Unexpectedly superior enantioselectivity for *trans*-stilbene *cis*-dihydroxylation over anchored triosmium carbonyl species in confined Al-MCM-41 channels†

Valérie Caps,‡ Ioannis Paraskevas and Shik Chi Tsang*

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Superior enantioselectivity in the dihydroxylation of *trans*-stilbene catalysed by anchored triosmium carbonyl species without using a chiral modifier is observed inside sterically congested MCM-41 channels; this effect is more pronounced through the introduction of surface Al sites into the silicate.

Catalytic asymmetric dihydroxylation of olefins to produce 1,2-diols is a key reaction in the fine chemicals industry. The 3-component process using a catalytic amount of soluble osmium tetroxide together with an oxidant and a pro-chiral ligand is well-documented.[1] However, the difficulty in recovering the expensive chiral ligand and the soluble Os species of an extremely toxic nature prompts economic and environmental concerns with this traditional process. Heterogenisation of this catalytic system is thus highly desirable.[2] Work has been reported on the immobilisations of chiral ligand(s) onto a polymer,[3] silica[4] or SBA-15.[5] It is noted that, using this approach, the toxic OsO_4 is still primarily used as a soluble species. Systems where catalytic osmium species are immobilised through precipitation onto nitrogen-containing polymers,[6] microencapsulation inside polymers[7] or ion-exchange onto charged ligands covalently bound to resin or silica,[8] followed by using soluble pro-chiral ligands, have also been reported.

In this communication, chemical vapour deposition (CVD) of $Os_3(CO)_{12}$ onto dried, freshly prepared MCM-41 or Al-MCM-41 mesoporous silicate was carried out; the Os loaded sample was then tested for the dihydroxylation of *trans*-stilbene in liquid phase using *N*-methylmorpholine *N*-oxide as an oxidant. We noted an unexpectedly high enantioselectivity for this catalysed reaction, *without using a chiral ligand or oxidant*.

MCM-41 was prepared using a standard method as previously reported.[9] Highly acidic Al-MCM-41 was prepared by adding aluminium isopropoxide in the hydrothermal synthesis of the mesoporous silicate.[10] The transmission electron micrographs of this material showed the same hexagonal array of channels of 30–40 Å, as MCM-41. The BET surface area (1233 m^2 g^{-1}) was slightly below that of MCM-41 (1344 m^2 g^{-1}). The actual incorporation of aluminium inside the silicon framework was evidenced by FTIR. Elemental analysis gave a Si/Al molar ratio of 3 : 4, indicating a high Al content. XPS gave a surface Si/Al atomic ratio of 5. The binding energy of 103.6 eV for Si 2p3/2 was similar to the one found in pure silica MCM-41 (103.6 eV). The binding energy of 75.4 eV for Al 2p also corresponded to a highly oxidised state of Al (binding energy for Al^0 is 72.9 eV), which was expected to be more acidic than in aluminas (74.7 eV) and aluminosilicates (75.0 eV). Thus, this Al-MCM-41 surface contains a high concentration of highly electron deficient, *i.e.* strongly Lewis acidic, Al sites.

$Os_3(CO)_{12}$ (99%) was purchased from Strem Chemicals, stored in a dry, air-tight glove-box to avoid air/moisture contamination and used without further purification. It was then applied to the freshly prepared MCM-41 or Al-MCM-41 support using a previously reported CVD technique.[9] Basically, all manipulations were carried out under an inert atmosphere or vacuum. The support was dried by heating under vacuum for 4 h at 150 °C. A predetermined amount of the $Os_3(CO)_{12}$ precursor (32 mg) was placed in a Schlenk tube together with 200 mg of the dried support. The tube was then evacuated, sealed and heated at 120 °C for 40 h to allow for the reaction between the metal precursor and the support to take place. Unattached species were subsequently removed by heating in a vacuum at 120 °C for 1 h. After the reactor tube was cooled to room temperature and exposed to air, the resulting material is referred to as the "as-synthesised" (AS) sample. A subsequent calcination of the AS samples to 220 °C in air for 2 h was also carried out for comparison. Detailed methodologies concerning testing the catalyst materials for the reaction and product analysis can be found in the ESI.†

It is noted from Table 1 that all these immobilised $Os_3(CO)_{12}$-derived species, with and without calcination, catalyse, in the presence of the *N*-methylmorpholine *N*-oxide oxidant, the oxidation of *trans*-stilbene to 1,2-diphenyl-1,2-ethanediol with a high yield (>64%). Greater than 78% selectivity to the principal

Table 1 Stereoselectivity in the dihydroxylation of the *trans*-stilbene over $Os_3(CO)_{12}$ species immobilised by CVD inside mesoporous silicates

Catalyst	Yield of diol (%)	Selectivity (%) *meso*	*(R,R)*	*(S,S)*
$32mgOs_3(CO)_{12}$/MCM-41[AS][b]	68.9	0	22.4	77.6
$32mgOs_3(CO)_{12}$/Al-MCM-41[AS][b]	64.0	0	5.2	94.8
$32mgOs_3(CO)_{12}$/MCM-41[220C][c]	80.4	0	45.9	54.1
$32mgOs_3(CO)_{12}$/Al-MCM-41[220C][b]	75.9	0	47.5	52.5

[a] Reaction conditions: substrate 1 mmol, NMO 1 mmol, 18 mg Os catalyst in acetone (18 cm^3) and water (2 cm^3) at 40 °C for 96 h (refer to ESI). Os contents determined in solids *ca.* [b] 7 wt% and [c] 3 wt% (derived from TGA).

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† Electronic supplementary information (ESI) available: characterisation of $Os_3(CO)_{12}$ deposited MCM-41 and related structures. See http://www.rsc.org/suppdata/cc/b4/b417787h/

‡ Present address: CNRS, Institut de Recherches sur la Catalyse, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France. E-mail: valerie.caps@catalyse.cnrs.fr

*s.c.e.tsang@reading.ac.uk

diol product with minor selectivities towards benzaldehyde, benzoin and benzyl was achieved.[9] Analysis of the diol product suggests that this heterogeneous reaction is a diastereospecific reaction (no *meso* configuration of the diol is observed), like the homogeneous counterpart, where a concerted [3 + 2] cycloaddition of the carbon–carbon double bond onto the single Os catalytically active site *via* two oxygen atoms is proposed. When the MCM-41- or Al-MCM-41-immobilised $Os_3(CO)_{12}$ CVD samples are calcined at 220 °C (2 h), they give a nearly racemic mixture of the *syn* configurations (*R*,*R*) and (*S*,*S*) despite their different Os contents (3 wt% and 7 wt%, respectively). However, it is surprising to observe a high enantiomeric excess (ee) towards the (*S*,*S*) configuration of the 1,2-diphenyl-1,2-ethanediol over the as-synthesised catalysts with no chiral ligand nor oxidant blended in the reaction medium. Careful repeated measurements of the chirality of products confirm reproducibility of the results (see ESI†). To ensure that the catalysis is heterogeneous in nature, the solid and filtrate (colourless) from the product solution were separated from each other and repeatedly tested by adding more batches of the same substrate contents. No activity (<1% conversion) was found using the filtrate. Instead, the solid catalyst gave a lower yield (41.5%) on the second test indicating a degree of deactivation but a very similar (*R*,*R*) and (*S*,*S*) product distribution was achieved. In addition, a soluble $Os_3(CO)_{12}$ (13 μmol) species without adding chiral modifier to replace the solid catalyst was tested under identical conditions. A very poor selectivity to the diol (56.3%) with selectivities to benzaldehyde (40.6%), benzoin (2.6%) and benzil (0.5%), respectively were obtained. Analysing the diol clearly showed the racemic mixture in this homogeneous system, as expected. Thus, as noted from Table 1, the (*S*,*S*) configuration is favoured by 55% on using the MCM-41 solid support and by 90% with the Al-MCM-41 support. This 90% ee towards the (*S*,*S*) configuration is higher than those reported using a homogeneous OsO_4–NMO–acetone : water system containing a chiral ligand (78%).[11] It is noted that the highest reported chirality is obtained using an Os catalytic system with a chiral modifier in ionic liquids which can give 94–97% ee towards the (*S*,*S*) configuration.[12]

FTIR characterisations of the as-synthesised MCM-41-immobilised $Os_3(CO)_{12}$ compared with MCM-41 show a strong and characteristic absorption band near 1382 cm^{-1} (Figs. 1a and b). This band is attributed to Os–H–Os vibrations.[9] More than 8 absorption peaks including 2124, 2116, 2076, 2067, 2026, 2017, 1995 and 1987 cm^{-1} vibrations are found in the enlarged CO-stretching frequency region (Fig. 1b). These absorption peaks outnumber those of pure $Os_3(CO)_{12}$ (2069, 2037, 2016 and 2005 cm^{-1} of D_{3h}), which implies a decrease in the symmetry when the molecule is adsorbed on the MCM-41 surface or a simultaneous presence of more than one surface species or very likely a result of both. Immobilisation of $Os_3(CO)_{12}$ *via* CVD onto various amorphous inorganic oxides including silica was widely reported in the eighties.[13] Detailed characterisation, including the uses of EXAFS and FTIR, showed that (μ–H)$Os_3(CO)_{10}$(μ–OSi–) species, with the triangular osmium framework anchored *upright* on the silica surface, can be synthesised at high surface coverage.[13] Many of our observed FTIR vibrations indeed match the reported values, indicating that the volatile $Os_3(CO)_{12}$ is likely to react with the MCM-41 silicate in a similar way as with those silicas, probably through oxidative addition of surface silanol groups into an Os–Os bond to yield the trinuclear anchored complex (μ–H)$Os_3(CO)_{10}$(μ–OSi–).

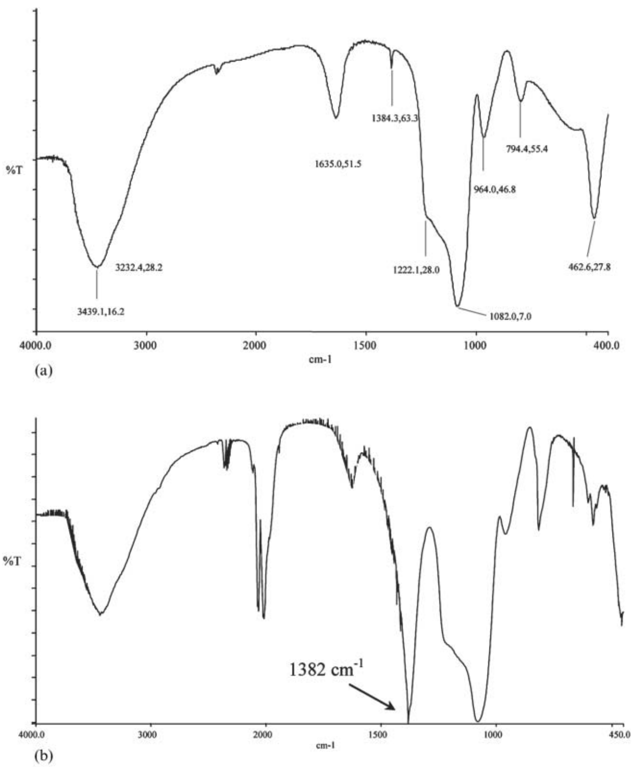

Fig. 1 (a) FTIR spectrum of pure MCM-41(upper curve); (b) FTIR spectrum of 32mg$Os_3(CO)_{12}$/MCM-41[AS] (lower curve).

However, careful study of CO_2 evolution during temperature programmed decomposition (TPDe) of the anchored species in a flowing stream of helium suggested more than one type of surface species.[9,14] In particular, the high temperature shoulder peak at 400 °C becomes more prominent in those samples with lower initial $Os_3(CO)_{12}$ loadings ($\leqslant$3 wt%, see ESI†) or when using the Al-MCM-41 support with more reactive acidic sites, as presently shown in Fig. 2. It is believed that, in these cases, the triangular clusters are likely to align themselves "parallel" to the MCM-41 channel surface, with possibly more than one anchor point per

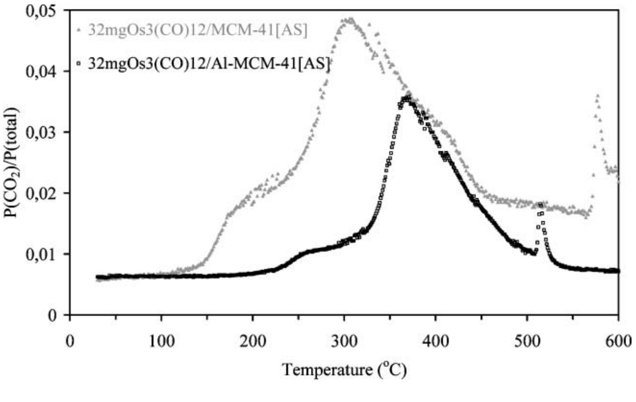

Fig. 2 Temperature programmed decomposition (CO_2 evolution monitored by on-line mass spectrometry) of anchored $Os_3(CO)_{12}$ on MCM-41 and Al-MCM-41 (as-synthesised samples) obtained by ramping the samples at 10 K min^{-1} in He (10 mL min^{-1}).

trinuclear cluster from the surface oxygen (eliminating more CO from the complex). It is noted that TGA-DTA (not shown) indeed indicates similar Os content (7 wt%) for both the Al-MCM-41 and the MCM-41 supports but the signal of the CO_2 evolution (Fig. 2) is clearly reduced in this acidic catalyst, which suggests the presence of less carbonyl species available from the Al-MCM-41 support. A similar surface species of a tri-Os carbonyl cluster with a bidentate oxygen donor from a silica surface has been previously suggested.[13] On the other hand, after calcination of the as-synthesised samples at 220 °C, the numbers of CO stretching bands in both MCM-41/Al-MCM-41 samples have been substantially decreased as compared to the free $Os_3(CO)_{12}$ cluster. Three principal FTIR CO-stretching vibrations are now observed at 2130, 2040 and 2000 cm^{-1}, in agreement with the previous observations that heat treatment of silica anchored $(\mu\text{–}H)Os_3(CO)_{10}(\mu\text{–}OSi\text{–})$ species can produce mononuclear surface species $Os(CO)_x$ (x = 2 or 3) with C_{2v} or C_{3v} symmetry through the cluster degradation.[9,13]

From the above characterisation, it may not be possible to work out the precise origin of the exciting enantioselectivity observed in the as-synthesised mesoporous samples. However, it is apparently clear that the *mononuclear* Os species anchored on the MCM-41 surface give a racemic mixture with no enantioselectivity in *trans*-stilbene oxidation. On the other hand, the *trinuclear* Os species anchored onto MCM-41, and in particular onto Al-MCM-41 (which accommodates more trinuclear Os species), give a very high enantioselectivity for the same reaction. It has recently been reported that placing chiral catalysts in confined porous structures, such as mesoporous silicates, could significantly boost the ee values.[15] Thus, it is thought that our impressive ee in the case of Al-MCM-41 is a result of the introduction of surface Al sites into MCM-41 for immobilisation of more trinuclear species, hence generating a more sterically crowded environment at higher coverage. Perhaps the most intriguing difference between our results and the literature is that no chiral ligand/modifier or oxidant is used in our case. Thus, we believe that upon immobilisation on the MCM-41 or related surfaces, a favourable chiral orientation of the triosmium complex precursor must have taken place, resulting in a new surface chiral catalytic species.

In summary, we have made an unprecedented observation that heterogenisation of $Os_3(CO)_{12}$ on the internal surface of Al-MCM-41 using simple chemical vapour deposition gives a superior enantioselectivity in the dihydroxylation of *trans*-stilbene without adding a chiral modifier. The present enantiomeric excess observed reaches 90%, rendering these materials potential heterogeneous catalysts akin to enzymes for the asymmetric dihydroxylation of alkenes in liquid phase. The precise nature of the surface chiral species is yet to be disclosed.

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Valérie Caps,‡ Ioannis Paraskevas and Shik Chi Tsang*
The Surface and Catalysis Research Centre, School of Chemistry,
University of Reading, Whiteknights, Reading, UK RG6 6AD.
E-mail: s.c.e.tsang@reading.ac.uk; Fax: +44 118 931 6632;
Tel: +44 118 931 6346

Notes and references

1 H. C. Kolb, M. S. VanNieuwenhze and K. B. Sharpless, *Chem. Rev.*, 1994, **94**, 2483; L. Ahrgren and L. Sutin, *Org. Process Res. Dev.*, 1997, **1**, 425.
2 D. E. De Vos, B. F. Sels and P. A. Jacobs, *Adv. Catal.*, 2002, **46**, 1; A. Severeyns, D. E. De Vos and P. A. Jacobs, *Top. Catal.*, 2002, **19**, 125.
3 D. Pini, A. Petri, A. Nardi, C. Rosini and P. Salvadori, *Tetrahedron Lett.*, 1991, **32**, 5175; P. Salvatori, D. Pini and A. Petri, *J. Am. Chem. Soc.*, 1997, **119**, 6929; C. Bolm and A. Gerlach, *Eur. J. Org. Chem.*, 1998, 21.
4 C. Bolm, A. Maischak and A. Gerlach, *Chem. Commun.*, 1997, 2353.
5 I. Motorina and C. M. Crudden, *Org. Lett.*, 2001, **3**, 2325.
6 W. A. Herrmann, R. M. Kratzer, J. Blümel, H. B. Friedrich, R. W. Fischer, D. C. Apperley, J. Mink and O. Berkesi, *J. Mol. Catal. A: Chem.*, 1997, **120**, 197.
7 S. Kobayashi, T. Ishida and R. Akiyama, *Org. Lett.*, 2001, **3**, 2649.
8 B. M. Choudary, N. S. Chowdari, M. L. Kantam and K. V. Raghavan, *J. Am. Chem. Soc.*, 2001, **123**, 9220; B. M. Choudary, N. S. Chowdari, K. Jyothi and M. L. Kantam, *J. Am. Chem. Soc.*, 2002, **124**, 5341.
9 V. Caps, I. Paraskevas and S. C. Tsang, *Appl. Catal., A*, 2003, **252**, 37.
10 A. Matsumoto, H. Chen, K. Tsutsumi, M. Grün and K. Unger, *Microporous Mesoporous Mater.*, 1999, **32**, 55.
11 H.-L. Kwong, C. Sorato, Y. Ogino, H. Chen and K. B. Sharpless, *Tetrahedron Lett.*, 1990, **31**, 2999.
12 C. E. Song, *Chem. Commun.*, 2004, 1033–1043.
13 R. Psaro, C. Dossi, A. Fiso and R. Ugo, *Res. Chem. Intermed.*, 1991, **15**, 31; J. Evans, *Spectrochim. Acta*, 1987, **43**, 1511.
14 V. Caps and S. C. Tsang, *Appl. Catal., A*, 2003, **248**, 19.
15 B. F. G. Johnson, S. A. Raynor, D. S. Shephard, T. Mashmeyer, J. M. Thomas, G. Sankar, S. Bromley, R. Oldroyd, L. Gladdenc and M. D. Mantlec, *Chem. Commun.*, 1999, 1167; J. M. Thomas, T. Maschmeyer, B. F. G. Johnson and D. S. Shephard, *J. Mol. Catal. A: Chem.*, 1999, **141**, 139; S. A. Raynor, J. M. Thomas, R. Raja, B. F. G. Johnson, R. G. Bell and M. D. Mantlec, *Chem. Commun.*, 2000, 1925; R. Raja, J. M. Thomas, M. D. Jones, B. F. G. Johnson and D. E. W. Vaughan, *J. Am. Chem. Soc.*, 2003, **125**, 14982; M. D. Jones, R. Raja, J. M. Thomas, B. F. G. Johnson, D. W. Lewis, J. Rouzaud and K. D. M. Harris, *Angew. Chem., Int. Ed.*, 2003, **42**, 4326.