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A cooperative effect between support and the heterogenised metalloporphyrins on electrocatalytic oxygen reduction

A. Fuerte[a,]*, A. Corma[b], M. Iglesias[c], E. Morales[d], and F. Sánchez[a,]*

[a]*Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*
[b]*Instituto de Tecnología Química, UPV-CSIC, Avda. de los Naranjos, s/n, 46022 Valencia, Spain*
[c]*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain*
[d]*Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

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A new general method to heterogenise porphyrins and different metalloporphyrins (Co, Fe) on silica, mesoporous MCM-41 and delaminated zeolites ITQ-2 and ITQ-6 yields stable materials, which act as active catalysts for the electrochemical oxygen reduction, without catalyst desorption from the electrode.

KEY WORDS: metalloporphyrins; heterogenised catalysts; electrocatalytic oxygen reduction.

1. Introduction

Cobalt and iron porphyrins have been proposed as a substitute to platinum as electrocatalyst for the O_2 reduction taking place at the cathode in a fuel cell [1]. However, its technological application seems limited by several reasons, mainly their instability due to the intermolecular self-oxidation and desorption of the catalyst from the electrode. A useful means to avoid these limitations is by heterogenisation of these transition metal complexes onto robust inorganic supports, due to the stable covalent binding established between catalyst and support and the demonstrated increased stability of the metallic complexes after supporting. Different methods have been used to heterogenise metalloporphyrins, namely, electrostatic binding [2], entrapment [3], polymerisation [4], covalent binding [5] or axial ligation of metal [6], but most of them suffer from a reversible binding under working conditions [2,6] or a fairly low porphyrin contents onto the solid matrix($\approx$0.02 mmol/g) [5]. 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 heterogenised porphyrins and metalloporphyrins. These systems and their homogeneous analogues have been comparatively tested for electrocatalytic oxygen reduction.

2. Experimental

2.1. Synthesis of ligand

Following the synthetic route developed in scheme 1, trietoxysilylaminopropyl isocyanate (1.56 ml, 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 a modified described method [7], (1.26 g, 2 mmol, 1 eq) in ethyl acetate (15 ml). After stirring for 16 h at refluxing of solvent, this was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (eluent:ethyl acetate-hexane 1:3) to yield the urea derivative 1. Yield 94%, elemental analysis ($C_{54}H_{52}N_6O_4Si$): Calc. C 73.94; H 5.98; N 9.58. Found C 73.82; H 6.01; N 9.40%. ^{1}H NMR ($CDCl_3$): δ 8.87 (2H, d, J = 4.9 Hz, 2,8-CH pyrrole); 8.83 (4H, s, 12, 13, 17, 18-CH pyrrole); 8.81 (2H, d, J = 4.9 Hz, 3,7-CH pyrrole); 8.26–8.14 (6H, m, *o*-H monosubst. phenyl); 8.11, 7.64 (4H, AA′BB′, J = 8.5 Hz, *p*-subst. phenyl); 7.78–7.68 (9H, m, *m,p*-H monosubst. phenyl); 6.63 (1H, s, PhNH); 5.12 (1H, t, J = 6,1 Hz, CH_2NH); 3.86 (6H, c, J = 7.0 Hz, CH_2CH_3); 3.35 (2H, dt, J = 6.1, 7.2 Hz, CH_2NH); 1.76 (2H, q, J = 7.2 Hz, $CH_2CH_2CH_2$); 1.25 (9H, t, J = 7.0 Hz, CH_2CH_3); 0.75 (2H, t, J = 7.2 Hz, CH_2Si); −2.79 (2H, s, NH pyrrole). ^{13}C NMR ($CDCl_3$): δ 155.5 (C=O), 142.1–118.5 (C-arom, C-pyrrole), 58.6 (OCH_2), 43.6 ($NHCH_2$), 23.4 ($CH_2CH_2CH_2$), 18.4 (CH_3), 7.8 (CH_2Si). IR (KBr pellets, cm^{-1}). ν 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). MS$^+$(*m*/*z*): 877 (M$^+$), 248, 176, 118, 102(100).

2.2. Heterogenisation of porphyrin ligand

This porphyrin **1** was heterogenised on silica based mesoporous and laminar silanols surface rich inorganic solids, such as silica gel, purely siliceous MCM-41 [8], and delaminated zeolites ITQ-2 [9] and ITQ-6 [10]. The textural characteristics of the solids are given in table 1.

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* To whom correspondence should be addressed.

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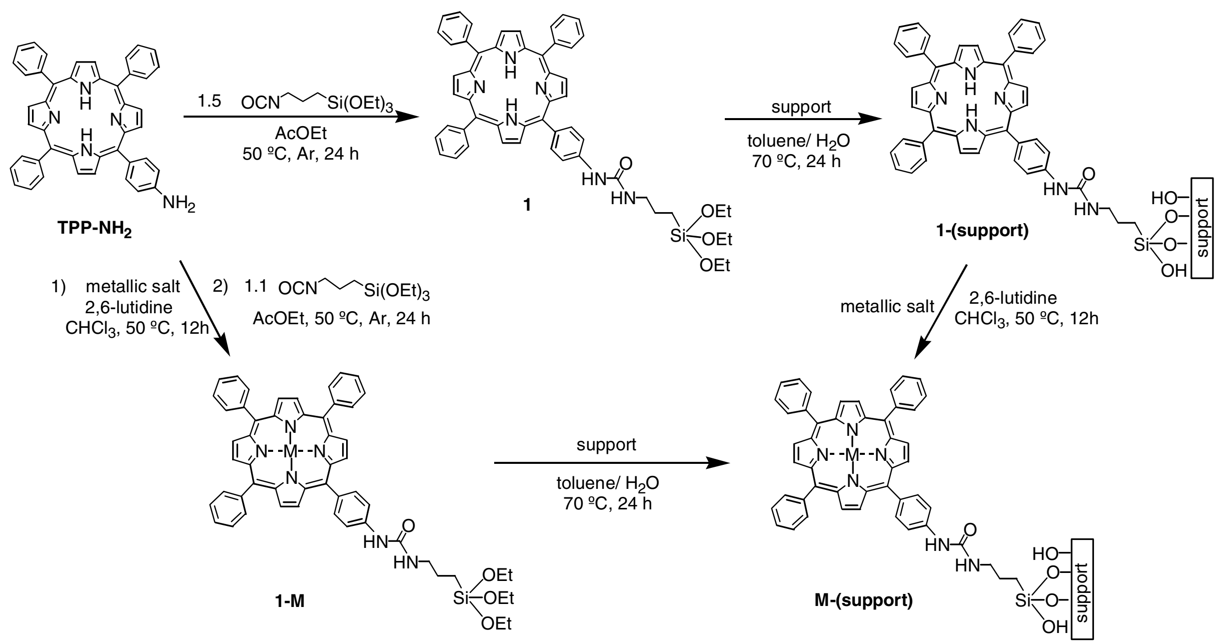

support: silica gel, MCM-41, ITQ-2, ITQ-6; **metallic salt**: $(AcO)_2Co·4H_2O$, $FeCl_2·4H_2O$; **M**: Co, FeCl

Scheme 1.

A typical procedure for the heterogenisation is as follows: a solution of **1** (876 mg,1 mmol) in toluene (10 ml) and 200 µl of water were added to a suspension of the inorganic support (1 g) in toluene (30 ml). After 16 h at 70 °C the solid was filtered off and 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 **1-(support)**.

2.3. Synthesis of metal complexes

Complexes were formed by addition of the corresponding metallic salt, cobalt (II) acetate (30 mg, 0.12 mmol, 1.2 eq) or $FeCl_2$ (100 mg, 0.5 mmol, 5 eq) and four drops of 2,6-lutidine to a suspension of the heterogenised porphyrins **[1-(support)]** (62 mg, 0.1 mmol, 1 eq) in chloroform (10 ml). After stirring for 12 h at reflux temperature of solvent, the solid crude was filtered and Soxhlet-extracted with chloroform for 7 h and heterogenised metalloporphyrins **[(M-support)]** were isolated. They were characterised using UV–Vis diffuse reflectance (figure 1) and FTIR spectroscopies; the content of ligand incorporated to the supports, measured by atomic absorption and inductively coupled plasma (AA/ICP), is reported in table 2.

2.4. Preparation of modified electrodes

The modified electrodes (pellets, 12-mm diameter) were built by mixing porphyrin powder (80% wt.), polymer binder (KF2801, Atochem) (20% wt.) and acetone (2 ml) in a mortar. After homogenisation and solvent evaporation, the active past (40 mg) was cold pressed (500 kg, 5 min) on a stainless steel grid. Following this procedure it was not possible to prepare a robust electrode with catalysts heterogenised on silica gel.

For electrodes charged with homogeneous catalyst (**H-M**) a mixture of Co- or FeCl-tetraphenylporphyrin, MCM-41 and binder was used, being the ratio between components similar to the heterogenised analogues. The amount of metalloporphyrin in the modified electrodes is reported in table 2.

Electrodes for cyclic voltammetry experiments at different scan rate were prepared in a similar manner by

Table 1
Textural characteristics of the solid supports

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

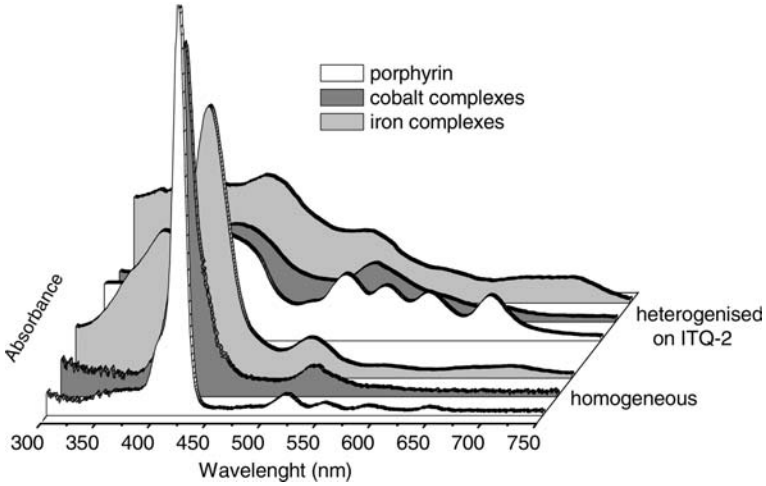

Figure 1. UV–Vis spectra of homogeneous porphyrins ($CHCl_3$.), heterogenised porphyrins (× 2.5) and the corresponding metallic complexes.

Table 2
Main characterisation results of heterogenised metalloporphyrins and porphyrin electrodes

Sample	Heterogenised metaloporphyrin loading of ligand[a]		Modified electrode surface covarage[b]	
	Co	Fe	Co	Fe
M-(Sil)	0.45	0.42	Φ	Φ
M-(MCM-41)	0.20	0.23	4.8	5.4
M-(ITQ-2)	0.30	0.13	3.5	2.9
M-(ITQ-6)	0.12	0.10	2.7	2.1
H-M	–	–	4.8	6.4

[Φ] unsuccessful preparation of modified electrode.
[a] measured by AA/ICP (mmol/g).
[b] content of porphyrin on the electrode (μmol/cm^2).

dispersing the metalloporphyrin (80 wt%), the polymer binder (10 wt%) and carbon back (Super P, 3 M) (10 wt%) was added to the mixture in order to increase the electrical conductivity.

2.5. Electrochemical measurements

All the measurements were carried out at room temperature. The electrical characterisation of the homo- and heterogenised metalloporphyrin samples were determined in DC conditions using a HP 6614C DC power supply connected to two HP 34401A digital multimeters. The conductivity ranges from 12 to 60 μS/cm, the higher values corresponding to the electrodes based on porphyrins heterogenised on zeolite ITQ-6.

Cyclic voltammetry experiments were performed using a Radiometer/Copenhagen Voltalab 32 potentiostat/galvanostat equipment. A three-electrode cell was used with a Ag/Ag+ reference electrode and an 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 with solution) 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 figure 2.

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-(MCM-41]** and iron **[Fe-(ITQ-6)]** heterogenised porphyrin. Plot of the relationship of the peak currents and potentials with scan rate for cobalt sample **[Co-(MCM-41]**is shown in figure 3.

3. Results and discussion

New heterogenised metalloporphyrins were obtained following the synthetic route developed in scheme 1. Porphyrin **1**, that bearing a $Si(OEt)_3$ group, was anchored to different inorganic supports by controlled hydrolysis of Si–OEt bond and reaction with the free silanols on the surface of the supports. The formation of complexes proceeded in good yields, the loading of metalloporphyrin in the heterogenised materials ranged

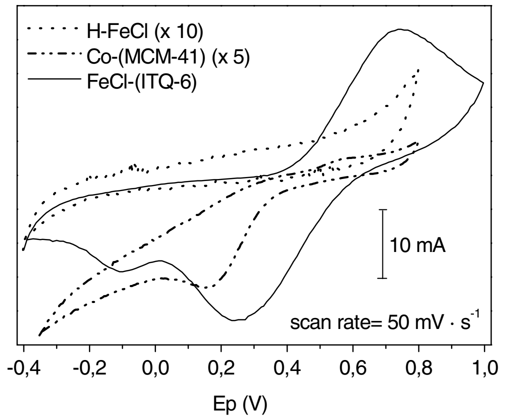

Figure 2. Cyclic voltammograms for homogeneous and heterogenised cobalt and iron porphyrins under oxygen saturated atmosphere at 273 K.

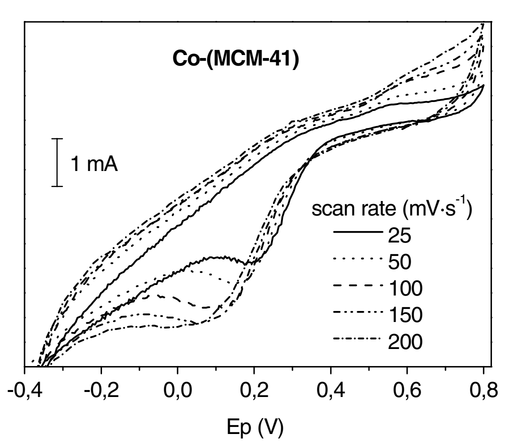

Figure 3. Changes of peak currents and potentials with the scan rate for the reduction of dioxygen on a modified electrode with **Co-(MCM-41)**. Electrode composition: 80% catalyst, 10% binder, 10% black carbon.

from 0.1 to 0.5 mmol/g (table 2), dependently on the support, and stoichiometry M/ ligand (1:1) was found.

Although the absorption spectrum of derivative **1** is typical of porphyrins (figure 1); the ratio of the intensities between the Soret (high intensity and high energy band) and Q bands (four low intensity and low energy bands) is ca. 17, the intensity of Soret band decreases markedly and the ratio is reduced to ca. 1.3, when porphyrin is bounded to the inorganic support [figure 1, **1-(ITQ-2)**]. This phenomenon can be explained by the effect of the extreme light scattering at wavelengths below 500 nm [11].

On the other hand, for metallic complexes (figure 1) a slight shift of Soret band and a decrease in the number of the Q bands is clearly visible. An additional band appears at 380 nm for iron complexes. Furthermore, IR spectrum of these metallic complexes shows an increased intensity for band at 1350 cm^{-1}, corresponding to C=N stretching [12], and an additional band near 1000 cm^{-1}. These contributions directly argue for the formation of the corresponding metallic complexes [13,14].

In order to demonstrate that metal is exclusively coordinated to the core of the porphyrin and not to the support, the formation of metallic complex was carried out in a previous step to the immobilisation (via **1-M** complex, scheme 1). The heterogenisation of the cobalt complex **(1-Co)** on MCM-41 yielded a new material practically indistinguishable from **Co-(MCM-41)**, prepared via **1-(MCM-41)**.

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. In the absence of oxygen, the heterogenised catalysts and their homogeneous analogues exhibit a clear and reversible response at 0.57 V and 0.74 V versus Ag/AgCl, for Co (III/II) and Fe(III/II) couples, respectively. 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 figure 2. In the case of the heterogenised catalyst, a reduction wave was observed with a 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, which can be assigned to the catalysed oxygen reduction. For homogeneous samples **(H-Co** and **H-Fe)**, where the porphyrin complex is non-covalently bounded to the support, the peak current corresponding to the oxygen reduction decreased with repetitive scans and a gradual change in coloration of electrolyte was observed. Thus, the lack of activity for this catalysts is probably due to the metalloporphyrin desorption from the electrode.

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 experiments of oxygen reduction on the modified electrodes the currents are higher when scan rate is increased and the peak shifts to more negative potentials (figure 3). It was found that the peak currents increased linearly with the square root of the scan rate, suggesting that the electrocatalytic processes are controlled by O_2 diffusion. From these experiments, considering a typical irreversible reaction, the number of exchanged electrons for the reduction can be estimated [15], leading to a value of 2.1 for **Co-(MCM-41)** and 2.2 for **FeC1-(ITQ-6)**. These facts conclude that under the catalysis of these heterogenised metalloporphyrins, O_2 reaching the electrode by diffusion is mainly reduced through a two-electron mechanism to H_2O_2.

The comparison of characterisation results with catalytic behaviour suggests that new heterogenised metalloporphyrins can be easily synthesised by a widely applicable methodology, bearing an stable covalent bond with support. 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, as well as the conductivity of new materials are directly related to the catalytic activity. 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, having an extended catalytic life.

Based on these results it could be expected that dimeric coupled heterogenised porphyrins will be a promising catalyst for the four-electron reduction of oxygen to water in the cathode of fuel cells and their study is in progress.

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