Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

The role of isolated active centres in high-performance bioinspired selective oxidation catalysts

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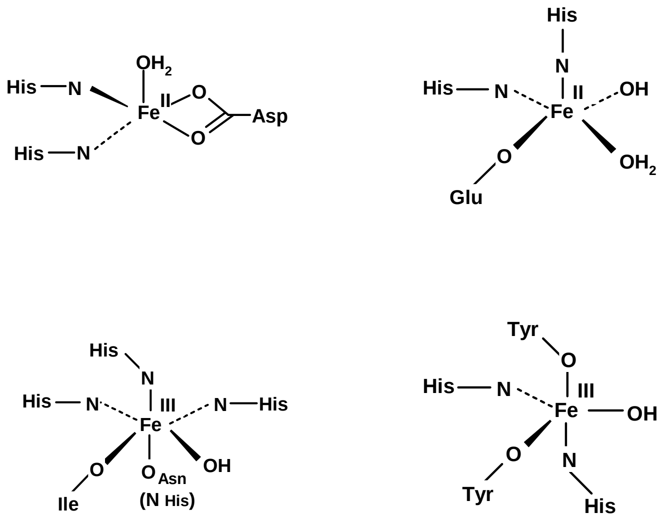


Scheme S1. Mononuclear iron active centres in non-heme enzymes that are responsible for substrate and oxygen activation.

Experimental

Iron acetate (Fe(CO$_2$CH$_3$)$_2$ (99.995%), fumed silica (99.8%), aluminum isopropoxide (99.99+%), Zeolite Y, cyclohexane (99.5%), benzyl alcohol (99+%), tert-Butyl hydroperoxide (TBHP) (70wt.% in water), mesitylene (98%), methanol and 1,2- dichloroethane both analytical reagent grade were purchased from Sigma-Aldrich. L-proline (>95.5%), triethylamine (Et$_3$N) (99.5%) were acquired from Fluka. Analytical grade sodium hydroxide (NaOH) and dimethyl sulfoxide (DMSO) were obtained from Fisher Scientific.
All reagents were used as received.

Fe^{3+}-Proline synthesis

The Fe^{3+}-Proline complex was prepared according to the methods described previously in the literature [1,2]. Proline (0.49g, 4,34 mmol) was dissolved in 10ml of MeOH. To this solution 0.6 ml of triethylamine (Et$_3$N) was added and the mixture was stirred for 0.5 h. The addition of iron acetate (0.37g, 2.17mmol) resulted in the formation of a yellow-grey precipitate. After stirring for 1h the resulting precipitate was collected by filtration, washed with methanol and dried in the air.

Fe^{3+}-Proline-X synthesis

The Fe^{3+}-Proline complex was encapsulated within the supercages of Zeolite-X using the '*zeolite synthesis method*' [3]. The silicate gel was prepared by stirring the 1.4 g of fumed silica, 1.06 g of NaOH, 0.1 g of Fe^{3+}-Proline and 3ml of water. Addition of the aluminate solution (aluminium isopropoxide 3 g, NaOH 1.06 g and water 2 ml) resulted in a pale-orange slurry. To this mixture 12 ml of water was added. The slurry was transferred to a polypropylene bottle with stirring for 24 h at room temperature and subsequently heated at 80^{o}C for 15 h. Complexes adsorbed on the exterior surface were removed by Soxhlet extraction technique. The resulting solid was dried at 80^{o}C for 24h.

Fe^{3+}-Proline-Y synthesis

Zeolite FeY was prepared by using the *'flexible ligand method'* in which metal complex is synthesized *in situ* in the zeolite cavity by reaction of the ligand with the previously exchanged metal cations [4].

2.5 g of NaY zeolite was suspended in 50 mL of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) aqueous solution (0.4 mmol) and the mixture was stirred for 24 h at room temperature. The solid fraction was then filtered, washed with deionized water and dried at 120°C for 12h to obtain FeY. 0.43 g of FeY was placed in round bottom flask and 20 ml of water was added. The pH was adjusted to 10 by using either a NaOH or HCL solution. To this suspension excessive amount of proline ligand (0.87 mmol) was added ($n_{\mathrm{ligand}}/n_{\mathrm{metal}}$=2.17). The complexation was carried out at room temperature for 24 h. Uncomplexed ligands and the complex molecules adsorbed on the exterior surface were removed by a thorough Soxhlet extraction with methanol and 1,2-dichloroethane.

Catalytic oxidation

The aerobic oxidation of benzyl alcohol using the neat Fe^{3+}-Proline complex and its corresponding zeolite-encapsulated heterogeneous analogue were performed in a high-pressure, stainless-steel catalytic reactor (Parr 4842) and comparative experiments with tert-butyl hydroxyperoxide (70% wt) were carried out using a glass-lined reactor. In both cases, the catalytic oxidations were studied at 98^{o}C. The reaction products were analysed by GC (PerkinElmer, Clarus 400) employing Elite Wax capillary column and Flame Ionisation Detector (FID). The identity and the quantification of the products were established by using mesitylene as an internal standard using the calibration method.

The identities of the products were first confirmed using authenticated standards and their individual response factors were determined using a suitable internal standard (mesitylene) by the calibration method. The overall yields were normalized with respect to the (GC) response factors obtained as above and the conversions and selectivities were determined by the following equations:

Conv. % = [(moles of initial substrate – moles of residual substrate) / (moles of initial substrate)] x 100

Sel. % = [(moles of individual product) / (moles of total products)] x 100

For the internal standard GC method, the response factor (RF) and mol % of individual products were calculated using the following equations:

RF = (mol Product/mol Standard) × (Area Standard/Area Product)
Mol % Product = RF x Mol Standard × (Area Product/Area Standard) x 100/Mol Sample

The identity of the products was further confirmed using GCMS. Hot filtration experiments and ICP measurements of the aqueous and organic mixtures were independently (and regularly) carried out to rule out the possibility of leaching. In most cases, the catalysts have been re-used 3 times without appreciable loss in catalytic activity or selectivity. Further, experiments analogous those reported earlier [5, 6], were carried out to rule out the possibility of leaching, and analysis of the resulting filtrate at the end of reaction by ICP and AAS revealed only trace amounts (< 5 ppb) of dissolved metal ions (Mn, Cr).

Catalyst characterisation

FTIR spectra were recorded using a Nicolet 380 spectrometer to confirm the structural integrity of the neat and encapsulated complexes. The purity of the complex was confirmed by elemental analysis.

X-Ray powder diffraction patterns were collected employing a Siemens D5000 diffractometer using Cu Kα1 radiation.

The UV-Vis spectra were recorded on Perkin-Elmer Lambda 900 DR UV-Vis with WinLab 900 software.

N_2 adsorption measurements were performed at liquid nitrogen temperature. Samples were first dehydrated and degassed in vacuum at 80°C. Surface area and micropore volume were determined by nitrogen adsorption-desorption isoterms using Micromeritics ASAP 2020. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the pore size was calculated using the Barrett-Joyner-Helenda (BJH) method.

The EPR experiments were performed using Bruker EMX spectrometer consisting of an electromagnet and X-band (9.8 GHz) microwave bridge ER 041XG in conjunction with a Bruker ER 4105D double rectangular resonator with a helium-gas flow cryostat. The temperature was varied in the range from 300 K to 10 K (±1 K) by an Oxford Instruments auto-tuning temperature controller ITC503.

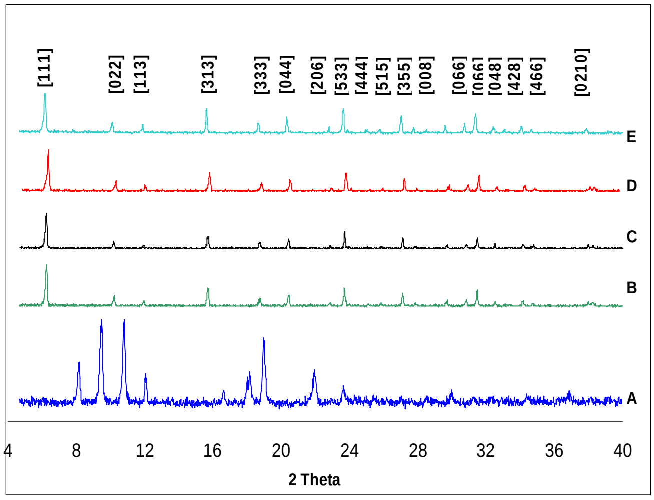
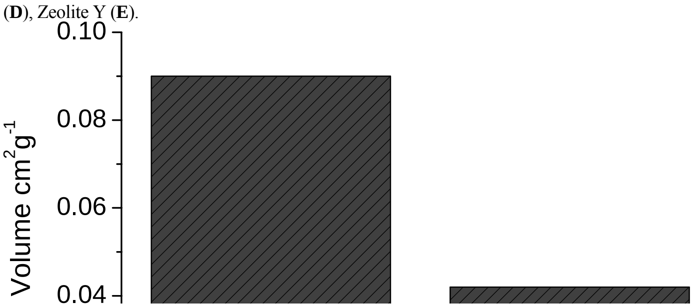


Fig.S1. Powder XRD patterns of Fe $^{3+}$-Proline (**A**), Fe $^{3+}$-Proline-X (**B**), Fe $^{3+}$-Proline-Y (**C**), Zeolite X (**D**), Zeolite Y (**E**).



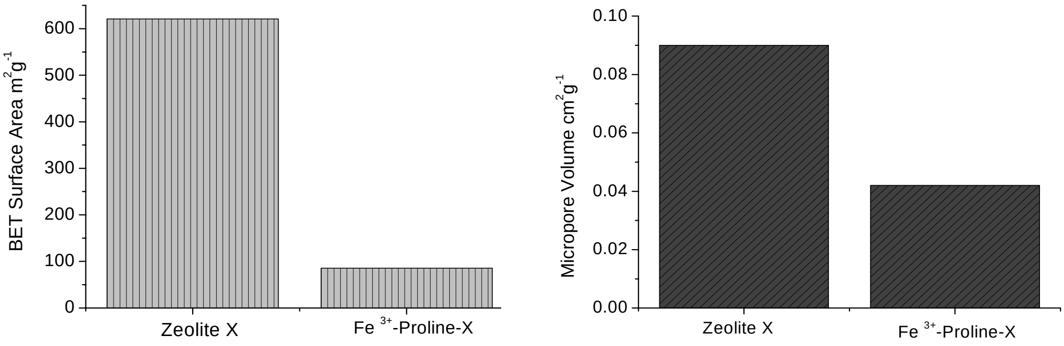


Fig. S2. Surface area and micropore volume measurements for Zeolite X and Fe^{3+}-Proline-X.

References

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