Oxidation of alkanes with H_2O on $Ir(acac)_3$ supported on a carbon fiber-anode

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$Ir(acac)_3$ supported on a carbon fiber-anode catalyzed the oxidations of alkanes (cyclohexane, *n*-hexane, adamantane) by generating strong electrophilic oxygen species from H_2O at 1.3 V (Ag|AgCl) with high current efficiency, for example, 45% for cyclohexanone formation.

Direct oxidation of alkanes is one of the key oxidation processes expected in the 21st century. On the other hand, the electroorganic synthesis of chemicals is also expected to be a key technology in green chemistry because the electrolysis can be operated under mild conditions. However, it is not so easy to realize direct oxidation of alkanes by electrolysis because their redox potentials [1.85 V (*vs.* NHE) for cyclohexane to 2.25 V for methane in aqueous solutions at pH = 0[1]] are higher than those of solvents and electrolytes. Some work on the anodic oxidation of alkanes in aqueous media > 358 K has been reported but current densities were < 0.1 mA cm^{-2} and the product was CO_2.[2] In non-aqueous media, oxidation of adamantane to adamantane derivatives was performed at > 2.0 V and 303 K but the current density was < 4 mA cm^{-2}.[3] Most of all successful electrochemical systems for the oxidation of alkanes applied an electrochemical reductive activation of O_2 at the cathode, indirect electrochemical oxidation, though the current efficiency of the produced oxygenates were low at $< 10\%$.[4]

We have recently reported an indirect anodic epoxidation of propene to propene oxide on PtO_2/Pt-anode and oxidation of benzene to benzoquinone on a carbon fiber-anode at 293 K.[5,6] A membrane electrolysis cell was assembled as [reactant | porous anode | silica wool membrane impregnated with H_3PO_4 aq. | porous Pt-graphite-cathode | H_2O(g), He]. An advantage of this system compared with conventional ones is that the separation procedure of the products from electrolyte is quite easy. We proposed that a nascent oxygen species generated on the anode from H_2O would oxidize propene and benzene, *i.e.* indirect electrochemical oxidation at the anode.[5,6] However, the two anodes mentioned above were not active at all for the oxidation of alkanes. Therefore, the purpose of this work was to design a new active anode for the oxidation of alkanes with H_2O by using the membrane electrolysis cell.

Fig. 1 shows the catalytic activities of various anodes for the oxidation of cyclohexane during electrolysis of H_2O in H_3PO_4 (aq) (0.7 mol l^{-1}) at 298 K. The anodes were prepared by the hot-press method from various electrocatalyst powders [metal blacks and metal compounds (0.5 mol%) supported on carbon fibers (CF)] and poly(tetrafluoroethylene) (PTFE) powder[4] with a geometric surface of *ca.* 2 cm^2. The membrane electrolysis cell attached to various anodes was assembled and the anode compartment was filled with pure cyclohexane (40 ml). The electrocatalytic oxidation of cyclohexane with H_2O was carried out by applying the anode potential; 1.5 V (Ag | AgCl) at Pd-black, Pt-black, Ir-powder, Ir-black anodes and 1.8 V at FeCl(TPP)/CF, Co_2O_3/CF, MnO_2/CF, Ir/CF, IrO_2, $IrCl_3$/CF, $IrCl_4$/CF anodes. Products were cyclohexanone (CyO), cyclohexanol (CyOH), adipic acid (AA), CO_2 and O_2. The results in Fig. 1 indicate that Ir compounds, especially $Ir(acac)_3$ supported on carbon fiber (CF), are active for the CyO formation, though current efficiencies (CE) estimated from eqn. (1) were not good. Therefore, attention was paid to the electrocatalytic function of the most active $Ir(acac)_3$/CF anode.

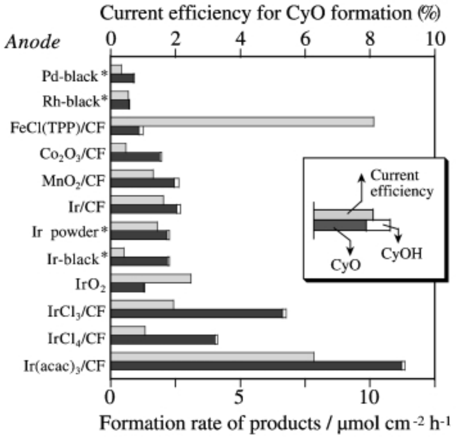

Fig. 1 Electrocatalytic oxidation of cyclohexane with H_2O over various anodes at 1.8 V (Ag | AgCl) or 1.5 V(*) at 298 K.

$$\text{cy-}C_6H_{12} + H_2O \rightarrow \text{cy-}C_6H_{10}O + 4\ H^+ + 4\ e^- \qquad (1)$$

To increase electrocatalytic activity for the oxidation of cyclohexane, (i) preparation conditions of the Ir-anode [types of carbon material, amounts of $Ir(acac)_3$ loading (0–2 mol%), amounts of PTFE (1–50 mg) and impregnation methods] were tested. The best components of the Ir-anode were [$Ir(acac)_3$ (0.025 mol%)/CF] (50 mg) and PTFE (5 mg). (ii) The study on the effects of various electrolytes (H_3PO_4, HCl, $HClO_4$, H_2SO_4, HNO_3, Na_2SO_4, NaOH and KOH) in the membrane and their concentrations on the oxidation of cyclohexane indicated that the best electrolyte was H_2SO_4 (aq) (1 mol l^{-1}).

Fig. 2(a) shows the formation rates of the products as a function of the anode potential by using the best anode and electrolyte described above. In the upper part (b), the current density and the current efficiency (CE) were plotted. When the anode potential was increased above 1.3 V (Ag | AgCl), the current density and the formation rates of CyO and CO_2 rapidly increased. The potential of 1.3 V for the onset of oxidation is far lower than the theoretical oxidation potential of 1.65 V (1.85 V *vs.* NHE) at pH = 0.[1] This result suggest that an indirect electrochemical oxidation of cyclohexane proceeds on the Ir-anode. The maximum formation rate of CyO was obtained at *ca.* 1.5 V. Here, the turnover number of Ir for CyO formation exceeded 110 in 1 h. In contrast, the formation rates of CO_2 and O_2 continuously increased when increasing the anode potential further. The decrease in the formation rate of CyO above 1.5 V may be due to the desorption of active oxygen species on the Ir-anode to the gas phase or to the consumption of the active oxygen in the successive oxidation of CyO to adipic acid or CO_2. Thus, the CE for the CyO formation decreased from 20 to 8% upon increasing the anode potential.

Effects of solvents (CH_2Cl_2, CCl_4, Et_2O, DMF and THF) on the oxidation were studied to optimize the oxidation. When a mixture of CH_2Cl_2 and cyclohexane (50 : 50 vol%) was used for the oxidation at 1.5 V, the CE for CyO formation dramatically

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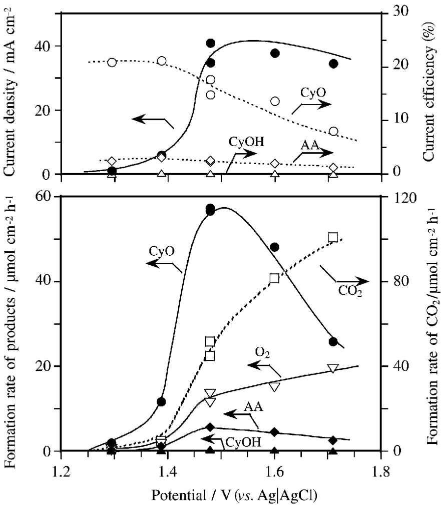

Fig. 2 Effects of anode potentials on (a) the formation rates of products and (b) current and current efficiency for the oxidation of cyclohexane on the Ir(acac)$_3$/CF anode with H_2O at 289 K.

increased from 15 to 45% while retaining a high formation rate of CyO. The increase in the CE was due to the decrease in both current and formation rates of CO_2 and O_2. If these by-products are formed through eqns. (2)–(4), their CE are estimated to be 18, 0.1, 10 and 15% for adipic acid, CyOH, CO_2 and O_2 respectively, giving a sum of CE of 88% at 1.5 V.

$$\text{cy-}C_6H_{12} + 4\ H_2O \rightarrow C_4H_8(CO_2H)_2 + 10\ H^+ + 10\ e^- \quad (2)$$

$$\text{cy-}C_6H_{12} + 12\ H_2O \rightarrow 6\ CO_2 + 36\ H^+ + 36\ e^- \quad (3)$$

$$\text{cy-}C_6H_{12} + H_2O \rightarrow \text{cy-}C_6H_{11}OH + 2\ H^+ + 2\ e^- \quad (4)$$

On the other hand, the CE for the formation of H_2 at the cathode was almost 100% within experimental error of ±2%. These results suggest the formation of undetectable products or oxidation of the anode itself.

A conventional H-type cell with the same [Ir(acac)$_2$ (0.025 mol%)/CF] anode was applied for the oxidation of cyclohexane dissolved in MeCN or dispersed as micelles in aqueous H_2SO_4. However, the oxidation of cyclohexane did not proceed at all. Our membrane electrolysis method is unique for the oxidation. After the oxidation, no Ir compounds were present in the reaction mixture or H_2SO_4 (aq) in the membrane according to ICP analysis. This result strongly suggests that Ir species are fixed on the CF.

Fig. 3 shows cyclic voltammograms (CV) of (a) the [0.025 mol% Ir(acac)$_2$/CF] electrode and (b) the CF electrode in aqueous H_2SO_4 under atmospheric pressure of Ar (geometric areas of both electrodes was 0.02 cm^2). Several redox couples were observed in the CV (a) of Ir(acac)$_3$/CF not observed in the CV (b) of CF, except for the redox couple due to quinone/hydroquinone groups present on carbon surfaces. A redox couple at 0.8–0.9 V (Ag | AgCl) (Ox-1/Red-1) can be assigned to Ir^{3+}/Ir^0.[7] The ratio of peak areas of Ox-1, Red-1, Ox-2 and Red-2 in Fig. 3(a) were roughly estimated to be 1 : 1 : 1 : 1. These facts suggested that the couple at higher potential (Ox-2/Red-2) can be ascribed to the transfer of three electrons, probably the redox couple Ir^{6+}/Ir^{3+} according to eqn. (5) or (6).

$$Ir^{3+} \rightarrow Ir^{6+} + 3\ e^- \quad (5)$$

$$Ir^{3+} + H_2O \rightarrow [IrO]^{4+} + 2\ H^+ + 3\ e^- \quad (6)$$

We believe that the formation of such high oxidation state Ir species[8] on CF would catalyse the oxidation of cyclohexane at >1.3 V(Ag | AgCl).

To gain information about the reactivity of active species, oxidations of CyOH (4.8 mol l^{-1}), CyO (4.8), hexane (3.8) and adamantane (0.25) dissolved in CH_2Cl_2 were studied at an anode potential of 1.5 V (Ag | AgCl). CyOH was efficiently oxidized to CyO with a high CE of 73% (assuming 2e$^-$ oxidation). On the other hand, CyO was oxidized to adipic acid with a low CE of 17% (6e$^-$ oxidation). These results suggest that active species generated on the Ir-anode oxidizes cyclohexane to CyO through CyOH. Deep oxidations of CyO to adipic acid and CO_2 were not fast. In oxidation of hexane, hexan-2-one (CE 14.0%, assuming 4e$^-$ oxidation), hexan-3-one (13.9%, 4e$^-$ oxidation) and hexanoic acid (0.4%, 6e$^-$ oxidation) were produced. The relative reactivities of secondary and primary C–H bonds (2° : 1°) in hexane were estimated from the quantities of the oxygenated products and found to 250 : 1 when normalized per C–H bond. Thus the secondary C–H bond was selectively oxygenated on the Ir-anode. In oxidation of adamantane, 1-adamantanol (CE 4.9%, assuming 2e$^-$ oxidation) and 2-adamantanone (0.7%, 4e$^-$ oxidation) were produced. The low CE observed here was due to the low solubility of adamantane in CH_2Cl_2 solvent. The relative reactivities of tertiary and secondary C–H bonds (3° : 2°) was 42 : 1. These results suggest that the active species has very strong electrophilicity for the oxidation of alkanes. This strong electrophilicity must be caused by the high oxidation state of Ir species suggested by CV experiments (Fig. 3).

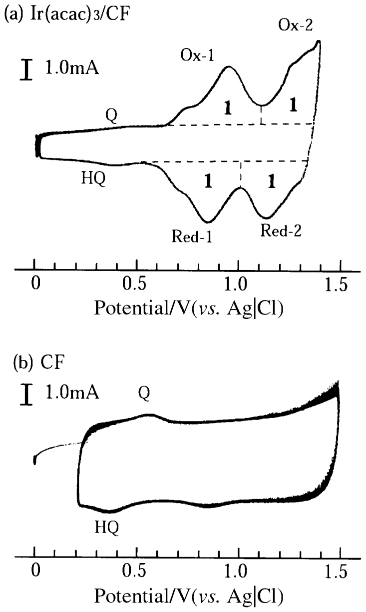

Fig. 3 Cyclic voltammograms of Ir(acac)$_3$/CF and CF electrodes in H_2SO_4 (aq) (1 mol l^{-1}) at atmospheric pressure of Ar. Scan speed 0.5 V s^{-1}.

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