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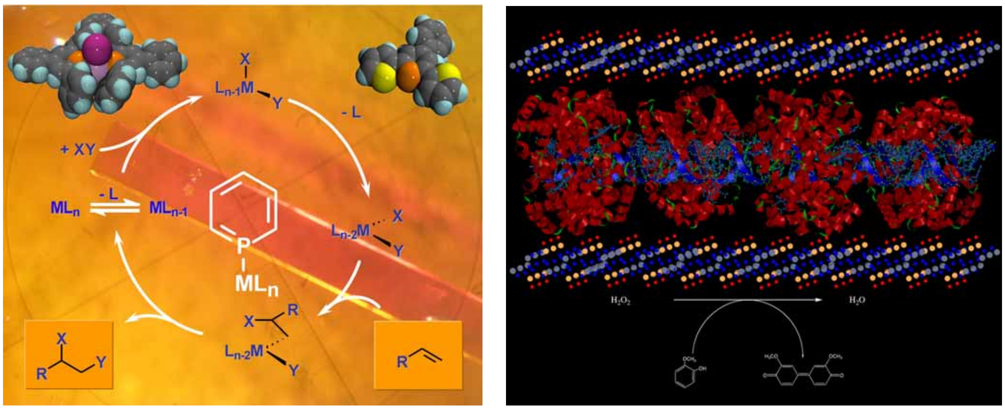

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Access to well-defined isolated Fe(II) centers on silica and their use in oxidation

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Well-defined Fe^{II} isolated sites are obtained by reaction of diaryl-*N*,*N*′-diazadiene bis(neosilyl) iron (**1**) with an aerosil silica, $SiO_{2\text{-}(700)}$. This system can be used as a precursor for the catalytic oxidation of cyclohexene into cyclohexene oxide, cyclohexenol and cyclohexenone in the presence of H_2O_2.

Introduction

The active sites of several oxygenases[1,2] and heterogeneous oxidation catalysts are based on Fe centers.[3–6] Notably, Fe-based zeolitic materials selectively oxidize benzene into phenol by N_2O, but the structure of the active site is still a matter of debate: isolated Fe center *vs.* binuclear Fe system (probably bonded through a μ-oxo bridge).[7] Recently, several bio-inspired homogenous catalysts have appeared using either mono- or binuclear Fe centers wrapped in a stabilizing ligand.[8–13] Using surface organometallic chemistry,[14] we report herein the reaction of 2,3-dimethyl-1,4-[(2′,6′)-diisopropylphenyl]-*N*,*N*′-diazadiene bis(neosilyl) iron (**1**)[15] with silica as a route to well-defined silica supported isolated Fe centers (**2**). Their activity as epoxidation catalyst precursors has been tested.

Experimental

All experiments were carried out by using standard air free methodology in a glove box under Ar, on a Schlenk line, or in Schlenk-type apparatus interfaced to high vacuum line (10^{-5} Torr). Ether and THF were distilled over a sodium–benzophenone mixture. CH_2Cl_2 was distilled over P_2O_5 and stored over 3 Å molecular sieves. All solvents were degassed by four freeze–pump–thaw cycles. The 2,3-dimethyl-1,4-[(2′,6′)-diisopropylphenyl]-*N*,*N*′-diazadiene bis(neosilyl) iron (**1**) was prepared according to the literature procedure.[15] Gas-phase analysis was performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and Al_2O_3–KCl on a fused silica column (50 m × 0.32 mm).

Elemental analysis was performed at the CNRS Central Analysis Service of Solaize and at the Laboratory of Organometallic Synthesis and Electrosynthesis at Dijon. Infrared spectra were recorded on a Nicolet 550-FT by using an infrared cell equipped with CaF_2 windows, allowing *in situ* studies. Typically 16 scans were accumulated for each spectrum (resolution, 2 cm^{-1}).

The X-ray absorption spectra were acquired at the SRS of the CCLRC at Daresbury, UK, on beam line 7.1. The sample studied, a solid resulting from the grafting of **1** onto $SiO_{2\text{-}(700)}$ (*vide infra*), was loaded within a nitrogen filled glove-box in a double-airtight sample holder equipped with Kapton windows. The sample was studied at room temperature, at the iron K-edge, in the transmission mode and using a double-crystal Si-(111) monochromator detuned to eliminate most of the higher harmonics content of the beam. Additionally, the spectra were recorded between 11 600 and 12 400 eV. The analysed spectrum was the result of the averaging of three acquisitions. The data analyses were performed by standard procedures using the programs developed by Alain Michalowicz, in particular the EXAFS fitting program RoundMidnight.[16] The background absorption, μ_0, was calculated by using a theoretical expression developed by Lengeler and Eisenberger and the single atomic absorption of the absorber, μ_1 was interpolated by a sixth degree polynomial between 11 600 and 12 400 eV.[17]

Fitting of the spectrum was done on the k^3 weighted data using the following EXAFS equation where $S_0{}^2$ is the scale factor; N_i is the coordination number of shell i; F_i is the EXAFS scattering function for atom i; R_i is the distance to atom i from the absorbing atom; λ is the photoelectron mean free path; σ_i is the Debye–Waller factor; Φ_i is the EXAFS phase function for atom i; and Φ_c is the EXAFS phase function for the absorbing atom:

$$\chi(k) \cong S_0^2 \sum_{i=1}^{n} \frac{N_i S_i(k, R_i) F_i(k, R_i)}{k R_i^2} \exp\left(\frac{-2R_i}{\lambda(k, R_i)}\right) \times \exp\left(-2\sigma_i^2 k^2\right) \sin\left[2kR_i + \Phi_i(k, R_i) + \Phi_c(k)\right]$$

The program FEFF7 was used to calculate theoretical values for S_i, F_i, λ, Φ_i, and Φ_c based on model clusters of atoms. The refinements were performed by fitting the structural parameters N_i, R_i, σ_i and the energy shift, ΔE_0. The fit residue, ρ, was calculated by the following formula:

$$\rho = \frac{\sum_k \left[k^3\chi_{\text{exp}}(k) - k^3\chi_{\text{cal}}(k)\right]^2}{\sum_k \left[k^3\chi_{\text{exp}}(k)\right]^2}$$

Where $\chi_{\text{exp}}(k)$ and $\chi_{\text{cal}}(k)$ designate respectively the experimental and simulated oscillatory parts of the absorption coefficient. The smaller this parameter is (in % in Table 1), the better is the agreement between experimental and simulated spectrum.[18]

Grafting of 1 on $SiO_{2\text{-}(700)}$ monitored by infrared spectroscopy. Representative procedure

In an IR-cell 50–100 mg of silica were pressed into a 18 mm self-supporting disk, which was put into a sealed glass high-vacuum

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reactor equipped with CaF_2 windows, and partially dehydroxylated under vacuum (500 °C, 12 h and 700 °C, 4 h). The silica disk was then immersed in a pentane solution of **1** at 25 °C for 3 h followed by two pentane washings and a drying step under dynamic vacuum at room temperature. After this step an IR spectrum was recorded.

Preparation of [1–$SiO_{2\text{-}(700)}$] by impregnation. Representative procedure

A mixture of **1** (80 mg, 0.13 mmol, 1.15 equiv. per surface silanols) and $SiO_{2\text{-}(700)}$ (500 mg) in pentane (8 mL) was stirred at 25 °C for 3 h. After filtration, the solid was washed 3 times with pentane, and all volatile compounds were condensed into another reactor (of known volume) in order to quantify the TMS evolved during grafting. The resulting green powder was dried under vacuum (10^{-5} Torr, 2 h) to yield 535 mg of **2** [**1**–$SiO_{2\text{-}(700)}$]. Analysis by gas chromatography indicated the formation of 0.09 mmol of Me_4Si during the grafting (0.85 Me_4Si–Fe). Elemental analysis of **2**: Fe: 1.13%$_{wt}$, C: 6.95%$_{wt}$, H: 0.87%$_{wt}$, N: 0.67%$_{wt}$.

Cyclohexene epoxidation. Representative procedure

Cyclohexene was degassed by four freeze–pump–thaw cycles and dried over freshly activated molecular sieves (3 Å). In a 10 mL batch reactor, 60 mg (0.012 mmol Fe) of catalyst were loaded followed by 1 mL of cyclohexene (substrate : catalyst ~750). At t = 0, 200 µl of a 30% solution of H_2O_2 in H_2O (substrate : oxidant = 5, oxidant : catalyst ~150) were added, and the reaction mixture was stirred at 60 °C. Small aliquots (40 µl) were analyzed at different times by GC using dodecane as an external standard. Fe lixivation was investigated by titrating the Fe present in the solution using colorimetric measurements: the reaction mixture was filtered, 1 mL of supernatant was brought to 10 mL with a 0.1 M nitric acid aqueous solution, and this resulting solution was diluted 250 times, treated with the indicator HI93746 and the Fe content was measured with a HANNA colorimeter instrument indicating the presence of less than 2% of initial Fe content.

Results and discussion

After immersing a silica disk partially dehydroxylated at 700 °C ($SiO_{2\text{-}(700)}$) for 3 h in a purple solution of 2,3-dimethyl-1,4-[(2′,6′)-diisopropylphenyl]-*N*,*N*′-diazadiene bis(neosilyl) iron (**1**)[15] in pentane at 25 °C (1.2 equiv. with respect to surface silanols; 0.26 mmol accessible OH g^{-1} of silica), the silica disk turned green; it was washed twice with pentane to remove the excess complex and then dried under vacuum (10^{-5} Torr, 2 h). Monitoring the reaction by IR spectroscopy showed that the band attributed to isolated silanol groups at 3747 cm^{-1} disappeared (Fig. 1), but a broad band (ν_0) appeared in agreement with the presence of remaining silanols interacting with organometallic moieties (3740–3550 cm^{-1}, ~15% of the original SiOH intensity). Moreover, two groups of bands appeared in the 3000–2850 cm^{-1} and 1470–1350 cm^{-1} regions. These bands, ν_{2-3} and δ_{6-7}, are assigned to $\nu_{(CH)}$ and $\delta_{(CH)}$ vibrations of the alkyl ligands respectively. Additionally, two other bands appeared at 3065 (ν_1) and 1586 cm^{-1} (ν_5), which were respectively assigned to $\nu_{(=C-H)}$ and $\nu_{(C=N)}$ vibrations.

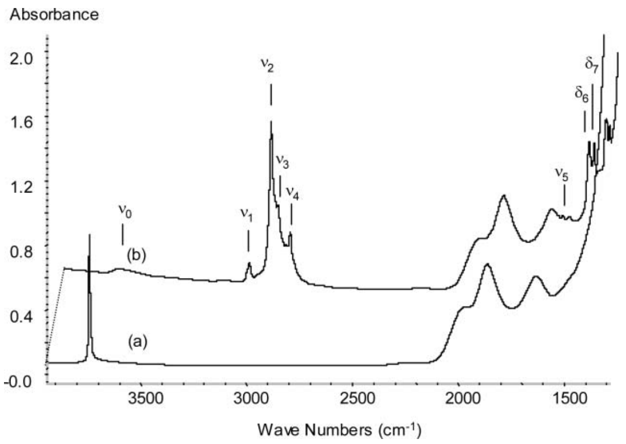
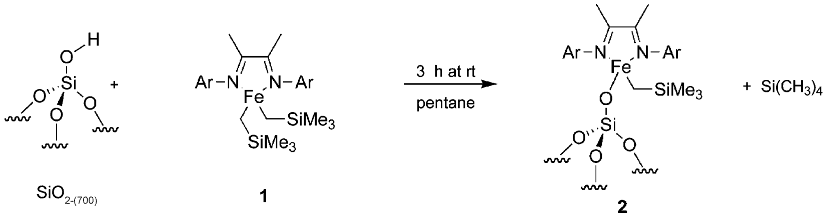


Fig. 1 Monitoring of the grafting of **1** on $SiO_{2\text{-}(700)}$ by IR spectroscopy. (a) $SiO_{2\text{-}(700)}$ pellet (50 mg). (b) After immersing $SiO_{2\text{-}(700)}$ in a pentane solution of 2,3-dimethyl-1,4-[(2′,6′)-diisopropylphenyl]-*N*,*N*′-diazadiene bis-neosilyl iron at 25 °C for 3 h followed by two washings with pentane and drying under vacuum.

Grafting of **1** was also carried out by impregnation in pentane at 25 °C with larger quantities of $SiO_{2\text{-}(700)}$. Iron elemental analysis on the resulting solid varies between 1.09–1.13%$_{wt}$, which corresponds to ~0.19–0.20 mmol Fe g^{-1}, confirming that most surface silanols have reacted (80% based on 0.26 mmol OH g^{-1} of $SiO_{2\text{-}(700)}$), which is consistent with what has been observed by *in situ* IR spectroscopy (*vide supra*). During grafting, 0.9 ± 0.1 equiv. of Me_4Si/grafted Fe was released. Moreover, carbon and nitrogen elemental analyses are 6.95 and 0.53%$_{wt}$, respectively, which correspond to 29 ± 3 C/Fe (expected 32 for **2**) and 1.9 ± 0.2 N/Fe (expected 2.0 for **2**). Furthermore, hydrolysis of the solid gives 0.8 ± 0.1 equiv. of Me_4Si (expected 1.0). All these data are consistent with the formation of **2** as the major surface species (Scheme 1).

Iron K-edge EXAFS studies on [**1**–$SiO_{2\text{-}(700)}$] provided further insight into the structure of the Fe surface species (Fig. 2): an average of one oxygen atom at 1.85 Å, one carbon atom at 1.97 Å and two nitrogen atoms at 2.10 Å in the coordination sphere of



Scheme 1 Proposed structure of the major surface species **2** (Ar = 2,6-diisopropylphenyl).

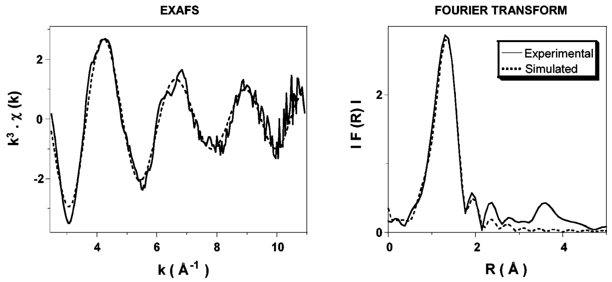


Fig. 2 Iron K-edge k^3-weighted EXAFS (left) and Fourier transform (right) of solid (**2**). Dashed lines: spherical wave theory, solid lines: experimental.

iron, which is consistent with **2** being the major species (Table 1). The Fe–C and Fe–N bond distances measured by EXAFS are in good agreement with those obtained by X-ray crystallography for **1** (Fe–C ~ 2.042 Å and Fe–N ~ 2.025 Å).[15,19,20] Finally, the Fe–OSi bond length is also very close to measured values of similar Fe molecular complexes (1.86–1.91 Å).[5,21]

Table 1 EXAFS Parameters for the solid **2**.[a] The errors generated by the EXAFS fitting program "RoundMidnight 2005"[16] are indicated between parentheses

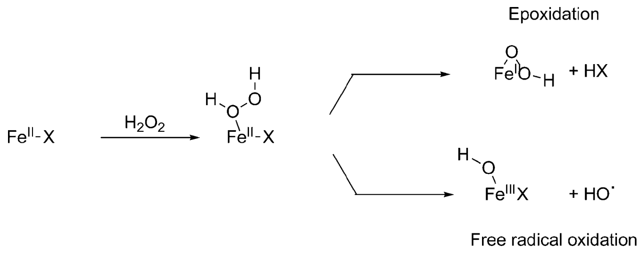
Neighbouring atom of Fe	Coordination number	Distance from Fe/Å	Debye–Waller factor/σ^2 Å^{-2})
–OSi	1	1.85(2)	0.004(2)
$–CH_2Si(CH_3)_3$	1	1.97(4)	0.002(1)
Ar–N=C–	2	2.10(3)	0.007(2)

[a] Δk: [2.4–10.9 Å^{-1}] – ΔR: [0.2–2.2 Å]; $\Delta E^0 = -4.8 \pm 1.4$ eV (the same for all shells); $S_0^2 = 1.0$; Fit residue: $\rho = 6.0\%$.

With **2** in hand, the epoxidation of cyclohexene was carried out. No reaction was observed when ^{t}BuOOH was used, and using CH_3CO_3H with or without catalyst gave cyclohexene oxide in 95% yield within 15 min. With H_2O_2 (30% in H_2O, 150 equiv.) in CH_3CN, cyclohexene (750 equiv.) is slowly converted into cyclohexene oxide along with 2-cyclohexenol and 2-cyclohexenone in the presence of **2** (1 equiv.), while no conversion was observed in the presence of pure silica. After one hour, 7.3% conversion is achieved, and the selectivity in epoxide is 24%, the major products being 2-cyclohexenol (32%) and 2-cyclohexenone (44%). Increasing the reaction time, however, decreased the yield of epoxide. The obtained selectivities are close to those reported by Tilley *et al.* using an isolated Fe^{III} siloxy species, and no Fe leaching was observed.[5] While the epoxide could probably be formed from the putative Fe^{II}OOH species, this species may readily decompose to generate hydroxyl radicals, so that the major pathway corresponds to Fenton chemistry as evidenced by the formation of 2-cyclohexenol and 2-cyclohexenone (Scheme 2).[22]

Conclusions

A route to well-defined isolated Fe^{II} centers dispersed onto a silica surface has been described. The alkyl derivative **2** has been fully characterised by elemental analysis, IR and EXAFS spectroscopies. In the presence of H_2O_2, this system catalyses the epoxidation of cyclohexene, but Fenton chemistry is the major pathway of oxidation leading to 2-cyclohexenol and 2-cyclohexenone. Further studies are currently under way to generate stable single-site Fe oxidation catalysts.



Scheme 2 Reactivity of Fe^{II} centers with H_2O_2 (X = CH_2SiMe_3 in **2** and X = OH during the catalytic cycle).

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