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A study of the electrochemical hydrogenation of o-xylene in a PEM hydrogenation reactor

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1. Introduction

1.1. General introduction

Hydroprocessing is commonly used in the petroleum refining industry. Current industrial hydro-processes operate over a range of temperatures (\sim 300–425 °C) and pressures (20–130 atm). Much of the hydrogen that is used in the refining industry comes from the steam reformation of natural gas. Steam reforming has a high energy demand to provide the endothermic heat of reaction plus the sensible heat needed to attain its high operating temperature. It also generates a large amount of carbon dioxide that contributes to climate change.

The current study examines a technique that might decrease both the energy demand for hydroprocessing and the accompanying quantity of greenhouse gases. Electrochemical hydrogenation can be performed at a much lower temperature and pressure than hydroprocessing, but requires an input of electrical power. The overall intent is to reduce the amount of energy required. Both electrochemical hydrogenation and hydroprocessing produce hydrogenated hydrocarbons, H₂S, and NH₃ as products. Capture and storage of the carbon dioxide from the steam reforming reaction is a financial burden to the petroleum industry which can be eliminated by replacing steam reforming with electrochemical hydrogenation.

ABSTRACT

In this study, we investigate the electrochemical hydrogenation of o-xylene in a proton exchange membrane hydrogenation reactor (PEMHR). The reactor was operated isothermally over the temperature range 20–68 °C and at a pressure of 1 atm in a semi-batch mode. Hydrogen was fed into the anode compartment and o-xylene into the cathode. The hydrogenation efficiency was investigated at different current densities and temperatures. Results obtained show that the hydrogenation efficiency increases with temperature but decreases with current density. At low current densities the hydrogenation efficiency approaches 100%. A zero dimensional model was used to fit the data and extract a rate constant for the hydrogenation reaction. The activation energy for this reaction was found to be 28 kJ/mole.

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Hydrogenation is also an important process in the food industry. In the hydrogenation of unsaturated fats to saturated fats in the vegetable oil industry, the high temperature and pressure used often results in the formation of trans-fats that have been associated with coronary heart disease. High temperatures and pressures also cause a break down in good but unstable saturated fats.

As an alternative to hydroprocessing, a number of researchers have recently investigated electrochemical hydrogenation using a proton exchange membrane (PEM) reactor. In a PEM hydrogenation reactor (PEMHR), hydrogen, introduced directly or produced at the anode by the electrolysis of water, is oxidized at the anode to produce protons that migrate through the proton conducting membrane in response to the applied potential. At the cathode, the protons in the electrolyte are reduced to hydrogen atoms adsorbed on the electrode metal, which can react to hydrogenate unsaturated compounds flowing through the cathode compartment. PEMHRs offer several advantages over conventional catalytic hydrogenation reactors. High temperatures and elevated pressures are not required. The lower temperatures reduce energy consumption and allow thermally unstable molecules to be hydrogenated. The rate of supply of hydrogen to the cathode is easily controlled, by adjusting the current.

In this study we report the results of the electrochemical hydrogenation of o-xylene. The o-xylene molecule has an aromatic ring and two methyl groups. It was chosen to be a model of the larger complex aromatic compounds that have both condensed aromatic rings and side chains, and form a major part of the heavy oils in the Canadian oil sand deposits.

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Fig. 1. Schematic illustrating the experimental set-up.

1.2. Hydrogenation in PEMHR

Research on PEMHRs has been relatively limited. In pioneering work, Langer et al. [1–4] studied the electrogenerative hydrogenation of a number of alkenes. Ogumi et al. [5–7] have studied the electrohydrogenation of olefins as well as a number of other organic reduction and oxidation reactions. More recently, Pintauro et al. [8–11] have studied both the hydrogenation of edible oils in a PEMHR as well as the electrochemical hydrogenation of glucose [12,13]. A series of studies have been carried out by Ma and coworkers [14–16] using a PEMHR to hydrogenate a variety of organic compounds. Recently, Sedighi and Gardner [17] have studied the electrochemical hydrogenation of ethylene in a PEMHR.

2. Experimental

2.1. Cell and membrane electrode assembly

Experiments were made using a single PEM electrochemical cell having a 25 cm² surface area manufactured by ElectroChem Inc. The membrane electrode assembly (MEA) used in these experiments had a carbon supported platinum catalyst at both the anode and cathode (loading: 1 mg Pt cm⁻²) and used NafionTM 115 as membrane material. Pure hydrogen, which had been humidified by bubbling it through water (Fig. 1), was fed to the anode continuously on a once-through basis and this electrode was used as a reference electrode for the measurement of the cathode potential.

In this study, a batch of o-xylene was stored in an external tank and then pumped through the cathode compartment of the PEMHR and then recycled back to the storage tank. Molecular hydrogen is oxidized at the anode to form protons that migrate across the Nafion membrane in response to the applied potential. At the cathode, atomic hydrogen is generated on the platinum catalyst surface by the reduction of these protons as shown in Eq. (1).

$$H^{+} + e^{-} + S \Leftrightarrow H - S; \quad \vec{k}_{H,red}$$
(1)

The electrogenerated hydrogen atoms at the cathode then either react with the aromatic bonds in the o-xylene (Eq. (2)) or else combine in an unwanted side reaction to form molecular hydrogen (Eq. (3)).

$$-CH=CH-+2H-S \rightarrow -CH_2-CH_2-+2S; \quad k_{hvdrog}$$
(2)

$$2H - S \Leftrightarrow H_2 + 2S; \quad \vec{k}_{H,des}, K_H$$
 (3)

where S represents a surface site on the platinum catalyst.

In our experimental set-up, any hydrogen gas that is evolved is carried with the o-xylene back to the o-xylene storage tank where it is separated and its rate of production measured (Fig. 1). It is then exhausted into the fume hood. The rate of hydrogen production was measured as a function of current to determine the efficiency of the hydrogenation process as per Eqs. (4) and (5).

The reaction was carried out at a constant flow rate of o-xylene and at temperatures ranging from 25 °C to 68 °C. The input pressure of the hydrogen to the flow meter was maintained at 377 kPa. The total pressure in the anode and cathode compartments of the PEMHR was maintained at 1 atm. The hydrogen gas inflow rate was controlled using a rotameter. The hydrogen flow rate was kept at about 100 ml/min, significantly higher than the amount required to support the maximum current (approximately 77 ml/min at 10 A). The o-xylene recycle flow rate in the cathode was maintained at 300 ml/min to ensure the system was isothermal. The recycle flow rates that are needed to maintain thermal equilibrium and to remove the evolved hydrogen are many orders of magnitude higher than the rate of removal of o-xylene through hydrogenation. At a 10 A current, a maximum of 1.25×10^{-2} ml/min is required to support the hydrogenation reaction. The results that we report for the rates of hydrogen production and utilization are thus expected to be independent of o-xylene flow rates at practical flow rate values.

Since hydrogen is the only gaseous entity in the exit flow, the amount of hydrogen that was consumed or utilized in the hydrogenation reaction per second, $V_{reacted}$, is deduced by subtracting the measured amount of hydrogen in the cathode exit, V_{out} , from



Fig. 2. Comparison of the theoretical and measured rate of hydrogen production at the cathode with no o-xylene present at the cathode: electrode area = 25 cm^2 corresponding to a maximum current of 10 A.

the theoretical amount of hydrogen that migrates across the membrane, V_{theor} , in response to the current flow as shown in Eq. (4).

$$V_{reacted} = V_{theor} - V_{out} = \frac{IRT}{2PF} - V_{out}$$
(4)

The hydrogenation efficiency can then be defined as

$$\eta_{hydrog.} = \frac{V_{reacted}}{V_{theor}} \times 100 = 100 \times \left(1 - \frac{2PFV_{out}}{IRT}\right)$$
(5)

A hydrogen production experiment (Fig. 2) carried out without o-xylene at the cathode confirmed that the amount of hydrogen produced agreed with the amount expected theoretically and that there was no significant permeation of hydrogen gas through the membrane.

2.2. Electrochemical measurements and data acquisition

A Kikusui Model PBX 20-10 Bi-Polar Power Supply, connected in parallel with the electrochemical cell, was used to control the cell current. The power supply was programmable so that the cell could be cycled through a predetermined current profile. A Fluke Hydra data logger was used to monitor and capture cell potential and current for final analyses using a desktop computer. One channel of the data logger was directly connected to the electrochemical cell to measure the cell potential while a second channel monitored cell current from a connection on the bipolar power supply. Constant current measurements were made at specific currents over a current range from 0 to 10A to determine the efficiency of the hydrogenation process. Polarization curve experiments were performed, by ramping the current from 0 to 10A at a rate of 20 mA/s.

3. Results and discussion

3.1. Effects of current density and temperature on the hydrogenation efficiency

The hydrogenation efficiency (Eq. (5)) was measured as a function of current density and temperature. As explained in the experimental section, to do this the rate of molecular hydrogen gas production was measured as a function of current and then the o-xylene hydrogenation reaction or utilization rate is deduced by subtracting the measured amount of hydrogen in the cathode exit from the theoretical amount of hydrogen that migrates across the



Fig. 3. Rate of hydrogen production at the cathode with o-xylene present at the cathode; electrode area = 25 cm^2 corresponding to a maximum current of 10 A.

membrane based on the current that is being passed through the cell (Eq. (4)). Results for the rate of molecular hydrogen gas evolution from the cathode as a function of current and temperature are shown in Fig. 3. The results show clearly that the amount of hydrogen that is evolved generally decreases with increasing temperature indicating that more hydrogen is being consumed in the hydrogenation reaction as the temperature increases.

Fig. 4 shows the rate of hydrogen utilization, $V_{reacted}$, as a function of current and temperature. The results show that the hydrogen utilization rate increases up to some value and then remains essentially constant. There are two possible explanations for this constant value that is reached: (a) the rate is limited by the hydrogenation rate; or else (b) it is limited by the rate of diffusion of o-xylene through the gas diffusion layer (GDL) to the cathode. Calculation shows that it is unlikely that the rate is being limited by the rate of diffusion of o-xylene to the cathode. Using typical values for the GDL thickness and porosity [18], we estimate that only 2.5% of the o-xylene contained in the GDL would be consumed to support the 10 A current for 1 min. This conclusion is also supported



Fig. 4. Rate of hydrogen utilization at the cathode with o-xylene present at the cathode at various temperatures: electrode area = 25 cm² corresponding to a maximum current of 10 A.



Fig. 5. Change in cell potential as a function of time in response to a 9 A to 1 A current step.

by potential step measurements. Fig. 5 shows how the cell potential changes in response to a step from 9A to 1A. If the rate was being controlled by the rate of diffusion of o-xylene to the cathode, it would be expected that the cell potential would slowly decrease as the concentration of o-xylene increased when the current was stepped from 9A to 1A. This behaviour is not observed. The small increase in cell potential is consistent with a reduction in hydrogen atom concentration at the lower current (potential). We thus conclude that the rate of hydrogen utilization is being limited by the rate of hydrogenation and not by the rate of diffusion. The limiting hydrogen utilization rate is strongly temperature dependent indicating that the hydrogenation rate is increasing with temperature as might have been expected.

Fig. 6 shows the effects of current density on the hydrogenation efficiency of the PEM reactor at various temperatures. At low current densities, the hydrogenation efficiency can approach 100%. Similar results have also been reported [11] for the hydrogenation of vegetable oils. Increasing the temperature (Fig. 7) generally results in an increase in the hydrogenation efficiency presumably because of an increase in the hydrogenation rate constant. The reason for the decrease observed in the 10 A curve at high temper-



Fig. 6. Hydrogenation efficiency as a function of current density at various temperatures.



Fig. 7. Hydrogenation efficiency as a function of temperature at various current densities.



Fig. 8. Polarization curves: (a) hydrogen at the cathode; (b) o-xylene at the cathode.

atures is unclear but probably results from increased experimental uncertainty at the higher temperatures.

3.2. Cathodic polarization curves

Fig. 8 shows the polarization curves at 46 °C for the cases where o-xylene is flowing through the cathode compartment (hydrogenation and hydrogen evolution) and where the cathode compartment contains only hydrogen (hydrogen evolution). Noticeable in this figure is the positive shift of the open circuit cathode potential at low current densities when o-xylene flows through the cathode compartment compared to hydrogen gas being at both electrodes. This positive shift results from the reduction in hydrogen partial pressure at the cathode as a result of the hydrogenation reaction. While the hydrogen pressure at the cathode is reduced as a result of the hydrogenation reaction. The shift in cathode potential can be related to the hydrogen pressure at the cathode by the Nernst equation:

$$\Delta \eta_C = \frac{RT}{2F} \ln \left[\frac{P_{\text{anode}}^{\text{H}_2}}{P_{\text{cathode}}^{\text{H}_2}} \right]$$
(6)

The observed shift in cathode potential (\sim 0.03 V) corresponds to an equilibrium hydrogen pressure of only about 0.1 atm at low current density indicating that the hydrogenation reaction consumes a substantial portion of the hydrogen that migrates across the membrane into the cathode compartment under these conditions. At very low currents, the hydrogenation reaction occurs spontaneously and does not involve the consumption of external power. The main loss mechanism in the reactor is, in fact, due to IR loss in the membrane. Selection of the optimum operating current for the reactor will depend on a trade-off between operating and capital costs.

4. Modelling o-xylene hydrogenation

4.1. Hydrogenation mechanism

In our studies, we have not analysed the product stream and do not know if significant amounts of mono- or di-enes are being formed. It is our assumption, that similar to the catalytic hydrogenation of benzene [19], once the first bond in an o-xylene is hydrogenated, hydrogenation of the other bonds will follow to give a completely saturated product. The anodic reaction can be written as

$$6H_2 \Leftrightarrow 6H^+ + 6e^- \tag{7}$$

While the cathodic reaction is assumed to be

$$6H^+ + 6e^- + o$$
-xylene $\Leftrightarrow 1, 2$ -dimethylcyclohexane (8)

The overall reaction in the cell is assumed to be the hydrogenation of o-xylene to form 1,2-dimethylcyclohexane according to the reaction:

$$6H_2 + o$$
-xylene $\Leftrightarrow 1, 2$ -dimethylcyclohexane (9)

The above equations describe the overall reactions in the cell but do not describe the detailed mechanism by which the hydrogenation occurs. Of the many mechanisms postulated for the hydrogenation of unsaturated hydrocarbons, the following three, based on experiments with ethylene, are often referenced:

4.1.1. Jenkins-Rideal mechanism

In the Jenkins–Rideal mechanism [20], the hydrogen radical that is absorbed on the platinum catalyst is assumed to react directly with the unadsorbed unsaturated hydrocarbon.

4.1.2. Horiuti-Polanyi mechanism

The Horiuti–Polanyi mechanism [21] postulates that unsaturated hydrocarbon is first adsorbed on the catalyst surface with hydrogenation then proceeding via reaction with atomic hydrogen radicals that were dissociatively adsorbed on the catalyst surface. Polanyi and Greenhalgh [22] extended this concept to the hydrogenation of benzene.

4.1.3. Twigg mechanism

The Twigg mechanism [23] combines features of both of the above models in that it is assumed that molecular hydrogen from the gas phase reacts with adsorbed hydrocarbon to add one of its hydrogen atoms to the hydrocarbon with the other forming an adsorbed hydrogen radical and that further hydrogenation occurs with the addition of an atomic hydrogen radical.

All three of these mechanisms result in the same final products. We have given preference, however, to the Jenkins–Rideal mechanism because, of the three, it appears to be most applicable to electrochemical hydrogenation and we have used this mechanism in our model. This mechanism is expected to be dominant because hydrogen is being continuously transferred from the anodic compartment to the cathodic compartment by the current and, as a result, adsorbed hydrogen radicals are expected to become readily available on the cathode catalyst. We suspect that any adsorbed oxylene will be quickly removed and replaced by adsorbed hydrogen radicals.

In initial attempts at modelling the hydrogenation of o-xylene, we attempted to fit the hydrogen utilization and polarization data to a Jenkins-Rideal type model assuming that once the initial aromatic bond had been hydrogenated by two hydrogen atoms, the hydrogenation of the remaining bonds proceeded very rapidly once again with the consumption of 6 hydrogen atoms. Using this assumption, we found we were unable to fit both the polarization and hydrogen utilization data adequately. The high rate of hydrogen consumption shifts the cell potential to higher positive potentials than are observed experimentally at low currents. We found, however, that we were able to get a good fit to the experimental data using the Jenkins-Rideal model if we assumed that the hydrogenation of each aromatic bond proceeded sequentially and that after one aromatic bond had been hydrogenated, then the next two pi bonds would begin to be rapidly hydrogenated in series at the same rate. As mentioned earlier, in our experiments we have not analysed the product stream to determine if significant amounts of mono- or di-enes are being formed but based on previous studies with benzene [19] in our model we assume that 1,2-dimethylcyclohexane and molecular hydrogen are the only products.

4.2. Modelling results

A zero-dimensional model, similar to that used by Zhang [24], has been used to model the reactions at the cathode. In this model it is assumed that the cathode chamber is perfectly mixed and that diffusion across the gas diffusion layer is rapid so that bulk concentrations are present at the catalyst surface. The cathode reactions are assumed to consist of the reversible hydrogen adsorption/desorption reaction, the reversible hydrogen electro-oxidation/reduction reaction as well as an irreversible xylene hydrogenation reaction as shown in Eqs. (1)–(3).

Adopting a zero dimensional model leads to the following set of equations for the rates of these reactions:

$$r_{\rm H,red} = -r_{\rm H,ox} = -2\vec{k}_{\rm H,ox}\theta_{\rm H} \sinh\left(\frac{\alpha F\eta_{\rm C}}{RT}\right)$$
(10)

Eq. (10) gives the rate at which protons are reduced at the cathode to form adsorbed hydrogen atoms as shown in Eq. (1).

$$r_{hydrog.} = \overline{k}_{hydrog.} C_{oX} \theta_{H}^{2}$$
(11)

Eq. (11) gives the rate of the desirable o-xylene hydrogenation reaction as shown in Eq. (2).

$$r_{\mathrm{H},des} = -r_{\mathrm{H},ads} = \vec{k}_{\mathrm{H},ads} K_{\mathrm{H}} \theta_{\mathrm{H}}^2 - \vec{k}_{\mathrm{H},ads} P_{\mathrm{H}_s}^b \theta_0^2; \quad \theta_0 = 1 - \theta_{\mathrm{H}} \quad (12)$$

Eq. (12) gives the rate of the undesirable reaction, the formation of hydrogen gas. Since the hydrogen atom surface coverage, $\theta_{\rm H}$, is potential dependent, all of the above rates (Eqs. (10)–(12)) are expected to be potential (current) dependent.

Using the rate expressions given above, the following set of six coupled ordinary differential equations can be derived considering the time dependence of the surface species, $\theta_{\rm H}$, the material balance at the cathode ($C_{\rm oX}^{\rm b}$, $C_{\rm dMC}^{\rm b}$, $P_{\rm H_2}^{\rm b}$ and $\nu_{\rm H_2}$) and conservation of charge at the cathode (η_c). All of these parameters depend on current and time and are thus variable in the calculation.

Using the rate expressions given above, the time dependence of the hydrogen surface coverage can then be expressed as follows.

$$\frac{d\theta_{\rm H}}{dt} = \frac{1}{F\gamma C_t} (r_{\rm H,ads} - r_{\rm H,ox} - r_{hydrog.})$$
(13)

The material balance for species i in the cathode chamber can be written as follows.

$$V\frac{dC_{i}^{b}}{dt} = \nu_{0}C_{i}^{0} - \nu C_{i}^{b} - N_{i}A = \nu_{0}C_{i}^{0} - \nu C_{i}^{b} - \frac{r_{i}A}{n_{i}F}$$
(14)

If the reactor is treated as a well stirred batch reactor of volume *V*, there is no net inflow or outflow of o-xylene (oX) or 1,2-dimethylcyclohexane(dMC) from the reactor and, for these species, Eq. (14) reduces to:

$$V\frac{dC_i^b}{dt} = -\frac{r_i A}{n_i F} \tag{15}$$

In Eq. (14), N_i represents the flux of species *i* to the surface which involves one or more of the rate expressions. This then leads to the following equation for the time dependence of the oX and dMC concentrations in the reactor.

$$\frac{dc_{\rm oX}^b}{dt} = -\frac{A}{6VF}r_{hydrog.} \tag{16}$$

$$\frac{dc_{\rm dMC}^b}{dt} = \frac{A}{6VF} r_{\rm hydrog.} \tag{17}$$

To calculate the material balance equation for the hydrogen, account must be taken of the hydrogen that flows out from the reactor, $\nu C_{H_2}^b$, and both the second and third terms of Eq. (14) must be retained. Conversion of the hydrogen concentration term to partial pressures using the ideal gas and Dalton's laws, $C_{H_2} = P_{H_2}/RT$, gives the following expression for the time variation of the gas partial pressure in the cathode compartment.

$$\frac{dP_{\rm H}^b}{dt} = \frac{ART}{2FPV} [P_{\rm H_2}^b - P] r_{\rm H,ads}$$
(18)

The rate of hydrogen production in the reactor is governed by the difference in the rate of hydrogen reduction and the rate of hydrogenation and is given by the equation

$$\frac{d\nu_{\rm H_2}}{dt} = \frac{ART}{2FP}(-r_{\rm H,ox} - r_{hydrog.})$$
(19)

From the charge conservation consideration, the following expression is obtained for the time dependence of the cathode potential.

$$\frac{d\eta_C}{dt} = \frac{A}{C_{dl}}[j - r_{\mathrm{H,ox}}]$$
(20)

The double layer capacitance, C_{dl} , appears in Eq. (20) because, when there is a change in potential, some of the current is used for double layer charging. A typical literature value [24] has been used for C_{dl} in our calculation.

The resulting system of six coupled ordinary differential equations (ODE – Eqs. (13), (16)–(20)) were solved using Scilab[®] software. In our simulations, literature values [24] for $K_{\rm H}$, $k_{\rm H,ads}$ and $k_{\rm H,ox}$ have been used and are included in Table 1. The only kinetic parameter that was adjusted to fit the modelled data to the experimental data was the hydrogenation rate constant, k_{hydrog} . A full list of the parameters and symbols used in our calculations is given in Table 1. The values of k_{hydrog} . at various temperatures were obtained by fitting the calculated hydrogen production data to the experimental data. Several of these fits are shown in Fig. 9. A comparison of the experimental and calculated hydrogenation efficiencies of the reactor is shown in Fig. 10. It is seen that the fitted data generally agrees well with the experimental data.

From the temperature dependence of the hydrogenation rate constant (Fig. 11), the activation energy for the electrochemical o-xylene hydrogenation reaction is determined to be 28 kJ/mole. This value is close to the value of 25 kJ/mole obtained [25] for the electrochemical hydrogenation of ethylene at a platinum electrode. The activation energy for hydrogenation at a gas–solid (platinum) interface [25] is almost double this value (45.8 kJ/mole). This higher



Fig. 9. Comparison of the measured and calculated rate of hydrogen production at various temperatures: electrode area = 25 cm² corresponding to a maximum current of 10 A.



Fig. 10. Comparison of the measured and calculated hydrogenation efficiencies at various temperatures.



Fig. 11. Plot of log(hydrogenation rate constant) vs 1/T to determine the activation energy.

Table 1		
Symbols and	model	parameters.

Symbol	Definition	Value	Units	Symbol	Definition	Value	Units
F	Faraday constant	96,485	$\rm Cmol^{-1}$	$P_{\rm H_2}^b$	Partial pressure of hydrogen	Variable	atm
Α	Surface area	25	cm ²	r _{hvdrog}	Hydrogenation reaction rate	Variable	A cm ⁻²
$k_{\mathrm{H,ox}}$	Hydrogen oxidation constant	4	$\mathrm{Acm^{-2}atm^{-1}}$	r _{H,ads}	Hydrogen adsorption reaction rate	Variable	$A cm^{-2}$
$k_{\mathrm{H,ads}}$	Hydrogen adsorption constant	402	$\mathrm{Acm^{-2}atm^{-1}}$	r _{H,ox}	Rate of hydrogen oxidation/reduction	Variable	$A cm^{-2}$
K _H	Hydrogen adsorption equilibrium constant	0.5	A cm ⁻² atm ⁻¹	j	Current density	Variable	A cm ⁻²
k _{hydrog}	Xylene hydrogenation constant	Variable	A cm ⁻² atm ⁻¹	η_c	Cathode overpotential	Variable	V
V	Volume		cm ³	C_{dl}	Double layer capacitance	0.45	
ν	Volumetric outlet flow rate	Variable	cm ³ min ⁻¹	γ	Electrode roughness factor	100	
v_0	Volumetric inlet flow rate	0	cm ³ min ⁻¹	Ni	Molecular flux of species i	Variable	mol cm ⁻²
С	Concentration	Variable	mol cm ⁻³	C_t	Pt atom mole density per cm ²	$2.2 imes 10^{-9}$	
Ι	Current	Variable	А	$\theta_{\rm H}$	Fraction of surface covered by H atoms	Variable	
R	Gas constant	8.314	J mol ⁻¹ K ⁻¹	θ_0	Fraction of surface uncovered	Variable	
Т	Temperature	298-346	K	α	Transfer coefficient	0.5	
Р	Total pressure	1	atm	n _i	Number of electrons		
c_{ox}^{b}	Bulk concentration of o-xylene	Variable	mol/l	$v_{\rm H_2}$	Outlet flow rate of hydrogen	Variable	cm ³ min ⁻¹
c_{dMC}^{b}	Bulk concentration of 1,2-dimethylcyclohexane	Variable	mol/l	-			

activation energy for thermochemical hydrogenation presumably is associated with the dissociation of molecular hydrogen on the platinum surface.

An insight into the effect of current density on the hydrogenation process can be obtained from the simulated results showing how the model parameters change during a 0-10A sweep at 20 mA/s (a 500 s sweep time). From Fig. 12, it is seen that, at low current densities, both the hydrogen surface coverage (Fig. 12a) and the hydrogen pressure (Fig. 12b) are held low as a result of the hydrogenation reaction which removes the hydrogen atoms that are formed at the electrocatalyst surface. Fig. 12d shows that the hydrogen production rate is also initially low and then increases linearly at the higher current densities. Fig. 12c illustrates the consumption of o-xylene during the current sweep. The starting o-xylene concentration corresponds to pure o-xylene (8.3 mole/l). Over the short time of the sweep (500 s), only a minor decrease in o-xylene concentration occurs as a result of hydrogenation.

The results presented have been interpreted in terms of two competing reactions: the hydrogenation of o-xylene to form 1,2dimethylcyclohexane and the undesirable reaction of two adsorbed hydrogen radicals to form hydrogen gas. At very small currents all of the protons entering the cathode are used to hydrogenate o-xylene.



Fig. 12. Effect of current density on the various parameters in the calculation: (a) hydrogen surface coverage; (b) hydrogen pressure in the cathode compartment; (c) o-xylene concentration; (d) hydrogen production rate.

As the current increases the protons are used for both reactions. When the current has been increased sufficiently, a limiting rate of o-xylene hydrogenation is reached beyond which all of the incremental protons entering the cathode are used to form hydrogen gas. The limiting rate increases with increasing temperature.

5. Conclusions

The results of this study have shown that o-xylene can be hydrogenated in a PEM reactor at low temperatures. Increasing the temperatures or decreasing the current density increases the hydrogenation efficiency. The efficiency of hydrogenation can approach 100% at low current densities. The experimental results have been shown to be consistent with a zero dimensional model of the hydrogenation process based on a Jenkins–Rideal type mechanism whereby adsorbed hydrogen reacts with o-xylene in the liquid phase. The activation energy for the hydrogenation reaction was determined to be 28 kJ/mole.

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References

 S.H. Langer, H.P. Landi, Journal of the American Chemical Society 85 (1963) 3043.

- [2] S.H. Langer, H.P. Landi, Journal of the American Chemical Society 86 (1964) 4694.
- [3] S.H. Langer, I. Feitz, C.P. Quinn, Journal of the American Chemical Society 93 (1975) 1092.
- [4] S.H. Langer, G.P. Sakellaropoulos, Journal of the Electrochemical Society 122 (1975) 1619.
- [5] Z. Ogumi, K. Nishio, S. Yoshizawa, Electrochimica Acta 26 (1981) 1779.
- [6] Z. Ogumi, S. Ohashi, Z. Takehara, Electrochimica Acta 30 (1985) 121.
- [7] Z. Ogumi, et al., Electrochimica Acta 28 (1983) 1687.
- [8] W. An, J.K. Hong, P.N. Pitauro, K. Warner, W. Neff, Journal of the American Oil Chemists Society 75 (1998) 917.
- [9] W. An, J.K. Hong, P.N. Pintauro, Journal of Applied Electrochemistry 28 (1998) 947.
- [10] W. An, J.-K. Hong, P.N. Pintauro, K. Warner, W. Neff, Journal of the American Oil Chemists' Society 76 (1999) 215.
- [11] P.N. Pintauro, M.P. Gil, K. Warner, G. List, W. Neff, Industrial & Engineering Chemistry Research 44 (2005) 6188.
- [12] V. Anantharaman, P.N. Pintauro, Journal of the Electrochemical Society 141 (1994) 2729.
 [13] V. Anantharaman, P.N. Pintauro, Journal of the Electrochemical Society 141
- (1994) 2742. [14] X.-Z. Yuan, Z.-F. Ma, Q.-Z. Jiang, W.-S. Wu, Electrochemistry Communications
- 3 (2001) 599. [15] Z.-F. Ma, X.-Z. Yuan, W.-S. Wu, J.-X. Zhou, Q.-Z. Jiang, 201st ECS Meeting Abstracts, vol. 2002-1, Philadelphia, No. 1123 (2002).
- [16] X.-Z. Yuan, Z.-F. Ma, Q.-G. He, J. Hagen, J. Drillet, V.M. Schmidt, Electrochemistry Communications 5 (2003) 189.
- [17] S. Sedighi, C.L. Gardner, Electrochimica Acta 55 (2010) 1701.
- [18] M. Saeys, M.-F. Reyniers, M. Neurock, G.B. Marin, Journal of Physical Chemistry B 109 (2005) 2064.
- [19] C. Xu, T.S. Zhao, Q. Ye, Electrochimica Acta 51 (2006) 5524.
- [20] G.I. Jenkins, E. Rideal, Journal of the Chemical Society (1955) 2490.
- [21] J. Horiuti, M. Polanyi, Transactions of the Faraday Society 30 (1934) 1164.
- [22] M. Polanyi, R.K. Greenhalgh, Journal of the Chemical Society 85 (1939) 520.
- [23] G.H. Twigg, Discussions of the Faraday Society 8 (1950) 152.
- [24] J. Zhang, Investigation of CO tolerance in proton exchange membrane fuel cells, Ph.D. Dissertation. Worchester Polytechnic Institute. June 2004.
- [25] A.J. Wieckowski, et al., Journal of the American Chemical Society 107 (1985) 5910.