deactivation of the excited state. This remains a theoretical hypothesis, however, since the two viologens cannot be distinguished by spectroscopic means. Even so, it seems reasonable to anticipate that highly directional electron transfer can be induced by environmental effects of the type proposed here.

Experimental Section

The syntheses of **1**, **2**, and **3** starting from readily prepared 4,4′-bis(methylene-4,4′-bipyridinium)-2,2′-bipyridyl bis(hexafluorophosphate) have been reported.[7] Solvents were purified by standard methods, and dielectric constants were taken from the literature.[13] For all laser spectroscopic studies, excitation was carried out at 565 nm with a 0.3-ps laser pulse delivered from a Nd-YAG pumped pyromethene dye laser similar to that described in ref. [14].

1: Yield: 64 mg, 70%; ^{1}H NMR (360 MHz, CD_3COCD_3, 298 K): $\delta = 6.15$ (s, 4H), 6.25 (s, 4H), 7.55–7.79 (m, 12H), 7.90 (s, 4H), 7.91–8.11 (m, 4H), 8.23 (m, 4H), 8.51 (d, 4H, $J = 6.2$ Hz), 8.70–8.85 (m, 6H), 9.33–9.55 (m, 8H); FAB-MS (nitrobenzyl alcohol(NBA)/CH_3CN matrix): m/z: 1737 $[M - PF_6]^+$, 1591 $[M - 2PF_6]^+$, 1446 $[M - 3PF_6]^+$.

2: Yield: 40 mg, 68%; ^{1}H NMR (360 MHz, CD_3COCD_3, 298 K): $\delta = 3.45$–3.48 (m, 4H), 3.61–3.63 (m, 8H), 3.69–3.72 (m, 8H), 3.79–3.85 (m, 12H), 3.93–4.10 (m, 4H), 6.10 (s, 4H), 6.23 (s, 4H), 6.26 (s, 4H), 7.57–7.73 (q, 4H, $J = 7.5$ Hz), 7.92–7.94 (d, 2H, $J = 6$ Hz), 7.98 (s, 4H), 8.00–8.02 (d, 2H, $J = 5.3$ Hz), 8.02–8.22 (m, 10H), 8.23–8.31 (q, 4H, $J = 7.8$ Hz), 8.34–8.36 (d, 2H, $J = 5.7$ Hz), 8.82–8.87 (m, 6H), 8.98 (m, 4H), 9.34–9.36 (d, 4H, $J = 5$ Hz); ES-MS ($CH_3CN/H_20/HCOOH$): m/z: 661 $[M - 3PF_6]^{3+}$, 460 $[M - 4PF_6]^{4+}$, 339 $[M - 5PF_6]^{5+}$.

3: Yield: 100 mg, 20%; ^{1}H NMR (360 MHz, CD_3COCD_3, 298 K): $\delta = 3.46$ (m, 8H), 3.61 (m, 8H), 3.89–3.93 (m, 16H), 6.08 (s, 4H), 6.15 (s, 4H), 7.94 (m, 2H), 8.00 (s, 4H), 8.10–8.14 (2 × d, 8H, $J = 8$ Hz), 8.18 (m, 2H), 8.90–8.92 (d, 2H, $J = 5$ Hz), 9.27–9.29 (d, 4H, $J = 5.2$ Hz), 9.32–9.34 (d, 4H, $J = 7$ Hz); FAB-MS (NBA matrix): m/z: 1569 $[M - PF_6]^+$, 1425 $[M - 2PF_6]^+$, 1280 $[M - 3PF_6]^+$, 1135 $[M - 4PF_6]^+$.

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[1] J. Deisenhofer, H. Michel, *Angew. Chem.* **1989**, *101*, 872; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 829.
[2] R. Huber, *Angew. Chem.* **1989**, *101*, 849; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 848.
[3] O. El-Kabbani, C.-H. Chan, D. Tiede, J. R. Norris, M. Schiffer, *Biochemistry* **1991**, *30*, 5361.
[4] H. Treutlein, K. Schulten, A. T. Brünger, M. Karplus, J. Deisenhofer, H. Michel, *Proc. Natl. Acad. Sci. USA* **1992**, *89*, 75.
[5] M. A. Steffen, K. Lao, S. G. Boxer, *Science* **1994**, *264*, 810.
[6] B. A. Heller, D. Holten, C. Kirmaier, *Science* **1995**, *269*, 940.
[7] a) A. C. Benniston, P. R. Mackie, A. Harriman, *Tet. Lett.* **1997**, *38*, 3577: b) D. Philp, J. F. Stoddart, *SynLett.* **1991**, *7*, 445, and references therein.
[8] D. B. Amabilino, P.-L. Anelli, P. R. Ashton, G. R. Brown, E. Cordova, L. A. Godinez, W. Hayes, A. E. Kaifer, D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, M. S. Tolley, D. J. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 11142.
[9] P.-L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193.
[10] E. H. Yonemoto, R. L. Riley, Y. L. Kim, S. J. Atherton, R. H. Schmehl, T. E. Mallouk, *J. Am. Chem. Soc.* **1992**, *114*, 8081.
[11] Calculated from redox potentials and corrected for electrostatic effects according to J. Kroon, J. W. Verhoeven, M. N. Paddon-Row, A. N. Oliver, *Angew. Chem.* **1991**, *103*, 1398; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1358.
[12] R. A. Marcus, *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.
[13] J. A. Riddick, W. B. Bunger in *Organic Solvents. Physical Properties and Methods of Purification. Techniques of Chemistry Vol II* (Ed.: A. Weissberger) Wiley-Interscience, New York, **1970**.
[14] J.-P. Collin, A. Harriman, V. Heitz, F. Odobel, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 5679.

Solid-Phase Immobilization of a New Epoxidation Catalyst**

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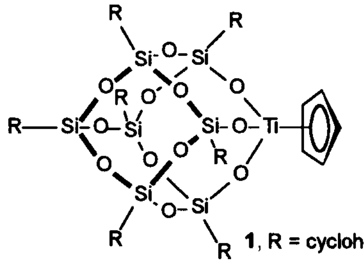
Rutger A. van Santen

The heterogenization of homogeneous catalysts is an important topic in liquid-phase oxidation catalysis.[1] Recently we reported on the use of the titanium(IV) silsesquioxane $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}Ti(\eta^5\text{-}C_5H_5)]$ **1**[2] as an active and robust homogeneous catalyst for alkene epoxidation.[3] Under the catalytic conditions employed, **1** is stable and does not leach titanium, which makes it an attractive candidate for heterogenization. Here we report on the immobilization of **1** in an MCM-41 molecular sieve,[4] for which we especially exploited its strong adsorption in the MCM-41 channel. The resulting self-assembled materials are active, truly heterogeneous, and recyclable catalysts for alkene epoxidation in the liquid phase.



1, R = cyclohexyl

The adsorption of the silsesquioxane **1** from hexane into an MCM-41 molecular sieve occurs quickly and can be followed easily by UV/Vis spectroscopy in solution by monitoring its intense 216 nm band. We investigated MCM-41 molecular sieves with Si/Al ratios of 42, 125, and ∞. The adsorption kinetics of **1** are typical for "single-file diffusion",[5] indicating that its actual adsorption takes place inside the MCM-41 channels. Because of this fast and complete adsorption, the loading of **1** can be adjusted easily by varying its total amount in solution. The maximum loading for the MCM-41 host with a Si/Al ratio of 42 was found to be 97 milligrams of **1** per gram

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of MCM-41 (i.e. 4.3 mg Ti/g MCM-41). FT-IR analysis of MCM-41 materials (KBr pellet) with a maximum loading of **1** showed, superimposed on the vibration bands characteristic for MCM-41, bands typical for **1**: cyclohexyl and cyclopentadienyl C–H vibrations (2854, 2928 cm^{-1}) together with a very characteristic cyclopentadienyl C–C vibration (1449 cm^{-1}).

The titanium silsesquioxane containing materials efficiently catalyze the epoxidation of cyclooctene at 50°C with *tert*-butyl hydroperoxide (Table 1, Figure 1). The scope of the reaction includes also the epoxidation of norbornene and 1-octene.[3] With the aluminum-free MCM-41 molecular sieves, in particular, high catalytic activity and heterogeneity was obtained. The data show that the presence of aluminum in MCM-41 reduces the activity of the catalyst (Table 1, entries 2–7).[6] Moreover, under epoxidizing conditions these catalysts quantitatively leached **1** from its aluminum-containing mesoporous host, thus rendering the catalysis homogeneous.

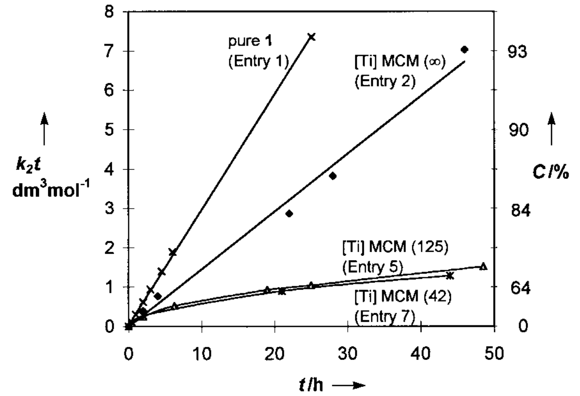

Figure 1. Second-order rate parameter k_2t for the catalytic epoxidation with [Ti] catalysts (Table 1, entries 1, 2, 5, 7). Left axis: $k_2t = 1/[A]_t - 1/[A]_0$ ($[A]_t$ = concentration of cyclooctene at time t and $[A]_0$ = concentration of cyclooctene at $t = 0$). Right axis: conversion C versus time t. All reactions were performed with equimolar amounts of alkene and dried *tert*-butyl hydroperoxide (7.2 mmol each) in hexane (4.0 mL).

Table 1. Activity of **1** immobilized in mesoporous MCM-41 or silica for the epoxidation of cyclooctene.[a]

Entry	[Ti] Catalyst (Si/Al ratio)	Silylated samples[c]	Heterogeneous?[d]	Conv. [%][e]	TOF[f] [mol mol $^{-1}$ h^{-1}]
1	**1**	–	–	95	287
2	[Ti]-MCM (∞)	–	yes	84	202
3	[Ti]-MCM (∞)	silylated	yes	77	184
4	[Ti]-MCM (125)	–	no	–[g]	–
5	[Ti]-MCM (125)	silylated	yes	65	160
6	[Ti]-MCM (42)	–	no	–[g]	–
7	[Ti]-MCM (42)	silylated	yes	55	178
8	[Ti]-silica	–	no	–[g]	–
9	[Ti]-silica	silylated	no	–[g]	–
10	MCM (∞)	–	–	10	–
11	MCM (125)	–	–	21	–
12	MCM (42)	–	–	14	–

[a] All reactions were performed with equimolar amounts of alkene and dried *tert*-butyl hydroperoxide (1.8 mmol each) in hexane (1.0 mL) and with 60 mg catalyst. [b] Catalysts with the prefix [Ti] contain complex **1** (1.2 mg Ti/g MCM-41); otherwise reference is being made to blank experiments without **1**. [c] $SiCl_2Ph_2$ was used as the silylating agent. [d] Catalysts are defined as heterogeneous when at 30% conversion and after direct filtration, no subsequent conversion takes place in the filtrate. [e] Conversion of cyclooctene determined by ^1H NMR spectroscopy after 22 h. Selectivities towards the epoxide >95%. [f] Initial turnover frequency (TOF) determined after 2 h. [g] Since the reaction was homogeneous the conversion is not relevant.

Fortunately, the undesired leaching of the aluminum-containing catalysts can be completely stopped when the MCM-41 molecular sieves are treated with the silylating agent $SiCl_2Ph_2$ prior to catalysis (Table 1, entries 3, 5, 7).[7] The unresolved phenyl signals of the $(\text{-O-})_2SiPh_2$ functions are found in the ^{13}C MAS NMR spectrum (100 MHz) at $\delta = 127.3$ and $\delta = 134.3$. BET analysis on an impregnated MCM-41 sample clearly showed a decrease in both pore diameter and mesopore volume upon adsorption of the silsesquioxane **1** as well as an increase in surface area due to the additional surface of **1** (Table 2). The effect of the silylation is also expressed in both a reduced pore diameter and a reduced mesopore volume.

Table 2. BET results for the series of aluminum-free MCM-41 materials employed in catalysis.[a]

Entry[b]	Cat.	Surface area [m^2g^{-1}]	Modus pore diameter [nm]	Micropore volume [cm^3g^{-1}]	Mesopore volume [cm^3g^{-1}]
10	MCM (∞)	552	2.9	0.20	0.15
2	[Ti]-MCM (∞)	610	2.7	0.20	0.10
3	[Ti]-MCM (∞) silylated	540	2.3	0.16	0.05

[a] All data have a maximum error of 5%; the error in the mesopore volume is roughly 20%. The [Ti]-MCM-41 samples were loaded with 25 milligrams of **1** per gram of MCM-41. [b] Entries as in Table 1.

The activity of the aluminum-containing heterogeneous catalysts obtained by the silylation procedure decreased in the course of alkene epoxidation (see Figure 1). Interestingly, the aluminum-free catalyst showed no deactivation at all, in either silylated or nonsilylated form. The kinetic data obtained for heterogeneous catalysis employing [Ti]-MCM-41 (∞) and for homogeneous catalysis by the complex **1** can be described by overall second-order rate equations (see Figure 1). All heterogeneous catalysts can be easily recovered by filtration; the aluminum-free catalyst can even be reused at least three times without an apparent loss of activity.

Even when a smaller silylation agent like $SiCl_2(CH_3)_2$ is used, an active, heterogeneous, nonleaching catalyst is obtained. This result indicates that the apolarity of the framework determines whether the catalyst will leach its active complex **1**, and not that **1** is physically trapped by the silylating agent.

The influence of the polarity of the framework on the adsorption of substrates was investigated by monitoring the competitive adsorption of 1,2-epoxyoctane and 1-octene. When an aluminum-containing MCM-41 molecular sieve was used, the 1,2-epoxyoctane/1-octene ratio decreased from 1 to 0 in several minutes, while in the case of an aluminum-free MCM-41 this ratio levels off at about 0.2. This demonstrates that the affinity of the hydrophilic aluminum-containing MCM-41 for the more polar epoxide is higher than that of the relatively hydrophobic aluminum-free MCM-41 framework. This observation is supported by thermogravimetric analysis, which indicated that both the water content and the dehydration temperature for the aluminum-free MCM-41 (1%, 49°C) are much lower than that of the the aluminum-containing MCM-41 (5%, 60°C). The higher polarity of the aluminum-containing MCM-41 materials is likely to induce leaching.[8] In contrast, the degree of apolarity of an aluminum-free MCM-41 molecular sieve is ideal for both strong adsorption of the catalyst, leading to a heterogeneous system, and diffusion of the organics through the MCM-41 channel. In contrast to physically enclosed systems, this will lead to a *self-assembled heterogeneous catalyst* that is prone to neither leaching nor deactivation.[9]

Conventional silica gel (Silica Grace SG360, total pore volume ca. 0.9–1.0 $cm^3 g^{-1}$, surface area roughly 600 $m^2 g^{-1}$) also adsorbs complex **1**. During catalyst testing, however, this material undergoes a significant degree of leaching (see Table 1). From this finding we conclude that a silica with channel-type pores such as an aluminum-free MCM-41 molecular sieve is essential for an irreversible adsorption of the silsesquioxane complex.

Experimental Section

The different MCM-41 samples were prepared following the procedure used by Beck et al.[10] and adapted by Busio et al.[4] In a typical adsorption experiment 50 mL of a 10^{-3} M solution of **1**[2b] in hexane (p.a., Acros) was added slowly to a suspension of 2 g of dried MCM-41 in hexane (50 mL), and the suspension was stirred for 24 h. The impregnated MCM-41 was subsequently filtered off, washed with hexane (3 × 20 mL), and dried in air at 80°C for 24 h.

In a typical silylation experiment 0.5 g of a dried and degassed impregnated MCM-41 sample was refluxed in a solution of 70 mL of hexane with 2.5 g of dichlorodiphenylsilane (96%, Acros) under an inert atmosphere for 72 h. The obtained material was filtered off, washed with hexane (3 × 20 mL) and acetone (p.a., Acros, 3 × 20 mL), and dried in air at 80°C for 24 h.

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[1] Different procedures with this goal have been reported: isomorphous substitution: a) M. Taramasso, G. Perego, B. Notari (Enichem), US Pat. **1983** 4410501; *Chem. Abstr.* **1981,** *95*, 206272k; for a recent review see: b) I. W. C. E. Arends, R. A. Sheldon, M. Wallau, U. Schuchardt, *Angew. Chem.* **1997**, *109*, 1190; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1144; grafting of complexes in molecular sieves: c) T. Maschmeyer, F. Rey, G. Sankar, J. M. Thomas, *Nature* **1995**, *378*, 159; ship-in-a-bottle catalysts, for a review see: d) D. E. De Vos, F. Thibault-Starzyk, P. P. Knops-Gerrits, R. F. Parton, P. A. Jacobs, *Macromol. Symp.* **1994**, *80*, 157; for a recent publication: e) K. J. Balkus, Jr., A. K. Khanmamedova, K. M. Dixon, F. Bedioui, *Appl. Catal. A* **1996**, *143*, 159. For a recent highlight see: R. Murugavel, H. W. Roesky, *Angew. Chem.* **1997**, *109*, 491; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 477.

[2] a) F. J. Feher, T. A. Budzichowski, K. Rahimian, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3859; b) I. E. Buys, T. W. Hambley, D. J. Houlton, T. Maschmeyer, A. F. Masters, A. K. Smith, *J. Mol. Catal.* **1994**, *86*, 309.

[3] H. C. L. Abbenhuis, S. Krijnen, R. A. Van Santen, *Chem. Commun.* **1997**, 331.

[4] M. Busio, J. Jänchen, J. H. C. Van Hooff, *Microporous Mater.* **1995**, *5*, 211.

[5] J. Kärger, M. Petzold, H. Pfeifer, S. Ernst, J. Weitkamp, *J. Catal.* **1992**, *136*, 283.

[6] A. Corma, P. Esteve, A. Martínez, *J. Catal.* **1996**, *161*, 11.

[7] For a related approach involving enzymes in MCM-41 materials: J. F. Díaz, K. J. Balkus, Jr., *J. Mol. Catal. B Enzymes* **1996**, *2*, 115.

[8] a) J. Jänchen, M. Busio, M. Hintze, H. Stach, J. H. C. Van Hooff, *Stud. Surf. Sci. Catal.* **1997**, 105, 1731; b) C. Y. Chen, H. X. Li, M. E. Davis, *Microporous Mater.* **1993**, *2*, 17.

[9] K. T. Wan, M. E. Davis, *Nature* **1994**, *370*, 449.

[10] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgens, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834.

A Biomimetic Synthesis of a Porphobilinogen Precursor Using a Mukaiyama Aldol Reaction**

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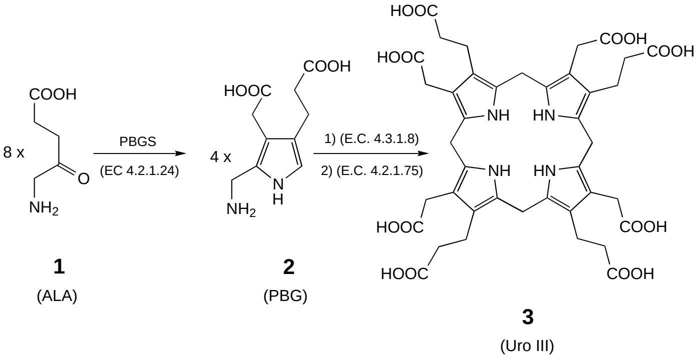
Dedicated to Professor Dieter Seebach
on the occasion of his 60th birthday

The tetrapyrrolic "pigments of life" fulfill many different functions and therefore have a special position among natural pigments.[1] The structures of the intermediates (δ-aminolevulinic acid (ALA, **1**) and porphobilinogen (PBG, **2**)) leading to uroporphyrinogen (Uro) III (**3**), the precursor of all tetrapyrroles, were determined in the early 1950s (Scheme 1).[2] Even early on, the second and third steps of this elegant and convergent biosynthesis could be mimicked chemically.[3]



Scheme 1. Biosynthesis of uroporphyrinogen III (**3**). PBGS = porphobilinogen synthetase.

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