of the cell voltage (cathode potential vs. anode one) or the applied voltage across the cell (anode potential vs. cathode one). The zero in the abscissa means the short-circuit conditions. As can be seen in this figure, the charge passed or the current increased with increasing the cell voltage giving the

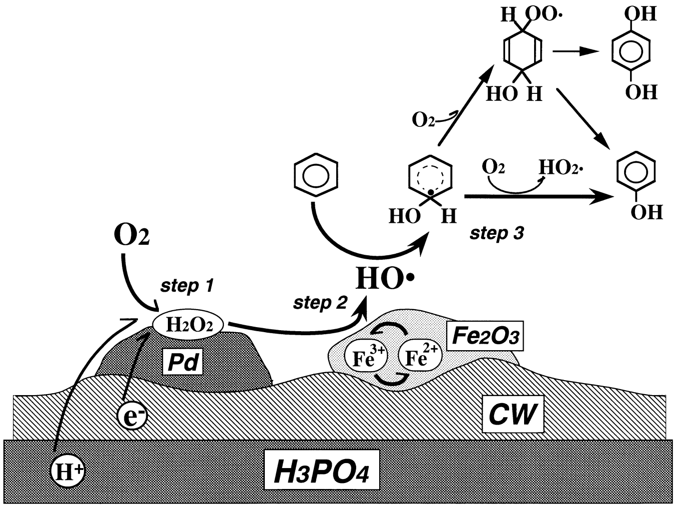

Fig. 9. Reaction scheme for the hydroxylation of benzene to phenol and hydroquinone at Pd-black and Fe_2O_3/carbon whisker cathode during H_2–O_2 fuel cell reactions.

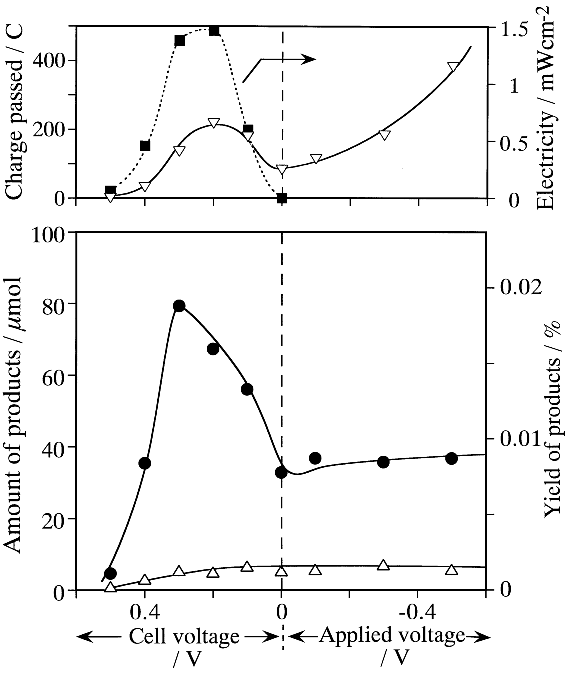

Fig. 10. Effects of cell voltages and applied voltages on the formation rates of phenol and hydroquinone and electricity at $CuSO_4$/carbon whisker cathode during H_2–O_2 fuel cell reactions. T=300 K, reaction time=3 h, superficial area of the cathode= 3.1 cm^2. The fuel cell as [O_2 (101 kPa), benzene (40 ml), cathode | H_3PO_4 aq. (1 mol l^{-1}) in silica wool disk | anode, H_2 (98 kPa), H_2O (3.3 kPa)]. Cathode: $CuSO_4$ (0.5 mol%)/CW (70 mg), anode: Pt-black (20 mg)/Gr (50 mg). Phenol (●), hydroquinone (△), charge passed (▽), electricity (■).

maximum at a cell voltage of 0.20 V. The electric power output shows the maximum at a cell voltage of 0.2 ~ 0.3 V. The amount of phenol formed shows the maximum at 0.3 V. For the right hand side in Fig. 10, the applied voltage increases the charge passed due to the acceleration in the rate of reduction of oxygen into water at the cathode. The increase in the current with a rise in the applied voltage does not enhance the rate of formations of phenol and hydroquinone. Although the formation rate of active oxygen ($HO^{\bullet}$) or that of reduced oxygen species ($HO_2^{\bullet}$, H_2O_2, etc.) may also be accelerated, their further reduction into water must as well be enhanced with a rise in the applied voltage.

The effect of content of $CuSO_4$ in the cathode on the formation of phenol and hydroquinone was examined at a cell voltage of 0.3 V. The rates of phenol and hydroquinone formations were enhanced markedly by increasing the content of $CuSO_4$ at a low content region <0.03 mol% in the carbon whisker. Turnover number per copper cation for the formation of the oxygenates was about seven at a $CuSO_4$ content of 0.01 mol%. It is clear that copper cation works as an electrocatalyst for the formation of oxygenates.

The effects of cell voltage and applied voltage indicated in Fig. 10 were very similar for the cathodes with other copper compounds. For all the cathodes with copper compounds examined in this work gave the maxima in the rate of phenol formation as well as in the electricity output at a cell voltage of ca. 0.30 V.

Table 2
Synthesis of phenol and hydroquinone from benzene over carbon whisker cathode added with Cu compounds

Cathodes [a] power	C.P. (10^2C)	Products [b] (μmol)			Electric output (Wh)
		PhOH	HQ	Total	
Under a terminal voltage +0.3 V					
CuO/CW	1.60	70.1	5.4	76.4	15.4
$CuSO_4$/CW	1.42	78.6	6.0	85.1	13.7
$Cu(NO_3)_2$/CW	1.34	70.4	5.3	76.2	12.9
$Cu(OAc)_2$/CW	1.32	69.5	5.0	75.1	12.7
$CuCl_2$/CW	1.73	37.1	4.2	41.8	16.7
CuCl/CW	1.61	63.9	6.4	69.9	15.5
Under short circuit condition					
CuO/CW	1.00	38.0	5.9	44.1	0
$CuSO_4$/CW	0.87	32.8	5.8	38.6	0
$Cu(NO_3)_2$/CW	0.99	33.9	5.0	39.2	0
$Cu(OAc)_2$/CW	0.78	29.7	4.3	34.2	0
$CuCl_2$/CW	0.72	12.6	2.4	15.2	0
CuCl/CW	0.78	22.4	4.5	27.4	0

[a] CW: carbon whisker.

[b] PhOH: phenol, HQ: hydroquinone. T=300 K, reaction time=3 h, superficial area of the cathode=3.1 cm ^{2}. The fuel cell as [O_2 (101 kPa), benzene (40 ml), cathode | H_3PO_4 aq. (1 mol l^{-1}) in silica wool disk | anode, H_2 (98 kPa), H_2O (3.3 kPa)]. Cathode: copper salts (0.5 mol%)/CW (70 mg), anode: Pt-black (20 mg)/Gr (50 mg).

The results under short-circuit conditions and at the cell voltage of 0.30 V are shown in Table 2 for the cathodes with different copper compounds. It is apparent that the formations of phenol and hydroquinone were accelerated when the electric power output was cogenerated.

The cathode potential for the $CuSO_4$/CW under short circuit conditions during the progress of the reaction in Fig. 10 was ca. −0.21 V vs. Ag|AgCl. The potential at a cell voltage of 0.30 V was 0.06 V vs. Ag|AgCl. Under these cathode potentials, we can expect the following reduction of copper cations Eqs. (23)–(25) as well as the formation of $HO^\bullet$ radicals through Eq. (26) and Eq. (27)[28].

$$Cu^{2+} + e^- \rightarrow Cu^+ \ (E^0 = -0.044\,V \text{ vs. } Ag|AgCl) \tag{23}$$

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \ (E^0 = 0.140\ V) \tag{24}$$

$$Cu^+ + e^- \rightarrow Cu^0 \ (E^0 = 0.324\ V) \tag{25}$$

$$O_2 + 2Cu^+ + 2H^+ \rightarrow H_2O_2 + 2Cu^{2+} \tag{26}$$

$$H_2O_2 + H^+ + Cu^+ \rightarrow OH^\bullet + H_2O + Cu^{2+} \tag{27}$$

$$C_6H_6 + HO^\bullet + Cu^{2+} \rightarrow C_6H_5OH + Cu^+ + H^+ \tag{28}$$

The $HO^\bullet$ attacks benzene, forming phenol in Eq. (28). The increase in current by putting a load in the outer circuit must decelerate the reduction of Cu^+ to Cu^0, which enhances the formation of $HO^\bullet$ in Eq. (26) and Eq. (27), consequently accelerates the current as well as the oxidation of benzene into phenol. Therefore, a key factor for the hydroxylation of benzene and the reduction of O_2 (current) is redox of Cu^{2+}/Cu^+ over CW.

3.5. *Oxidation of light alkanes by using H_2–O_2 fuel cell*

Partial oxidation of light alkanes such as CH_4, C_2H_6, and C_3H_8 into their oxygenates has been one of the most desired reactions from the standpoint of utilization of natural gas as a chemical feed stock. However, catalytic oxidation of these light alkanes under mild conditions has not been successful because high activation energy is required for breaking their

C–H bonds. As described in this paper, the selective oxidation of benzene and hexanes were possible at room temperature by reductively activated oxygen at the cathode during H_2–O_2 fuel cell reactions. However, the oxidation of CH_4, C_2H_6, and C_3H_8 were not successful by applying the same cathodes used for the oxygenations of benzene and hexanes. After the tests of the carbon whisker cathodes without and with many kinds of metal oxides, metal-salts and metal blacks, we concluded that the carbon whisker without any additives was the best cathode for the partial oxidation of C_3H_8 into Me_2CO in the gas phase at room temperature [29]. The cathodes prepared from other carbon materials such as graphite, active carbon cloth, active carbon fiber, and carbon black were less active than the carbon whisker.

Fig. 11 compared the rates of oxidation of CH_4, C_2H_6, and C_3H_8 on the carbon whisker cathode at 301 K. A mixture of light alkane and O_2 was passed through the cathode compartment. No products were observed under open circuit conditions. It should be noted that although the product is CO_2, CH_4 can be oxidized at 301 K. In C_2H_6 oxidation, CO_2 was also the main product but a little MeCHO was produced. In contrast with the results of CH_4 and C_2H_6, the selectivity to useful oxygenate (Me_2CO) in the case of C_3H_8 exceeded 65% on the basis of C_3H_8 reacted. The rate of alkane oxidation increased as $CH_4 < C_2H_6 < C_3H_8$ as expected. We speculate that the activation of light alkanes would take place by the free $HO^{\cdot}$ evolved into the gas phase at the vicinity of the electrode/electrolyte interface.

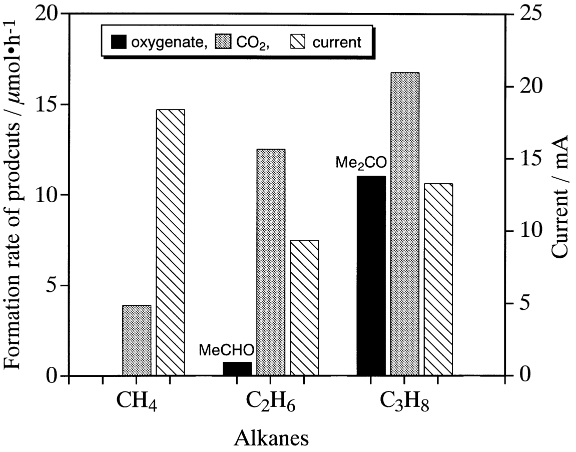

Fig. 11. Oxidation of light alkanes in the gas phase at carbon whisker cathode during H_2–O_2 fuel cell reactions. T=298 K, supecific area of the electrodes 2 cm^{-2}, the fuel cell as [O_2 (50 kPa), alkanes (50 kPa), cathode | H_3PO_4 aq. (1 mol l^{-1}) in silica wool disk | anode, H_2 (50 kPa), H_2O(4 kPa)], total flow rates 20 ml min^{-1}. Cathode:CW (70 mg)+PTFE (5 mg), anode: Pt-balck (20 mg)+Gr(50 mg)+PTFE (5 mg). (■): MeCHO from C_2H_6 or Me_2CO from C_3H_8, (▒): CO_2, (▨): current.

The specific surface area of the CW used as the cathode was 22 m^2g^{-1} and this carbon material had almost no micropores of less than 10 nm. The high outer surface area of the CW together with the absence of metal cation additives must be suitable for both the generation of $HO^{\bullet}$ and its evolution into the gas phase under steady state conditions. The presence of additives would accelerate not only the formation of $HO^{\bullet}$ but also its further reduction into H_2O on the surface. Under these circumstances, the evolution of $HO^{\bullet}$ may be decreased. Further studies are needed to clarify the active oxygen species and the reaction mechanism for the oxidation of the light alkanes in the gas phase.

3.6. Dual oxidations at the cathode and the anode

In contrast to the reductive activation of O_2 during H_2–O_2 fuel cell reactions described so far, the reverse reaction, i.e., the electrolysis of acidic water might oxidatively activate O^{2-} of water at the anode Eq. (29) as follows.

$$H_2O \rightarrow O^{**} + 2H^+ + 2e^- \tag{29}$$

$$RH + O^{**} \rightarrow ROH \tag{30}$$

The so-formed active oxygen O^{**} can be expected to also oxygenate hydrocarbons Eq. (30) under mild conditions. On the basis of this concept, we have tested many kind of anode electrocatalysts including noble metal blacks for epoxidation of 1-hexene. Among the noble metal blacks tested, the most active and selective anode electrocatalyst was Pt-black [30,31]. XPS studies on various Pt black samples suggested that a PtO_2 phase was associated with the active oxygen for the epoxidation [31]. The Pt black sample active for the epoxidation of 1-hexene catalyzed also the epoxidation of propylene to propylene oxide at room temperature and atmospheric pressure [31].

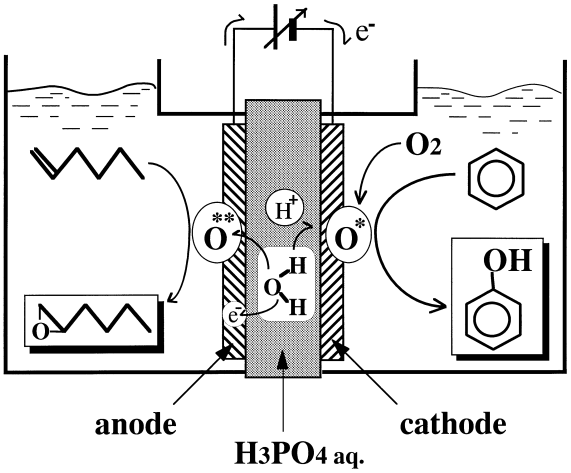

Fig. 12. Diagram of the reactor for simultaneously epoxidation of 1-hexene at anode and the hydroxylation of benzene at cathode.

It should be noted that the reaction at the cathode during the epoxidation of alkenes described above is the evolution of hydrogen.

$$\text{(Cathode)}\,2H^+ + 2e^- \rightarrow H_2 \qquad (31)$$

If benzene and O_2 are introduced into the cathode compartment, we can expect the hydroxylation of benzene at the cathode during the epoxidation of alkenes at the anode at the same time. We have demonstrated this simultaneous oxidations by introducing 1-hexene and benzene in the anode and the cathode compartments, respectively [30]. The reactor used and the principle of the method are shown schematically in Fig. 12. The anode was Pt-black (a mixture of PtO_2 and Pt^0) and the cathode was a mixture of Pd black, Fe_2O_3 and carbon whisker. The electrocatalytic functions of the cathode have already been described earlier. Fig. 13 shows the results of the dual oxidations of 1-hexene and benzene at the anode and the cathode, respectively. The amount of products in 2 h by using the electrodes of 3 cm^2 (superficial area) are plotted as functions of the applied voltage. The results in Fig. 13 show that the optimum applied voltage is 1.5∼1.7 V for the syntheses of both 1,2-epoxyhexane and phenol under the experimental conditions in this work.

On the basis of the same idea, we expect that various anode and cathode oxidations described earlier can be combined and be performed under applied voltage at mild reaction conditions.

4. Possible extensions

In principle, the electrochemical cell reactor described for the oxidation of alkenes using alkenes–O_2 fuel cell systems can be applied to many oxygenation reactions of hydrocarbons if we chose appropriate anode electrocatalysts and electrolytes.

The concept described for the oxidations in this work could be extended to the hydrogenations of alkynes, alkenes and NO_x by using [substrate | H_3PO_4 | H_2] cell reactions. We demonstrated already the selective hydrogenation of acetylene in abundant ethylene [32], hydroformylation of ethylene to propionic aldehyde [33], and selective hydrogenation of NO to NH_2OH [34] by using the electrochemical cell reactions.

The H_2–O_2 cell systems generated very active oxygen species (ex. $HO^\bullet$, $Sm^{(3-\delta)+}(HO_2^{\delta+})$) which enabled the hydroxylation of aromatics and the oxidation of methane, ethane and propane at room temperature. The system may be also applied to other difficult oxidations such as epoxidation of alkenes, oxidative degradation of toxic compounds, and to the treatment of waste waters containing organic compounds and to cleaning the air contaminated with CO or bad odor.

5. Conclusion and perspectives

Catalytic oxidation systems can be converted into electrochemical cells which control the reaction rate and selectivity easily by a variable resister or potentiostat in the outer circuit. We demonstrated this idea in Wacker type and π-allyl type oxidations.

The hydroxylation of benzene to phenol and of oxidation of light alkanes could be realized at room temperature by applying H_2–O_2 fuel systems. The reverse of H_2–O_2 cell reaction, i.e., H_2O electrolysis enabled the epoxidation of propylene into propylene oxide at room temperature. The combination of the

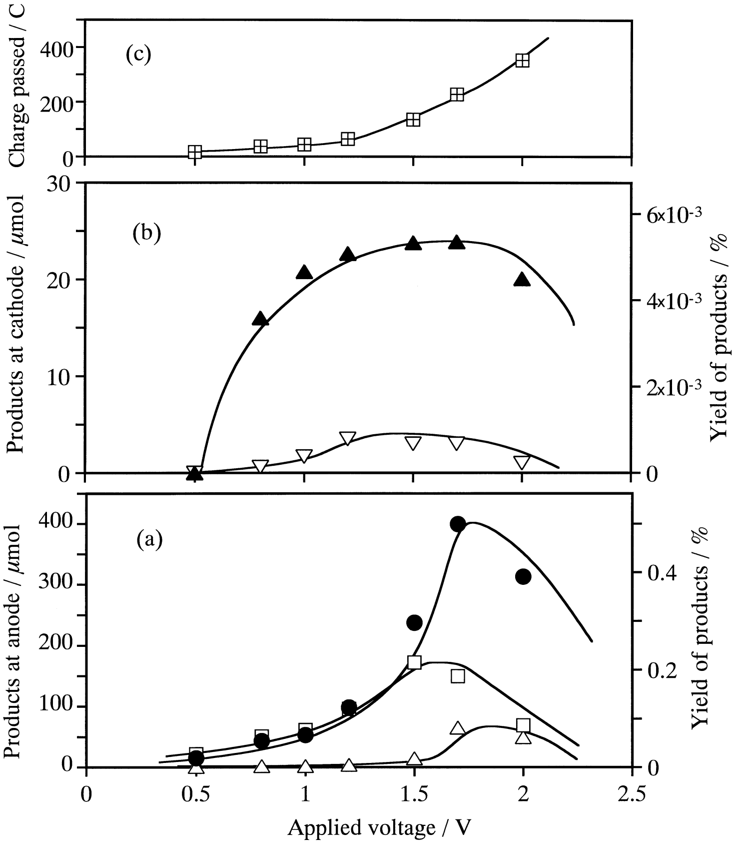

Fig. 13. Effects of applied voltages on simultaneous epoxidation of 1-hexene at the anode (a) and the hydroxylation of benzene (b) at the cathode. $T=298$ K, the cell as [1-hexene (10 ml), CH_2Cl_2 (30 ml) anode | H_3PO_4 aq. (1 mol l^{-1}) in silica wool disk | cathode, O_2 (101 kPa), benzene (40 ml)]. Anode:Pt-black (70 mg)+PTFE(1 mg), cathode:Pd-black (20 mg)+Fe_2O_3 (5 mg)+CW (50 mg). At anode; 1,2-epoxyhexane (●), 2-hexanone (□), others (△). At cathode; phenol (▲), hydroquinone (▽). Current (⊞).

two systems made it possible to synthesize phenol and the epoxide at the cathode and the anode, respectively, at the same time.

However, the problem to be solved for all the systems described in this report is to improve the current or the rate of oxygenations. These should be increased one to two orders of magnitude for commercial application. Therefore, better electrocatalysts and appropriate electrolytes are definitely to be developed. On the other hand, the method should be applied for the synthesis of fine chemicals to compensate the low reaction rate and current efficiency. Cogeneration of electric power output and valuable chemicals could be an alternative application of electrochemical cell reactors.

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