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Electrochemically promoted olefin isomerization reactions at polymer electrolyte fuel cell membrane electrode assemblies

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Abstract

The isomerization of 2-3-dimethyl-1-butene was enhanced over a thousand fold (vs the open circuit value) by spillover protons generated by low currents (electrochemical promotion) on carbon supported Pd catalysts in a polymer electrolyte fuel cell. There was substantial proton spillover catalyzed shift of the double bond of 2-3-dimethyl-1-butene. With 3-3-dimethyl-1-butene, the proton spillover catalyzed methyl shift occurred at low levels and 2-2-dimethyl-butane was the primary product from the simple reduction reaction. Although the substantial non-Faradaic electrochemical modification of catalysis (NEMCA) of the double bond isomerization of an olefin was further demonstrated, the more challenging electrochemical promotion of an olefin methyl shift at the polymer electrolyte Pd/C cathode was less pronounced.

1. Introduction

The Non-Faradaic Electrochemical Activation of Catalytic Activity (NEMCA) or electrochemical promotion of catalysts was discovered by Vayenas [1, 2] using a yttria-stabilized zirconia (YSZ) oxide conductor in a solid oxide fuel cell configuration. Ethylene and oxygen were co-fed over the three phase interfaces at the Pt catalyzed anode. The expected catalytic oxidation of ethylene was observed at open circuit.

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{1}$$

When the cell potential was adjusted to initiate oxygen reduction at the cathode, concomitant with O^{2-} migration to the anode where the Faradaic oxidation of ethylene (eq. 2)

$$C_2H_4 + 6O^{2-}(YSZ) \rightarrow 2CO_2 + 2H_2O + 12e^- \tag{2}$$

occurs, an unexpected enhancement of the non-Faradaic catalytic process (Equation 1) was observed. The Equation 1 process was enhanced by up to 5 orders of magnitude greater than the $(I/2F)$ supply of O^{2-} from the cathode. Vayenas defined the rate enhancement ratio ρ, the enhancement factor Λ, and an approximate relationship between the absolute value of Λ and the exchange current I_o as follows:

$$\rho = \frac{r}{r_o}; \quad \Lambda = \frac{(r - r_o)}{(I/2F)} \quad |\Lambda| \approx 2Fr_0/I_0 \tag{3}$$

where r is the catalytic rate at a current I and r_o is the open-circuit rate of ethylene oxidation. A parameter used by Vayenas for the quantitative description of electrochemical promotion was the exchange current, I_o, for spillover O^{2-} redox in the presence of the co-fed reactant (e.g. ethylene).

We were first to report the electrochemical promotion of non-redox, unimolecular catalytic reactions, specifically the isomerization of alkenes on high surface area Pd/C cathodes of polymer electrolyte fuel cell membrane electrode assemblies (MEAs) [3]. FTIR and deuterium isotope studies elucidated the mechanism of electrochemically promoted 1-butene isomerization to cis- and trans-2-butene [4]. The predominant pathway is acid catalyzed isomerization at the metal surface with the initial step involving abstraction of a proton from the catalytic surface for addition to the C-1 carbon concomitant with return of a proton from the C-3 carbon, Figure 1.

The Pd/C was located at the fuel cell cathode (Figure 2). Hydrogen and olefins were delivered to the anode and cathode, respectively, via grooves cut into graphite flow field plates. The flow fields contact porous carbon diffusion backing layers. The highly porous diffusion layers (e.g. carbon cloth or carbon paper) have the dual functions of conducting electrons between the

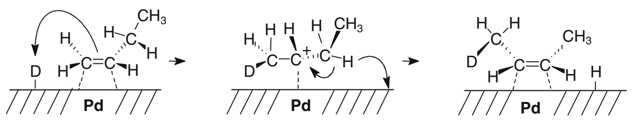

Fig. 1. Mechanism of proton spillover promoted 1-butene isomerization elucidated by deuterium isotope measurements.

flow field plates and the catalytic layers, while at the same time permitting reactants to flow freely to and from the catalytic layers. The catalytic layers sandwich the Nafion 117 polymer electrolyte membrane.

The gas diffusion layers, typically carbon paper at the anode and carbon cloth at the cathode, are about 300 μm thick. The catalytic layers are about 5–7 μm thick and the hydrated polymer membrane electrolyte (e.g. Nafion^{TM} 117) is about 200 μm thick. The catalyst inks, prepared by dispersing the catalysts into alcoholic solutions of soluble Nafion^{TM}, are deposited either on the diffusion layers or the polymer electrolyte surface before hot pressing. When the diffusion layers are catalyzed, the MEA is referred to as a 5-layer integrated MEA. This technology for MEA fabrication was pioneered by Raistrick [5, 6] and enhanced by Wilson [7]. The state-of-the-art MEA is a highly optimized porous electrode system. The advantage of porous electrodes for chemical transformations stem from the large interfacial area per unit volume of porous electrode (e.g. 10^4 cm^{-1}) [8]. This is coupled to the advantage of using a fuel cell configuration where the potential of the hydrogen anode is sufficiently negative to yield a galvanic cell when coupled to the olefin isomerization electrode [3]. The fuel cell configuration enables chemical transformations coupled to power generating Galvanic processes [9].

Figure 3 schematizes proton spillover onto the nanostructured Pd catalyst. Protons generated at the Pt anode, migrate through the Nafion membrane and chemisorb, with some charge compensation, onto the Pd surface concomitant with adsorption of the olefin at the Pd–Nafion interface. The source of the catalyst Nafion overlayer is solubilized Nafion (Aldrich) included in the catalyst ink. The Nafion overlayers are submicron layers that are required for ionic transport to the catalytic surfaces. The spillover protons effect acid catalyzed reactions prior to participation in electroreduction processes (i.e. reduction of the olefin). The catalytic activity and the selectivity of the three phase interface can be tuned by controlling the proton spillover rate via the electrode potential.

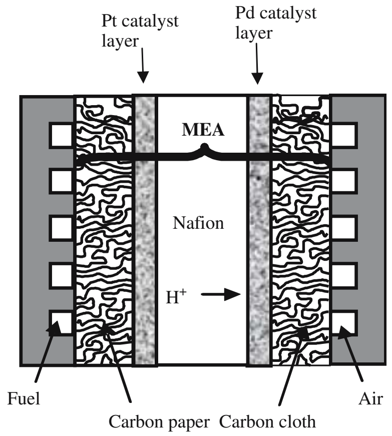

Fig. 2. Schematic of a polymer electrolyte fuel cell.

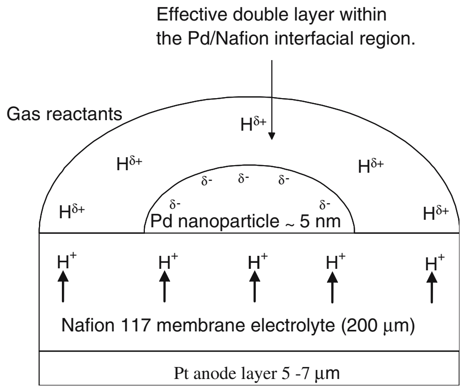

Fig. 3. Proton spillover onto a Pd catalyst particle (over coated with a thin film of Nafion from the catalyst ink prepared with solubilized Nafion) adhered to the Nafion 117 membrane electrolyte. The $H^{\delta+}$ are the result of spillover protons accompanied by their compensating charge in the metal forming an effective double layer.

Since isomerization reactions are not redox processes, the lack of an exchange current density [10] to relate to the electrode process motivated the introduction of the spillover proton enhancement factor, K, as the ratio of $(r - r_o)$ to the proton flux (Equation 4), where r is the rate at current I, r_o is the open-circuit rate and F is Faraday's constant [3].

$$\mathrm{K} = \frac{(r - r_o)}{(I/F)} \tag{4}$$

The maximum K value, obtained by Ploense in a galvanic fuel cell operating at 70 °C, for isomerization of 1-butene to both *cis*- and *trans*-butene (≈28) corresponds to the number of butene molecules isomerized per electro-migrated proton prior to consumption of the proton along with the electrochemical reduction of the olefin to butane [3]. The dependence of K on the catalyst composition and preparative method has not yet been established.

Here we extend the study of proton spillover promoted isomerization reactions to substituted olefins with an aim to effect skeletal rearrangement reactions in solvent free systems at low temperature. Such acid catalyzed isomerization reactions, an important area of research in the petroleum industry, are usually conducted on Pt or Pd supported on zeolites or clays. The acidic supports which function through their ability to accept and release protons serve to build up carbonium ions which are important intermediates in acid catalyzed reactions. The long term stability of the zeolites and or clay supports may pose a problem. In this work, the super acidic Nafion^{TM} is a substitute for the more traditional zeolites or clay support. The organic substrates selected were 2-3-dimethyl-1-butene and 3-3-dimethyl-1-butene.

2. Experimental

A Pd/C catalyst ink was prepared by dispersing 0.15 g of 30 wt%, Pd/C (Engelhard, Industries, Inc.) into 1 g of solubilized Nafion^{TM} (5% solution, Aldrich) and stirred (24 h). A Pt-black ink was prepared similarly (0.1 g Pt-black, Alfa Aesar Fuel Cell Grade and 0.35 g Nafion). Catalyst decals were prepared by repetitively brush painting ink onto a 5 cm^2 sheet of Teflon, annealing (120 °C, 20 min.), and weighing, until the desired catalyst loading (28 mg of Pd/C and 30 mg of Platinum black) was attained. The Pt and Pd/C decals were hot-pressed onto opposite faces of a Nafion^{TM} 117 sheet (130 °C, 100 psig, 30 sec). The temperature and pressure were increased (140 °C, 300 psig) and pressing continued for an additional 40 s. After cooling to room temperature, the Teflon sheets were peeled off leaving catalytic films on both faces of the Nafion^{TM}. The catalytic layers were overlaid with 20-wt. % Teflonized porous carbon cloth and inserted into the fuel cell assembly. The hot pressing of the membrane electrode assembly dehydrates the polymer electrolyte. Thus the electrodes must be conditioned prior to attempting to obtain reproducible results as previously discussed. Conditioning involves delivering humidified hydrogen and air to the anode and cathode respectively and then cycling the cell from open circuit to about 300 mV for several hours using a load unit. Although there are as many formulas for conditioning as there are workers in the field, all involve re-wetting of the catalysts with hydrated Nafion [11].

Although the load units are adequate for the conditioning process, they are not sufficiently precise for galvanic control of the cell at the very low currents required for study of non-Faradaic processes. Thus a Pine AFRDE5 Bi-Potentiostat was then connected to the fuel cell assembly at open circuit voltage to control the current through the 5 cm^2 fuel cell while reaction products were analyzed by gas chromatography. The cathode was purged with humidified N_2 at 100 standard cubic cm per minute at open circuit prior to introduction of the olefin. The liquid olefins were delivered, using an ISCO pump, to a modified GC injector port set at 85 °C. The vaporized olefin was then delivered via a venturi tube to a mixing chamber where the olefin was blended with a nitrogen carrier gas. Humidified hydrogen is delivered to the fuel cell anode. Cathode products were analyzed on-line using a Perkin Elmer Auto System gas chromatograph equipped with temperature controlled Arnel gas sampling valves with a 56.4 µl sample loop. An 80/100 *n*-octane/Porasil column was used for separation with a flame ionization detector for analysis of products.

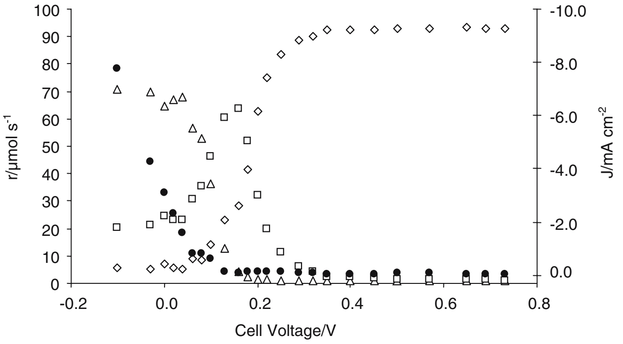

Fig. 4. Product distribution and proton spillover current of the isomerization and reduction of 2-3-dimethyl-1-butene (◇, 2,3DM1BE) versus cell potential. 2-3-dimethyl-butane (Δ, 2,3DMBA); 2-3-dimethyl-2-butene (□, 2,3DM2BE), current density (•).

3. Results and Discussion

Figure 4 shows the results of the 2-3-dimethyl-1-butene double bond shift study. The open circuit voltage with 2-3-dimethyl-1-butene at the Pd/C cathode and humidified hydrogen at the anode was 720 mV. From open circuit voltage to about 0.15 V, the only observed product was 2-3-dimethyl-2-butene. The isomerization reaction dramatically increased at approximately 300 mV positive of the current onset potential. The maximum rate of formation of the isomerized product occurred at about 0.15 V. At potentials lower than 0.15 V, the reduction to the alkane, 2-3-dimethy-butane, began to dominate. This is a striking demonstration of proton spillover promoted isomerization of an olefin. This NEMCA effect can be quantified using the rate enhancement ratio (ρ) as described by Vayenas, $\rho = r/r_o$ where r and r_o were defined earlier [12]. Table 1 shows that the maximum ρ value, attained at 0.16 V, was 1230.

Figure 5 shows the maximum value for spillover proton enhancement, K occurs at 0.16 V. Unfortunately, the reduction process begins to dominate and masks the electrochemically promoted isomerization process at lower potentials.

Figure 6 shows the product distribution resulting from the reaction of 3-3-dimethyl-1-butene (3,3DM1BE) at a Pd cathode. The primary product was 2-2-dimethyl-butane (2,2DMBA) generated during the simple reduction of the olefin. The formation of 2,2DMBA essentially tracked the current potential characteristics of the fuel cell. At −0.39 V there were low levels of the skeletal rearrangement product (2-3-dimethyl-butane) along with low levels of 2-methyl-butane that resulted from the loss of one methyl group. The latter two products were observed at potentials about 600 mV negative of the current onset. The isomerization products 2-3-

Table 1. The 2,3DM1BE isomerization rate enhancement ratio as a function of cathode potential

Potential/V	0.35	0.25	0.16	0.08	0
$\rho = r/r_o$	28	200	1230	677	464

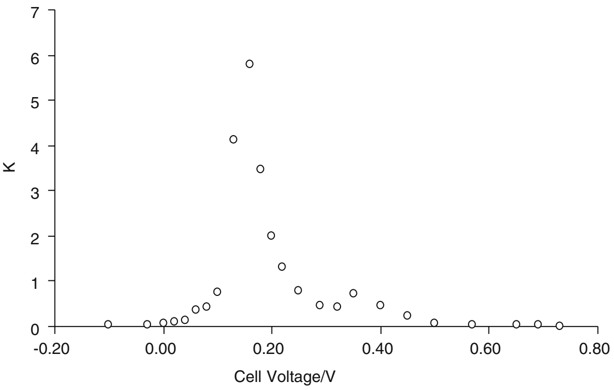

Fig. 5. Proton flux enhancement factor (*K*) of the isomerization of 2-3-dimethyl-1-butene.

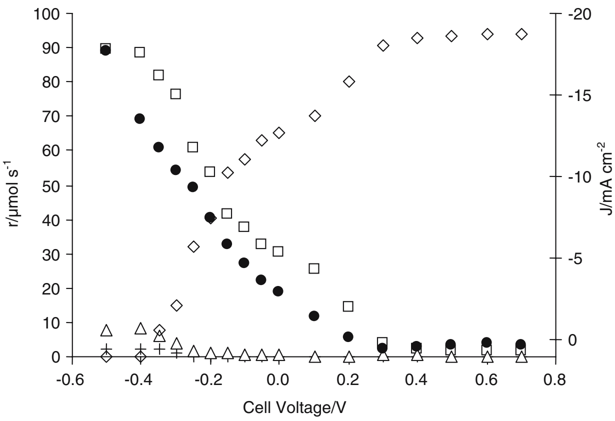

Fig. 6. Product distribution of the reaction of 3-3-dimethyl-1-butene (◇, 3,3DM1BE) at a Pd cathode. 2-methyl-butane (Δ, 2MBA); 2-2-dimethyl-butane (□, 2,2DMBA); 2-3-dimethyl-butane (+, 2,3DMBA); current density (•).

dimethyl-1-butene and 2-3-dimethyl-2-butene were not observed.

4. Conclusions

A dramatic proton spillover enhancement of the isomerization of 2-3-dimethyl-1-butene to 2-3-dimethyl-2-butene is observed to initiate at about 350 mV vs a hydrogen counter electrode in a galvanic fuel cell. The isomerization reaction is at a maximum at about 150 mV, after which the process is damped by the reduction of the olefin to the alkane. The ρ value for the isomerization reaction is over 1200 at 0.16 V with a proton flux enhancement of about 6.

In the case of 3-3-dimethyl-1-butene, the observed products were 2-2-dimethyl-butane, 2-3-dimethyl-butane and 2-methyl-butane. The skeletal rearrangement product, 2-3-dimethyl-butane, and the de-methylated product 2-methy-butane were found at relatively low levels. The primary product, resulting from the simple reduction of the double bond of the starting material essentially tracked the current potential characteristics of the fuel cell. The evidence for NEMCA promoted skeletal rearrangement of 3-3-dimethyl-1-butene at a Pd/C cathode is very weak. Low levels of the reduced skeletal rearrangement product were observed only at potentials very negative of the current onset.

In summary, although the spillover promoted isomerization of the substituted olefin, 2-3-dimethyl-1-butene, was dramatic, the proton spillover promoted skeletal rearrangement reaction of 3-3-dimethyl-1-butene remains elusive. The reduced product of a skeletal rearrangement reaction was observed at potentials substantially negative to the current onset potential. Experiments with alternative catalysts along with temperature dependent studies are now in progress.

Acknowledgements

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