From Zeolites to Porous MOF Materials – the 40th Anniversary
of International Zeolite Conference
R. Xu, Z. Gao, J. Chen and W. Yan (Editors)

Bio-inspired manipulation of catalytic sites via immobilization of metal ion complexes in zeolites

A. M. Beale[a], J. G. Mesu[a], K. Kervinen[a], T. Visser[a], F. Soulimani[a], P. C. A. Bruijnincx[b], R. J. M. Klein Gebbink[b], G. van Koten[b] and B. M. Weckhuysen[a]

[a]Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

[b]Organic Chemistry and Catalysis, Department of Chemistry, Utrecht University, Padualaan 8, 3584 CA Utrecht, The Netherlands

ABSTRACT

By careful selection of the appropriate preparation parameters we show how it is possible to immobilize transition metal ion complexes within the supercages of zeolite Y to create molecular species, which mimic the active sites of enzymes and their catalytic function. In particular, we demonstrate the use of 3,3-bis(1-methylimidazol-2-yl)propionate (MIm_2Pr) combined with Cu^{2+} to imitate enzyme actives sites based on the 2-His-1-carboxylate facial triad motif and the use of histidine moieties (His) to replicate the active site of galactose oxidase. Characterization of these active site mimics using a variety of advanced spectroscopic techniques, has also been performed in order to understand why they possess this improved catalytic activity.

1. INTRODUCTION

A robust catalyst that delivers the performance of enzymes is the ultimate dream of many catalyst scientists. A first step in realizing this dream is to understand further the chemistry of enzymes. This is often attempted by studying a compound that resembles an enzyme active site. For example, Cu^{2+}-(His) complexes are known to play a key-role in many metallo-enzymes, and thus have been well studied in order to obtain better insight into the working mechanisms [1-3]. A logical next step towards the design of bio-inspired heterogeneous catalysts was the incorporation of Cu^{2+}-(His) complexes in layered and porous crystalline inorganic hosts; the general idea being to combine the activity of the enzyme in solution with the shape-selective control induced by the zeolite pores/channels [3-6]. In addition, we observe that the host material can impart additional stability and/or modified activity. For instance, immobilization of these and similar complexes in the micropores of a zeolite matrix results in the stabilization of structural mimics of the active site of galactose oxidase and for enzymes based on the 2-His-1-carboxylate facial triad motif [3-6]. However determining the active site responsible for the catalytic activity in these materials is difficult. For example, for the Cu^{2+}-(His) system it has previously been observed (using various techniques such as UV/Vis/NIR, multi-frequency EPR as well as pulsed EPR, such as ESEEM and ENDOR techniques) that two complexes (**A** and **B**) tended to form within the zeolite cages of which

the absolute and relative abundance depended on the Cu^{2+}-(His) concentration in the ion exchange solution and on the Si:Al ratio of the zeolite material [6-8]. Complex **A** was concluded to contain Cu^{2+} species attached to one (His) ligand and was anchored directly to the zeolite framework. In contrast complex **B** was proposed to connect to 2 (His) ligands; one coordinating to Cu^{2+} via 2 nitrogen (imidazole/amine) atoms and the other via coordination of imidazole and the oxygen of the carboxyl group [6-9]. Despite this work, the precise effect of the host material on the coordinating preferences of Cu^{2+}-(His) complexes was not fully understood. However, knowledge of this effect is essential, as it may influence the catalytic properties of the transition metal ion complex after immobilization. Particularly since it has been proposed that the enzyme's activity originates from the geometric and electronic distortions (caused by the large protein structures) around the metal ion resulting in an 'energised state' and enhanced lability [10]. It is therefore reasonable to assume that a combination of a multidentate ligand and zeolite structure could induce such geometric strain on the copper species leading to the lowering of the redox potential (a process known as entasis) [10].

Here, we report on some of our recent attempts to further characterise the Cu^{2+}-(His) species immobilized in zeolite Y and our efforts to craft single stable enzyme active site mimics within the zeolite's supercages [5, 6].

2. EXPERIMENTAL

For this work, two commercially available zeolite support materials were used: NaY zeolite (AKZO Nobel, Si/Al ratio of 2.5, surface area of 900 m^2/g and pore volume of 0.34 ml/g) and DAY (dealuminated zeolite Y) zeolite (Wessalith, Si/Al ratio of 100, surface area of 700 m^2/g and pore volume of 0.29 ml/g). Immobilization of the copper complexes was carried out using either ion exchange (Cu^{2+} and His moieties) or via "ship-in-a-bottle" type methods (Cu^{2+} and MIm_2Pr_2) [11, 12]. For the Cu-MIm_2Pr complexes, ion exchange was first performed at pH 7.3 (maintained using 0.1 M HNO_3 or NaOH) for 48 h at room temperature on Na^+ forms of both zeolites using $Cu(NO_3).3H_2O$ as the Cu^{2+} source. The ligand MIm_2Pr was subsequently introduced in the zeolite material by the incipient wetness impregnation method. For immobilization of Cu^{2+}-(His) species a solution of the copper salt and L-histidine in a 1:5 ratio at pH = 7.3 was mixed with the zeolite for 48 h at room temperature. The ion-exchanged zeolite Y was then washed and filtered three times, dried and the copper content was determined by XRF. Characterization of the complex-containing zeolites was performed using UV/Vis, EPR, IR and XAFS spectroscopy.

3. RESULTS AND DISCUSSION

Critically it appeared that for both systems studied, immobilization lead to a direct interaction between the complexes and the zeolite Y framework resulting in a stabilized enzyme 'mimic species'. We discuss first the results obtained from our attempts to identify the different types of Cu^{2+}-(His) complexes in the zeolite followed by the use of the MIm_2Pr ligand to stabilise one type of active complex.

Our study combined UV/Vis/NIR, EPR and X-ray absorption analysis to obtain complementary information on the molecular structure of Cu^{2+}-(His) complexes immobilized in the cage of the zeolite supports NaY and DAY. Our results suggest that complex **A**, contains one His molecule coordinating to Cu^{2+} in a tridentate facial manner with the remaining equatorial position occupied by an oxygen from the zeolite. (Fig. 1) In complex **B**,

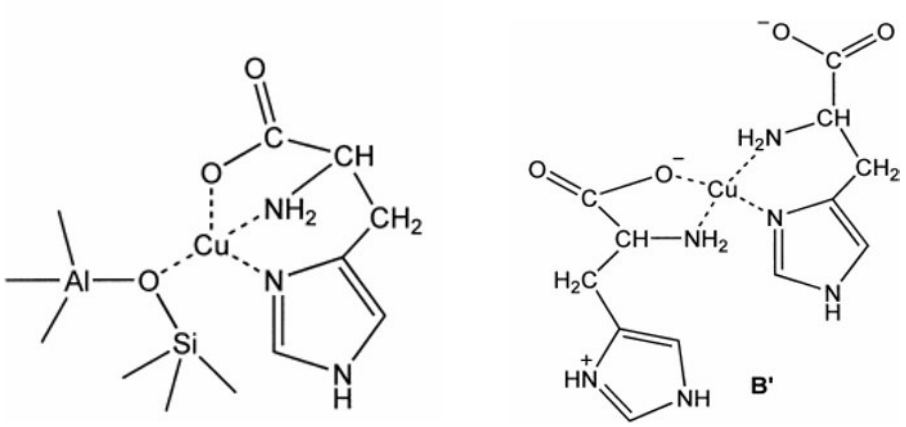

Fig. 1. Proposed refined structures of Cu^{2+}-(His) complexes A (left) and B (right) immobilized in zeolite Y [6].

one His ligand coordinates in a glycine-like coordination (N_{amine}, $O_{carboxylate}$), but the other one takes a histamine-like chelation (N_{amine}, $N_{imidazole}$). This complex is trapped in the supercage *via* the positive charge on the non-coordinating imidazole ring and matches with the preferred structure of the Cu^{2+}-(His) complex in aqueous solution at this pH [13]. On the other hand, complex **A** differs from the structure it occupies in solution, which implies that zeolite host materials are able to alter the coordination and orientation of the guest molecules. In addition it illustrates that zeolites are not just inorganic supports that can be used for site isolation and shape selectivity, but actively participate in the coordination chemistry by imposing a different chemical environment than in e.g., aqueous solution. This mutual interaction is well illustrated by the enhanced reducibility of Cu2+ to Cu+ in complex A (in comparison to complex B) on exposure to X-ray radiation (Fig. 2.). The trend from Cu2+ towards Cu1+ in complex A is probably due to a distortion of the square pyramidal geometry of Cu2+ towards the favored trigonal structure of Cu1+. The result is an energised or entactic state – a similar state to that seen for active copper species in many enzymes [6, 10].

In Fig. 3 we show the comparative UV-Vis and XANES spectra of the Cu(MIm2Pr)2 homogeneous complex in solution and the zeolite immobilized Cu(MIm2Pr)ZY sample. According to our results it is clear that the spectra for the homogeneous and zeolite immobilized samples are different. These data for the Cu(MIm2Pr)2 complex suggest that the Cu2+ environment is centrosymmetrical containing 4 nitrogen atoms in the equatorial plane around the copper (NNNN type coordination) and 2 carboxylate oxygens coordinating in axial positions [5]. Such a structure is uncharged and therefore difficult to stabilize within the pore system of the zeolite Y and is easily washed out. In contrast, samples with a Cu:L ~ 1 result in the formation of $Cu(MIm_2Pr)ZY$ complex, which remains in the zeolite supercage upon washing. It is characterised by a shift in the d-d transition from 590 nm to 690 nm (Fig. 3) and a decrease in $A_{||}$ and increase in $g_{||}$ values, indicating that some of the nitrogen atoms present in $Cu(MIm_2Pr)_2$ are replaced by oxygen atoms in $Cu(MIm_2Pr)ZY$. Indeed, a fivefold superhyperfine splitting pattern is observed which points towards the presence of only a total of two nitrogen atoms around the copper. XAFS analysis confirms that the structure of $Cu(MIm_2Pr)ZY$ is "half" of $Cu(MIm_2Pr)_2$, i.e., one of the ligands has been removed, with the rest of the ligands around the Cu^{2+} being oxygen atoms from the zeolite Y lattice and/or from

a water molecule. In addition both XANES and EXAFS analysis revealed that the Cu^{2+} coordination environment possesses a distorted five-fold geometry. We rationalize that this 'under-coordinated' state would provide a free site for catalytic activity and may explain the successful oxidation of benzyl alcohol at room temperature with tert-butylhydroperoxide as the oxidant with good selectivity to benzaldehyde [5].

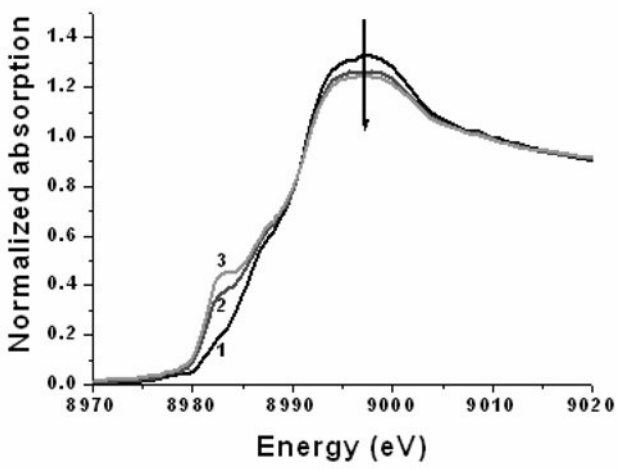

Fig. 2. The development of the X-ray absorption near edge structure in time of the Cu^{2+}-(His)/NaY sample with the lowest copper concentration. Note the numbers represent the order in which the scans were recorded and illustrate how a feature at 8983 eV due to Cu^{+} grows with duration of X-ray exposure.

4. CONCLUSIONS

Zeolites have been successfully employed as supports to create new catalysts with active sites that resemble those of enzymes. In particular we highlight how the zeolite stabilises an unusually distorted four coordinate geometry (Cu^{2+}-(His) complex **A**), which undergoes facile reduction in an X-ray beam. We propose that the combination of zeolite and one His ligand forces the Cu^{2+} complex into an activated, entactic state by the interaction with the zeolite material; this observation may explain why complex A is catalytically more active for alkene epoxidation. In addition we showed that immobilization inside the zeolite Y supercages proved to be an efficient method to isolate a mononuclear, monoligand complex [$Cu(MIm_2Pr)ZY$] with different catalytic properties, which cannot be stabilized as a homogeneous complex thus demonstrating further the significant potential of using this synthetic approach to develop new catalytic materials. These results demonstrate that the immobilization of transition metal ion complexes in inorganic support materials may open new perspectives in the design of new catalyst materials with novel applications.

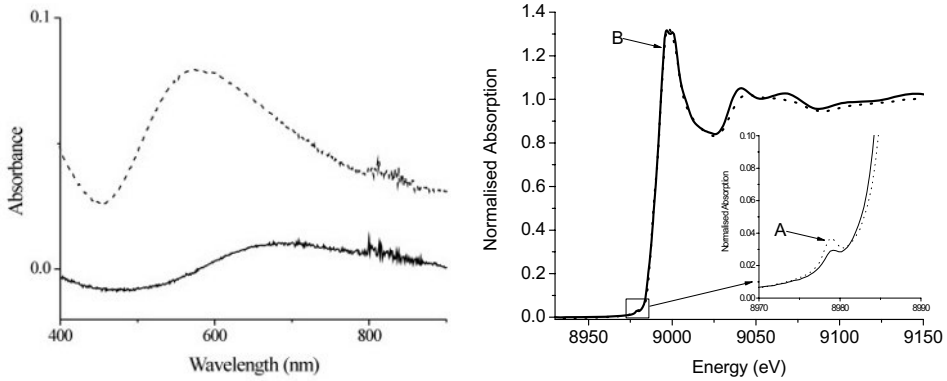

Fig. 3. (Left) DRS spectra around the d-d transition region of $Cu(MIm_2Pr)_2$ sample (dashed line) and the $Cu(MIm_2Pr)ZY$ sample (solid line). (Right) Comparative XANES spectra of $Cu(MIm_2Pr)_2$ (solid line) and $Cu(MIm_2Pr)ZY$ (dashed line) with inset highlighting the differences in the intensity of the 1s-3d transition (feature A) at 8979 eV. Since the intensity of the 1s-4p transition is similar for both samples (feature B) a change of symmetry from the centrosymmetric distorted octahedra in the $Cu(MIm_2Pr)_2$ to that of a non centrosymmetric environment is the most likely cause of the increase in feature A.

ACKNOWLEDGEMENTS

Financial support from NWO-CW (VICI project) and National Research School Combination – Catalysis (NRSC-C) as well as beamtime from NWO are kindly acknowledged. The authors would also like to thank Marijke Groothaert and Robert Schoonheydt (Leuven University, Belgium) for the opportunity to use and the assistance with the EPR measurements as well as Ad van der Eerden for the XRF measurements.

REFERENCES

[1] I. Bertini, A. Sigel and H. Sigel (eds.) Handbook on Metalloproteins, Marcel Dekker, Inc., New York, 2001.
[2] K. Buchholz, V. Kasche and U. T. Bornscheuer, Biocatalysts and Enzyme Technology, Wiley-VCH, Weinheim, 2005.
[3] B. M. Weckhuysen, A. A. Verberckmoes, J. A. Pelgrims, P. L. Buskens, P. A. Jacobs and R. A. Schoonheydt, Angew. Chem. Int. Ed. 34 (1995) 2652.
[4] L. Fu, B. M. Weckhuysen, A. A. Verberckmoes and R. A. Schoonheydt, Clay Minerals 31 (1996) 491.
[5] K. Kervinen, P. C. A. Bruijnincx, A. M. Beale, J. G. Mesu, G. van Koten, R. J. Klein Gebbink and B. M. Weckhuysen J. Am. Chem. Soc. 128 (2006) 3208.
[6] J. G. Mesu, T. Visser, A.M. Beale, F. Soulimani and B. M. Weckhuysen, Chem. Eur. J. 12 (2006) 7167.
[7] R. Grommen, P. Manikandan, Y. Gao, T. Shane, J. J. Shane, R. A. Schoonheydt, B. M. Weckhuysen and D. Goldfarb, J. Am. Chem. Soc. 122 (2000) 11488.
[8] B. M. Weckhuysen, A. A. Verberckmoes, L. Fu and R. A. Schoonheydt, J. Phys. Chem. 100 (1996) 9456.
[9] D. Baute, D. Arieli, F. Neesse, H. Zimmermann, B. M. Weckhuysen and D. Goldfarb, J. Am. Chem. Soc. 126 (2004) 11733.
[10] P. Comba, Coord. Chem. Rev. 200-202 (2000) 217.

[11] D. E. De Vos, P. P. Knops-Gerrits, R. F. Parton, B. M. Weckhuysen, P. A. Jacobs and R. A. Schoonheydt, J. Inclus. Phen. Mol. Rec.Chem. 21 (1995) 185.
[12] N. A. Caplan, F. E. Hancock, P. C. Bulman Page and G. J. Hutchings, Angew. Chem. Int. Ed. 43 (2004) 1685.
[13] J. G. Mesu, T. Visser, F. Soulimani, E.E. van Faassen, P. de Peinder, A.M. Beale and B. M. Weckhuysen, Inorg. Chem. 46 (2006) 1960.