Electrochemical synthesis at pre-pilot scale of 1-phenylethanol by cathodic reduction of acetophenone using a solid polymer electrolyte.

Alfonso Sáez, Vicente García-García, José Solla-Gullón, Antonio Aldaz , Vicente Montiel*.

Instituto de Electroquímica, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain.

Abstract

The pre-pilot scale synthesis of 1-phenylethanol was carried out by the cathodic hydrogenation of acetophenone in a 100 cm² (geometric area) Polymer Electrolyte Membrane Electrochemical Reactor. The cathode was a Pd/C electrode. Hydrogen oxidation on a gas diffusion electrode was chosen as anodic reaction in order to take advantage of the hydrogen evolved during the reduction. This hydrogen oxidation provides the protons needed for the synthesis. The synthesis performed with only a solid polymer electrolyte, spe, has lower fractional conversion although a higher selectivity than that carried out using a support-electrolyte-solvent together with a spe. However, the difference between these two cases is rather small and since the work-up and purification of the final product are much easier when only a spe is used, this last process was chosen for the pre-pilot electrochemical synthesis of 1-phenylethanol.

Keywords: 1-phenylethanol, PEMER, solid polymer electrolyte, electrochemical hydrogenation, acetophenone.

* Corresponding author

Email address: vicente.montiel@ua.es (Vicente Montiel)

Phone: +34-965903400 (3628)

1. Introduction

Electrochemical hydrogenation is a useful process for the conversion of ketones into alcohols. Acetophenone is used for the synthesis of 1-phenylethanol, an attractive product for fine chemical, pharmaceutical and cosmetic industries. In a previous paper [1], we studied the electrochemical hydrogenation of acetophenone yielding 1-phenylethanol as main product and ethylbenzene and hydrogen as by-products.

In this previous work, two types of supporting electrolyte media were employed: the first one was a sulphuric acid solution together with a solid polymer electrolyte (spe), and the second one was a spe on its own. In addition, hydrogen oxidation was chosen as the anodic reaction in order to take advantage of the hydrogen evolved and to lessen the effect of current efficiency on the economic parameters of the synthesis.

In addition, it is worth noting that the elimination of the supporting electrolyte during the purification of the product it is an expensive task and therefore, this should be avoided if possible for industrial purposes. In this regard, the use of an ion exchange membrane as solid supporting electrolyte and only the initial reactant, if the latter is a liquid, or dissolved in a solvent if it is a solid, could make many organic electrosyntheses economically feasible. Consequently, this approach could help to awaken the chemical industry to the use of electrochemical syntheses, a type of process that this industry has contemplated so far with suspicion.

A type of reactor that can be employed for this type of synthesis is that described in the literature as Polymer Electrolyte Membrane Electrochemical Reactor (PEMER) [5] based on the structure of direct organic fuel cells. Nowadays, industrial interest in this

type of fuel cell has increased and cells of large dimensions are available making easier the scale-up of industrial electrochemical synthesis when a spe is employed.

The aim of this communication is, therefore, to show a pre-pilot scale synthesis of 1-phenylethanol from the cathodic reduction of acetophenone using a spe and a PEMER of 100 cm² geometric area whereby 1-phenylethanol is obtained in a simple yet inexpensive manner.

2. Material and methods

All cathodes were manufactured by air-brushing a catalytic ink onto a carbonaceous support (Toray Paper TGPH-90). The catalytic ink was made by dispersing a home-made Pd/C 30 wt% catalyst in isopropanol and Nafion solution 5 wt% as previously described [1]. The Pd catalytic loading and Pd/C/Nafion ratio were 0.1 mg cm⁻² and 60/40, respectively. The PEMER was built by home machining a flow distributor (see bottom right in fig. 1) on two graphite plates (type 2114-45, Mersen Ibérica, S.A; dimensions 240 x 140 x 8 mm). The available electrode geometric area of the reactor was 100 cm². The cell consisted of a cathode manufactured as described above and a gas diffusion electrode as anode, formed by a Pt catalytic layer (Vulcan XC-72 4.5 mg cm⁻², ratio Pt Vulcan/PTFE of 40/60), on 20 wt% teflonated Toray Paper TGPH-90. The composition of the Pt catalytic layer was Pt/C 20 wt% (HisPEC 3000 Fuel Cell Catalyst, Johnson Matthey) and Nafion with a ratio of 60/40 and a final Pt catalytic loading of 1 mg cm⁻². As spe a Nafion 117 membrane was used. The components were pressed between two carbon plates which act as current collectors. The scheme is shown in the upper right of fig. 1.

The initial concentration of acetophenone was 0.5 M and the solvent was ethanol 96%/water (90/10 v/v) with and without 0.1M H₂SO₄. For all experiences, a peristaltic pump (Ismatel Reglo DIG MS/CA 2–8C) provided a catholyte flow of 24 mL min⁻¹. The anodic reaction was the oxidation of hydrogen (Praxair, purity: 99.999%) that was fed to the anode at 1 atm without humidification and with a flow of 50 mL min⁻¹ measured with the MTS-module A-150 of a ElectroChem system. The gas diffusion anode was pressed on the membrane using the carbon current collector. The electrochemical hydrogenation was carried out at room temperature and at constant current using an EA-PS 2032-050 power supply.

The catholyte was analyzed by HPLC using a high-resolution liquid chromatograph Agilent 1200 with a Hypersil ODS column 4 x 250 mm, 5 µm (Agilent Technologies). A mixture of acetonitrile/water (1/1 v/v) (acetonitrile isocratic HPLC grade from Panreac, water type II, >5 MΩ cm, Elix 3 from Millipore) was used as eluent. The eluent flow was 1 mL min⁻¹ and the injection volume was 100 µL. Detection was carried out at 220 nm and the response was found to be linear between 20-100 ppm with standards prepared from samples supplied by Sigma-Aldrich. The test temperature was 303 K. The results of the synthesis are given as fractional conversion of acetophenone (X_R) defined as:

$$X_R = \left(1 - \frac{n_{\text{acetopheno}}}{n_{\text{acetopheno}}^o} \right) 100$$

where:

$n^o_{\text{acetophenone}}$: starting moles of acetophenone.

$n_{\text{acetophenone}}$: remaining moles of acetophenone.

and as product yield (η) defined as:

$$\eta = \left(\frac{n_{1\text{-phenylethanol or ethylbenzene}}}{n^o_{\text{acetophenone}}} \right) 100 \quad \text{and} \quad \eta = \left(\frac{2 n_{2,3\text{-diphenyl-2,3-butanediol}}}{n^o_{\text{acetophenone}}} \right) 100$$

where:

$n_{1\text{-phenylethanol or ethylbenzene}}$: moles of 1-phenylethanol or ethylbenzene obtained.

$n_{2,3\text{-diphenyl-2,3-butanediol}}$: moles of 2,3-diphenyl-2,3-butanediol obtained.

3. Results and discussion

The electrochemical hydrogenation of acetophenone yields 1-phenylethanol as major product and ethyl benzene and hydrogen as by-products. 2,3-diphenyl-2,3-butanediol can also be obtained in neutral or basic media. The anodic reaction was hydrogen oxidation that yields hydronium cations that maintain the conductivity of the cation exchange membrane, at the same time providing the protons required for the reduction of the acetophenone. A scheme of this process is shown in figure 1a.

It is important to note that, with a view to developing an industrial process, we performed the synthesis in a batch mode, trying to keep as low as possible, the amount of initial reagent at the end of the reaction.

The performance of the electrochemical hydrogenation with and without sulphuric acid and using a charge of 6F is compared in figure 2. As shown in figure 2a, the fractional conversion of acetophenone is around 90% (with sulphuric acid) and 80 % (without

sulphuric acid) For both cases, similar product yield for 1-phenylethanol was obtained, figure 2b. However, a higher production of ethylbenzene (undesired by-product) was observed when the electrolysis was carried out in presence of sulphuric acid, figure 2c. Taking into account that in order to yield 1-phenylethanol i) the work-up of the final solution is much more difficult if sulphuric acid is present, ii) a higher amount of ethylbenzene is obtained in presence of sulphuric acid and iii) the product yield and fractional conversion are for both cases not very different, we have chosen the use of starting solution without sulphuric acid and a spe for the pre-pilot synthesis. As result of the use of a hydrogen anode, the applied potential is very low (0.2 V-0.3 V) that means a low energy consumption per kg of the product. Obviously, the cost of the hydrogen should be taken into account. However this cost can be decreased using the evolved hydrogen in the cathodic reaction. Table 1 shows the energy consumption.

Experiences with the same starting solution and current densities of 15 and 20 mA cm⁻² were also carried out with the aim of studying the influence of the current density on the fractional conversion. As the reaction time was not modified, more electrical charge is passed, namely 9 and 12 F (450% and 600% of the theoretical charge assuming a two electron process). Also, two different Pd catalytic loadings (0.1 and 0.2 mg cm⁻²) have been studied. Figure 3 shows the fractional conversion and yields for the products synthesized under these different conditions. The increase in the catalytic loading does not produce any significant improvement in the process. However, an increase in the current density increases the formation of a racemic mixture of 2,3-diphenyl-2,3-butanediol (figure 3b). This product is produced via the formation of an anion radical in the first electron transfer. The coupling of this radical yields 2,3-diphenyl-2,3-butanediol [6]. We also obtained 1-phenylethanol, but with a lower product yield than that obtained at 10 mA.cm², and ethylbenzene, with a product yield of 5% (similar to

those obtained so far), with a charge passed of 1.5 and 2.0 times higher than that previously used (figure 3 b and c). A plausible explanation for the formation of 2,3-diphenyl-2,3-butanediol is that an increase in the current density shifts the potential of the cathode to more negative values at which the reduction of acetophenone on carbon takes place [6].

4. Conclusion

The electrochemical synthesis at pre-pilot scale of 1-phenylethanol by cathodic reduction of acetophenone dissolved in a hydroalcoholic medium and using a spe, a Pd/C electrode and a PEMER (100 cm² geometric area) was carried out. In order to take advantage of the evolved hydrogen at the cathode, hydrogen oxidation was chosen as anodic reaction. The influence of the current density and Pd loading on the synthesis were studied. Ethylbenzene and 2,3-diphenyl-2,3-butanediol were also obtained depending on reaction conditions. Since the anodic reaction was hydrogen oxidation, the energetic cost is very low (0.3-0.4 kWh kg⁻¹). However, the cost of the hydrogen spent in the anodic reaction must be obviously added. However, this cost can be decreased by using the hydrogen formed in the cathodic reaction.

Acknowledgements

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Figure captions.

Figure 1. a) Scheme of the electrochemical reduction reactions of acetophenone, b) scheme of the polymer electrolyte membrane electrochemical reactor (PEMER).

Figure 2. Influence of the presence of sulphuric acid on the synthesis: a) fractional conversion of acetophenone; b) product yield of 1-phenylethanol and c) product yield of ethylbenzene. Starting solutions: $\diamond$ EtOH(96%)/H₂O (90/10 v/v) + 0.1 M H₂SO₄; $\blacksquare$ EtOH(96%)/H₂O (90/10 v/v). Pd catalytic loading: 0.1 mg cm⁻². Current density: 10 mA cm⁻². Charge passed 6 F.

Figure 3. . Influence of current density on: a) fractional conversion; b) product yield of 2,3-diphenyl-2,3-butanediol; c) product yield of 1-phenylethanol and d) product yield of ethylbenzene. Starting solution 0.5 M PhCOMe in EtOH(96%)/H₂O 90/10. Current density (mA cm⁻²): 10 (green) 15 (black), 20 (red). Pd catalytic loading (mg cm⁻²): $\square$ 0.1, $\triangle$ 0.2.

Table.Table 1. Energy consumption (kW kg^{-1}) for synthesis of 1-phenylethanol.

Charge / F	PhCOMe 0.5 M EtOH(96%)/H ₂ O (90/10 v/v)
	Energy consumption / kWh (kg)^{-1}
1	0.33
2	0.38
3	0.37
4	0.38
5	0.43
6	0.48

Figure 1.

Figure 2

Figure 3