Preparation of MCM-41 type silica-bound manganese(III) Schiff-base complexes

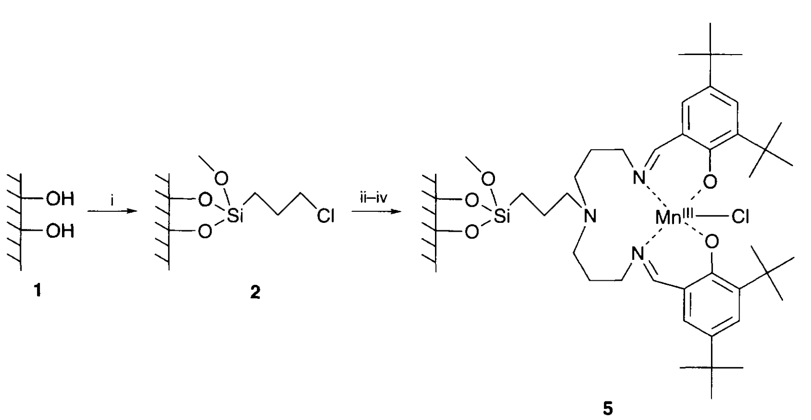
Pierre Sutra and Daniel Brunel

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618-CNRS-ENSCM-Ecole Nationale Supérieure de Chimie, 8 rue Ecole Normale, 34053-Montpellier Cedex 1, France

Pentadentate ligands (salpr) anchored to the surface of MCM-41 type silica through covalently linked organic moieties are further converted into Mn^{III} (salpr) complexes by ligand exchange without loss of the regular porous structure of the support.

Transition-metal-complex promoted oxidation reactions are of considerable current interest because of their relevance to organic chemistry.[1,2] Manganese(III) Schiff-base complexes have become highly valuable catalyst in homogeneous alkene epoxidation reactions using readily available oxygen donors such as NaOCl, H_2O_2 or PhIO.[3–5] On the other hand, immobilization of transition-metal complexes on solid supports can provide catalysts which are easier to handle and which may possibly exhibit improved selectivities and activities because of the support environment.[6–10] The advantages to be gained in heterogenizing, *e.g.* Schiff-base transition-metal complexes through polymer attachment have been previously described.[11–13] However, as far as we are aware, no example of immobilization of such transition-metal complexes on mineral supports through covalent linkages has been reported. The interest in mineral solids as supports for improvement of catalytic site properties lies in application of solids possessing high surface areas in addition to their insolubility in organic solvents. Here, we report the grafting of Mn^{III} Schiff-base complexes onto the internal surface of mesoporous MCM-41 type silica **1** through Si–O–Si bonds. These new silica materials[14,15] synthesized by silicate condensation around surfactant micelles provide ideal inorganic supports[16] due to their regular arrays of uniformly sized channels with pore diameters in the mesoporous range of 20–100 Å. Until now, these materials have received widespread interest because of their acid catalytic potential when they contain isomorphously substituted framework aluminium. For reactions involving high molecular mass hydrocarbons, low diffusion resistance is observed due to the large pore diameters.[17] In order to encompass applications to catalytic reaction types other than acidic processes such as selective oxidation of hydrocarbons,[18,19] many efforts have been recently made towards the synthesis and characterisation of transition-metal-containing mesoporous molecular sieves.[20–26] However, the activities and the selectivities as well as the structural preservation of these types of catalytic sites during the oxidation processes are, as yet, disappointing. This prompted us to attempt covalent attachment of Mn-salen type complexes to the MCM-41 silica surface in the hope that it might provide an efficient route to obtaining well defined catalytic sites. 3-[*N*,*N*′-Bis-3-(3,5-di-*tert*-butylsalicylidenamino)propyl]amine (*t*-salpr) was bound to the surface through partial nucleophilic displacement of chlorine of previously grafted 3-chloropropylsilane moieties (Cl-MPS) **2** by the basic amino group of the *t*-salpr ligand (Scheme 1). The grafting of *t*-salpr ligands was attempted chiefly because we believe it would lead to catalytic sites more isolated from each other, owing to their larger steric hindrance relative to the salpr analogue. Nevertheless, the grafting of the latter complex **3b** was also studied in order to compare more readily the physicochemical characteristics of the corresponding organic chains grafted at higher concentration. This allowed us to ascertain the best control of the efficiency of the coupling reaction. Spectroscopic characterization of the corresponding soluble transition-metal 3-[*N*,*N*′-bis-(3-salicylidenamino)propyl]methylamine (smdpt) complex was also investigated for supplementary verification.

In a typical surface modification process, activated MCM-41 silica **1** (3 g, 423 K, under vacuum) was first treated with a refluxing anhydrous toluene solution (50 ml) of 3-chloropropyltriethoxysilane (9×10^{-3} mol) followed by washing with diethyl ether–CH_2Cl_2 in a Soxhlet apparatus yielding covalently anchored 3-chloropropylsilane moieties **2** (1.17×10^{-3} mol g^{-1}). The latter (1 g) was then treated with a toluene solution (60 ml) of an excess of salpr (4×10^{-3} mol) leading to salpr–MPS with simultaneous elimination of HCl removed as HsalprCl. The structures of the anchored organic moieties were characterized by IR spectroscopy† and by ^{13}C NMR from comparison of the spectra of salpr–MPS **3b** (MAS) and salpr (in $CDCl_3$ solution).‡ The organic content was established by



1 **2** **5**

Scheme 1 Synthesis of ClMn^{III}(salpr) complexes linked to MCM-41 silica. *Reagents and conditions*: i, $(MeO)_3(CH_2)_3Cl$, refluxing toluene, 3 h; ii, salpr (excess), refluxing toluene, 24 h; iii, Mn^{II}(acac)$_2$, methanol, 355 K; iv, saturated NaCl solution, air, 24 h.

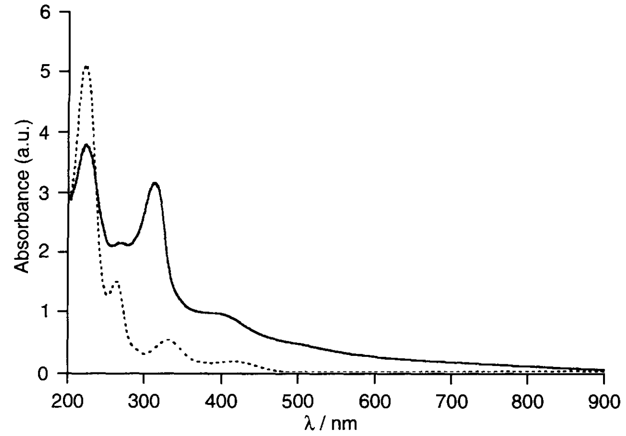


Fig. 1 UV–VIS diffuse reflectance spectra of **3a** (——) and **5** (– – – –)

elemental analysis and thermogravimetry. The anchored *t*-salpr and salpr moieties were obtained from partial Cl elimination in 6 and 31% yield, respectively. As already reported in previous work,[16] the modified mesoporous silicas feature a decrease in surface area and mesoporous volume as a function of the content and the size of the grafted organic chains.§

The introduction of metal atoms was achieved by reacting surface *t*-salpr ligands with $\mathrm{Mn^{II}(acac)_2}$ in MeOH at 355 K under argon. The EPR spectrum of the grafted $\mathrm{Mn^{II}}$ (*t*-salpr) complexes **4**, after successive washing with MeOH, dmf and EtOH under argon, shows a distorted sextuplet signal at $g = 2$ typical of an unsymmetrical complex. The complexation reaction yield determined by the amount of penta-2,4-dione obtained by ligand exchange was nearly quantitative. The grafted $\mathrm{Mn^{II}}$ complexes suspended in saturated brine were air-oxidized to give $\mathrm{ClMn^{III}}$(*t*-salpr)–MPS, the amount of which, as determined by elemental analysis, was nearly the same as that of the parent grafted *t*-salpr ligands and corresponded to the previously measured value for the $\mathrm{Mn^{II}}$ complexation yield.

The efficiency of the complexation method is illustrated by UV–VIS diffuse reflectance spectroscopy. The *t*-salpr–MPS spectra before and after Mn complexation (Fig. 1) show similar bands to the absorption spectra of the parent *t*-salpr ligand and the corresponding Mn complex in $\mathrm{CH_2Cl_2}$ solution (λ = 262, 327 nm, *cf.* 264, 330, 414 nm).

The preservation of the regular porosity during the different transformations was verified by X-ray diffraction using Cu-Kα radiation (θ = 1.16°, d_{100} = 37.95 Å, hexagonal lattice parameter a = 43.82 Å) and nitrogen sorption analysis.§

In conclusion, MCM-41 type silicas can be functionalized with well defined Mn Schiff-base complexes without loss of their regular pore structure. The pentadentate ligand linked to the silica surface by stable covalent Si–O–Si–C bonds possesses an additional apical ligand usually added to tetradentate salen complexes in order to improve their catalytic activity.[27]

We thank Dr F. Di Renzo for fruitful discussions on mesoporous materials and Dr A. Finels and Professor D. Lerner for their help with NMR and UV measurements respectively.

Footnotes

† IR: characteristic bands of modified solids in addition to the C–H vibration bands around 2900–3080 cm^{-1}; **3a**, 1689, 1635, 1606, 1588 cm^{-1}; **3b**, 1688, 1635.5, 1606, 1589 cm^{-1}; **5**, 1689, 1610, 1586, 1559, *1524.5* cm^{-1}. Corresponding IR bands of the salpr-type molecules and their $\mathrm{Mn^{III}Cl}$ complexes in $\mathrm{CCl_4}$ solution: *t*-salpr: 1633, 1596, 1469, 1457 cm^{-1}; $\mathrm{ClMn^{III}}$(*t*-salpr): 1652, 1626, 1615, 1553, *1535*, 1477, 1463 cm^{-1}; smdpt, 1635, 1584, 1496, 1462.5 cm^{-1}; $\mathrm{ClMn^{III}}$(smdpt), 1620.5, 1598, *1545*, 1469, 1446 cm^{-1}.

‡ ^{13}C CP MAS–NMR of **3b** and solution ^{13}C NMR ($\mathrm{CDCl_3}$) (in parentheses) of salpr: δ 9.8 ($C\mathrm{H_2Si}$), 49–57 (55) ($C\mathrm{H_2N}$), (57) ($C\mathrm{H_2N{=}C}$), 25.8 (28.4) ($C\mathrm{H_2CH_2N}$), 118.9 (116.8), 120.8 (118.7), 128.5 (131.2, 131.9) (aromatic CH), 122.5 (118.7), 151.9 (160.7) (aromatic C), 156.6 (164.9) (C=N).

§ $\mathrm{N_2}$ sorption: **1**; surface area (S) = 930 m^2 g^{-1}, mesoporous volume (V_m) (cm^3 g^{-1}) = 0.74. For **2**; S = 901, V_m = 0.49. For **3a**; S = 755, V_m = 0.41. For **3b**; S = 633, V_m = 0.36.

References

1 H. Mimoun, *J. Mol. Catal.*, 1980, **7**, 1.
2 B. Meunier, *Bull. Soc. Chim. Fr.*, 1986, **4**, 578.
3 K. Srinivasan, P. Michaud and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2309.
4 K. A. Jorgensen, *Chem. Rev.*, 1989, **89**, 431.
5 W. Zhang and E. N. Jacobsen, *J. Org. Chem.*, 1991, **56**, 2296.
6 G. L. Linden and M. Farona, *J. Catal.*, 1977, **43**, 284.
7 K. R. Kumar, B. M. Choudary, Z. Jamil and G. Thyagarajan, *J. Chem. Soc., Chem. Commun.*, 1986, 130.
8 P. Hernan, C. del Pino and E. Ruiz-Hitzky, *Chem. Mater.*, 1992, **4**, 49.
9 Y. G. Akopyants, S. A. Borisenkova, O. L. Kalya, V. M. Derkacheva and E. A. Lukyanets, *J. Mol. Catal.*, 1993, **83**, 1.
10 A. Corma, M. Iglesias and F. Sanchez, *Catal. Lett.*, 1995, **32**, 313.
11 D. S. Drago, J. Gaul, A. Zombeck and D. K. Straub, *J. Am. Chem. Soc.*, 1980, **102**, 1033.
12 C. Bied-Charreton, M. Frostin-Rio, D. Pugol, A. Gaudemer and J. P. Idoux, *J. Mol. Catal.*, 1982, **16**, 335.
13 S. K. Das, A. Kumar Jr., S. Nandrajog and A. Kumar, *Tetrahedron Lett.*, 1995, **36**, 7909.
14 J. S. Beck, C. T.-W. Chu, I. D. Johnson, C. T. Kresge, M. E. Leonowicz, W. J. Roth and J. C. Vartuli, Mobil Oil Corporation, WO 91/11390, 1991.
15 C.-Y. Chen, H.-X. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 17; 27.
16 D. Brunel, A. Cauvel, F. Fajula and F. Di Renzo, *Stud. Surf. Sci. Catal.*, 1995, **97**, 173; A. Cauvel, D. Brunel, F. DiRenzo and F. Fajula, *Proc. 53rd Int. Meeting Phys. Chem. 'Organic Coatings', Am. Inst. Phys.*, 1996, **354**, 477.
17 E. Armengol, M. L. Cano, A. Corma, H. Garcia and M. T. Navarro, *J. Chem. Soc., Chem. Commun.*, 1995, 519.
18 A. Corma, M. T. Navarro and J. P. Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147.
19 A. Tuel, S. Gontier and R. Teissier, *J. Chem. Soc., Chem. Commun.*, 1996, 651.
20 S. Gontier and A. Tuel, *Zeolites*, 1995, **15**, 601; *Microporous Mater.*, 1995, **5**, 161.
21 D. Zhao and D. Goldfarb, *J. Chem. Soc., Chem. Commun.*, 1995, 875.
22 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159.
23 A. Tuel and S. Gontier, *Chem. Mater.*, 1996, **8**, 114.
24 K. M. Reddy, I. Moudrakovski and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1994, 1059.
25 J. S. Reddy and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1995, 2231.
26 A. Jentys, N. H. Pham, H. Vinek, M. Englisch and J. A. Lercher, *Microporous Mater.*, 1996, **6**, 13.
27 J. Skarzewski, A. Gupta and A. Vogt, *J. Mol. Catal.*, 1995, **103**, L63.

Received, 7th August 1996; Com 6/05512E