

Electrochemical activation of catalytic activity in the isomerization of hydrocarbons

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Abstract

The electrochemical activation of catalytic activity or NEMCA effect was investigated in a non-redox catalytic reaction by conducting the cathodic isomerization of 2,3dimethyl-1-butene (2,3DM1BE) in a Polymer Electrolyte Fuel Cell (PEFC). Experimental results showed that the selectivity, yield, rate of reaction and proton enhancement factor were modified by the electrically induced and controlled spillover of protons from the solid polymer electrolyte (Nafion) onto the metal surface (Pd). The isomerization of 2,3DM1BE is an acid-catalyzed process in which the double bond shift caused the rearrangement of the molecule to yield the most stable isomer.

Introduction

The use of electrochemistry to activate and precisely tune heterogeneous catalytic processes is a new development, which was first described by Vayenas as the Electrochemical Activation of Heterogeneous Catalysis or non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA). The first study of the NEMCA effect was accomplished by co-feeding the reactants (e.g., H₂, O₂ /Pt-black/Nafion/Pt-black/O₂) on the working electrode of a solid electrolyte cell, using the working electrode both as an electrode and as a catalyst for the catalytic oxidation of hydrogen by co-fed oxygen. This catalytic reaction was enhanced by the electro-oxidation of hydrogen coupled to an oxygen cathode. Results showed that there is a non-faradaic catalysis, that the reaction on the working electrode between H₂ and O₂ occurred as well and that it was depended upon the potential difference across the electrode [Vay 88]. NEMCA has been studied for over 40 catalytic reactions [Vay92] on Pt [Sob93], Pd [Vay90], Rh [Pli95], Ni, Au, Cu, and Ag [Beb92] surfaces interfaced to a variety of solid electrolytes, such as yttria-stabilized-zirconia (YSZ) [Cav93], β''-Al₂O₃ [Kar96], CaF₂, CsHSO₄, CaZr_{0.9}In_{0.1}O_{3-α}, SrCe_{0.95}Yb_{0.05}O_{3-α}, [Chi93], Nafion [Tsi97], TiO₂ and aqueous alkaline solutions [Neo94]. In order to quantify the NEMCA phenomenon, Vayenas defined the rate enhancement ratio ρ and the enhancement factor Λ, which are given by:

$$\rho = \frac{r}{r_o}; \quad \Lambda = \frac{(r - r_o)}{(I / 2F)}$$

where r is the catalytic rate at a current I and r_o is the open-circuit catalytic rate. It was found that the induced reversible change in catalytic rate (expressed in mol/s) can be up to 100 times larger than the catalytic rate before current application, i.e., there is up to a 10 000% rate increase. Furthermore, this rate increase can be up to 10⁵ times larger than the rate, I/nF, of supply of ions (e.g. O²⁻, Na⁺, H⁺) to the catalyst surface (where I is the applied current, n the ion charge and F is Faraday's constant). This implies that each ion supplied to the catalyst can cause up to 10⁵ adsorbed reactants to react and produce up to 10⁵ product molecules [Vayenas, 99]. Ploense and Smotkin [Plo97, Plo99] were the first to study the NEMCA effect

for non-redox catalytic reactions. For these processes, the net reaction for the electrochemical process differs from the catalytic reaction; therefore, the enhancement factor Λ was modified. Thus, Smotkin [Pl097, Pl099] defined K as the proton enhancement factor, as the ratio of $(r - r_0)$ to the proton flux:

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

Experimental

The membrane electrode assembly (MEA) was prepared by the method of Wilson [Wil92]. A Pd/C ink was prepared by dispersing 0.14g of 30 wt% Pd/C (Engelhard, Industries, Inc.) into 0.58 ml of solubilized Nafion (5% solution, Aldrich), then stirring for 24 h. Similarly, a Pt black ink was prepared using 0.1g of Pt/black (Alfa-Aesar Fuel Cell Grade) with 0.2 ml of Nafion solution. Catalyst layers of Pd/C ink and Pt/black ink were applied to a 20 wt% Teflonized porous carbon cloths (5 cm²), respectively. After annealing (120°C, 20 min), these catalyzed carbon cloths were hot-pressed onto the Nafion sheet (130°C, 400 psig) for 1 min. Temperature and pressure were increased (140°C, 1500 psig) for 1 min. The resulting MEA contained 4.5 mg/cm² of Pd/C and 5 mg/cm² of Pt/black on opposite faces of a Nafion sheet. The MEA was overlaid with a 20 wt% Teflonized porous carbon cloth and sandwiched between graphite blocks of a Fuel Cell Assembly.

The experimental apparatus is shown schematically in Figure 1. The complete reaction system consisted of the feed section, the PEM fuel cell and the analysis system. Fifteen temperature channels controlled by Labview software were used to control temperatures and avoid condensation of the liquids. Humidified H₂ and 2,3DM1BE/N₂ were delivered to the anode and cathode of the fuel cell, respectively. Humidification of gases was conducted at 75°C before being introduced to the fuel cell. The flow rates were 60 sccm of H₂, 0.5 μl/min (2,3DM1BE). The cathode potential was stepped from open circuit, V_{oc} , to negative potentials (reductive potentials) in small increments with simultaneous current measurement and quantification of cathodic products at isothermal conditions, 70°C. A Pine Potentiostat was utilized to carry out the electrochemical measurements and cathodic products were analyzed with a Chromatographer, Perkin Elmer Auto System with Arnel gas sampling valve and a FID detector including a 56.4 μl gas loop. Injections were performed onto a column packed with 80/100 N-Octane/ Porasil.

Results and Discussion

Figure 2 represents the product distribution of the cathodic isomerization and hydrogenation of 2,3DM1BE to 2,3DM2BE. When the potential was stepped from open circuit potential to negative potentials (reductive potentials), the concentration of the reactant, 2,3DM1BE decreased progressively. From open circuit potential to 0.15V, a single compound was detected with a significant rate of reaction, which was identified as 2,3 dimethyl-2-butene (2,3DM2BE), the isomer of 2,3DM1BE. This product was formed from a non-faradaic reaction (no electron transfer) as demonstrated by the low values of current in this interval of potentials. The isomerization of 2,3DM1BE to 2,3DM2BE was caused by a re-arrangement of the molecule by a double bond shift reaction, from 0.3 to 0.15V, the production of 2,3DM2BE increased dramatically, reaching a maximum at the latter potential. When the potential was stepped to more negative values than 0.15V, a faradaic reaction (with electron transfer) took

place, as demonstrated by the significant increase of the current. The only product formed from this reaction was identified as 2,3dimethylbutane (2,3DMBA).

The distribution of the rate enhancement ratio (ρ) as function of potential for the cathodic isomerization of 2,3DM1BE to 2,3DM2BE is presented in Figure 3. These results provided the evidence that the catalytic rate of reaction was enhanced by the applied electrical potential and that the catalytic activity of Pd/C was altered dramatically by supplying protons at the metal catalyst surface by applying an electrochemical potential. The maximum rate enhancement ratio in the production of 2,3DM2BE was obtained at 0.16V. The enhanced catalytic rate was 1230 times larger than the open circuit catalytic rate of reaction. Another key parameter for describing the electrochemical activation of heterogeneous catalysis is the proton flux enhancement factor, K, defined by Smotkin [Pl097, Pl099] as:

$$K=(r-r_0)/(I/F)$$

K shows how many molecules of 2,3DM1BE undergo isomerization per electromigrated proton prior to consumption of the proton by the electrochemical reduction of 2,3DM1BE to 2,3DMBA. The distribution of the proton enhancement factor as potential dependent for the cathodic isomerization of 2,3DM2BE is presented in Figure 4. When the electrical potential reached 0.16V, six molecules of 2,3DM1BE were isomerized due to the electromigration of one proton from the anode to the cathode of the fuel cell.

The distribution of the yield as potential dependent for the cathodic hydrogenation and isomerization of 2,3DM1BE is presented in Figure 5. The 2,3DM2BE yield shows a maximum yield of 0.66 at 0.16V and the production of 2,3DMBA shows a maximum yield of 0.75 at -0.1V. These results show that the use of electrochemistry can decrease efforts in the synthesis of new catalysts and that using a single catalyst, the reaction presents a variety of yields that can be selected by applying a specific potential to the fuel cell.

A proposed mechanism for the formation of 2,3DM2BE in a polymer electrolyte fuel cell is illustrated in Figure 6. The addition of a proton to an adsorbed molecule of 2,3DM1BE would yield a secondary carbonium ion, followed by abstraction of a proton from the C3 carbon, forming 2,3DM2BE via the catalytic reaction. Regarding the electrocatalytic reaction, 2,3DM1BE is reduced to the saturated hydrocarbon 2,3DMBA.

Conclusions

We view the isomerization of 2,3DM1BE to 2,3DM2BE as an acid-catalyzed process that occurred in the cathode three-phase boundary: solid polymer electrolyte, metal catalyst and reactant. We consider that the double bond shift reaction of the cathodic isomerization of 2,3DM1BE to 2,3DM2BE is a non-faradaic process, in which the double bond shift caused the rearrangement of the molecule to yield the more stable isomer. We have shown that the rate of reaction, proton enhancement factor, selectivity and yield, in the isomerization of 2,3DM1BE have been modified by the electrically induced and controlled spillover of protons from the solid polymer electrolyte (Nafion) onto the metal surface (Pd), which confirms the presence of the NEMCA effect in this reaction.

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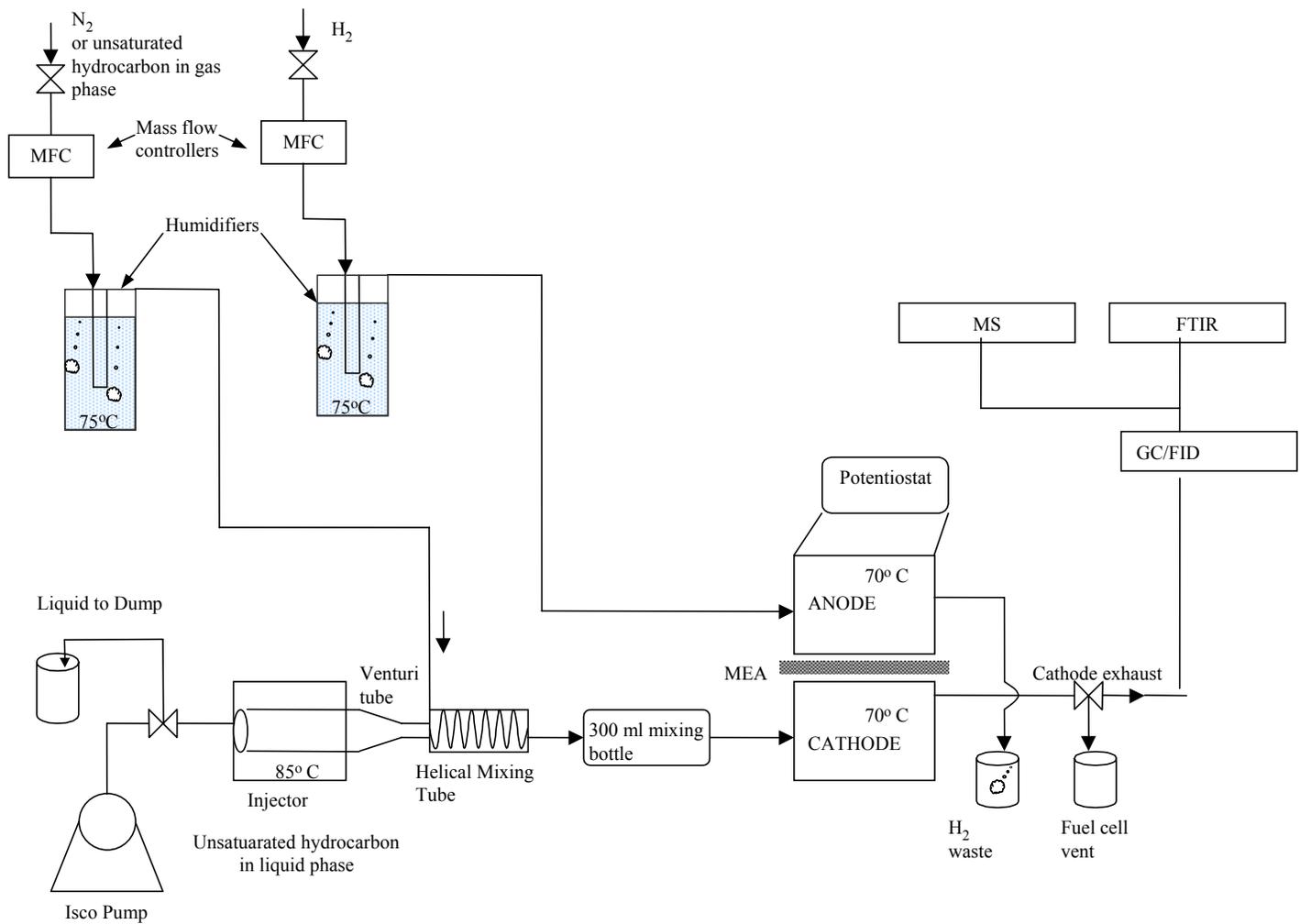


Figure 1. Schematic Drawing of the Experimental Set-Up for the Isomerization and Hydrogenation of Unsaturated Hydrocarbons in a Polymer Electrolyte Fuel Cell

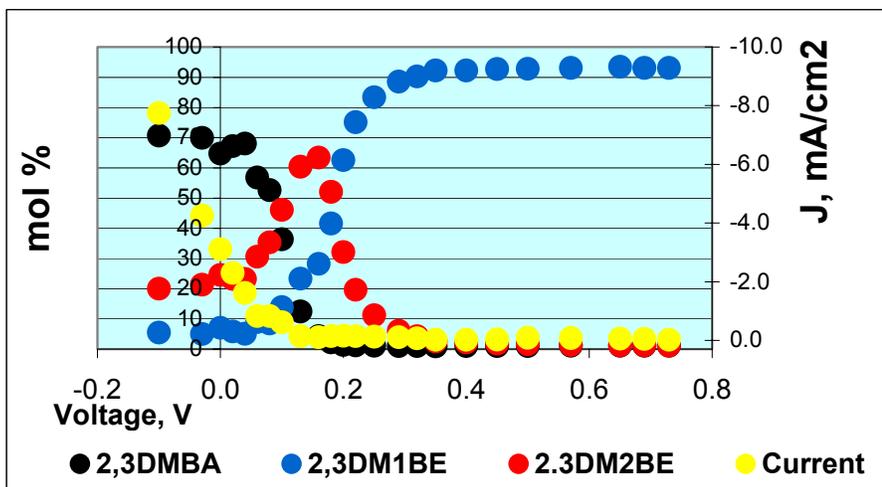


Figure 2. Product Distribution of the Cathodic Isomerization and Hydrogenation of 2,3DM1BE

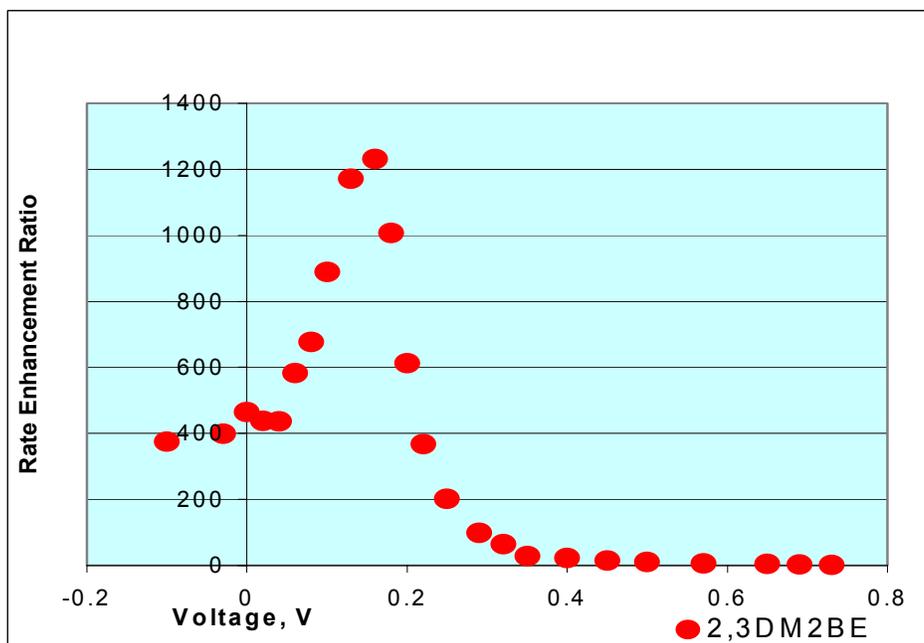


Figure 3. Distribution of the rate enhancement ratio. Cathodic Isomerization and Hydrogenation of 2,3DM1BE

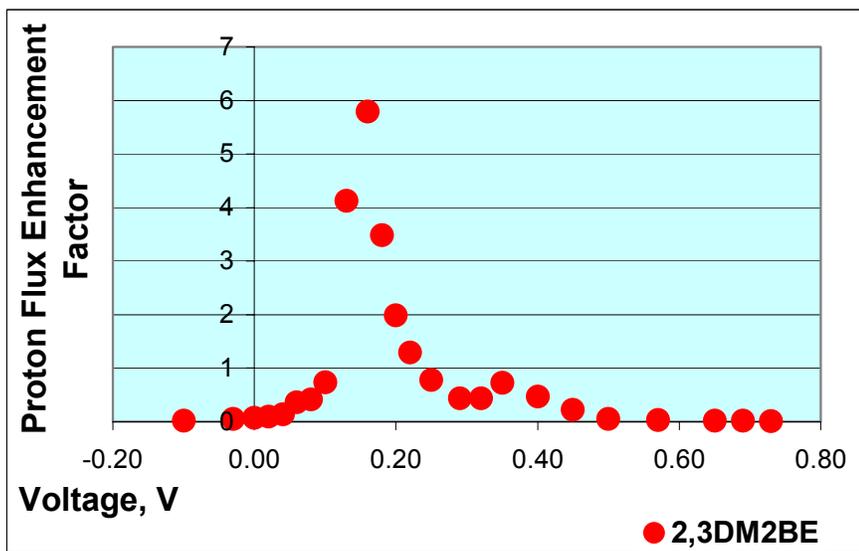


Figure 4. Distribution of the Proton Flux Enhancement Factor (K). Cathodic Isomerization and Hydrogenation of 2,3DM1BE

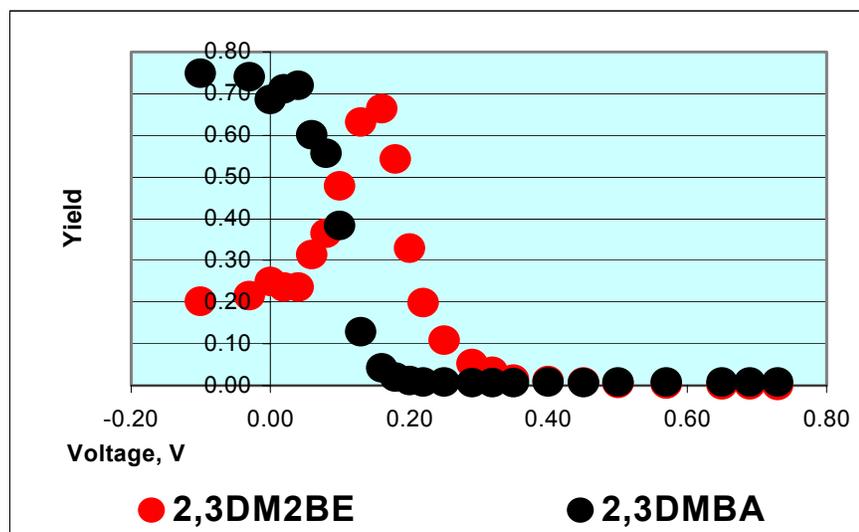


Figure 5. Distribution of Yields of 2,3DM2BE and 2,3DMBA. Cathodic Isomerization and Hydrogenation of 2,3DM1BE

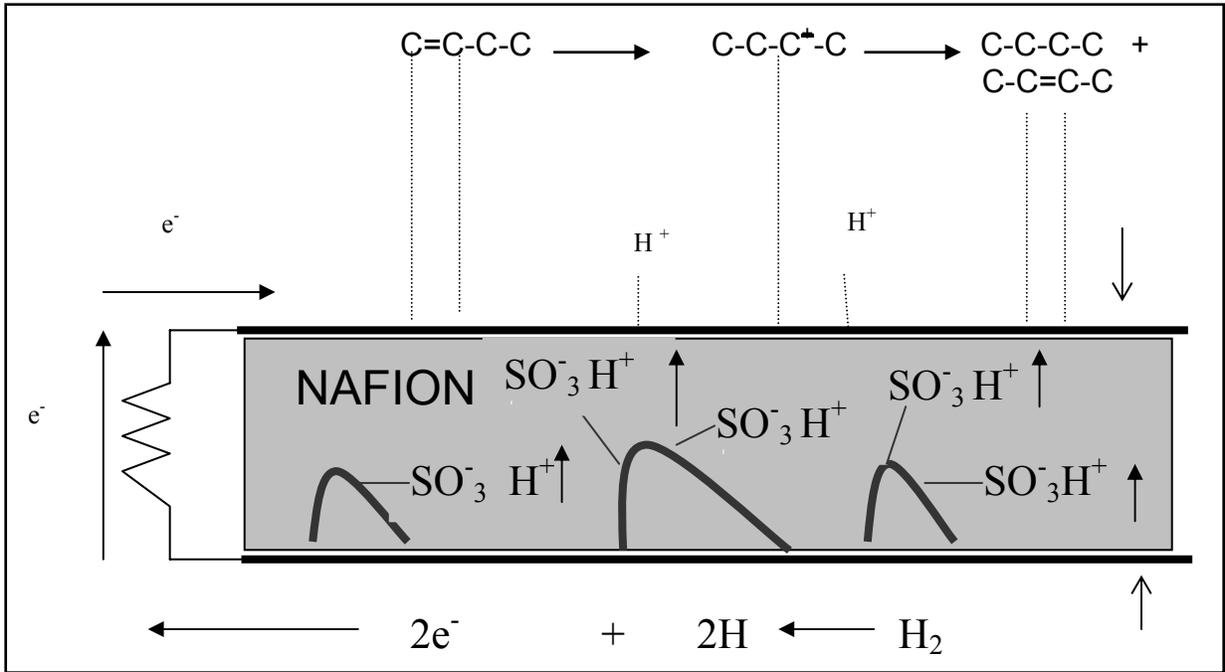


Figure 6 Proposed mechanism for the formation of Cathodic Isomerization and Hydrogenation of 2,3DM1BE