

## Proton Spillover Promoted Isomerization of *n*-Butylenes on Pd-Black Cathodes/Nafion 117

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The electrochemical activation of heterogeneous catalysis, described by Vayenas as non-Faradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion,<sup>1</sup> is currently attracting considerable interest. NEMCA, an effect ascribed to the electrochemically induced and controlled spillover of ions from a solid electrolyte onto a catalyst surface, takes place at the three-phase boundary between the electrode catalyst, electrolyte, and reactant vapor phase. Until now, NEMCA has been demonstrated only for non-Faradaic catalytic reactions which are identical to the net electrocatalytic process (e.g. H<sub>2</sub>, O<sub>2</sub>/Pt-black/Nafion/Pt-black/O<sub>2</sub>, where catalytic oxidation of hydrogen by co-fed oxygen is enhanced by the electro-oxidation of hydrogen coupled to an oxygen cathode). The rate enhancement ratio  $\rho$ , the enhancement factor  $\Lambda$ , and an approximate relationship between the absolute value of  $\Lambda$  and the exchange current  $I_0$  are given in eq 1.

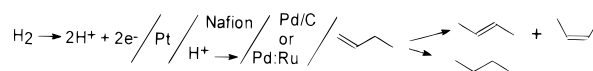
$$\rho = \frac{r}{r_0}; \quad \Lambda = \frac{(r - r_0)}{(I/2F)}; \quad |\Lambda| \approx 2Fr_0/I_0 \quad (1)$$

where  $r$  is the catalytic rate at a current  $I$  and  $r_0$  is the open-circuit catalytic rate. A key parameter for the quantitative description of NEMCA is the exchange current,<sup>2</sup>  $I_0$ , which expresses the rates of the anodic and cathodic processes of the electrocatalytic reaction at open circuit.<sup>3</sup>

NEMCA has been studied for over 40 catalytic reactions<sup>4</sup> on Pt,<sup>5</sup> Pd,<sup>6</sup> Rh,<sup>7</sup> Ni, Au, Cu, and Ag<sup>8</sup> surfaces interfaced to a variety of solid electrolytes, such as yttria-stabilized-zirconia (YSZ),<sup>9</sup>  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>,<sup>10</sup> CaF<sub>2</sub>, CsHSO<sub>4</sub>, CaZr<sub>0.9</sub>In<sub>0.1</sub>O<sub>3- $\alpha$</sub> , SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3- $\alpha$</sub> ,<sup>11</sup> Nafion,<sup>12</sup> TiO<sub>2</sub>, and aqueous alkaline solutions.<sup>13</sup>

We now report the first demonstration of NEMCA for nonredox catalytic reactions, specifically the isomerization of alkenes on high surface area Pd/C or unsupported Pd–Ru cathodes interfaced to Nafion with a Pt-black/H<sub>2</sub> counter electrode. A Nafion electrolyte fuel cell assembly (FCA)<sup>14</sup> was

### Scheme 1



used to study current–voltage and conversion–voltage relationships in the isomerization of 1-butene to *cis*- and *trans*-2-butene, shown in Scheme 1.

The catalytic–electrocatalytic reactor consists of a membrane electrode assembly (MEA), such as Pt-black/Nafion/Pd/C sandwiched between sheets of porous carbon cloth, housed in a FCA. The MEAs were prepared by the method of Wilson.<sup>15</sup> 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 (5% solution, Aldrich) and stirring (24 h). A Pt-black ink was prepared similarly (0.1 g of Pt-black, Alfa Aesar Fuel Cell Grade, and 0.35 g of Nafion). Catalyst decals were prepared by repetitively brush painting an ink onto a 5 cm<sup>2</sup> sheet of Teflon, annealing (120 °C, 20 min), and weighing, until the desired catalyst loading (28 mg of Pd/C and 30 mg of Pt-black) was attained. The Pt and Pd/C decals were hot-pressed onto opposite faces of a Nafion 117 sheet (130 °C, 100 psig, 30 s). The temperature and pressure were increased (140 °C, 1500 psig), and pressing was 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. The catalytic layers were overlaid with a 20 wt % Teflonized porous carbon cloth and inserted into the FCA. Current–voltage (*I*–*V*) data was obtained with a Pine potentiostat, used with the FCA anode shorted to the reference electrode input; the maximum current was <25 mA/cm<sup>2</sup> on high roughness factor (>250) electrodes. Thus, the H<sub>2</sub> anode is essentially a nonpolarizable reference electrode. The flow rates were 60 SSCM H<sub>2</sub> (15 psig) to the anode and 2.2–7.2 SCCM (0 psig) 1-butene to the cathode. The inlet feeds were saturated with H<sub>2</sub>O at 75 and 70 °C, respectively, with the FCA at 70 °C. Cathode products were quantified by GC-TCD/FID.

Figure 1 shows the *I*–*V* dependence of the steady state cathode exhaust component fluxes ( $\nu$ ) of *cis*- and *trans*-2-butene, and butane.

The NEMCA for the isomerization of 1-butene is apparent at low overpotentials and increases dramatically, even prior to 0.2 V where butane reduction becomes significant. Butane was the only reduction product detected by GC analysis; the butene reduction current efficiency was 100% from open circuit to short circuit. The striking electrochemical promotion of the isomerization of 1-butene to *cis*- and *trans*-butene is curtailed at 0.16 and 0.1 V, respectively, as the butene reduction current increases. Nafion-coated Pd/C exhibited no open circuit isomerization rate enhancement in comparison to bare Pd/C catalysts.<sup>16</sup> The  $\rho$  values for *cis*- and *trans*-butene at their maximum fluxes are approximately 38 and 46, respectively. Of the 40 reactions tabulated by Vayenas,<sup>1</sup> only two reactions have higher  $\rho$  values: the oxidation of ethylene by O<sub>2</sub> on Pt/YSZ at 260–450 °C ( $\rho = 55$ ) and the oxidation of ethylene by O<sub>2</sub> on Rh/YSZ at 250–400 °C ( $\rho = 90$ ). However, this is the first report of  $\rho$  values for nonredox reactions, and with the exception of hydrogen–oxygen recombination, the isomerization of butene at 70 °C is the lowest temperature reported for NEMCA.

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(16) A packed bed reactor was constructed with 316 stainless steel tubing (reactor volume 3 cm<sup>3</sup>). The catalysts (Nafion-coated Pd/C or bare Pd/C) were dispersed on glass wool prior to packing. The reactor was typically charged with ca. 0.5 g of Pd/C. Humidified 1-butene was fed (4 mL/min) at 70 °C. Analysis of the effluent by GC/FID showed comparable rates of 1-butene conversion (<2%) for Nafion-coated and bare Pd/C catalysts.

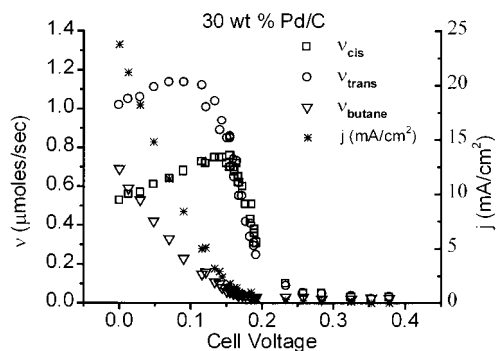


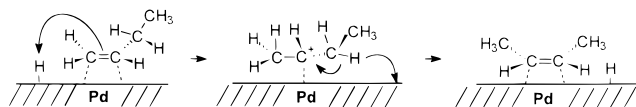
Figure 1.

Since the net reaction for the electrochemical process differs from the catalytic reaction, the relationship between  $\rho$  (for a nonredox process), the exchange current density for the electrochemical process ( $I_0$ ), and the enhancement factor ( $\Lambda$ ) requires clarification. Thus, we define  $K$  as the ratio of ( $r - r_0$ ) to the proton flux (eq 2).

$$K = \frac{(r - r_0)}{(I/F)} \quad (2)$$

The maximum value of  $K$  for the isomerization to both *cis*- and *trans*-butene is approximately 28. We view the above process as an acid-catalyzed isomerization reaction which occurs within the electrode double layer. Markovnikov<sup>17</sup> addition of a spillover proton to an adsorbed alkene to yield a secondary

### Scheme 2



carbonium ion, followed by abstraction of a proton from the C3 carbon would yield both isomers of 2-butene. This process can be schematized, as shown in Scheme 2, with spillover protons electromigrated from the hydrogen anode transiently available for the acid catalysis of 1-butene isomerization at the cathode three-phase boundary. On Pd/C, in this study, up to 28 molecules of butene undergo isomerization per electromigrated proton prior to consumption of the proton by the electrochemical reduction of butene to butane.

We attempted to measure the electrochemical promotion of another acid catalyzed reaction using the same fuel cell assembly (e.g., the esterification of acetic acid with methanol) and observed no enhancement; the esterification reactants lack carbon-carbon  $\pi$  clouds to facilitate adsorption to the Pd catalyst surface.

In conclusion, we have demonstrated the unprecedented electrochemical promotion of the heterogeneous catalysis of alkene isomerization. The  $\rho$  values for *cis*- and *trans*-butene formation in the galvanic fuel cell, at the maximum fluxes reported, are very high (approximately 38 and 46, respectively).

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