Platinum-Catalyzed Oxidations of Organic Compounds by Ferric Sulfate: Use of a Redox Fuel Cell to Mediate Complete Oxidation of Ethylene Glycol by Dioxygen at 80°C

Christopher B. Gorman, Steven H. Bergens, and George M. Whitesides

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

A number of alcohols, aldehydes, and carboxylic acids were oxidized under mild conditions (60–80°C, 3 M H_2SO_4 in water) by Fe(III) using a catalytic amount of Pt black to generate Fe(II) and protons. The extent of oxidation depended on the structures of the organic reductant and on reaction conditions. A redox fuel cell that catalyzed the complete oxidation of ethylene glycol by dioxygen at 80°C was assembled. Fe(II) generated by oxidation of ethylene glycol was reoxidized to Fe(III) at the anode of the cell. A V(V)/V(IV)/HNO_3/O_2 redox system was used to catalyze the electrochemical reduction of dioxygen. Both the anode and cathode consisted of WDF graphite felt, the surface of which had been oxidized by boiling concentrated nitric acid for 15 min. A maximum power density of 9.9 mW/ cm^3 of graphite felt was obtained at a cell voltage of 197 mV. © 1996 Academic Press, Inc.

INTRODUCTION

The catalytic oxidation of organic compounds using dioxygen as the ultimate oxidant is widely used in synthesis and is a prevailing strategy for removal of contaminants from waste streams and flue gases (1–3). We have found an inorganic redox system (Fe(III)/Fe(II)) that oxidized various alcohols, aldehydes, and carboxylic acids in the presence of a catalytic amount of platinum black. The system was made catalytic in Fe(III), and dioxygen was used as stoichiometric oxidant, by electrochemically reoxidizing Fe(II) to Fe(III) at the anode of a redox fuel cell. Figure 1 shows a schematic of the fuel cell. Fe(II) was electrochemically oxidized to Fe(III) at the anode, and O_2 was reduced to H_2O at the cathode using a V(IV)/V(V)/ HNO_3 redox system developed by Kummer and Oei (4–6). A Nafion membrane separated the anode and the cathode compartments of the cell and allowed transfer of protons from the anolyte to the catholyte. Both the anode and the cathode consisted of WDF graphite felt (Union Carbide) that was surface oxidized with boiling, concentrated nitric acid for 15 min. This scheme may have advantages in the design of fuel cells. Particularly, it is not clear how to

design a catalytically active electrode that has a substantial volume. However, with this scheme, it becomes difficult to compare performance with conventional fuel cells that employ planar electrodes (7, 8).

We previously reported such a redox fuel cell that operated with methane as fuel (9). In this paper we demonstrate both catalytic oxidation of a number of substrates with the Fe(III)/Pt system and complete oxidation of ethylene glycol to carbon dioxide under mild conditions using dioxygen as stoichiometric oxidant in a redox fuel cell operating at 80°C. This is the first report of a redox fuel cell operating with ethylene glycol as fuel (5, 10–12).

METHODS

Materials. Methanol, ethanol, and ethylene glycol were distilled before use. Acetic acid (glacial) was stirred with acetic anhydride and CrO_3 (2 g/100 ml) to remove water and trace aldehyde and distilled before use. Glycolic acid (Aldrich), glyoxyilic acid (50% solution, Aldrich), potassium oxalate (Mallinckrodt), glyoxal (40% solution, Aldrich), glycerol (Fisher), sorbitol (Aldrich), and glucose (Aldrich) were used as received. Platinum black (Aesar, fuel cell grade) was heated to 100°C under vacuum for 30 min before use. The activity of the platinum catalyst was determined to be 3.3×10^{-4} mol/g Pt (6.44% dispersion) by alternating titration with hydrogen and oxygen as described previously by other researchers (13). Ferric sulfate was purchased from Aesar (puratronic grade) and used directly or from Aldrich (as the pentahydrate) and recrystallized from 6 M H_2SO_4 before use. Solutions approximately 0.5 M in ferric sulfate and 0.8 M in sulfuric acid (Aesar, puratronic grade) were prepared and [Fe^{3+}] was determined by titrating aliquots of the solution with EDTA at 40°C using N-(4-methoxyphenyl)-1,4-phenylenediamine hydrochloride (Aldrich) as the indicator.

Open-circuit oxidation of methanol by Fe(III) on a platinized platinum gauze electrode. A two-compartment electrochemical cell similar to one described previously (14)
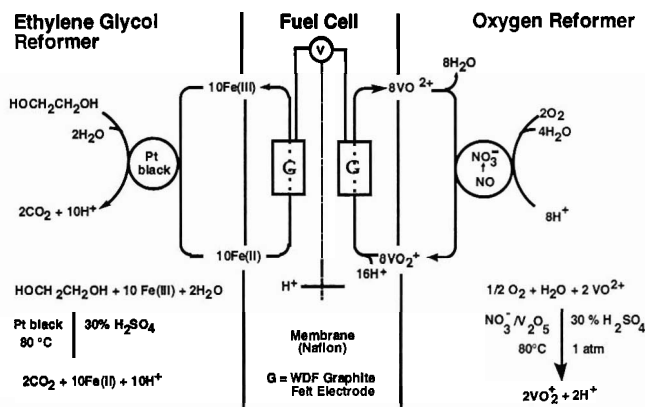
FIG. 1. Schematic of the ethylene glycol/oxygen fuel cell. Details of the cell components and operation are provided in the Methods section.

was used to study the oxidation. In this case, however, the cell compartments were separated by a Nafion membrane, a saturated calomel electrode was used as the reference electrode, and stirring was accomplished with a Teflon-coated magnetic stirbar. The catalyst/electrode (roughness factor of 684, geometric area of 6.25 cm^2) was prepared as previously described (15). The platinized catalyst/electrode was first carefully rinsed with a solution of 30% H_2O_2 in concentrated H_2SO_4 (~10% H_2O_2 solution in H_2SO_4 by volume) and then held at alternating potentials of +1.4 and −0.1 V in 1 M solutions of H_2SO_4 in water at 25°C until constant cyclic voltammograms (swept from 0 to 1.2 V at 50 mV/s) were obtained. It was finally held at +1.4 V for 20 s before being rinsed with water and transferred to the reaction vessel. The system was set up under an atmosphere of argon with equal volumes of Fe(III) solution (0.6 M, Fe(III)/Pt$_{surface}$ = 978:1) and of 3 M H_2SO_4 solution in the catalyst/electrode and reference electrode compartments, respectively. Control experiments showed that only slight variation in measured potentials of the catalyst/electrode occurred when the reference electrode was moved between cell compartments. The system was allowed to equilibrate in a 60°C bath before addition of methanol. The potential of the working catalyst/electrode varied little with stir rate unless stirring was stopped, which would typically result in an increase of potential by ~50 mV.

Oxidation reactions. Except for the oxidation of methanol (see below), all reactions were performed as follows. All reactions were performed under argon using argon-purged solutions. After heating the platinum black [3 mol% based on the number of reducing equivalents of fuel (x in Eq. [1] and Table 1)], the flask was cooled to the reaction temperature, and ferric sulfate solution (15 ml, [Fe(III)] = 0.586 M) was added. The stirring rate was established at 2400 rpm (1-in. Teflon-coated stirbar in a 100-ml, three-necked flask) using a stroboscope. After

allowing the reaction system to come to steady-state temperature (80°C) and pressure (1 atm), the stopcock to a gas buret filled with mineral oil was opened. The organic compound to be oxidized was added as a neat liquid or as an aqueous solution via syringe. The amount added was selected so that the ratio of Fe(III) to reducing equivalents of fuel was approximately 2:1. Reaction generally occurred after a short (1–2 min) initiation period and was evidenced by gas production (an increase in the volume of gas in the buret). During the reaction, the volume of the system was allowed to expand by maintaining the pressure of the system at atmospheric by means of a sidearm reservoir on the gas buret. Reaction was carried out until gas production had slowed to virtually zero or after approximately 3–4 h. Afterward, the reaction solution was filtered under argon atmosphere to remove the platinum black and titrated with a standard Ce^{4+} solution to determine the amount of iron reduced. In a control experiment, it was verified that small amounts of residual organics in the acidic solution were not directly oxidized by the ceric ion at a rate that would interfere with the redox titration of the ferrous ion. Oxidation of methanol was carried out in a similar procedure except that 2 mol% of Pt based on the reducing equivalents of fuel was used, and the reaction was carried out at a temperature of 60°C.

Ethylene glycol fuel cell. The assembly and operation of the cell was similar to that described for a methane redox fuel cell (9). The oxidation of ethylene glycol at dispersed platinum black by Fe(III) and the reduction of dioxygen by V(IV) were carried out in separate reformer flasks. The anolyte and catholyte were circulated between reformer flasks and cell compartments using peristaltic pumps. The solutions in the reformer flasks were filtered through glass frits before being admitted to the fuel cell. The reduction of Fe(III) to Fe(II) due to oxidation of ethylene glycol was carried out for 2 h before the solution was admitted to the anode compartment and the cell was operated. Currents at various cell potentials were measured under steady-state conditions by varying the load across the cell. The cell compartments were 3 cm in diameter and 5.5 cm deep and were separated by a Nafion membrane. A saturated calomel electrode was placed in each compartment as a reference electrode. Both the solutions in the reformer flasks and the solutions in the fuel cell chambers were stirred with Teflon-coated magnetic stirbars.

The reformer flask for the anode consisted of a flask containing 75 ml of a 0.6 M $Fe_2(SO_4)_3$ solution in 30% H_2SO_4 solution, 1 ml of ethylene glycol [a four-fold excess relative to starting Fe(III)], and 79.8 mg of Pt black [0.9 mol% relative to starting Fe(III); 3.3×10^{-4} mol active sites/g Pt as determined by H_2/O_2 titrimetry (13) (6.4% dispersion)]. The oxygen-reforming reaction is discussed

in detail elsewhere by Kummer and Oei (4–6). Cyclic volt-ammograms of the catholyte and anolyte were identical to those of authentic solutions of V(V) and Fe(III), respectively.

Both the anode and the cathode of the fuel cell consisted of rectangles of WDF graphite felt (Union Carbide, 2 × 3 × 0.5 cm). The felt was surface oxidized with boiling, concentrated nitric acid for 15 min. The density of the felt before this treatment was 8.49×10^{-2} g/cm^3. The surface area and density of the felt after treatment with boiling nitric acid were not measured. The current collectors were Pt wires (0.5 mm in diameter and ∼4 cm long). Since this redox fuel cell scheme permits the use of porous felt electrodes (i.e., the electrode reaction can take place in the volume of a porous electrode) and since the cost of the graphite felt is relatively unimportant, but the volume of the felt is important, current densities are reported per unit volume of carbon felt used (15).

RESULTS

Oxidation of methanol. Methanol is rapidly and quantitatively oxidized to CO_2 by excess Fe(III) in the presence of a catalytic amount of platinum black (1 mol% Pt versus Fe(III); [Fe(III)] = 0.7 M; 60°C; 30% w:w H_2SO_4 in water; under argon). The rate of CO_2 evolution was effectively constant for the majority of reaction. The turnover frequency during this period was 0.39 turnover/atom Pt$_{surface}$/s (one turnover = production of 1 CO_2 or of 6 Fe(III), Pt$_{surface}$ is an active site on Pt black). Substantial evolution of CO_2 was observed even when methanol was in excess of Fe(III) (e.g., MeOH:Fe(III) ∼ 2:1; 12 reducing equivalents per Fe(III)), demonstrating that products of partial oxidation were more reactive than methanol.

We obtained information about the surface of an operating catalyst by measuring the open-circuit potential (the catalyst potential with no applied current or voltage) of a Pt catalyst/electrode while it catalyzed oxidation of methanol by Fe(III). The catalyst/electrode was a platinized (15) square of 52-mesh Pt gauze with a roughness factor of 684 (15). The potential of the catalyst/electrode was 1.15 V versus the standard hydrogen electrode (SHE; all potentials in this paper are reported versus SHE) before addition of methanol. This potential is consistent with that of a Pt surface covered with oxides (14). The oxides resulted from the method we used to prepare the catalyst/electrode surface (see the Methods section). Addition of excess methanol (MeOH:Fe(III) ∼ 3.3:1) resulted in immediate reduction of the catalyst/electrode potential to 0.65 V and evolution of CO_2 from the catalyst/electrode surface. The potential gradually decreased as Fe(III) was consumed, reaching a minimum (0.48 V versus SHE) at the end of reaction, when evolution of CO_2 had ceased. Addition of more Fe(III) (remaining MeOH:added

TABLE 1

Reaction Conditions and Resulting Stoichiometries for the Oxidation of Various Functionalized Fuels[a]

R	x (mol Fe(II)/mol fuel oxidized)[b]		z (mol CO_2/mol fuel oxidized)[b]	
	Expected	Found[c]	Expected	Found[d]
CH_3OH	6	6.4	1	0.94
$HOCH_2CH_2OH$	10	9.6	2	1.7
$HOCH_2COOH$	6	6.4	2	1.6
$OCHCHO$	6	6.6	2	1.8
$OCHCOOH$	4	4.6	2	1.8
$KOOCCOOK$	2	2.1	2	2.0
CH_3CH_2OH	12	5.8	2	0
CH_3COOH	8	≈0.02	2	0
$C_3H_8O_3$ (glycerol)	14	15.0	3	1.8
$C_6H_{12}O_6$ (glucose)	24	3.8	6	0
$C_6H_{14}O_6$ (sorbital)	26	7.2	6	0

[a] Conditions 80°C, 3 M H_2SO_4.

[b] From Eq. [1].

[c] Determined by potentiometric titration of Fe^{2+} produced with a standard Ce^{4+} solution and expressed as the ratio of [Fe^{2+}] at the end of the reaction to [R] at the beginning of the reaction. Error in this ratio is ±0.1.

[d] Determined by measuring the volume of gas produced at constant temperature and pressure using a gas buret. Error in z_{found} is ±0.1.

Fe(III) ≅ 16:1) caused a rapid increase of catalyst/electrode potential to 0.61 V and evolution of CO_2 to resume. We interpret this behavior as formation of the active catalyst during a short induction period by reduction of surface oxides by methanol (14), followed by catalytic oxidation by Fe(III). The potential of the catalyst/electrode during catalytic oxidation of methanol remained in the region (0.4–0.7 V) (15) where coverage of Pt by hydrides and by oxides is low. We believe, therefore, that two possible roles of Fe(III)/Fe(II) during this oxidation are to act as a sink for electrons and to maximize the number of active sites available on Pt for oxidation of methanol by keeping the surface of Pt free of oxides and hydrides.

Rates/stoichiometries for the $Pt/Fe_2(SO_4)_3$ oxidations of functionalized hydrocarbons. Oxidation of the substrates was carried out using the Fe(III)/Pt redox system:

$$R + yH_2O + xFe^{3+} \xrightarrow{Pt(0)} zCO_2 + xFe^{2+} + xH^+. \quad [1]$$

Table 1 summarizes the results of this reaction for various reductants (R). Our first interest was to establish the stoichiometries of these reactions. Reaction stoichiometry was quantified in two complementary ways: by measuring the amount of CO_2 produced using a gas buret and by measur-
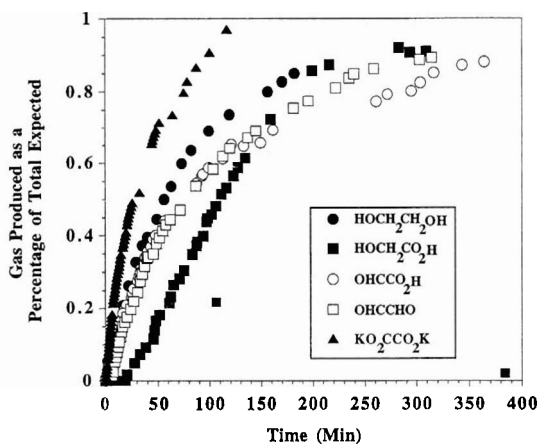
FIG. 2. Rates of carbon dioxide production measured by gas buret. Conditions are the same as those reported in Table 1.

ing the amount of ferric ion reduced to ferrous ion by redox titration.

The first general class of compounds listed in Table 1 is C_2 fuels in which each carbon atom is functionalized. These compounds were completely oxidized to CO_2 at 80°C. The extent of this reaction after 3–4 h was, at a minimum, 79% of completion as evidenced by the amount of CO_2 produced. By titration, it was found that at least enough ferric ion was reduced to correspond to the expected amount of fuel oxidized (16).

Ethanol and acetic acid both contain one unfunctionalized (methyl) carbon. Under the experimental conditions employed (80°C, 3–4 h reaction time), these reductants were not completely oxidized to CO_2. No gas evolution was detected. The reduction of ferric ion suggests, however, that partial oxidation of the ethanol occurred, probably to at least the oxidation level of acetic acid (expected $x = 4$; see Eq [1]). We suspect that complete oxidation of these species can be effected, albeit under conditions of higher temperature and pressure (9).

Functionalized fuels with greater numbers of carbons gave results on oxidation that depended on the structure. Glycerin (three carbons) was oxidized completely under these reaction conditions. When six carbon substrates (glucose, sorbital) were employed as fuels, no gas evolved and only a small fraction of the expected ferrous ion was produced. Dehydrations of sugars in acidic media to form functionalized furans are documented in the literature (17). Given the results presented in this work, it is likely that such fuels are difficult to oxidize under these conditions and that cyclization/aromatization may be occurring.

The rates of oxidation of several fuels to carbon dioxide were monitored with a gas buret; CO_2 was identified by GC/MS. Figure 2 summarizes rates. Interestingly, a long (20–30 min) initiation period was observed in the oxidation of glycolic acid. This observation was made in triplicate

oxidations using different samples of substrate in each. Experimentally, there is ambiguity about the mechanisms of oxidation at a platinum surface (18). Empirically, multielectron oxidation is possible under these conditions from functionalized carbon compounds with no detectable slow steps.

Operation of a fuel cell using ethylene glycol as the fuel. Ethylene glycol was oxidized completely to carbon dioxide in a prototype fuel cell similar to one using methane (9) that was reported previously. Oxidation of ethylene glycol to CO_2 was carried out in a separate reformer flask, and the reduced iron solution was pumped into the anode chamber of the fuel cell to deliver the electron equivalents produced in the oxidation reaction. Since the redox couple was the same as in the methane cell (9), the same electrochemical behavior is expected if ethylene glycol does not oxidize much directly at the electrode. Indeed, similar behavior was observed and is illustrated in Fig. 3.

DISCUSSION

In this article, it has been shown that several alcohols, aldehydes, and carboxylic acids were oxidized under mild conditions (60–80°C, 3 M H_2SO_4 in water) by Fe(III) using a catalytic amount of Pt black to generate Fe(II) and protons. Under these conditions, complete oxidization of several reductants was effected. On the basis of these results, a redox fuel cell that catalyzed the complete oxidation of ethylene glycol by dioxygen at 80°C was assembled. A maximum power density of 9.9 mW/cm^3 of graphite felt was obtained at a cell voltage of 197 mV. These results indicate that the oxidation of the ethylene glycol in the reformer section (Fig. 2) is not a limiting factor in the electrical performance of the cell. The power density in this porous felt electrode is not straightforwardly compared with those in planar and gas diffusion electrodes. However, as the porous felt employed has substantial surface area, it is clearly low compared to that in gas diffusion electrodes
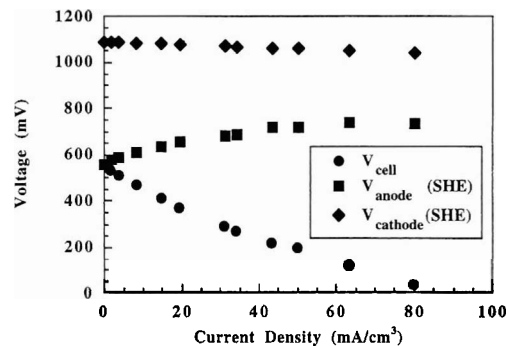

FIG. 3. Current/voltage characteristics of the ethylene glycol/oxygen fuel cell. Anode and cathode voltages were measured using separate reference electrodes in each compartment.

(7, 8). However, by decoupling the catalytic oxidation of the fuel from the electrochemical transfer of electrons to the circuit, redox fuel cells provide several advantages over conventional, direct fuel cells. The electrode material is constructed at substantially lower cost and with greater ease than the conventional gas diffusion electrode that has been employed in a methanol fuel cell (19). As we have shown previously, a high pressure and temperature reformer that catalyzes the complete oxidation of methane to carbon dioxide can be substituted for this reformer using the same cell scheme (9). Moreover, replacement and recovery of the catalyst is simpler and less expensive for liquid reformers than for conventional fuel cell stacks (7). Our results suggest that it is possible to develop redox fuel cells that oxidize a variety of fuels for both production of energy and for removal of contaminants from waste streams; such work is in progress in our group.

ACKNOWLEDGMENTS

REFERENCES

1. Sachtler, W. M. H., *Catal. Rev.* **4,** 27 (1970).
2. Kilty, P. A., and Sachtler, W. M. H., *Catal. Rev.* **10,** 1 (1974).
3. Langer, S. H., *J. Appl. Electrochem.* **23,** 745 (1993).
4. Oei, D.-G., *J. Appl. Electrochem.* **12,** 41 (1982).
5. Kummer, J. T., and Oei, D.-G., *J. Appl. Electrochem.* **12,** 87 (1982).
6. Kummer, J. T., and Oei, D.-G., *J. Appl. Electrochem.* **15,** 619 (1985).
7. Prentice, G., *Chemtech* **14,** 684 (1984).
8. Lindström, O., *Chemtech* **18,** 490 (1988).
9. Bergens, S. H., Gorman, C. B., Palmore, G. T. R., and Whitesides, G. M., *Science* **265,** 1418 (1994).
10. Carson, W. M., and Feldman, M. L., *Proc. Annu. Power Sources Conf.* **13,** 111 (1959).
11. Posner, A. M., *Fuel* **24,** 330 (1955).
12. Matsen, J. M., *Adv. Chem. Ser.* **64,** 277 (1967).
13. Carballo, L., Serrano, C., Wolf, E. E., and Carberry, J. J., *J. Catal.* **52,** 507 (1978).
14. DiCosimo, R., and Whitesides, G. M., *J. Phys. Chem.* **93,** 768 (1989).
15. Woods, R., *in* "Electroanalytical Chemistry: A Series of Advances" (A. J. Bard, Ed.), p. 1. Dekker, New York, 1976.
16. In all cases but one, slightly more ferric ion was reduced than expected, resulting in a higher than expected stoichiometry. This observation initially suggested that some of the platinum was oxidized to Pt(II) and/or Pt(IV). However, with glyoxal, for example, 4.92 mmol of Fe(III) was reduced, 4.45 mmol of which could be accounted for by complete oxidation of the glyoxal. If the rest of the iron oxidized the Pt(0), it would correspond to complete oxidation of the Pt(0) to Pt(IV), $(4.92–4.45)/4 = 0.12$ mmol of Pt(0) $\rightarrow$ Pt(IV) but 24.3 mg Pt(0) $\cdot$ (1 mmol/195.09 mg) = 0.12 mmol. Furthermore, substantial amounts of platinum black remained after the reaction. Within this experimental uncertainty, this stoichiometry does correspond to complete oxidation of these substrates.
17. Vinke, P., de Wit, D., de Goede, A. T. J. W., and van Bekkum, H., *in* "New Developments in Selective Oxidation by Heterogeneous Catalysis" (P. Ruiz, and B. Delmon, Eds.), p. 1. Elsevier, New York, 1992.
18. McNicol, B. D., *J. Electroanal. Chem.* **118,** 71 (1981).
19. Watanabe, M., Uchida, M., and Motoo, S., *J. Electroanal. Chem.* **199,** 311 (1986).