SUPPORTED MOLTEN-SALT ELECTROCATALYST FOR CO-GENERATION OF ACETALDEHYDE AND ELECTRICITY FROM ETHANOL IN A FUEL CELL

Sanjiv Malhotra and Ravindra Datta*

Department of Chemical and Biochemical Engineering
The University of Iowa, Iowa City, IA 52242.

ABSTRACT

A novel fuel cell has been developed for simultaneously generating electricity and acetaldehyde from ethanol, that is based on supported molten-salt electro-catalysts (SMSEC). The SMSEC used the Wacker homogenous catalyst, namely PdCl\textsubscript{2}/CuCl\textsubscript{2}, dissolved in a low-melting molten salt. Current densities of up to 3.5 mA/cm\textsuperscript{2} with good selectivity (85%) to acetaldehyde were obtained in the tetra-n-butylammonium trichlorostannate as the molten salt. Preliminary results for different molten salt catalysts and electrolytes are presented here.

INTRODUCTION

The utilization of the favorable free energy of reaction to drive fuel cells to produce desired chemicals and co-generate electricity is an attractive idea (1). In cogeneration fuel cell systems, selective electrocatalysis is employed to produce value-added chemicals, in contrast to fuel cells where complete combustion of the reactants and energy production is the usual goal. Further, attention being attributed to biomass-based chemical feedstocks has generated an interest in the usage of ethanol for producing other basic chemicals and for alternative energy generation.

Acetaldehyde is an important large scale industrial intermediate chemical. It is an intermediate in the production of a number of chemicals such as acetic acid, acetic anhydride, ethyl acetate, 1,3-butylene glycol, and peracetic acid, etc. There are several commercial routes for acetaldehyde production: 1) partial oxidation of ethylene, 2) oxidation or dehydrogenation of ethanol, 3) hydration of ethylene, now obsolete, and 4) partial oxidation of low molecular weight paraffin hydrocarbons. While more than 80% of the acetaldehyde is produced by the Wacker-Hoechst process involving partial oxidation of ethylene, some of it is also produced by the oxidation or, less commonly, by the dehydrogenation of ethanol. This work is concerned with the feasibility of a novel prototype fuel cell designed to simultaneously produce value-added acetaldehyde and electricity from renewable ethanol.

The fuel cell is based on the novel electro-catalytic usage of homogenous (liquid phase) catalysis to achieve high selectivity and reactivity at relatively low temperatures (~150°C). This has been made possible by the development of the technique of supported molten-salt catalysis (SMSC) (2). The fuel cell system described here possesses the following novel features:

Author to whom correspondence may be addressed.
- A homogenous supported molten salt electrocatalyst (SMSEC) for the cogeneration of acetaldehyde and electricity from ethanol.

- An electrolyte comprising of a low melting point molten salt supported on a Nafion® membrane.

- New chemistry for producing acetaldehyde from ethanol, which combines the chemistries of the Veba-Chemie method for producing acetaldehyde from ethanol and the Wacker process which is used for producing acetaldehyde from ethanol.

DESCRIPTION

Supported Molten-Salt Catalyst:

In the homogeneously catalyzed Wacker process for acetaldehyde synthesis there are some engineering problems: inefficient catalyst utilization, limited gas-liquid surface area, corrosion, and the required separation of the catalyst from the product. In fact, many of these problems are inherent to homogeneous catalysis, which have thus limited its industrial application, even though there are now many major industrial processes that employ soluble transition metal complexes as catalysts (3-4). Due to the dwindling raw material supplies, higher energy costs, and more stringent environmental standards, the use of more efficient homogeneous catalysis is expected to continue to grow because of its high selectivity, high activity, mild operating conditions, molecular dispersion of the catalyst, and better control of the nature of the catalytic species.

Several hybrid techniques (5) have been developed that seek to combine the attractive features of homogeneous catalysis with those of heterogeneous catalysis such as large interfacial area, use of conventional reactors such as packed-bed and fluidized-bed reactors, and ease of separation of catalyst from products. These techniques include polymer heterogenized metal complexes (5-6), zeolite entrapped complexes, supported liquid-phase catalysis (SLPC) (7), and supported molten-salt catalysis (2). At the present time none of these approaches have yielded a commercially viable catalyst. However, the SMSC approach, described below, offers some promise in this regard.

In the SMSC technique (2), a molten-salt containing the dissolved or dispersed transition metal complex catalyst is coated on the walls of a porous support so as to occupy a fraction of the pore space, much like a chromatographic packing supporting a liquid phase. The gaseous or vapor phase reactants diffuse through the residual gas pore space, as well as through the liquid, and react within the liquid catalyst film. The catalyst retains a dry external appearance and, thus, effectively combines the attractive features of homogeneous catalysis with those of heterogeneous catalysis. It virtually eliminates liquid-diffusion limitations, since the liquid is coated as a very thin film and the interfacial area is extremely large. The SMSC technique is a very powerful one since a large variety of molten salts is available for practically any temperature range. Co-catalysts or promoters can also be easily incorporated in the liquid. Further, molten salts have excellent solvent properties and can dissolve a wide variety of substances such as ionic substances, organic substances, gases, water, metal oxides, non-metallic elements and even metals (8-9). Thus, SMSC can be developed not only for homogeneous catalysts but also for
"heterogeneous" catalysts by dispersing crystallites of metals and inorganic metal compounds in supported molten salts (10).

Rao and Datta (2) have developed a SMSC Wacker catalyst by replacing the aqueous solvent (H₂O + HCl) with a eutectic melt of CuCl and KCl (m.p. 150 °C), which is highly active, affording almost complete utilization of the expensive Pd catalyst, has high selectivity, is extremely stable, and virtually eliminates the corrosion problems encountered in the industrial process. This catalyst forms the basis of the proposed SMSEC.

**Novel Catalysis for the Reaction:**

The reaction system chosen here is the Veba-Chemie process, i.e., the oxidative dehydrogenation of ethanol to form acetaldehyde. However, the traditional Veba-Chemie process oxidizes ethanol by passing ethanol vapors and air over a silver catalyst at a high temperature (~500 °C). We conduct this reaction by combining the chemistries of the Veba-Chemie and the Wacker-Hoechst processes in order to produce acetaldehyde from ethanol at a relatively mild temperature (~100-190°C) in a fuel cell. Experiments in our laboratory have indicated that this catalysis is feasible. The anticipated overall reaction mechanism, analogous to the Wacker process, is:

\[
\begin{align*}
\text{PdCl}_4^{2-} + \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{CHO} + \text{Pd}^0 + 2\text{HCl} + 2\text{Cl}^- \\
2\text{Cl}^- + \text{Pd}^0 + 2\text{CuCl}_2 & \rightarrow \text{PdCl}_4^{2-} + 2\text{CuCl} \\
2\text{CuCl} + 2\text{HCl} + \frac{1}{2}\text{O}_2 & \rightarrow 2\text{CuCl}_2 + \text{H}_2\text{O} \\
\text{C}_2\text{H}_5\text{OH} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}
\end{align*}
\]

**Supported Molted-Salt Electrocatalytic Fuel Cell:**

The new supported molten-salt electro-catalyst (SMSEC) design is shown schematically in Figure 1. A molten-salt containing the dissolved catalyst, is coated on the walls of porous carbon, which on account of its excellent corrosion resistance, electronic conductivity and cost, is a popular porous electrocatalyst support. The gaseous or vapor phase reactants diffuse through the residual gas pore space as well as through the molten-salt phase, and react within the catalyst layer. The anode and cathode are separated by a thin layer of supported electrolyte for the conduction of ions. The electrolyte used is either an appropriate acid which provide excellent ionic conductivities, or a supported molten-salt electrolyte. The electrolyte support material must be nonconducting.

Different molten salts as follows were employed as solvents for electrocatalysts:

**Catalyst Type A** had the Wacker homogeneous catalyst (PdCl₂ + CuCl₂) dissolved in a eutectic melt of 35 mol% KCl-65 mol% CuCl (m.p. = 150 °C) (Janz, 1969). The catalyst preparation procedure is described by Rao and Datta (2). It involves dissolving the above substances in a dilute aqueous solution of HCl in a volumetric ratio corresponding to the desired liquid loading. The mixture is gently stirred for about 24 hrs. Meanwhile the porous supports are kept in vacuum overnight to remove air from the pores. Then the vacuum pump is shut off and the catalyst solution is added to the porous supports. The supports are thus immersed for 24 hrs and then the supports are removed from the solution.
and placed in a vacuum oven at 110°C for about 12 hrs to evaporate the hydrochloric acid and water from the pores. The weight gain of support provides the amount of catalyst-salt mixture remaining in the pore space. The solvent loading (CuCl + KCl) was about 30% and the palladium chloride and copper(II) chloride concentration was 10.5 mmol/L and 0.13 mol/L respectively.

**Catalyst Type B** had the Wacker homogenous catalyst (PdCl₂ + CuCl₂) dissolved in an organic eutectic melt namely tetra-n-butylammonium trichlorostannate. The crystals of the melt were prepared by adding 100 ml of aqueous 1 M tetra-n-butylammonium chloride to a solution of 0.1 mol of SnCl₂·2H₂O at room temperature. The solution was stirred for about 15 minutes. A colorless oil separated. The residual oil crystallized on cooling. Recrystallization of the tetra-n-butylammonium trichlorostannate from ethanol gave white crystals with a melting point of around 60°C. The catalyst and the molten salt were mixed at around 90°C in a vacuum oven and spread uniformly on a graphite support thus allowing direct impregnation for a period of 24 hrs. The amount of the molten salt impregnated was 2.5 gms and the catalyst concentration was the same as that used in catalyst Type A.

**Catalyst Type C** had the Wacker homogenous catalyst dissolved in ethylene glycol. The volumetric solvent loading was around 24% with the same catalyst concentrations as in catalyst type A.

**Catalyst Type D** had Platinum catalyst supported on graphite discs. The method of preparation was the same as used for the Cathode, described in the next section. The platinum loading was around 1.2 mg/cm².

**Anode:**

The different electrocatalysts used at anode are listed in Table 1.

The anticipated half-cell reactions at the anode are:

\[
PdCl₄^{2-} + C₂H₅OH \rightarrow CH₃CHO + Pd⁰ + 2HCl + 2Cl⁻
\]

\[
2Cl⁻ + Pd⁰ + 2CuCl₂ \rightarrow PdCl₄^{2-} + 2CuCl
\]

\[
2CuCl + 2HCl \rightarrow 2CuCl₂ + 2H^+ + 2e⁻
\]

\[
C₂H₅OH \rightarrow CH₃CHO + 2H^+ + 2e⁻
\]

**Cathode:**

The cathode has platinum catalyst supported on graphite discs (Catalyst Type D). The graphite discs are immersed in a solution of chloroplatinic acid for a period of 5 days. The discs are then placed in a vacuum oven (85°C) for 12 hours. Then the catalyst is reduced with flowing hydrogen at 450°C for 6-7 hours. The half-cell reaction is:

\[
\frac{1}{2}O₂ + 2H^+ + 2e⁻ \rightarrow H₂O
\]
Electrolyte:

The different electrolytes tried include phosphoric acid, Nafion® membranes and a molten-salt eutectic (CuCl-KCl). Since the Nafion membrane is dehydrated and exhibits a loss in ionic conductivity at temperatures above 80°C, we saturated the membrane with phosphoric acid for 24 hrs in order to have it operational even at temperatures above 100°C. Alternatively, the Nafion membrane was impregnated with low melting molten salts possessing protonic conductivity. The different inert supports tried for the molten salt eutectic (CuCl-KCl) and phosphoric acid include porous vycor glass (40 Å pore size), alumina disc (0.125" thick and 5μm pore size), and aluminium nitride (0.125 " thick and 5 μm pore size) disc. A thin film of phosphoric acid was contained between two Nafion® membranes and nafion gel along with phosphoric acid was applied to the faces of the electrodes which were in contact with the nafion membranes. In another set of experiments, a thin disc of glass wool (1mm thick) was saturated with phosphoric acid and contained between two Nafion® membranes which had been impregnated with the acid for 24 hours. This reduced the possibility of the acid evaporating during the fuel cell operation.

Experimental Apparatus and Test Procedure:

Ethanol was supplied by means of a liquid pump (Eldex, Model No. A-60-S) and, upon evaporation in a vaporizer with controlled temperature, was carried by He into the anode compartment. Air (or O2) was supplied to the cathode compartment. The fuel cell is made of stainless steel. The reactant inlet and product outlet connections from each half cell have the shell-and-tube exchanger design, with the tubes (1/8" and 1/4" O.D) placed concentrically in each opening. This minimizes the number of connections to the fuel cell and hence the possibility of leaks. The temperature of the vaporizer was controlled using a Omega temperature controller (CN9100A). The flow rates were controlled by needle valves and measured with mass flow meters (Omega, FMA 1700/1800 series). The pressure in the reactant gas line and in the fuel cell was measured by means of a Matheson pressure gage. Two three way valves allowed the feed stream as well as the product stream to be analyzed on a continuous basis by means of an on-line gas chromatograph (Gow-Mac, Series 580) utilizing a Porapak-Q column. Another set of three-way valves allowed the monitoring of products and reactants in the two electrode compartments (anode and cathode) separately. Heating tape was used for the gas lines to avoid condensation of product stream leading from the fuel cell to the G.C. The temperature of the fuel cell was controlled with a temperature controller (Omega, CN9000A) and heating tapes.

The rate of formation of the product on the basis of ethanol converted, the selectivity to acetaldehyde and the current efficiencies for the products were studied. The current efficiency can be calculated by measuring the total electric charge passed with the help of the coulometer, and dividing this by the amount of electric charge that should be stoichiometrically produced with the measured amount of the products produced.

RESULTS AND DISCUSSION

Different combinations of the electro-catalysts at the anode and the cathode along with different electrolytes were studied for carrying out initial feasibility studies (Table 1). Initially, Catalyst Type A was studied both at the anode and the cathode with CuCl-KCl.
eutectic supported on porous vycor glass as the electrolyte medium. The current density obtained was only around 0.05mA/cm² with a low conversion at around 180°C. Catalyst Type A was discarded for the cathode since it was found that the Pt catalyst supported on graphite discs was far more suitable for the reduction reaction (Catalyst Type D). In order to improve the ionic contact and to circumvent the problem due to the fragility of the porous vycor glass, a nafion membrane with a thin film of phosphoric acid was used as the electrolyte. Current densities of around 1mA/cm² were obtained with acetaldehyde selectivity of around 75%. However, this was not reproducible due to the fact that phosphoric acid evaporated at 180°C. Then ethanol was fed along with 5% phosphoric acid - 5% water to the anode side. In different experimental runs carried out with the above solution as the anode feed, the current densities obtained were around 1-1.3 mA/cm² but substantial amount of ethylene was also formed due to the acidic nature of the anode, thus reducing the selectivity to acetaldehyde.

Since, Nafion® membrane is dehydrated above 100°C, a liquid solvent such as ethylene glycol was used for the wacker catalyst at the anode (Catalyst C). Platinum on graphite was used at the cathode and a nafion membrane impregnated with phosphoric acid with a thin film of ethylene glycol on the electrode surface in contact with the Nafion® membrane was used as the electrolyte. Current densities of around 0.3mA/cm² with 65% selectivity to acetaldehyde were obtained, but the catalyst deactivated after an initial run of 5 hrs at around 90°C due to the evaporation of the liquid solvent.

Next, an organic molten salt (tetra-n-butylammonium trichlorostannate) was used as the melt for dissolving the catalyst for two primary reasons:

- To have a low melting point molten salt so that the low operating temperatures reduce the rate of evaporation of the phosphoric acid contained between the nafion membranes.

- To have a molten salt with a good protonic conductivity, thus facilitating protonic conduction from the catalytic site to the electrolyte interface.

The reason for the relatively low current densities compared to the circuit voltages obtained from the various set of experiments is probably due to the thickness (0.125") of the electrodes. The high resistance to diffusional transfer provides the overpotential losses. To avoid this loss, we plan on next employing very fine weave carbon cloth electrodes (0.4 mm thick) obtained from Electrosynthesis Corp. The electrode will be characterized using cyclic voltammogram and SEM techniques in order to study the active catalyst layer.

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| Anode | Cathode | Electrolyte | Temperature | Current Density | Voltage | Current Efficiency | Selectivity |
|-------|---------|-------------|-------------|----------------|---------|--------------------|-------------|
| Type A | Type A  | CuCl-KCl    | 180°C       | 0.05 mA/cm²    | 0.15 V  | 45%                | 65%         |
| Type A | Type D  | Nafion 1*   | 180°C       | 1.0 mA/cm²     | 0.25 V  | 82%                | 75%         |
| Type A | Type D  | Nafion 2$   | 180°C       | 1.3 mA/cm²     | 0.27 V  | 47%                | 41%         |
| Type B | Type D  | Nafion 1*   | 90°C        | 3.5 mA/cm²     | 0.53 V  | 87%                | 83%         |
| Type C | Type D  | Nafion 1*   | 90°C        | 0.3 mA/cm²     | 0.36 V  | 67%                | 65%         |
| Type D | Type D  | Nafion      | 70°C        | 1.6 mA/cm²     | 0.45 V  | 81%                | 72%         |
| Type D | Type B  | Nafion 1*   | 90°C        | 0.9 mA/cm²     | 0.46 V  | 73%                | 70%         |

*Nafion 1: Phosphoric acid contained between two Nafion membranes.

$Nafion 2: 5% Phosphoric acid fed along with ethanol to the anode.

Table 1: Results of Feasibility Study of Supported Molten-Salt Electrocatalysts.

![Figure 1: Schematic of SMSEC Fuel Cell for Co-Generation of Acetaldehyde and Electricity from Ethanol.](image)

780