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Approaches to the synthesis of heterogenised metalloporphyrins Application of new materials as electrocatalysts for oxygen reduction

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Abstract

Porphyrins and different metalloporphyrins have been synthesised and heterogenised on robust inorganic solids such as silica gel, purely siliceous MCM-41, and delaminated zeolites ITQ-2 and ITQ-6. Two different strategies for preparation of these catalysts have been explored, mainly based on immobilisation of a functionalisated porphyrin (route A) or heterogenisation of an aromatic aldehyde and consecutive porphyrin formation (route B). Route A yields stable materials and allows introduction of a larger quantity of metalloporphyrin onto the support (contents ranged from 0.3 to 0.4 mmol g^{-1}) whereas route B was unsuccessful and no evidence was found to support the porphyrin formation. A multitechnique approach is employed for characterisation of samples and their catalytic behaviour has been tested in the electroreduction of oxygen. A cyclic voltammetry investigation, at varying scan rate, was carried out in an attempt to elucidate the net reaction for the oxygen reduction. The synthesised metalloporphyrins are active for electrocatalytic reduction of oxygen by a two-electron mechanism, producing hydrogen peroxide. The comparison between homogeneous and heterogenised catalysts confirms that heterogenisation avoids the catalyst desorption (lost of activity) from the electrode. Catalytic activity is directly related with the content of metalloporphyrin in heterogenised materials that are addressable electronically.
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Keywords: Metalloporphyrins; Heterogenised catalysts; Electrocatalytic oxygen reduction

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are efficient and non-polluting electrical power generators based on two electrochemical reactions: the oxidation of hydrogen and the reduction of oxygen [1,2]. These fuel cells work at low temperature (<80 °C) and for that they require the use of catalysts to generate noticeable currents; up to now, platinum or platinum-based catalysts are the most active materials [3]. To reduce cost and to become competitive with more conventional electrical generators new alternatives are sought to replace these expensive and noble metal-based catalysts. The use of non-noble metal catalysts is excluded in PEMFC for their chemical stability because these fuel cells are operating at too low pH (≈1) [4]. However, some metal N_4-macrocycles, such as porphyrins, phthalocyanines and tetraazaannulenes, have been found to be able to catalyse the oxygen reduction [5] and also stable in acidic medium. Thus, cobalt and iron porphyrins have been proposed as a substitute to platinum as electrocatalyst for the O_2 cathode in a fuel cell [6,7]. Unfortunately, its technological application seems limited by several reasons, such as the desorption of the catalyst from the electrode or the catalyst instability due to the intermolecular self-oxidation. A useful way to avoid these limitations is by heterogenisation of these transition metal complexes onto robust inorganic supports, such as zeolites [8]. Furthermore, anchoring metalloporphyrins to solid supports can have a marked influence on the chemistry of these systems, improving their thermal and mechanical stability, and providing the local environment of the reaction. Other obvious advantage of such systems can include easier oxygen diffusion due to the structural characteristics of the supports, specially their high surface area.

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Much effort has been made to attach metalloporphyrins to solids, namely, adsorption, [9] electrostatic binding, [10] entrapment, [11] polymerisation, [12,13] covalent binding [14–16] or axial ligation of metal, [17] but most of them suffer from a reversible binding under work conditions, specially in polar solvents like water or methanol [8], or a fairly low porphyrin contents onto the solid matrix (≈0.02 mmol g^{-1}).

In order to achieve a stable binding between ligand and support and increased loading of metallic complex we have developed a simple way to synthesise different heterogenised porphyrins and metalloporphyrins. Two synthesis strategies have been explored for the preparation of cobalt- and iron-porphyrins supported on silica based mesoporous and laminar inorganic solids, such as silica gel, purely siliceous MCM-41, and delaminated high surface zeolites ITQ-2 and ITQ-6. One strategy is basically based on the heterogenisation by covalent binding of a functionalised porphyrin whereas the alternative way involves the previous immobilisation of an aromatic aldehyde on the support and consecutive porphyrin formation. The heterogenised systems and their homogeneous analogues ones have been comparatively tested for oxygen electrocatalytic reduction.

2. Experimental procedure

2.1. Instruments and reagents

Pyrrole and the silylating agent $OCN(CH_2)_3Si(OEt)_3$ were distilled before use. C, H and N analysis were carried out with a Heraeus apparatus. Metal content was analysed by using inductively coupled plasma (ICP) with a Perkin–Elmer Plasma 40-ICP spectrometer. ^{1}H- and ^{13}C NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers; chemical shifts are given in ppm with tetramethylsilane as internal standard. Infrared spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) as KBr pellets. UV–vis absorption spectra were performed with a Shimadzu UV-2401 spectrophotometer.

The inorganic supports are silica gel, a mesoporous MCM-41 [18] and delaminated zeolites ITQ-2 [19] and ITQ-6; [20] the main characterisation of the solids is given in Table 1.

Table 1
Main characterisation of the solid supports

Support	BET surface area ($m^2 g^{-1}$)	Micropore surface ($m^2 g^{-1}$)	External surface (or mesoporous) ($m^2 g^{-1}$)
Silica	540	–	540
MCM-41	1030	0	1030
ITQ-2	830	130	700
ITQ-6	618	10	608

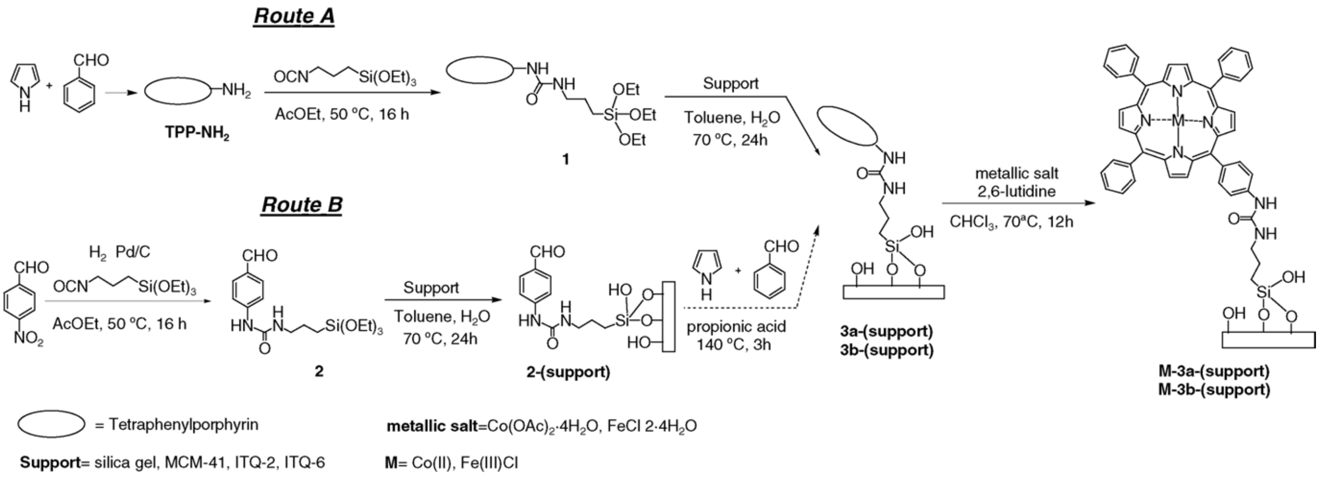
2.2. Synthesis of heterogenised metalloporphyrins

Two different strategies were explored to synthesise heterogenised metalloporphyrins by cyclocondensation of aryl aldehydes with pyrrole in propionic acid, see Scheme 1. In both cases metallic complex was formed after heterogenisation, although the formation of metallic complex before heterogenisation was also investigated.

2.2.1. Synthesis of heterogenised porphyrins

2.2.1.1. Route A. This approach is mainly based on the functionalisation of a porphyrin ring, by including a trietoxysilyl group available for grafting, and further inmobilisation on the support.

*2.2.1.1.1. 1-(3-Trietoxysilylpropyl)-3-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-urea (**1**).* Trietoxysilylaminopropyl isocyanate (6 mmol, 3 eq) was added, under argon atmosphere, to a solution of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin ($TPP-NH_2$), which was prepared according to the literature method, [21] (2 mmol, 1 eq) in ethyl acetate (15 ml). The reaction mixture was stirred for 16 h at refluxing of solvent. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel using ethyl acetate–hexane (1:3) as eluent to yield the urea derivative 1. Yield: 94%. $C_{54}H_{52}N_6O_4Si$: calc. C 73.94; H 5.98; N 9.58. Found C 73.82; H 6.01; N 9.40%. Spectroscopic data, ^{1}H NMR, ^{13}C NMR, IR and MS, are summarised in Table 2.



Scheme 1. Alternative routes explored to synthesize heterogenised metalloporphyrins (–, successful; · · ·, unsuccessful).

Table 2
Spectroscopic data of porphyrin **1** and aldehyde **2**

	^{1}H NMR[a]				^{13}C NMR[a] (ppm)	
	ppm	No. of H	Mult.	J (Hz)		
Compound **1**						
C=O					155.5	IR (KBr, cm^{-1})
2,8-CH pyrrole	8.87	2	d	4.9	142.1–118.5	3350 (NH); 3060–2860 (C—H); 1642 (C=O); 1596 (C=C); 1542 (N—CO); 1350 (C=N); 1102 (C—Si); 1075 (Si—O); 796 (CH)
12,13,17,18-CH pyrrole	8.83	4	s			
3,7-CH pyrrole	8.81	2	d	4.9		
o-H monosubstituted phenyl	8.26–8.14	6	m			
p-Substituted phenyl	8.11, 7.64	4	AA′BB′	8.5		
m,*p*-H monosubstituted phenyl	7.78–7.68	9	m			
PhNH	6.63	1	s			
CH_2NH	5.12	1	t	6.1		MS$^+$ (m/z)
CH_2CH_3	3.86	6	c	7.0	58.6	877 (M$^+$), 248, 176, 118, 102 (100)
CH_2NH	3.35	2	dt	6.1, 7.2	43.6	
$CH_2CH_2CH_2$	1.76	2	q	7.2	23.4	
CH_2CH_3	1.25	9	t	7.0	18.4	
CH_2Si	0.75	2	t	7.2	7.8	
NH pyrrole	−2.79	2	s			
Compound **2**						
C=O					156.3	IR (KBr, cm^{-1})
CHO	9.79	1	s		191.4	3364 (NH); 2970–2860 (C—H); 1675 (CHO); 1664 (C=O); 1592 (C=C); 1542 (N—CO); 1350 (C=N); 1107 (C—Si); 1078 (Si—O)
PhNH	9.02	1	s		147.8, 131.1, 1304.4, 117.9	
Ph	7.71	4	s			
CH_2NH	6.44	1	t	6.2		
CH_2CH_3	3.75	6	c	7.0	58.6	
CH_2NH	3.17	2	dt	6.2, 7.3	42.3	MS$^+$ (m/z)
$CH_2CH_2CH_2$	1.58	2	q	7.3	23.1	368 (M$^+$), 338, 202 (100), 160, 137, 104, 79, 45
CH_2CH_3	1.16	9	t	7.0	18.1	
CH_2Si	0.57	2	t	7.3	7.5	

[a] Deuterated solvent: $CDCl_3$.

*2.2.1.1.2. Heterogenised porphyrins [**3a-(support)**].* This porphyrin **1**, that bears a $Si(OEt)_3$ group, was heterogenised on different inorganic supports following a well-known procedure: a solution of **1** (1 mmol) in toluene (10 ml) and 200 μl of water were added to a suspension of the inorganic support (1 g) in a toluene (30 ml). The slurry was heated at 70 °C for 16 h and the solid was filtered off and washed successively with toluene, petroleum ether, ethanol, ethyl ether, and were Soxhlet-extracted with chloroform and ethanol for 7 h to remove all organic material non-covalently bounded to the support. The solid was dried under vacuum to afford the heterogenised porphyrins **3a-(support)**. The content of ligand incorporated to the supports, measured by atomic absorption (AA), is reported in Table 3. The structure of these new materials was confirmed by UV–vis diffuse reflectance (Fig. 1) and FTIR spectroscopies.

2.2.1.2. Route B. Route B involves the previous inmobilisation of an aromatic aldehyde, that bears a $Si(OEt)_3$ group, and consecutive porphyrin formation by cyclocondensation between the heterogenised aldehyde [**2-(support)**], benzaldehyde and pyrrol.

*2.2.1.2.1. 1-(4-Formylphenyl)-3-(3-triethoxysilylpropyl)-urea (**2**).* A mixture of *p*-nitrobenzaldehyde (13 mmol), Pd/C (100 mg) in ethyl acetate (120 ml) was stirred at room temperature under hydrogen atmosphere. The reaction was monitored by TLC using ethyl acetate–hexane (1:1) as eluent. After 24 h the reaction was filtered and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using ethyl acetate–hexane (1:3) as eluent to yield 2. Yield: 77%. Spectroscopic data, ^{1}H NMR, ^{13}C NMR, IR and MS, are summarised in Table 2.

Table 3
Content of ligand (aldehyde, porphyrin or metalloporphyrin) anchored to the support (mmol g^{-1})

Support	**2-(support)**[a]	**3a-(support)**[a]	**Co-3a-(support)**[b]	**FeCl-3a-(support)**[b]
Silica	0.53	0.45	0.45	0.42
MCM-41	0.55	0.23	0.20	0.23
ITQ-2	0.54	0.36	0.30	0.13
ITQ-6	0.39	0.13	0.12	0.10

[a] Measured by elemental analysis.
[b] Metal content measured by AA/ICP.

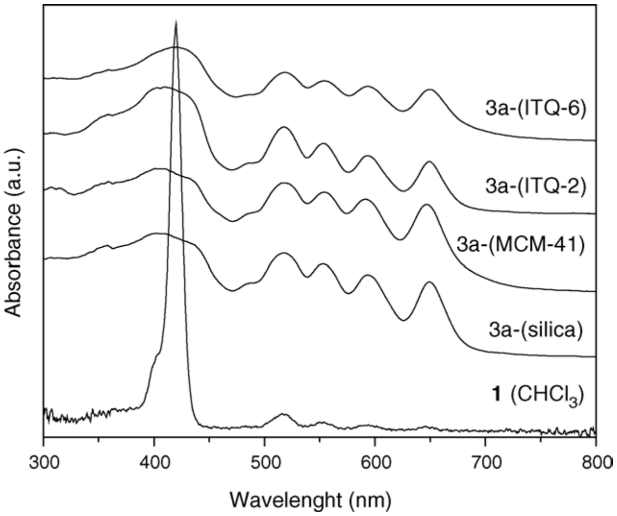


Fig. 1. UV–vis spectra of porphyrins heterogenised following route A [**3a-(support)**] and their homogeneous analogue (**1**).

*2.2.1.2.2. Heterogenised aldehydes [**2-(support)**].* Aldehyde **2**, that bears a $Si(OEt)_3$ group, was heterogenised on different inorganic supports following the procedure described above to yield the anchored aldehydes **2-(support)**. The main characterisation of these materials is reported in Table 3 and Fig. 2.

*2.2.1.2.3. Heterogenised porphyrins [**3b-(support)**].* Trying to synthesise the porphyrin ring, benzaldehyde (2.1 mmol), pyrrole (2.7 mmol) and $BF_3{\cdot}Et_2O$ (0.21 mmol, 1 M, CH_2Cl_2) were added to a suspension of the corresponding heterogenised aldehyde [**2-(support)**] (0.42 mmol) in dry dichloromethane (25 ml) and the mixture was stirred at room temperature for 3 h. DDQ (0.63 mmol) was then added, the dark brown mixture was stirred for 60 min, and then neutralised with 2.5 ml of triethylamine. The solid was filtered off and washed successively with toluene, petroleum ether, ethyl ether, and were Soxhlet-extracted with chloroform for 7 h. After drying under vacuum the obtained solids [**3b-(support)**] were studied by UV–vis diffuse reflectance spectroscopy (Fig. 2).

2.3. Preparation of cobalt and iron complexes

Homogeneous cobalt and iron complexes of 5,10,15,20-tetraphenylporphyrin were prepared following a typical procedure: [22] an excess of the corresponding metallic salt (7.5 mmol) was added to a solution of porphyrin (1 mmol) in $CHCl_3$ (100 ml) and 0.3 ml of 2,6-lutidine. After refluxing for 16 h the mixture was poured into equal volume of ice water. The organic phase was washed with water twice, dried over anhydrous Na_2SO_4 and evaporated to dryness to isolate the solid complex.

2.3.1. Heterogenised metalloporphyrins

Following a similar method, see above, a representative experimental procedure to prepare heterogenised metalloporphyrins is as follows: $(CH_3CO_2)_2Co{\cdot}4H_2O$ (0.11 mmol) or $FeCl_2{\cdot}4H_2O$ (0.75 mmol), and 2,6 lutidine (15 drops) were added to a suspension of the corresponding heterogenised porphyrin [**3a-(support)** or **3b-(support)**] (0.1 mmol) in chloroform (10 ml). The reaction mixture was stirred at reflux of solvent for 16 h. Then, the mixture was allowed to cool and the solid was filtered off and washed thoroughly with chloroform, water, ethyl ether and Soxhlet-extracted with chloroform for 7 h. The solid was dried under vacuum to afford the corresponding anchored metalloporphyrins **M-3a-(support)** and **M-3b-(support)**. The content of ligand incorporated to the support and UV–vis diffuse reflectance spectra of these materials are reported in Table 3 and Fig. 3, respectively.

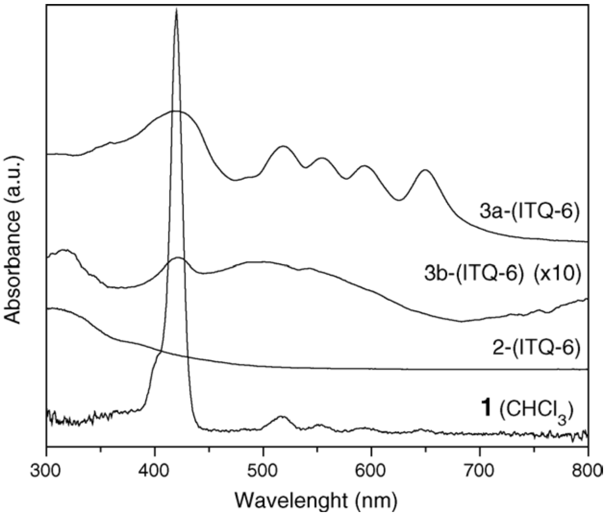


Fig. 2. UV–vis spectra of ITQ-6-heterogenised aldehyde [**2-(ITQ-6)**], porphyrin heterogenised following both routes [route A: **3a-(ITQ-6)**; route B: **3b-(ITQ-6)**] and porphyrin reference (**1**).

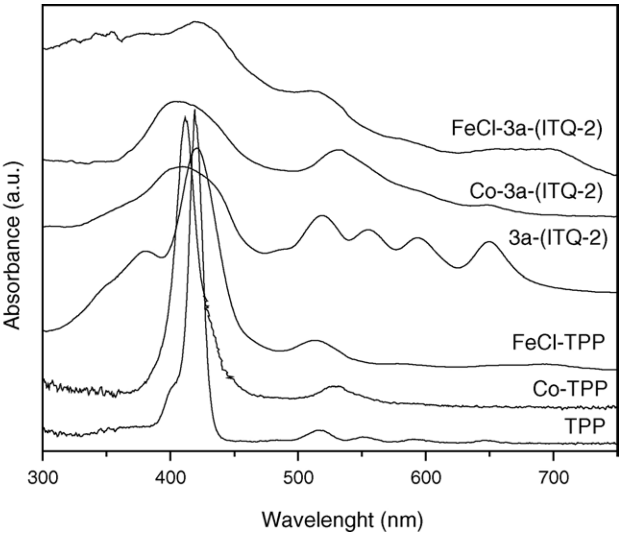
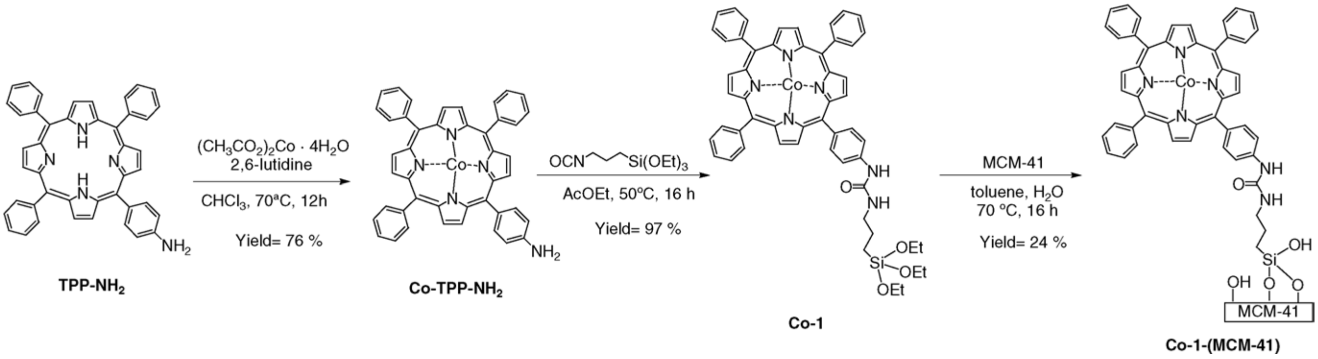


Fig. 3. UV–vis spectra of route A-heterogenised porphyrin [**3a-(ITQ-2)**], its corresponding metallic complexes [**M-3a-(ITQ-2)**]) and their homogeneous analogues (TPP derivatives, in $CHCl_3$).



Scheme 2. Synthesis of heterogenised metalloporphyrins with previous formation of metallic complex.

2.4. *Alternative synthesis of heterogenised metalloporphyrins by preformed homogeneous metalloporphyrins*

The formation of metallic complex in a previous step to heterogenisation was carried out, starting from 5-*p*-aminophenyl-10,15,20-triphenylporphyrin (**TPP-NH$_2$**), see Scheme 2.

2.4.1. *Co(II)-5-(4-aminophenyl)-10,15, 20-triphenylporphyrin (**Co-TPP-NH$_2$**)*

Following the general procedure, $(CH_3CO_2)_2Co{\cdot}4H_2O$ (0.11 mmol) and 2,6 lutidine (15 drops) were added to a solution of porphyrin (**1**) (0.1 mmol) in chloroform (10 ml). The reaction mixture was stirred for 16 h at reflux of solvent. Then, the mixture was allowed to cool and the solid crude complex was isolated by precipitation using ethyl ether. Yield: 76%. IR (KBr, cm^{-1}): $\nu = 3436$ (NH$_2$); 3049–2851 (C–H); 1598 (C=C); 1351 (C=N); 1005 (Co–N). MS$^+$(*m*/*z*): 686 (M$^+$, 100). UV–vis (CHCl$_3$): λ_{max} 413 (Soret), 532 nm.

2.4.2. *Co(II)-1-(3-trietoxysilylpropyl)-3-[4-(10, 15,20-triphenylporphyrin-5-yl)-phenyl]-ureate (**Co-1**)*

To a solution of this metallic complex (**Co-TPP-NH$_2$**) (0.22 mmol) in ethyl acetate (15 ml), under argon atmosphere at 50 °C, 3-triethoxysilylpropylisocyanate (0.22 mmol) was added dropwise. The reaction was monitored by TLC using ethanol as eluent. After the reaction was completed (12 h) the solvent was evaporated under reduced pressure and the purple solid was dried in vacuo. Yield: 97%. $\nu = 3420$ (NH$_2$); 2970–2860 (C–H); 1646 (C=O); 1596 (C=C); 1542 (N–CO); 1350 (C=N); 1102 (C–Si); 1075 (Si–O); 1005 (Co–N); 796 (CH). MS$^+$ (*m*/*z*): 933 (M$^+$, 100), 686, 613. UV–vis (CHCl$_3$): λ_{max} 412 (Soret), 531 nm.

2.4.3. *Preparation of heterogenised metalloporphyrin [**Co-1-(MCM-41)**]*

The solid complex **Co-1** was heterogenised on MCM-41 following the process described above. Characterisation of the obtained product [**Co-1-(MCM-41)**] shows that these heterogenised metalloporphyrin is practically indistinguishable from **Co-3a-(MCM-41)**, which was prepared following route A.

2.5. *Preparation of modified electrodes*

The modified electrodes (pellets, 12 mm diameter) were built by mixing porphyrin powder (80 wt.%), polymer binder (KF2801, Atochem) (10 wt.%), black carbon (Super P, 3 M) (10 wt.%) and acetone (2 ml) in a mortar. After homogenisation and solvent evaporation, the active paste (40 mg) was cold pressed (500 kg, 5 min) on a stainless steel grid. Following this procedure it was no possible to prepare a robust electrode with catalyst heterogenised on silica gel. Although in preliminary studies electrodes were prepared in the absence of black carbon (data not shown), the voltammetric behaviour was slightly low so in final modified electrodes black carbon was incorporated to provide electrical conductivity to the substrate. Polymer KF2801 is added to bind the particles including black carbon.

For electrode charged with homogeneous catalyst (**M**–**H**) a mixture of Co- or FeCl-tetraphenylporphyrin, MCM-41, binder and black carbon was used, being the ratio between components similar to the heterogenised analogues. The amount of metalloporphyrin in the modified electrodes is reported in Table 4.

2.6. *Electrochemical measurements*

All the measurements were carried out at room temperature. The electrical characterisation of the homo- and heterogenised metalloporphyrin samples was determined in DC conditions using a HP 6614C DC power supply connected to two HP 34401A digital multimeters.

Cyclic voltammetry experiments were performed using a Radiometer Copenhagen Voltalab 32 potentiostat/galvanostat

Table 4
Main characterisation of modified electrodes

Catalyst	Metallophorphyrin content[a] (10^{-3} mmol cm^{-2})	
	Co	Fe
M-3a-(MCM-41)	4.8	5.4
M-3a-(ITQ-2)	3.5	2.9
M-3a-(ITQ-6)	2.7	2.1
M-H	4.8	6.4

M = Co, FeCl.
[a] Based on metal content measured by AA/ICP.

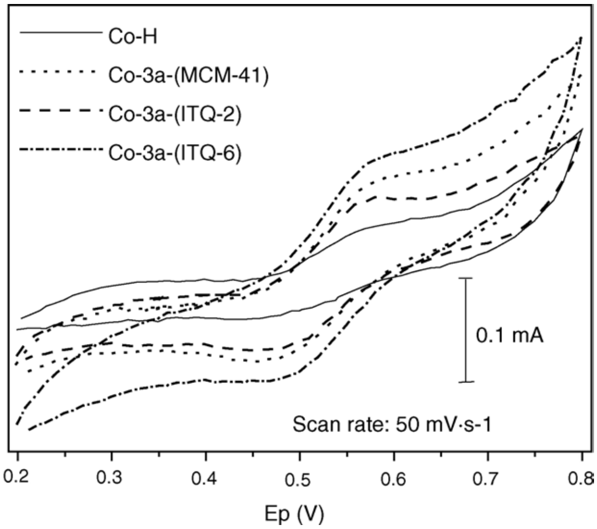


Fig. 4. Cyclic voltammograms for electrodes modified with cobalt homogeneous (**Co-H**) and heterogenised porphyrins [**Co-3a-(support)**]. Electrode composition (ratio catalyst/binder): 80:20 [**Co—H** and **Co-3a-(ITQ-6)**]; 70:30 [**Co-3a-(MCM-41)** and **Co-3a-(ITQ-2)**].

equipment. A three-electrode cell was used with an Ag/AgCl reference electrode and a stainless steel plate as contraelectrode.

Prior to the oxygen reduction experiments, modified electrode under study was immersed directly in the electrolyte (aqueous 0.5 M H_2SO_4) for 1 h and oxygen was then bubbled through the solution during 10 min. Results obtained heterogenised metalloporphyrins and their homogeneous analogues are represented in Figs. 4 and 5.

In an attempt to elucidate the net reaction for the oxygen reduction, voltammetric experiments, at varying scan rate, were carried out with a representative cobalt [**Co-3a-(MCM-41)**] and iron [**Fe-3a-(ITQ-6)**] heterogenised porphyrin. Plot of the relationship of the peak currents and potentials with scan rate for these samples is show in Fig. 6(A and B).

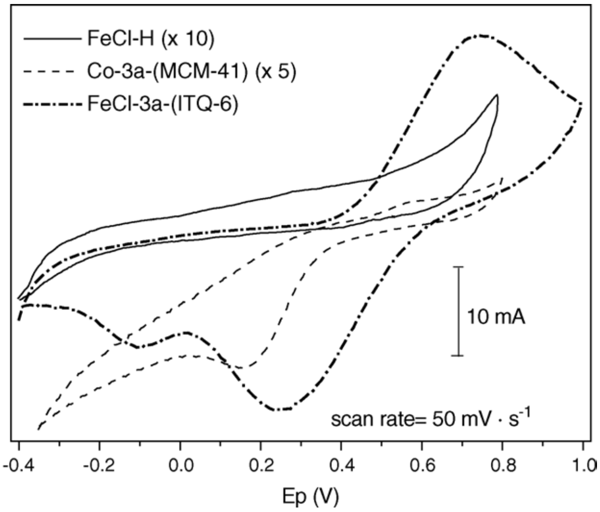


Fig. 5. Cyclic voltammograms for O_2 reduction at modified electrodes with homogeneous (**FeCl—H**) and heterogenised metalloporphyrins [**Co-3a-(MCM-41)** and **Fe-3a-(ITQ-6)**].

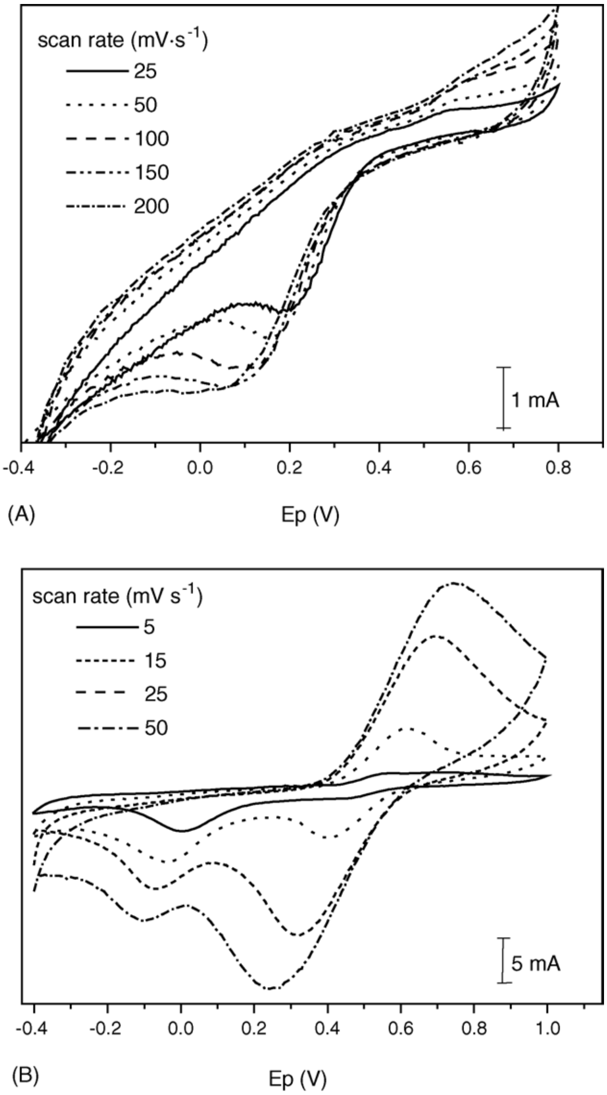


Fig. 6. Changes of I and E_p with the scan rate for the reduction of dioxygen on a electrode modified with (A) **Co-3a-(MCM-41)** or (B) **Fe-3a-(ITQ-6)**.

3. Results and discussion

3.1. Synthesis of heterogenised porphyrins

Two synthetic strategies have been explored for the preparation of heterogenised cobalt- and iron-porphyrins. Firstly, following route A (Scheme 1), the urea derivative **1** was prepared and fully characterised. This porphyrin **1**, that bears a $Si(OEt)_3$ group, was anchored to different inorganic supports (silica gel, purely siliceous MCM-41, and delaminated zeolites ITQ-2 and ITQ-6) by controlled hydrolysis of Si-OEt bond at room temperature and reaction with the free silanols on the surface of the supports. Solids were Soxhlet-extracted to remove all organic material non-covalently bounded to the support. The loading of porphyrin in these heterogenised materials [**3a-(support)**], based on N-contents from elemental analysis data, is reported in Table 3 and it ranges from 0.1 to 0.5 mmol g^{-1} dependently on the support. These values have been used for calculating the ratio catalyst/substrate in the reaction tests.

The content of porphyrin incorporated to the support is related to different factors: surface area, structural characteristics of supports and number of silanol groups that are accessible for grafting. Both silica and MCM-41 are short range amorphous materials containing a large number of silanol groups available for grafting. In the case of MCM-41, the material presents a long range ordering of hexagonal symmetry with regular monodirectional channels of 3.5 nm diameter. On the other hand, ITQ-2 and ITQ-6 delaminated zeolites present both, short and long range order, together with a large-well structured external surface in which the silanol groups act as grafting centres. However, there are structural differences between the two delaminated zeolites. Indeed, in the case of the ITQ-2 there are "cup-like" apertures to the external surface with ∼0.8 nm × 0.8 nm dimensions, while in the case of the ITQ-6 these "cups" are less deep (∼0.3 nm). In both delaminated zeolites the structured silanols are located at the borders of those "cups" [23]. On the basis of the percentage of porphyrin incorporated to the different supports it can be concluded that the structural characteristics of these materials, based on channels, sheets or cups, are decisive in the incorporation of a bulky molecule as porphyrin. Thus, silica where the steric constraints are minimised, is the support that incorporates a higher content of ligand although the surface area in this case is lower than in the other supports.

The presence of the porphyrin unit on the surface of support was confirmed by UV–vis diffuse reflectance (Fig. 1) and IR spectroscopies of the systems. UV–vis spectra of these new heterogenised porphyrins show five bands in the expected range for Soret band (∼415 nm, high intensity and high energy band) and Q bands (∼500–650 nm, four low intensity and low energy bands). Comparing these absorption spectra with the obtained one for derivative **1,** whose spectrum is typical of porphyrin, it was observed that the ratio of the intensities between the Soret and Q bands decreases markedly from ca. 17 to ca. 1.3 when porphyrin is bounded to the inorganic support. This phenomenon can be explained by the effect of the extreme light scattering at wavelengths below 500 nm and it has been observed previously for this type of materials [24].

Cobalt and iron were selected as metal-ions for being incorporated to the porphyrin based on its redox-active nature. The formation of complexes using the corresponding metallic salt proceeded in good yields (76–80%) to give the new heterogenised metalloporphyrins [**M-3a-(support)**]. The content of metalloporphyrin anchored to the supports is summarised in Table 3 and it ranges between 0.10 and 0.45. Although similar results have been observed with different metals (Co and Fe) using the same support, it must be noted that ITQ-2 incorporates a lower content of iron(III)porphyrin in comparison to cobalt(II)porphyrin probably due to its higher surface polarity [19].

The combined use of UV–vis and IR spectroscopy gives evidence that complexes are formed. In all cases it is possible to observe a slight shift of Soret band with the formation of the metallic complex and a decrease in the number of the Q bands (Fig. 3); an additional band appears at 380 nm for iron complexes. Furthermore, IR spectra of these metallic complexes shows an increased intensity for band at 1350 cm^{-1}, corresponding to C=N stretching [25], and an additional band near 1000 cm^{-1}. These contributions directly argue for the formation of the corresponding metallic complexes [26,27].

In order to demonstrate that metal is exclusively co-ordinated to the core of the porphyrin and not to the support, metallation reaction was carried out in a previous step to heterogenisation. The cobalt complex of porphyrin derivative **1** was synthesised and fully characterised, and its heterogenisation on MCM-41 yielded a new material practically indistinguishable from **Co-3a-(MCM-41)**. The successful synthesis of the supported catalysts was confirmed by IR and diffuse-reflectance UV–vis spectroscopies.

Based on these results it can be concluded that the species are covalently bounded to the surface and the coordination sphere around the metal is the same for the unsupported complexes under these reaction conditions.

Although we have developed a useful methodology to synthesise heterogenised porphyrins and taking into account the low to moderate yields achieved for targeted porphyrins, due to the tedious purification from the resulting reaction mixtures, we have designed and tested an alternative route (route B, Scheme 1). It is mainly based on the previous heterogenisation of an aromatic aldehyde on the support and consecutive porphyrin formation via co-condensation of pyrrole, benzaldehyde and heterogenised aldehyde. In this way, *p*-nitrobenzaldehyde was reduced, using Pd/C as catalyst, and treated in situ with trietoxysilylpropyl isocyanate to yield the urea derivative **2**. The reductive atmosphere avoids the polymerisation of *p*-aminobenzaldehyde and allows the one-pot reaction between amine group and isocyanate. The amount of Pd/C was adjusted to minimise the double addition of isocyanate to the amine group, for instance, using 2.5% (w/w) of this catalyst the reduction of nitro group was not completed and a mixture (45:55) of **2** and product from double addition was obtained. No products from hydrolysis of Si–OEt bonds in the reaction media could be detected.

Heterogenisation on different supports of compound **2**, which bears a triethoxysilyl group, yields the new materials **2-(support)**. Based on the analytical data of C, H and N, the content of aromatic aldehyde anchored to the support varies from 0.4 to 0.55 mmol g^{-1} (Table 3). Due to the molecular size of compound **2**, the content of ligand incorporated to the support is higher than in the case of a voluminous molecule, such as porphyrin **1**, is heterogenised. Further co-condensation between heterogenised aldehydes **2-(support)** with pyrrol and benzaldehyde yielded **3b-(support)** samples. Unfortunately, it was not possible to calculate the real content of porphyrin incorporated to the support for these samples, due to the presence of other organic compounds, such as heterogenised aldehydes without condensing or adsorbed specimens.

In Fig. 2, UV–vis spectra of the ITQ-6-heterogenised aldehyde [**2-(ITQ-6)**] and the corresponding **3b-(ITQ-6)** are shown; similar results are obtained for the different supports. All heterogenised aldehydes, independently on the support, show a broad band near 300 nm. This band is also visible in the spectra of [**3b-(support)**] samples, indicating that certain percentage of heterogenised aldehyde remains without condensing. Although an additional band appears in the region of Soret bands (∼415 nm), Q bands are scarcely observable in the spectra of these heterogenised porphyrins synthesised following route B. On the other hand, it is not possible to distinguish any variation in the spectra when the corresponding metallic complexes are formed.

Thus, it can be concluded that unfortunately, under these conditions, there are no evidence to confirm the formation of porphyrin ring. It seems to be formed but in a very low percentage and most of the heterogenised aldehyde remains without reacting. This fact could probably due to the adsorption of pyrrol on acid centres but further studies are required in order to fully confirm this conclusion.

3.2. *Catalytic properties*

The conductivity of new metalloporphyrin modified electrodes, measured in DC conditions, ranges from 12 to 60 μS cm^{-1}. Although conductivities were in general very similar and slightly low, the higher values corresponded to the electrodes based on porphyrins heterogenised on zeolite ITQ-6.

Oxidation and reduction potentials of new cobalt and iron porphyrins as well as their catalytic activity towards O_2 reduction were determined by cyclic voltammetry. Previous studies of zeolite-encapsulated complexes [8] demonstrated the possibility of electrochemical characterisation of physically entrapped metal complexes inside the zeolite cavities by using the pressed powder-composite electrodes.

In the absence of oxygen, the heterogenised catalysts and their homogeneous analogues exhibit a clear and reversible response at 0.57 and 0.74 V versus Ag/AgCl, for Co (III/II) and Fe (III/II) couples, respectively, independently on the support. Cyclic voltamograms for homogeneous and heterogenised cobalt porphyrins are shown in Fig. 4.

Although all new catalysts were screened for the oxygen reduction, only the cyclic voltammograms of representative homogeneous and heterogenised porphyrin electrodes, with comparable intensity, are shown in Fig. 5. No response was observed when metalloporphyrins heterogenised following route B, **M-3b-(support)** samples, were used, probably because of the extremely low content or absence of metalloporphyrin in these materials. However, in the case of the catalyst heterogenised following route A, **M-3a-(support)**, a reduction wave was observed with a well-defined peak potential at about 0.19 V for cobalt complexes, and at −0.10 V for iron ones at an scan rate of 50 mV s^{-1}, which can be assigned to the catalysed oxygen reduction. Further reduction of hydrogen peroxide to water was not observed to more negative potentials under working conditions. For homogeneous samples (**Co–H** and **FeCl–H**), where the porphyrin complex is non-covalently bounded to the support, the peak current corresponding to the oxygen reduction decreased with repetitive scans until disappearing and a gradual change in coloration of electrolyte was observed. Thus, the lack of activity for these catalysts is probably due to the metalloporphyrin desorption from the electrode. On the other hand, in the case of heterogeneous materials no significant decrease of the current densities was detected in a test of various oxidation–reduction cycles, indicating that it was not leached off during the experiments and electroactive species are strongly retained on the material surface.

Dioxygen can be reduced at the chemically modified electrodes by a two-electron process to H_2O_2 or via a direct four-electron reduction to H_2O. In an attempt to elucidate the net reaction for the oxygen reduction with these new modified electrodes, cyclic voltammetry experiments at varying scan rate were carried out (Fig. 6(A and B)). In these experiments, under oxygen saturated atmosphere, the currents were higher when scan rate was increased and the peak shifted to more negative potentials.

It was found that the peak currents increased linearly with the square root of the scan rate between 25 and 200 mV s^{-1} for [**Co-3a-(MCM-41)**] or 5 and 50 mV s^{-1} for [**Fe-3a-ITQ-6)**], suggesting that the electrocatalytic processes are controlled by O_2 diffusion in modified electrode [28].

For a typical irreversible reaction, the relationship between peak current and scan rate is as follows [29,30].

$$I_\mathrm{p} = 0.4958 n F A c_0 \left(\frac{\alpha n_\alpha F}{RT}\right)^{1/2} \upsilon^{1/2} D_0^{1/2} \quad (1)$$

$$\Delta E_\mathrm{p} = \frac{1.15 RT}{\alpha n_\alpha F} \quad (2)$$

where n is the number of electrons transferred, A the surface area of the electrode (a surface area of 1.131 cm^2 was employed), D_0 and c_0 the oxygen diffusion coefficient and the bulk concentration, respectively, υ the scan rate in V s^{-1}, α the transfer coefficient, n_α the apparent number of electrons transferred in the rate-determining step and ΔE_p is the peak potential change when the scan rate increases 10-fold. Other symbols have their usual significance. In the air-saturated solution, ${D_0}^{1/2} c_0$ is calculated as 3.2×10^{-8} mol s$^{-1/2}$ cm^{-2} in the present experiment (obtained from the relation between I_p and $\upsilon^{1/2}$, referred to the reduction of oxygen to water at a bulk Pt electrode in the same solution). The potential shifts ΔE_p are determined to be 0.269 and 0.107 V for [**Co-3a-(MCM-41)**] and [**Fe-3a-(ITQ-6)**], respectively. The values of αn_α are calculated from Eq. (2), and replacing these values in Eq. (1) the number of electrons n for the reduction can be calculated as 2.1 for **Co-3a-(MCM-41)** and 2.2 for **FeCl-3a-(ITQ-6)**. These facts conclude that under the catalysis of these single heterogenised metalloporphyrins, O_2 reaching the electrode by diffusion is mainly reduced through a two-electron process to H_2O_2.

It has been shown [7] that presence of cofacial dimeric porphyrin specimens, whose distance between rings is adapted to accommodate an oxygen molecule, constitutes an important factor to achieve the four-electron reduction of oxygen. Thus, assuming that drawbacks of instability of catalyst by self-oxidation, its desorption from the electrode or the low contents of catalytic active material incorporated to the support has been solved following the proposed methodology, its application to synthesise stable heterogenised dimetalloporphyrins seems to be promising in the searching of new catalysts for oxygen electroreduction to water.

4. Conclusions

The comparison of characterisation results with catalytic behaviour suggests that new heterogenised porphyrins and metalloporphyrins can be easily synthesised by a widely applicable methodology, bearing a stable covalent bond with support. Synthetic route A allows to achieve high content of metalloporphyrin incorporated to the support ($\sim$0.2–0.4 mmol g^{-1}) whereas following route B there is no evidence of porphyrin formation. Mesostructured solids and well structured-all accessible delaminated zeolites seem to be suitable supports to immobilizing homogeneous porphyrins, both with very high surface areas and accessibility to reactants.

These catalysts are useful for oxygen electroreduction, to H_2O_2, with comparable results than referable monomer soluble porphyrins. The percentage of metallic complex incorporated to the support, which is higher in the case of MCM-41 with higher surface area and containing larger number of silanol groups available for grafting, are directly related to the catalytic activity. It should be noted that although the zeolite framework serves as relay between host species probably not all the metalloporphyrins present in the modified electrode are addressable for the electrochemical reaction. This factor as well as the electronic conductivity of the new materials is the main responsible for their catalytic activity so new strategies should be developed to improve the electrochemical accessibility of the encaged complexes.

On the other hand, it has been demonstrated that, independently of nature of support, the heterogenised porphyrins are very stable materials and no desorption from electrode were detected under usual operation conditions for several runs, having an extended catalytic life.

Based on these results it could be expected that dimeric coupled heterogenised porphyrins, with an appropriated linkage, will be a promising catalyst for the four-electron reduction of oxygen to water in the cathode of fuel cells and such study is presently in progress in our laboratory.

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References

[1] J. Larminie, A. Dicks, Fuel Cell System Explained, Willey, Chinchester, 2000.
[2] L. Carrette, K.A. Friedrich, U. Stimming, Chem. Phys. Chem. 1 (2000) 163.
[3] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345.
[4] S. Gottesfeld, T. Zawodzinski, Adv. Electrochem. Sci. Eng. 5 (1997) 195.
[5] R. Jasinki, Nature 201 (1964) 1212.
[6] T. Imaoka, S. Nakazawa, K. Yamamoto, Chem. Lett. (2001) 412.
[7] J.P. Collman, P.S. Wagenknecht, J.E. Hutchison, Angew. Chem. Int. Ed. Engl. 33 (1994) 1537.
[8] F. Bedioui, Coord. Chem. Rev. 144 (1995) 39.
[9] S.-i. Yamazaqui, Y. Yamada, T. Ioroi, N. Fujiwara, Z. Siroma, K. Yasuda, Y. Miyazaki, J. Electroanal. Chem. 576 (2005) 253.
[10] H.C. Saco, Y. Iamamoto, J.R. Lyndsay Smith, J. Chem. Soc. Perkin Trans. 2 (2001) 181.
[11] J.L. Zhang, Y.L. Liu, C.M. Che, Chem. Commun. (2002) 2906.
[12] E. Hasegawa, J.I. Nemoto, T. Kanayama, E. Tsuchida, Eur. Polym. J. 14 (1978) 123.
[13] U. Johanson, M. Marandi, V. Sammelselg, J. Tamm, J. Electroanal. Chem. 575 (2005) 267.
[14] E. Brulé, Y.R. De Miguel, Tetrahedron 43 (2002) 8555.
[15] F.G. Doro, J.R. Lyndsay Smith, A.G. Ferreira, M.D. Assis, J. Mol. Catal. A 164 (2000) 97.
[16] T. Stuchinskaya, N. Kundo, L. Gogina, U. Schubert, A. Lorenz, V. Maizlish, J. Mol. Catal. A 140 (1999) 235.
[17] P.R. Coke, J.R. Lyndsay Smith, Tetrahedron Lett. 33 (1992) 2737.
[18] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[19] A. Corma, V. Fornés, J.M. Guil, S. Pergher, T.L.M. Maesen, J.G. Buglass, Microporous Mesoporous Mater. 38 (2000) 301.
[20] A. Corma, U. Diaz, M.E. Domine, V. Fornés, Angew. Chem. Int. Ed. 39 (2000) 1499.
[21] W.J. Kruper, T.A. Chamberlin, M. Kochanny, J. Org. Chem. 54 (1989) 2753.
[22] V.V. Borovkov, J.M. Lintuluoto, I. Inoue, Synlett 1 (1999) 61.
[23] G. Sastre, C.R.A. Catlow, A. Corma, J. Phys. Chem. B 103 (1999) 5187.
[24] S. Cherian, C.C. Wamser, J. Phys. Chem. B 104 (2000) 3624.
[25] D.W. Thomas, A.E. Martell, J. Am. Chem. Soc. 78 (1956) 1338.
[26] T. An, Y. He, Y. Fang, X. Jin, H. Chen, J. Mol. Catal. A 159 (2000) 143.
[27] F.S. Vinhado, P.R. Martins, A.P. Masson, D.G. Abreu, E.A. Vidoto, O.R. Nascimento, Y. Iamamoto, J. Mol. Catal. A 188 (2002) 141.
[28] W. Lu, C. Wang, Q. Lv, X. Zhou, J. Electroanal. Chem. 558 (2003) 59.
[29] R.S. Nicholson, I. Shain, Anal. Chem. 36 (1964) 706.
[30] A.J. Bard, L.R. Faulkner, Electrochemical Methods-Fundamentals and Applications, Wiley, New York, 1980, Chapters 3 and 12.