

# Practical heterogenisation of an active manganese triazacyclononane epoxidation catalyst *via* surface glycidylation

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## A convenient immobilisation of triazacyclononane ligands on a glycidylated surface leads to a new group of active, heterogeneous manganese epoxidation catalysts.

The catalytic activity of complexes of Mn and 1,4,7-triazacyclononane (tacn) type ligands in oxidation catalysis has only recently been unveiled.<sup>1</sup> Working in the right solvent and temperature conditions can greatly improve epoxidation activity and selectivity, although both catalytic parameters are also largely influenced by the nature of the substituents on the nitrogen atoms.<sup>2</sup> We now exploit this knowledge in devising an easy procedure for covalently anchoring Mn–tacn complexes on a mesoporous MCM-41 support material. Considerable research has been devoted to the covalent anchoring of first-row transition-metal catalysts, but most of this work concentrated on porphyrins. These are heterogenised on inorganic carriers *via* substitution at the periphery of the macrocycle, or *via* a coordinative bond with a covalently attached axial ligand.<sup>3</sup> While some non-haem transition-metal complexes have been covalently attached to the MCM-41 surface,<sup>4</sup> there seem to be few reports on the catalytic activity of these systems. We now report that our anchoring of tacn on a glycidylated support provides a heterogeneous catalyst in which the catalytic activity of the Mn–tacn core is well preserved.

The mesoporous, siliceous MCM-41 material was synthesised by a slightly modified literature procedure.<sup>5</sup> Its quality was established by XRD and by sorption measurements. In the surface modification, the dried surface of MCM-41 was first reacted with (3-glycidyloxypropyl)trimethoxysilane in dry toluene.<sup>†</sup> IR spectroscopy shows that the reaction of the silanol groups ( $\nu_{\text{OH}}$  ca. 3745  $\text{cm}^{-1}$ ) is almost complete. Next tacn is added and reacts selectively with the glycidyloxypropyl (GP) residue, producing a 3-propoxy-2-hydroxypropyl substituent on the tacn macrocycle. This type of oxirane opening is well known from the preparation of 2-hydroxyalkyl-substituted tacn ligands.<sup>6</sup> In a third step, the remaining secondary amine groups of the anchored tacn are further functionalised, for instance through reaction with propylene oxide (Scheme 1). Careful Soxhlet extractions after the surface modification ensure that only covalently attached ligands reside on the host material. The different steps in the build-up at the surface were followed by <sup>13</sup>C MAS NMR, and by thermal analysis. For instance, after reaction with the glycidylating agent, the MAS NMR spectrum shows peaks at  $\delta$  73.4, 50, 44, 23 and 9, which is in close agreement with the peaks of the glycidyloxypropyltrimethoxysilane precursor. Only the CH<sub>2</sub>Si resonance is slightly shifted downfield (from  $\delta$  5.26 to 9) as a result of the surface bonding. Loadings with tacn were determined with

thermogravimetric analysis; a typical loading is 0.4 mmol tacn per gram of modified MCM-41. Porosity measurements indicate that the pore volume with a radius under 20 Å substantially decreases after anchoring of the tacn (from 1.62 to 0.98  $\text{ml g}^{-1}$ ). For the sake of comparison, tacn was also anchored on a silica, glycidylated *via* the same method (Sil-GP–tacn); a commercial chloropropyl functionalised silica was also reacted with tacn (Sil-P–tacn).

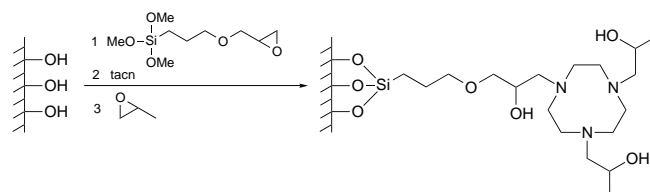
The metal-binding properties of the functionalised surfaces were thoroughly characterized by EPR spectroscopy. Therefore the materials were doped with a small amount of Mn<sup>2+</sup> or Cu<sup>2+</sup> probe ions, corresponding to 10% of the estimated metal binding capacity.<sup>‡</sup> The EPR parameters of Cu<sup>2+</sup> are highly sensitive to the composition of the primary coordination sphere, and can be used to distinguish between mono- and bis-chelated complexes [Table 1 and Fig. 1(a)–(c)].<sup>7</sup> In a Cu<sup>2+</sup> doped MCM-GP–tacn, Cu<sup>2+</sup> binds selectively on the bound ligand, and not on the siliceous surface. At low Cu<sup>2+</sup> concentrations, bis-complexes are formed. This shows that the mobility of the bound ligands and the surface coverage are sufficiently high to allow an interaction between neighbouring attached ligands. At contrast, not only bis- but also mono-complexes are observed with the Cu<sup>2+</sup> doped Sil-P–tacn sample. This proves that the metal binding sites are more isolated in this material. In the case of Mn<sup>2+</sup>–MCM-GP–tacn, the selective metal binding to the ligand is evidenced by the appearance of ‘non-central’ lines in the X-band EPR spectrum [Fig. 1(d)].<sup>8,9</sup>

Most importantly, the catalytic activity of Mn–tacn is preserved intact after this mild anchoring procedure. Before reaction, a solution of MnSO<sub>4</sub> (8  $\mu\text{mol}$ ) was reacted for 1 h with the heterogenised ligand (20 mg) under an N<sub>2</sub> atmosphere. Subsequently the alkene (1 mmol) and H<sub>2</sub>O<sub>2</sub> (2 mmol, diluted in the organic solvent in a 1 : 1 mass ratio) were added, bringing the oxidant : alkene : Mn ratio to 250 : 125 : 1. Results are given in Table 2. Especially encouraging are the high epoxide selectivities (up to 90%) obtained for styrene and cyclohexene

**Table 1** EPR parameters of crystalline and supported Cu–tacn complexes

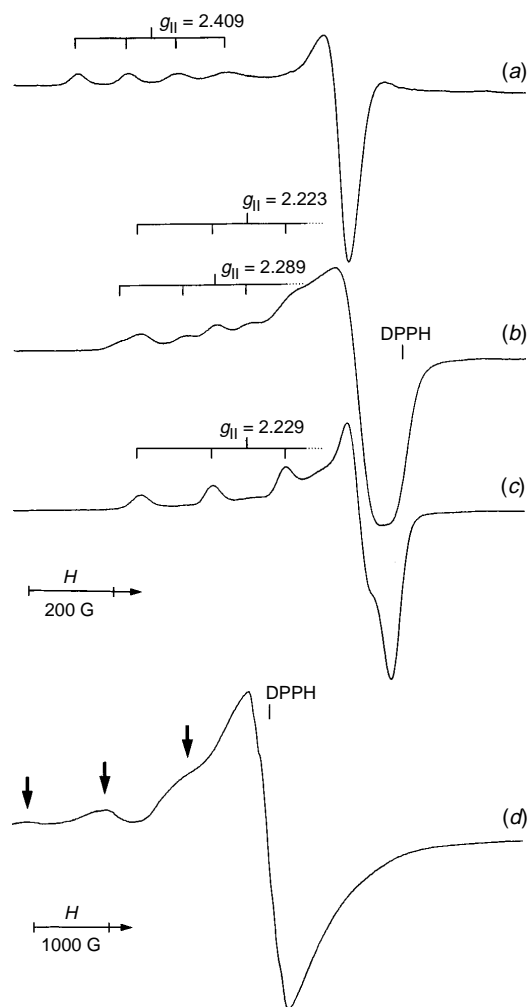
Complex	$g_{\parallel}$	$ A_{\parallel} ^a$	$g_{\perp}$
Cu <sup>2+</sup> on MCM-41	2.409	131	2.08
Cu <sup>2+</sup> on Sil-P–tacn	2.289	159	2.05–2.06
	2.223	181	2.05–2.06
Cu <sup>2+</sup> on MCM-GP–tacn	2.229	176	2.05
[Cu(tacn)Br <sub>2</sub> ] <sup>b</sup>	2.278	158	2.050
[Cu(tacn) <sub>2</sub> ] [Cu(CN) <sub>3</sub> ] <sup>b</sup>	2.229	177	2.055

<sup>a</sup> 10<sup>–4</sup> cm<sup>–1</sup>. <sup>b</sup> See ref. 7.



**Scheme 1**

with an Mn–MCM-GP-tacn modified with propylene oxide. This means that radical reactions are unimportant in product formation. In the particular case of styrene oxidation in methanol, the epoxide is further converted *via* acid catalysis into phenylacetaldehyde and phenylethandiol. As the siliceous



**Fig. 1** X-Band EPR spectra (130 K) of  $\text{Cu}^{2+}$ , adsorbed on (a) siliceous MCM-41, (b) Sil-P-tacn, (c) MCM-GP-tacn; (d) is the spectrum, recorded at 293 K under  $\text{N}_2$ , of  $\text{Mn}^{2+}$  on MCM-GP-tacn. The clear non-central transitions (indicated by arrows) prove a strong distortion of the  $\text{Mn}^{2+}$  coordination symmetry from spherical and thus coordination of  $\text{Mn}^{2+}$  by a surface-bound tacn macrocycle.

**Table 2** Catalytic activity of complexes of Mn and tacn, covalently anchored on silica carriers<sup>a</sup>

Substrate	Catalyst	Solvent	T.O. <sup>b</sup>	Selectivity <sup>c</sup>
Styrene	MCM-GP-tacn	Acetone	4.1	87 (88)
	MCM-GP-tacn <sup>d</sup>	Acetone	16	87 (90)
	MCM-GP-tacn <sup>d</sup>	Methanol	52	24 (76)
	MCM-GP-tacn <sup>d</sup>	Acetonitrile	15	62 (88)
	Sil-P-tacn	Acetone	2.6	79 (82)
	Sil-P-tacn <sup>d</sup>	Acetone	3.0	67 (82)
	Sil-GP-tacn	Acetone	6.1	72 (81)
Cyclohexene	Sil-GP-tacn <sup>d</sup>	Acetone	18	83 (89)
	MCM-GP-tacn <sup>d</sup>	Methanol	16	86

<sup>a</sup> Reaction conditions: 1 mmol of substrate, 2 mmol of aqueous 35%  $\text{H}_2\text{O}_2$ , 20 mg of support with the covalently attached ligand, 8  $\mu\text{mol}$  of  $\text{MnSO}_4$ , 1 g of solvent, 1 h, 273 K. <sup>b</sup> T.O. = turnover number, *i.e.* moles of epoxide and epoxide-derived products  $\text{h}^{-1}$  (mole Mn)<sup>-1</sup>. <sup>c</sup> Epoxide selectivity. Numbers within parentheses includes products directly derived from the epoxide, *e.g.* phenylacetaldehyde and phenylethandiol in the case of styrene. <sup>d</sup> Modified with propylene oxide.

MCM-41 is not acidic, the low pH of aqueous  $\text{H}_2\text{O}_2$  may well be at the basis of these reactions. A typical turnover number for reactions in methanol is 50. Somewhat lower turnover numbers were obtained with other solvents such as acetone and acetonitrile, but epoxide selectivities were higher. The glycidylation approach is not limited to the MCM support. Thus a considerable activity was obtained with tacn, anchored on a glycidylated silica surface. The catalytic data prove that for tacn anchoring, the newly proposed glycidylation approach is clearly more successful than the more traditional approach *via* substitution of a silica-bound chloropropyl chain.

Summarizing, our work presents to our knowledge the first example of a catalytically active, non-aromatic Mn complex which is covalently heterogenised on an inorganic support. The reaction of the glycidyl residue with tacn is not only a very facile anchoring step; the opening of the oxirane ring by tacn also creates a hydroxy group which can assist in the metal binding.

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### Footnotes

† 1.0 ml (4.5 mmol) of 3-glycidloxypropyltrimethoxysilane (Fluka) was added to 3.0 g of a freshly calcined MCM-41 in 25 ml of dry toluene and refluxed for 24 h in an  $\text{N}_2$  atmosphere. After reaction the resulting solid was filtered, washed thoroughly with toluene and methanol and subjected to toluene Soxhlet extraction. The oxirane ring on the glycidylated support (1 g) was opened with tacn (80 mg) in toluene (50 ml, 50 °C, 24 h). 2-Hydroxypropyl substituents were introduced by adding an excess of propylene oxide in ethanol (293 K, 10 h). For anchoring on silica supports, analogous procedures were adopted. Silica was from Fluka (70–230 mesh) and 3-chloropropyl silica was from Aldrich (230–400 mesh).

‡ For the EPR measurements, 0.1 g of the functionalised support was stirred for 2 h in 4 ml of a 1 mM  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  or  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution in methanol–water (9:1), and collected by filtration. For Mn, an inert atmosphere was used. The metal concentration was limited to avoid dipolar line broadening.

### References

- R. Hage, J. Iburg, J. Kerschner, J. Koek, E. Lempers, R. Martens, U. S. Racherla, S. W. Russell, T. Swarthoff, M. Van Vliet, J. Warnaar, L. van der Wolf and B. Krijnen, *Nature*, 1994, **369**, 637.
- D. E. De Vos and T. Bein, *Chem. Commun.*, 1996, 921; *J. Organomet. Chem.*, 1996, **520**, 195; D. E. De Vos, J. Heinershagen and T. Bein, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2211.
- A. W. van der Made, J. W. H. Smeets, R. J. M. Nolte and W. Drenth, *J. Chem. Soc., Chem. Commun.*, 1983, 1204; P. Battioni, E. Cardin, M. Louloui, B. Schöllhorn, G. A. Spyroulias, D. Mansuy and T. G. Traylor, *Chem. Commun.*, 1996, 2037; K. Miki and Y. Sato, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2385; G. Labat and B. Meunier, *J. Chem. Soc., Chem. Commun.*, 1990, 1414; P. R. Cooke and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1913.
- P. Sutra and D. Brunel, *Chem. Commun.*, 1996, 2485.
- J. S. Beck, J. C. Vartuli, W. Roth, M. Leonowicz, C. T. Kresge, K. D. Schmitt, C. Chu, D. H. Olson, E. W. Sheppard, S. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- A. A. Belal, P. Chaudhuri, I. Fallis, L. J. Farrugia, R. Hartung, N. M. McDonald, B. Nuber, R. D. Peacock, J. Weiss and K. Wieghardt, *Inorg. Chem.*, 1991, **30**, 4397.
- R. D. Bereman, M. R. Churchill, P. M. Schraber and M. E. Winkler, *Inorg. Chem.*, 1979, **18**, 3122; P. Chaudhuri, K. Oder, K. Wieghardt, J. Weiss, J. Reedijk, W. Hinrichs, J. Wood, A. Ozarowski, H. Stratemaier and D. Reinen, *Inorg. Chem.*, 1986, **25**, 2951.
- G. M. Woltermann and J. R. Wasson, *Inorg. Chem.*, 1973, **12**, 2366; H. W. De Wijn and R. F. van Balderen, *J. Chem. Phys.*, 1967, **46**, 1381; D. E. De Vos, B. M. Weckhuysen and T. Bein, *J. Am. Chem. Soc.*, 1996, **118**, 9615.
- D. Zhao and D. Goldfarb, *J. Chem. Soc., Chem. Commun.*, 1995, 875.

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