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Electrocatalytic activity of a polypyridyl ruthenium-oxo complex covalently attached to a graphite felt electrode

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The complex $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ grafted to a graphite felt electrode shows electrocatalytic activity toward primary and secondary alcohols. Kinetic analyses highlights the contribution of the immobilized catalyst to the oxidation of benzenemethanol to the corresponding aldehyde, whereas the formation of benzoic acid from benzaldehyde is mostly due to a direct oxidation at the graphite electrode. In contrast to the catalyst in solution, the immobilized catalyst exhibits poor activity toward compounds containing C–H bonds adjacent to unsaturated bonds.

Introduction

The ruthenium-oxo complex $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ (bpy is 2,2′-bipyridine and tpy is 2,2′:6′,2″-terpyridine) has been widely used in indirect electrolysis as a catalyst for the oxidation of alcohols[1–5] and C–H bonds adjacent to unsaturated bonds.[4–7] It is prepared by anodic oxidation of $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ in aqueous medium according to the following reactions:[8,9]

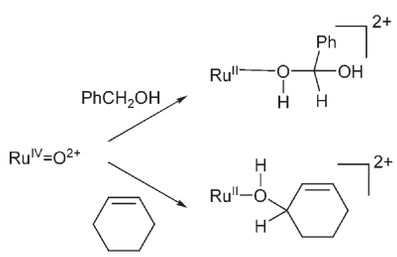
$$Ru^{II}(tpy)(bpy)(OH_2)^{2+} \rightleftharpoons Ru^{III}(tpy)(bpy)(OH)^{2+} + H^+ + e^- \quad (1)$$

$$Ru^{III}(tpy)(bpy)(OH)^{2+} \rightleftharpoons Ru^{IV}(tpy)(bpy)(O)^{2+} + H^+ + e^- \quad (2)$$

$$2Ru^{III}(tpy)(bpy)(OH)^{2+} \rightleftharpoons Ru^{II}(tpy)(bpy)(OH_2)^{2+} + Ru^{IV}(tpy)(bpy)(O)^{2+} \quad (3)$$

Mechanisms for the oxidation of alcohols[10] and unsaturated compounds[7] by $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ in solution have been proposed, involving a two-electron hydride transfer (Chart 1).

More recently, another mechanism was suggested by Meyer *et al.*[9,11] in which the initial step would be a C–H insertion:



The participation in oxidation of alcohols by Ru^{III}–OH^{2+} has also been reported,[10] though the reaction was slower than with Ru^{IV}=O. Ru^{III}–OH^{2+} is also able to catalyze the oxidation of olefin *via* a radical mechanism but this reaction also proceeds far more slowly than with Ru^{IV}=O.[11] In order to simplify the electrolysis procedure and to avoid the use of high quantities of the expensive catalyst, the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ complex has been immobilized on electrodes. This could be achieved using a polymer coating. Thus, the complex has been incorporated in Nafion films used as an electrostatic binding medium. Cyclic voltammetry of this modified electrode showed catalytic activity of the immobilized complex in the presence of benzenemethanol and 2-propanol.[12,13] Moreover, covalent attachment of the catalyst on a polymer film could be achieved by electropolymerization of the metal complex with pyrrol-substituted ligands.[14,15] The modified electrode could be used for electrocatalytic oxidations of benzenemethanol and α-methylbenzenemethanol on preparative scales.[15]

More recently, we showed that the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ complex could be immobilized on high-surface felt electrodes by anodic oxidation of bipyridine carboxylate ligand, giving rise to the covalent attachment of the complex directly onto the surface of the electrode.[16] We report here an analytical study of the electrocatalytic activity of this covalently modified electrode and the differences in reactivity observed between heterogeneous and homogeneous catalyses.

Experimental

Reagents and materials

Graphite felt was obtained from Le Carbone Lorraine (RVG 4000). 4-Nitrobenzenemethanol, benzenemethanol, 4-bromobenzenemethanol, 2-furanmethanol, α-hydroxybenzeneacetic acid, 1-phenyl-1,2-ethanediol, α-methylbenzenemethanol, α-phenylbenzenemethanol, toluene, 4-methylbenzoic acid,

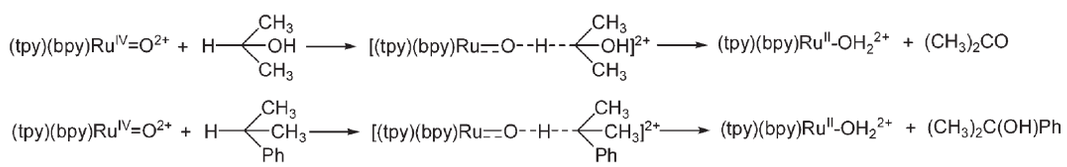


Chart 1

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cyclohexene, 1,2-diphenylethanone and 1-phenylethanone were purchased from Acros.

Instrumentation

Cyclic voltammetry, differential pulse voltammetry and controlled potential electrolyses were performed in the same divided flow cell using a graphite felt electrode (10 mm diameter, 12 mm thickness). The electrode was located between two counter-electrodes and the compartments were separated by cationic exchange membranes (Ionac 3470).[17]

HPLC experiments were performed on a Waters 600 instrument equipped with a Nova-Pak C_{18} column (3.9×150 mm). The eluent was water containing 10–50% of acetonitrile with 0.2% of triflic acid (0.4–1 ml min^{-1} flow rate). A UV-Vis detector was used for detection at 210 nm. Samples taken from the reaction medium were acidified with concentrated hydrochloric acid before being injected. The identification of the products and the calculation of their concentrations were based on HPLC comparison with authentic samples.

General procedure for the anodic oxidation of substrates on the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode

The anodic oxidation of the substrates ($n_{substrate} \simeq 100 \times n_{catalyst}$; $n_{catalyst}$ was measured by cyclic voltammetry) dissolved in 100 ml of phosphate buffer pH = 7.2 (NaH_2PO_4 0.25 M; Na_2HPO_4 0.25 M) was performed in the flow cell at 0.7 V_{SCE}, under nitrogen (SCE = saturated calomel electrode). The same buffer was used in the cathodic compartments. The electrolyte flowed through the porous electrode with recycling (8 ml min^{-1}). The reaction was stopped when it was completed or when the current fell to 40–60 μA (the initial current was around 1 mA).

Anodic oxidation of benzyl alcohol on oxidized graphite felt electrode

The anodic oxidation of benzyl alcohol (2.89×10^{-6} mol) in 100 ml of phosphate buffer pH = 7.2 (0.25 M) was carried out in the flow cell at 0.7 V_{SCE}, under nitrogen. The working electrode was previously prepared by anodic oxidation of graphite felt in phosphate buffer pH = 2.2 (NaH_2PO_4 0.25 M; H_3PO_4 0.25 M) for 1 h following a previously described procedure.[17] The electrolyte solution flowed through the electrode with recycling (flow rate: 8 ml min^{-1})

Results

$[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ was immobilized on the carbon felt according to a previously described procedure.[16] Anodic oxidation of the lithium salt of 4′-methyl-(2,2′-bipyridine)-4-acetic acid in phosphate buffer, pH = 2.2, led to the attachment of the bipyridine ligand to the electrode. The formation of oxides at the surface of the electrode simultaneously occurred during the grafting process. Further reactions with $Ru^{II}Cl_2(DMSO)(tpy)$ and then CF_3SO_3H, followed by addition of water, afforded the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode. Cyclic voltammetry analyses of the modified electrode were performed in phosphate buffer pH 7.2 (NaH_2PO_4 0.25 M; Na_2HPO_4 0.25 M) in the flow cell[17] and showed the presence of only one wave at 0.50 V_{SCE}[18] (Fig. 1). However, the differential pulse voltammogram performed in phosphate buffer pH 7.2 exhibited two peaks at 0.47 and 0.60 V_{SCE}. This analysis shows that the immobilized $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ compound can be electrochemically oxidized in its active oxo complex form and that the electrocatalysis using the modified electrode can then be investigated. The volume concentration of grafted compounds was roughly estimated by integration of the cyclic voltammograms using the Faraday law and was around $1–2 \times 10^{-8}$ mol cm^{-3} (Fig. 1).

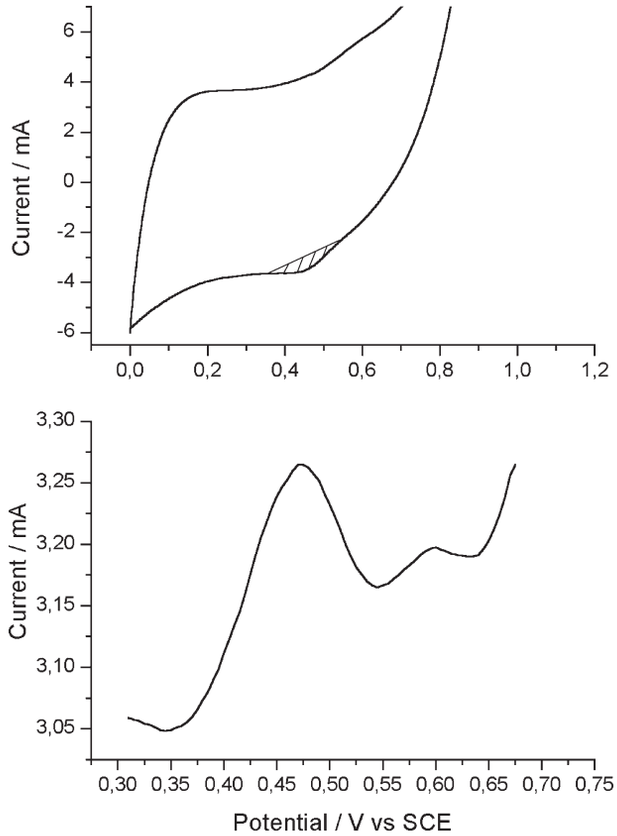


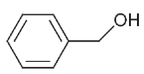
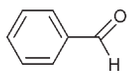
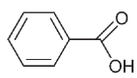
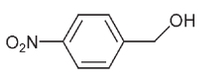
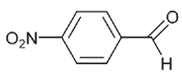
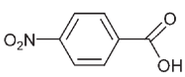
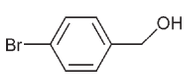
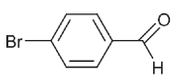
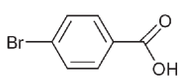
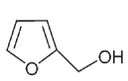
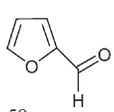
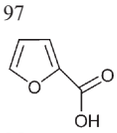
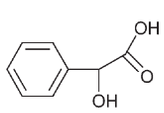
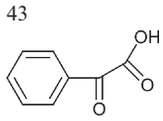
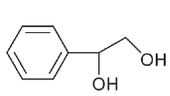
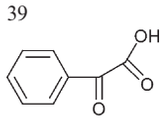
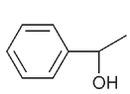
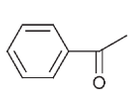
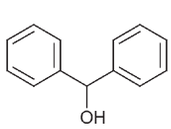
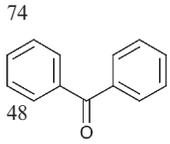
Fig. 1 Cyclic and differential pulse voltammograms of the $[Ru(tpy)(bpy)(OH_2)]^{2+}$ modified electrode in phosphate buffer pH = 7.2 (0.25 M). Cyclic voltammetry: scan rate 20 mV s^{-1}. Differential pulse voltammetry: scan rate 2 mV s^{-1}, pulse width 1.5 s, pulse height 70 mV, step width 2.5 s, step height 5 mV. Only the hatched area was considered to calculate the volume concentration.

Indirect electrolyses with modified graphite felt electrodes were carried out in the flow cell, in phosphate buffer pH 7.2 at 0.7 V, using 1 mol % of catalyst. The results of the electrocatalytic oxidations are summarized in Table 1. Primary alcohols were oxidized to their acidic derivatives *via* aldehyde intermediates (Table 1, entries 1 to 4). The reactions were not selective but the quantity of aldehyde obtained after a partial electrolysis was relatively high (63% yield after 1 h for benzaldehyde). This result can be considered for applications on preparative scales.

The variation in the concentrations of benzenemethanol, benzaldehyde and benzoic acid during electrolysis are given in Fig. 2(a). For comparison, an electrolysis of benzenemethanol was performed at a graphite felt electrode, previously oxidized in phosphate buffer pH = 2.2 for 1 h, in order to use an electrode without catalyst comparable to the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode (similar specific area and presence of oxides on the surface of the electrode).[16] The electrolysis was performed under the same conditions as with the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode and the corresponding variation of the concentrations of benzenemethanol, benzaldehyde and benzoic acid with time are given in Fig. 2(b).

In order to estimate the rate constants for the oxidation of benzenemethanol and benzaldehyde (Scheme 1), we considered two consecutive first-order reactions. The constant k_2 represents an overall rate constant taking into account the hydration of the aldehyde and its oxidation. The curves in Fig. 2(b) corresponding to the numerical resolution of the integrated rate from eqns (4–6)[19] fit well with the analytical results

Table 1 Oxidation of alcohols in phosphate buffer pH = 7.2 using the $[Ru(bpy)(tpy)(OH_2)]^{2+}$ modified electrode

Entry	Substrate	Time/h	Products % Yield[a]		% Unreacted substrate	% Current efficiency[b]	TON[c]
1							
		1[d]	63	19	22	28	101
		4	13	85	Traces	28	183
2							
		2[d]	48	52	Traces	22	152
		4	27	73	Traces	18	173
3							
		1[d]	36	58	6	41	152
		6.5	3	97	Traces	23	197
4							
		2[d]	58	35	10	25	128
		5.5	43	51	Traces	17	145
5							
		5	39		46	3	39
6							
		6	47		27	13	47
7							
		4	74		21	6	74
8							
		3	48		19	8	48

[a] Approximate yields calculated using the concentrations determined by HPLC analyses. [b] Current efficiency = 100 × theoretical charge/charge passed. [c] Turnover number (TON) = $(n_{aldehyde} + 2n_{acid})/n_{catalyst}$, where $n_{aldehyde}$, n_{acid} and $n_{catalyst}$ are the number of moles of aldehyde, acid and catalyst, respectively; $n_{catalyst}$, initially calculated from cyclic voltammetry, led to minimum values of the turnover number (these values could be multiplied by 5, see the discussion). [d] Electrolysis time corresponding to the maximum concentration of aldehyde.

and the calculated constants k_1 and k_2 are equal to 0.0028 and 0.01 min^{-1}, respectively.

$$[PhCH_2OH] = [PhCH_2OH]_0 e^{-k_1 t} \quad (4)$$

$$[PhCH(OH)_2] = \frac{[PhCH_2OH]_0 k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \quad (5)$$

$$[PhCOOH] = \frac{[PhCH_2OH]_0}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right] \quad (6)$$

We used the same kinetic model for the oxidation carried out with the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode considering that the concentration of catalyst was constant during electrolysis. The curves calculated from the integrated rate eqns (4–6) ($k_1' = 0.027$ min^{-1} and $k_2' = 0.009$ min^{-1}) also fit well with the experimental data [Fig. 2(a)]. k_1' is considered as the overall constant for the competitive oxidations of the alcohol directly on the electrode or *via* the catalyst and k_2' takes into account the two competitive oxidations and the hydration of the aldehyde.

To check the stability of the catalyst during electrolysis, the volume concentration of the grafted catalyst on the felt was measured by cyclic voltammetry. We noticed, for all substrates in Table 1, a severe decrease of the electrochemical signal (around 80%). Electrolyses either without substrate or with benzenemethanol (1 mol % of catalyst) were performed under the standard electrolysis conditions (in phosphate buffer pH

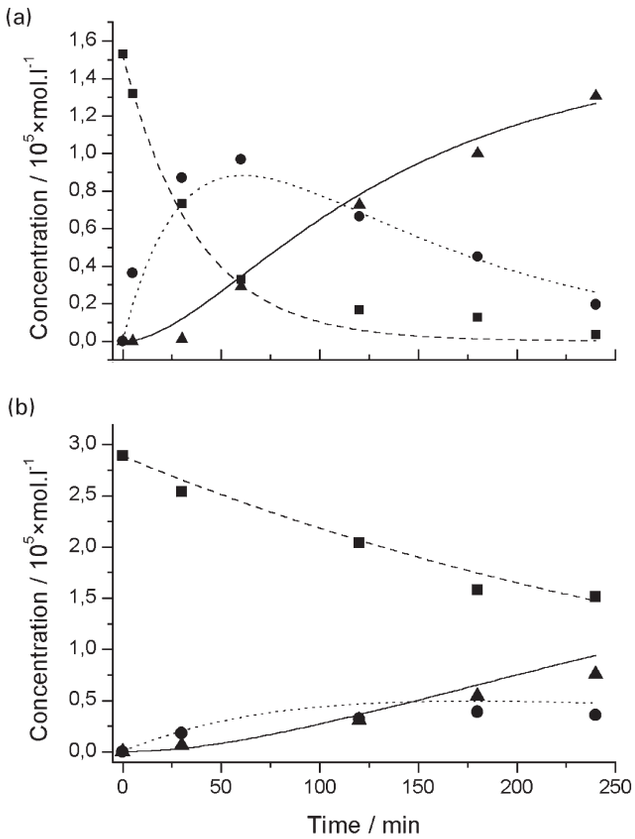
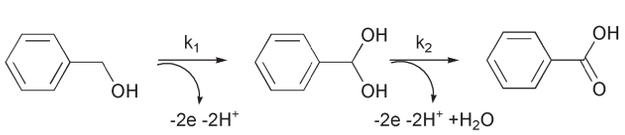


Fig. 2 Electrooxidation of benzenemethanol on: (a) $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified graphite felt electrode, (b) oxidized graphite felt electrode, in phosphate buffer of pH = 7.2. The symbols represent: (■) benzenemethanol, (●) benzaldehyde, (▲) benzoic acid. Curves were calculated from the integrated rate using: (---) eqn. (4), (···) eqn. (5), (—) eqn. (6).

7.2 at 0.7 V) and stopped at different reaction times. For each experiment a new felt was used. The variation of the amount of remaining catalyst during electrolysis are given in Fig. 3. A rapid decrease was observed at the beginning of the electrolysis, particularly in the absence of substrate.

Secondary alcohols could also be oxidized to the corresponding ketones (Table 1, entries 5 to 8). While the oxidation of α-methylbenzenemethanol led to 1-phenylethanone with good yield (74%; Table 1, entry 7), the other ketones were obtained in moderate yields. In all experiments, the presence of benzoic acid was not detected by HPLC.

Curiously, low current efficiencies were obtained for all electrolyses. To understand these results, electrolyses were carried out in phosphate buffer pH 7.2 (0.25 M) at 0.7 V without substrate and catalyst using an oxidized graphite felt electrode (*vide supra*). We noticed the presence of currents, similar to the currents observed during the electrolyses of the substrates. Cyclic voltammetry analyses revealed that the potential of the oxidation of water at a previously oxidized graphite felt electrode was lower than at a non-oxidized one. It seems that the oxygen overvoltage decreases when the graphite felt electrode has been previously submitted to an anodic oxidation in aqueous medium, as is the case for the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode. This behaviour would give



Scheme 1 Oxidation of benzenemethanol to benzoic acid.

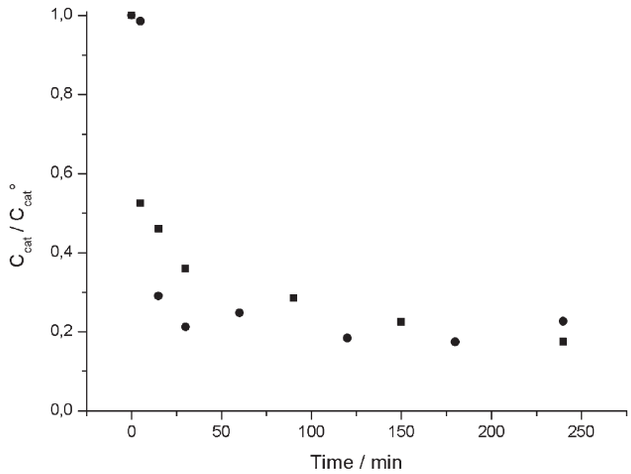


Fig. 3 Ratio of catalyst remaining on the felt after anodic oxidation at 0.7 V_{SCE}: (●) without substrate and (■) in the presence of benzenemethanol.

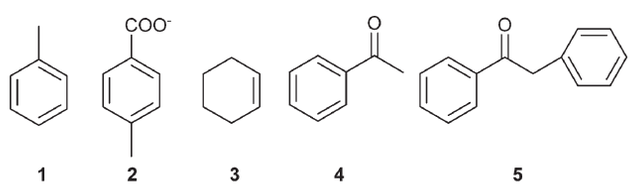
rise to a competition between the oxidation of the alcohols and the oxidation of water, leading to low current efficiencies.

Furthermore, we also studied the oxidation of compounds **1** to **5** (Scheme 2) using the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode. The oxidation of **1**, **4** and **5** in homogeneous catalysis led to benzoic acid.[4,6] However, the formation of benzoic acid could not be observed in heterogeneous catalysis. In the same manner, 1,4-benzenedicarboxylic acid and 2-cyclohexen-1-one, resulting from the homogeneous catalytic oxidation of **2** and **3**, respectively,[4,6] were not detected by HPLC. While the concentration of 4-methylbenzoic acid (**2**) and 1-phenylethanone (**4**) did not change, even after 6 h of electrolysis,[20] the concentration of 1,2-diphenylethanone (**5**) decreased significantly. HPLC analysis revealed the formation of 14% 2-hydroxy-1,2-diphenylethanone but no other products could be detected.

Discussion

Cyclic voltammetry analysis of the modified electrode showed only one system, at the same potential as the $Ru^{III/II}$ in solution.[17] A single system has also been obtained by cyclic voltammetry analysis at pH 7 for $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ immobilized on the electrode by electropolymerization.[15] UV spectroscopy showed that $[Ru^{IV}(tpy)(bpy)O]^{2+}$ was the final oxidized form of the complex. The authors attributed this electrochemical behaviour to the slowness of the $Ru^{III/II}$ couple in the polymer film. In our case, the $Ru^{IV/III}$ system observed at 0.62 V_{SCE} in solution[16] could be hidden by the large capacitive current and the water oxidation, as suggested by the occurrence of two waves in differential pulse voltammetry.

The results depicted in Table 1 show that secondary alcohols are oxidized to the corresponding ketones and primary alcohols to a mixture of the corresponding aldehydes and acids in modest-to-good yields, depending on the substrate. In order to determine the effects of the immobilization method of the catalyst on its catalytic activity, we compared our results to



Scheme 2 Investigated substrates containing C–H bonds adjacent to unsaturated bonds.

these of the literature. Primary alcohols were oxidized to acidic derivatives, as it was already observed for alcohols in homogeneous electrocatalysis on platinum electrode.[1] However, it has been reported that electrocatalysis of benzenemethanol led selectively to benzaldehyde when the catalyst was covalently attached to a polymer film.[15]

Kinetic analysis of the oxidation of benzenemethanol with an oxidized graphite felt revealed a slow oxidation to benzaldehyde ($k_2 = 0.0028$ min^{-1}) and a faster oxidation to benzoic acid ($k_1 = 0.01$ min^{-1}). We used the same kinetic model for the oxidation performed with the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode, considering that the volume concentration of catalyst in the felt was constant during electrolysis. The curves calculated from this kinetic model fit well with the experimental data and confirm the hypothesis that the volume concentration of catalyst in the felt does not decrease significantly during the electrolysis (4 h). However, cyclic voltammetry analyses showed a very strong decrease in the volume concentration of the catalyst after electrolyses. The measurement of the volume concentrations of catalyst during the electrolysis of benzenemethanol (Fig. 3) highlights a dramatic decrease during the first 30 minutes of the reaction. After this period, the concentration remains almost constant. Curiously, when the electrolysis is performed without substrate, the volume concentration of the catalyst decrease during the first 15 minutes to reach a practically constant value. A possible explanation[21] would be that the initial volume concentrations measured by cyclic voltammetry are overestimated, perhaps due to a contribution of the capacitive current. Thus, the concentration of the catalyst would be almost constant during the electrolysis, most probably around $0.2–0.4 \times 10^{-8}$ mol cm^{-3}.

The comparison of the rate constants $k_1 = 0.0028$ min^{-1} and $k_1' = 0.027$ min^{-1}, clearly shows that the presence of the catalyst on the graphite felt increases significantly the reaction rate. In contrast, the rate constant $k_2' = 0.009$ min^{-1} is similar to $k_2 = 0.01$ min^{-1}. These results seem to show that benzaldehyde is oxidized into the corresponding acid directly on the electrode[22] and that the catalyst only oxidizes the benzenemethanol to benzaldehyde. This would be in agreement with the selective oxidation of benzenemethanol to benzaldehyde observed when the modified electrode is covered by a polymer film.

The oxidations of compounds with C–H bonds adjacent to unsaturated bonds (**1** to **5**), already described in homogeneous catalysis,[4,6] surprisingly could not be achieved with the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified electrode. These results need to be confirmed using a smaller amount of substrate in the electrolysis medium.[23] Indeed, most of the reactions performed in homogeneous catalysis were described with a ratio of substrate to catalyst of around 10–15. Nevertheless, the oxidation of compounds **1** and **2** was quantitative after 100 catalytic cycles when the catalyst was in solution whereas we did not observe any formation of oxidized compounds with the modified electrode. These results stress the lower reactivity of the catalyst immobilized on the electrode, compared to the catalyst in solution. This property of the grafted catalyst could be very interesting to achieve selective oxidations of alcohols containing unsaturated bonds.

Conclusion

In conclusion, this work shows that the oxidation of alcohols can be achieved using $[Ru^{II}(tpy)(bpy)(O)]^{2+}$ covalently attached to the surface of a graphite felt. Kinetic analyses of the electrolysis of benzenemethanol highlighted the contribution of the electrode to the oxidation of benzaldehyde to benzoic acid. The investigation of the electrocatalytic activity of the grafted complex $[Ru^{II}(tpy)(bpy)(O)]^{2+}$ also revealed the poor activity of the immobilized catalyst toward compounds with C–H bonds adjacent to unsaturated bonds. This result can be promising to achieve selective oxidations of unsaturated alcohols.

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References

1 M. Navarro, W. F. De Giovani and J. R. Romero, *Synth. Commun.*, 1990, **20**, 399.
2 M. Navarro, W. F. De Giovani and J. R. Romero, *Tetrahedron*, 1991, **47**, 851.
3 M. Navarro, W. F. De Giovani and J. R. Romero, *J. Mol. Catal. A: Chem.*, 1998, **135**, 249.
4 B. A. Moyer, M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1980, **102**, 2310.
5 M. S. Thompson, W. F. De Giovani, B. A. Moyer and T. J. Meyer, *J. Org. Chem.*, 1984, **49**, 4972.
6 J. M. Madurro, G. Chiericato, Jr., W. F. De Giovani and J. R. Romero, *Tetrahedron Lett.*, 1988, **29**, 765.
7 M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 5070.
8 K. J. Takeuchi, M. S. Thompson, D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 1845.
9 L. A. Gallagher and T. J. Meyer, *J. Am. Chem. Soc.*, 2001, **123**, 5308.
10 M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4106.
11 L. K. Stultz, M. H. V. Huynh, R. A. Binstead, M. Curry and T. J. Meyer, *J. Am. Chem. Soc.*, 2000, **122**, 5984.
12 R. C. McHatton and F. C. Anson, *Inorg. Chem.*, 1984, **23**, 3935.
13 W. J. Vining and T. J. Meyer, *J. Electroanal. Chem.*, 1987, **237**, 191.
14 J. P. Collin, A. Jouaiti and J. P. Sauvage, *J. Electroanal. Chem.*, 1990, **286**, 75.
15 W. F. De Giovani and A. Deronzier, *J. Electroanal. Chem.*, 1992, **337**, 285.
16 F. Geneste, C. Moinet and G. Jézéquel, *New J. Chem.*, 2002, **26**, 1539.
17 F. Geneste, M. Cadoret, C. Moinet and G. Jézéquel, *New J. Chem.*, 2002, **26**, 1261.
18 The potential was calculated as follows: $(E_c + E_a)/2$, where E_c and E_a are the cathodic and anodic potentials, respectively.
19 P. W. Atkins, *Physical Chemistry*, ed. Oxford University Press, Oxford, 5th edn., 1994, ch. 25, pp. 883–884.
20 The solution of toluene and cyclohexene was not concentrated enough to be monitored by HPLC.
21 The initial waveshape could be obtained again when after electrocatalysis the felt was treated with $Ru^{II}Cl_2(DMSO)(tpy)$, CF_3SO_3H and H_2O. We are currently studying this phenomenon.
22 The oxidation of benzenemethanol to benzoic acid on a reference graphite felt (non-oxidized) was very low. But the reaction was improved on an oxidized electrode, probably due to the formation of oxides at the surface of the fibres. See, for example: D. C. Alsmeyer and R. L. McCreery, *Anal. Chem.*, 1992, **64**, 1528; P. Chen and R. L. McCreery, *Anal. Chem*, 1996, **68**, 3958; F. Regisser, M.-A. Lavoie, G. Y. Champagne and D. Bélanger, *J. Electroanal. Chem.*, 1996, **415**, 47. Thus, the oxidation of water was observed at more anodic potential using a reference felt compared to an oxidized one and the difference of reactivity between the two felts could be explained by the oxidation of alcohols by water oxidation intermediates..
23 To allow UV detection in the HPLC analyses, the concentration of substrates in the electrolysis medium could not be reduced.