# Selective Synthesis of Acetaldehyde using a Fuel Cell System in the Gas Phase

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The Pd|$H_3PO_4$|Pd fuel cell system produces acetaldehyde very selectively (>97%) in the gas phase at temperatures <395 K, which suggests several advantages over the Wacker process.

The Wacker reactions for single-step synthesis of acetaldehyde include oxidation of ethylene to acetaldehyde in aqueous solution.[1] This process, however, has some disadvantages from the engineering point of view. (a) Since the reactions are carried out in an aqueous phase, the reactants have to be absorbed into the solution and the acetaldehyde produced must be distilled and separated from the solution. (b) A major engineering concern is the corrosive nature of the aqueous solution of chlorides of palladium and copper. (c) There is a danger of forming explosive gas mixture of oxygen and ethylene.

A number of investigators have focussed a great deal of effort on inorganic oxidation in fuel cells. The purpose of the work was the rapid and complete oxidation of cheap feed stocks for generating electricity and heat. However, some of the investigators have demonstrated that fuel cells can cogenerate electricity and useful chemicals.[2—4] The purpose of this work is to apply this idea in the synthesis of acetaldehyde by partial oxidation of ethylene using a Pd-attached phosphoric acid fuel cell in the gas phase. The fuel cell reactor and the gas flow system are demonstrated in Figure 1. A Pd black-attached silica wool wafer (1.0 mm thickness, 21 mm diameter) containing phosphoric acid [85% $H_3PO_4$(aq.) 0.25 ml] was used as a separator for the two compartments. The apparent density of the Pd electrode was 10 mg cm$^{-2}$ for both sides of the wafer. No external load was applied, in order to get chemicals exclusively. Ethylene and water vapour were carried with helium into the left compartment and the oxygen into the right compartment of the cell in Figure 1. All the reactions were carried out under atmospheric pressure for both compartments. The experimental conditions were as follows: at anode compartment: $C_2H_4$:$H_2O$:He = 12:1:20, total flow rate = 33 ml min$^{-1}$; at cathode compartment: pure $O_2$ (25 ml min$^{-1}$). No leakage of the reactants through the separator was observed. Under open-circuit conditions only a trace of $CO_2$ was observed at temperatures 318—395 K. When the circuit was closed, current flowed and MeCHO was produced very selectively (>97%). The results observed at different temperatures are shown in Table 1. The rate of formation of acetaldehyde at any reaction temperature corresponds well to the current observed, assuming the following electrocatalytic reactions:

$$\text{Anode: } C_2H_4 + H_2O \longrightarrow \text{MeCHO} + 2H^+ + 2e^-$$

$$\text{Cathode: } 2H^+ + 2e^- + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

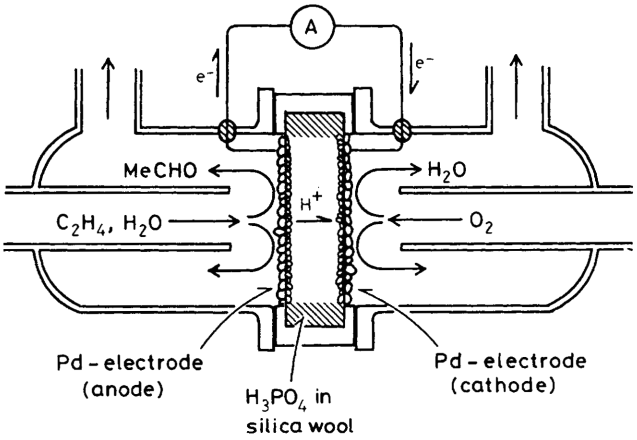

**Figure 1.** Diagram of the fuel cell type reactor.

Thus, the current efficiency at any temperature is 100% within the limits of experimental error (±5%) as can be seen from the right-hand column of Table 1. The rate of formation of acetaldehyde decreases only slightly over 23 hours' operation of the reaction at 356 K. The turnover number for the acetaldehyde produced in 23 hours per Pd atom on the anode is 5.9. These observations show that the Pd works as an electrocatalyst. When a mixture of $C_2H_4$ and $O_2$ ($C_2H_4$ : $O_2$ : He = 11 : 6 : 20, total flow rate = 37 ml min$^{-1}$) was passed over the Pd catalyst at 393 K in the anode compartment under open circuit conditions, only a trace of $CO_2$ was formed. This observation shows that the partial oxidation of $C_2H_4$ by $O_2$ does not occur on the Pd black attached to the wafer. Platinum black as electrocatalyst under closed-circuit conditions produced only $CO_2$ without any trace of acetaldehyde. Fine rhodium powder produced neither $CO_2$ nor acetaldehyde at temperatures 313—393 K. These facts suggest that Pd is a specific electrocatalyst for the formation of acetaldehyde.

Table 2 shows the results at 393 K when potential was applied between the Pd electrodes on both sides of wafer in

**Table 1.** Synthesis of MeCHO in the absence of applied potential at different temperatures.

| Cell temp. /K | Current /mA | Formation rate of MeCHO/a | % Selectivity | % Current efficiency |
|---|---|---|---|---|
| 318 | 0.27 | 0.092 | 96 | 102 |
| 336 | 0.70 | 0.140 | 99 | 104 |
| 356 | 1.10 | 0.259 | 98 | 106 |
| 375 | 1.29 | 0.276 | 97 | 101 |
| 395 | 3.95 | 0.981 | 97 | 101 |
| 395 (open) | — | 0.006 | 40 | — |

Experimental conditions: anode, $C_2H_4$:$H_2O$:He = 12:1:20; total flow rate = 33 ml min$^{-1}$; cathode, pure $O_2$ flow rate = 25 ml min$^{-1}$; a = $10^{-6}$ mol min.$^{-1}$

**Table 2.** Synthesis of MeCHO under applied potential at 356 K.

| Current /mA | Applied potential /V | Formation rate of MeCHO/a | % Selectivity | % Current efficiency |
|---|---|---|---|---|
| 9.85 | 0.288 | 4.36 | 99.2 | 101 |
| 18.91 | 0.610 | 8.49 | 98.9 | 98 |
| 29.52 | 0.925 | 13.40 | 99.2 | 103 |

Experimental conditions are the same as those for Table 1. a = $10^{-6}$ mol min.$^{-1}$

Figure 1. The selectivity for MeCHO was very high (>99%) and the rate of formation of MeCHO corresponded well to the current here, also.

We believe that the reaction is initiated by the $Pd^{2+}$ which may be generated electrochemically at the interface of the Pd electrode and $H_3PO_4$:

$$Pd^0 \longrightarrow Pd^{2+} + 2e^-$$

$$Pd^{2+} + C_2H_4 \longrightarrow Pd^{2+}\cdots C_2H_4$$

$$Pd^{2+}\cdots C_2H_4 + H_2O \longrightarrow Pd^{+}\text{–}CH_2CH_2OH + H^+$$

$$Pd^{+}\text{–}CH_2CH_2OH \longrightarrow MeCHO + H^+ + Pd^0$$

The advantages of this method are as follows: it is simple and the reactants and products can be handled easily in the gas phase; no corrosive aqueous solution of $PdCl_2$, $CuCl_2$ and HCl is needed; the reactants $C_2H_4$ and $O_2$ are separated by the diaphragm, so danger of explosion must be reduced; and the reaction cogenerates electricity and acetaldehyde.

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