DOI: 10.1002/adsc.200606165

Heterogenisation of Acylperrhenate on Mesoporous Materials and its Application in Catalysis

Draganco Veljanovski,[a] Ayyamperumal Sakthivel,[a] Wolfgang A. Herrmann,[a,*] and Fritz E. Kühn[a, b,*]

[a] Lehrstuhl für Anorganische Chemie der Technischen Universität München, Lichtenbergstrasse 4, 85747 Garching bei München, Germany
Fax: (+49)-89-289-13473; e-mail: wolfgang.herrmann@ch.tum.de or fritz.kuehn@ch.tum.de
[b] Department of Chemistry, Instituto Technológico et Nuclear (ITN), Estrada Nacional No. 10, 2686-953 Sacavém, Portugal
Fax: (+351)-21-984-6186; e-mail: fekuhn@itn.pt

Received: April 13, 2006; Accepted: June 2, 2006

Abstract: Acylperrhenate is grafted on the surface of mesoporous silicates and aluminiosilicate molecular sieves through available surface silanol and acidic hydroxy groups. The intactness of the mesoporous supports and the nature of the catalytic species is demonstrated by XRD, TEM, FT-IR, N_2 adsorption-desorption and elemental analysis. The grafted materials are applied for alkene epoxidation. The catalysts are found to be stable against decomposition on the surfaces and to exhibit good catalytic activity. However, during the course of repeated catalytic runs, some leaching associated with subsequent decomposition of the catalyst is observed, reducing the activity of the materials.

Keywords: catalysis; epoxidation; grafting; mesoporous materials; rhenium

Introduction

Epoxides, especially ethylene and propene oxides, are key raw materials for a large number of products such as glycols, glycol ethers, alkanolamines and polymers (e.g., polyester and polyurethane).[1] The first metal-catalysed epoxidation with alkyl hydroperoxide was reported by Hawkins in 1950.[2] The production of epoxides using alkyl hydroperoxides in the presence of homogeneous catalysts based on molybdenum, vanadium, tungsten, titanium and zirconium was reported almost simultaneously by Halcon[3] and Atlantic Richfield (ARCO)[4,5] in 1968. This so-called oxirane process is currently applied for roughly 45% of the 3 million tons of propene oxide produced annually.[1]

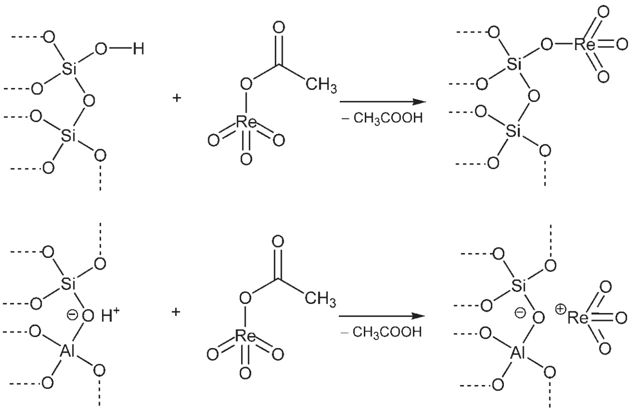
Despite the still widespread use of other oxidants in industries, hydrogen peroxide or pure oxygen are nowadays favoured as oxygenation reagents because of their clean reactivity and environmentally benign nature. The starting materials are inexpensive and, even more importantly, only water (in the case of H_2O_2) or no by-product (in the case of O_2) is formed. Oxidation reactions with these oxidants are mainly catalysed with homogenous catalysts based on tungsten,[6] manganese[7] and rhenium.[8]

A particularly strong interest in environmentally friendly oxidation catalysts has been noticed following the preparation of the versatile catalyst methyltrioxorhenium(VII) (MTO) throughout the last 15 years. The catalytic activity of MTO and its derivatives, the organorhenium oxides, was investigated in some detail and several of these compounds have gained significant importance as extremely active catalysts for olefin epoxidation reactions,[9] aldehyde olefination,[10] olefin metathesis,[11] etc. The by far most widely employed organorhenium(VII) oxide, however, still is MTO.[8,9] Among the numerous applications of MTO, olefin epoxidation with H_2O_2 as oxidising agent is one of the best examined and most successful.

An important drawback of the homogeneous catalysts of the organorhenium oxide family, however, is the not yet satisfyingly solved recyclisation. An essential step of applied chemistry is to combine the advantages of heterogeneous and homogeneous catalysis, in particular by immobilisation of homogeneous catalysts. Organorhenium oxides, were already heterogenised on various supports such as zeolites,[13] polymers,[14] ionic liquids[15] molecular sieves,[16] etc. and the reactivities in olefin oxidation, olefin metathesis and Bayer–Villiger reactions of these new materials were examined. However, in most cases the reactivity and selectivity are far below the reactivity and selectivity of the respective homogenous catalyst. Extensive leaching is an additional problem in several cases.

Among the various supporting materials studied, the mesoporous silicates, designated as MCM-41 and MCM-48 by Mobil scientists[17] with regular pore size, large surface areas, a large number of surface silanol groups, and high chemical and thermal stability are potential and promising candidates as both catalysts and catalyst supports.[18] Organorhenium species have been stabilised on the above mentioned mesoporous surfaces through silane linkers, however, they lack sufficient epoxidation ability.[16] In the present study our aim is to fix the trioxorhenium(VII) moiety directly on the surface of mesoporous materials. In this regard it is noteworthy that acylperrhenate ($AcOReO_3$),[19–21] which is an intermediate for the synthesis of MTO and its homologues, may be directly grafted through the available Si–OH or Si–O–Al groups of the mesoporous materials.

We have successfully grafted acylperrhenate ($AcOReO_3$) on MCM-41, MCM-48, Al-MCM-41, Al-MCM-48 materials, through available silanol and Al–OH groups, and evaluated the catalytic reactivity and selectivity of these systems in alkene epoxidation (Scheme 1). The materials grafted with acylperrhenale are designated as MCM-41-$OReO_3$, Al-MCM-41-$OReO_3$, MCM-48-$OReO_3$ and Al-MCM-48-$OReO_3$. The stability and the leaching properties of the received new materials are investigated as well. Trimethylsilyl perrhenate was also synthesised in solution under the same conditions as used in the grafting process in order to examine the nature of the bonding between the rhenium species and the surface.



Scheme 1. Grafting of $AcOReO_3$ on mesoporous materials.

Results and Discussion

Acylperrhenate ($AcOReO_3$) was synthesised as previously described[20] and the comparison of the ^1H NMR and ^{13}C NMR data proved that the complex is pure and identical with the compound described in the literature.[20]

The heterogenisation of $AcOReO_3$ was performed as described in the Experimental Section. The grafted samples are of a pale brown colour. The powder XRD patterns of the obtained MCM-41-$OReO_3$ and Al-MCM-41-$OReO_3$ materials are depicted in Figure 1, traces a and b. In each case all four reflections are observed in the 2θ range 2–8°, with an indexing corresponding to a hexagonal cell showing the (100), (110), and (200) and (210) planes. Figure 1, traces c and d show the XRD patterns of the MCM-48-$OReO_3$ and Al-MCM-48-$OReO_3$, which exhibit a main reflection corresponding to the (211) plane along with a shoulder peak derived from the (220) plane, typical for cubic cells. These peaks together with the sextet pattern observed between the 2θ angles 3–6°, are characteristic for a cubic mesoporous MCM-48 structure.

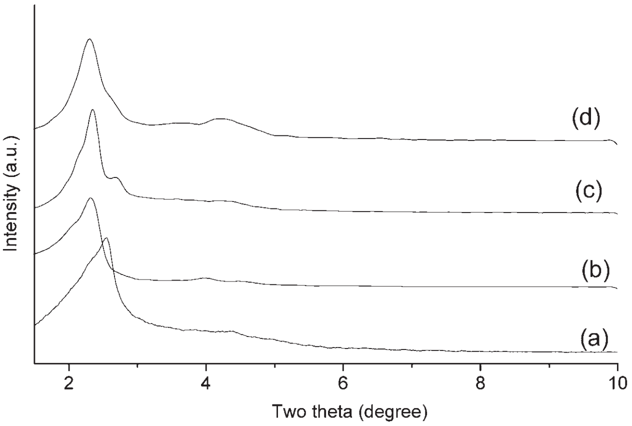


Figure 1. Power XRD pattern of (a) MCM-41-$OReO_3$, (b) Al-MCM-41-$OReO_3$, (c) MCM-48-$OReO_3$ and (d) Al-MCM-48-$OReO_3$.

The observed product reflections show some decrease in the relative intensity and a notable shift to higher 2θ values compared to the parent samples.[22f] These changes result from the contraction of the unit cell, because of the immobilisation of the acylperrhenate on the channels of the molecular sieves. However, the XRD patterns clearly indicate that the structures of the mesoporous materials remain intact throughout the grafting procedure. The modified mesoporous materials contain between 1–6 wt.% Re according to the elemental analysis.

The low temperature N_2 adsorption/desorption isotherms of parent MCM-41 and MCM-48 are of type (IV) according to the IUPAC nomenclature[24] and

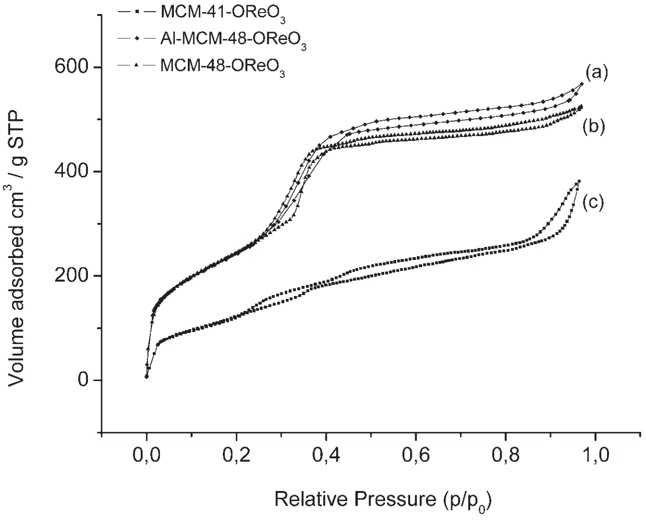


Figure 2. N_2 adsorption/desorption isotherms of (a) Al-MCM-48-OReO$_3$ (b) MCM-48-OReO$_3$ (c) MCM-41-OReO$_3$.

characteristic for mesoporous solids (Figure 2). A well-defined sharp inflection is observed between the relative pressure (p/p_0) of 0.3–0.4 due to capillary condensation of nitrogen inside the primary mesoporous channels of the molecular sieves. The calculated textural parameters using XRD and adsorption/desorption isotherms are summarised in Table 1. All grafted samples show a decrease in the unit cell value, surface area and the pore volume. This is probably due to the grafting of the acylperrhenate complex on the internal surfaces of the mesoporous materials. The TEM images (Figure 3) of the grafted samples show a high uniformity in pore size, providing strong evidence that the mesoporous structures retain long-range ordering[17,18] throughout the grafting process and the channels remain accessible. A representative electron diffraction pattern of the (100) and (110) planes supports further the long-range ordering of the grafted samples.

The FT-IR spectra of parent Al-MCM-41/Al-MCM-48 and the grafted samples are depicted in Figure 4. The bands at 3500, 960, 1080 and 800 cm^{-1} are attributed to stretching vibration of the surface (Si–OH, Si–O–Re, Si–O–Si and Si–O–Si).[25] The peak broadening between 930 and 970 cm^{-1} is an indication for the presence of the trioxorhenium species, its asymmetric stretching vibration [Re=O]$_{vs}$ appearing usually at 920–960 cm^{-1}.[20] The symmetric stretching vibration [Re=O]$_w$ that should be detectable[20] around 980 cm^{-1} is, unfortunately, masked by the strong [Si–O–Si] vibration of the carrier material in this region.

A Model of the Grafting Process

The determination of the exact nature of the catalyst precursor grafted on MCM-41 and MCM-48 proved to be quite difficult. In order to confirm the possible grafting mode of acylperrhenate and to develop an idea what the structure of the grafted complex may look like, a similar reaction in the liquid phase using trimethylsilanol as a model for the surface was performed (Scheme 2). This liquid phase reaction proceeding under the same conditions as the grafting process was monitored by ^{1}H NMR.

It can be clearly seen that the peak at 0.099 ppm [9H, $(CH_3)_3Si$] originating from the trimethylsilanol moiety decreases in intensity and a new peak at 0.483 ppm, representative for trimethylsilyl perrhenate is formed (Figure 5). After crystallisation, colourless crystals are isolated. The analytical and spectroscopic results (^{1}H NMR, ^{13}C NMR, elemental analysis) are identical with the literature data for trimethylsilyl perrhenate.[19,26]

This reaction supports that the Si–O–Re moiety is formed under the reaction conditions applied, and accordingly the assumption of the formation of –SiOReO$_3$ building blocks on the surface seems to be reasonable.

Table 1. Textural properties of the non-grafted and the grafted samples.

Sample	Re [wt %]	Interplane distance [nm][a]	Unit cell parameter [nm][b]	BET surface area [m^{2}g^{-1}]	Pore volume [cm^{3}g^{-1}]
Al-MCM-41	-	3.75	4.33	-	-
Al-MCM-41-OReO$_3$	0.9	3.75	4.33	-	-
Al-MCM-48	-	3.79	9.28	-	-
Al-MCM-48-OReO$_3$	1.3	3.82	9.36	941	0.8
MCM-41	-	3.80	4.38	839	0.8
MCM-41-OReO$_3$	2.8	3.46	3.99	489	0.6
MCM-48	-	3.97	9.72	1043	1.2
MCM-48-OReO$_3$	6.0	3.72	9.12	938	0.8

[a] d_{100} for MCM-41 and d_{211} for MCM-48.

[b] $\bar{a} = 2d_{100}/\sqrt{3}$ for MCM-41; $\bar{a} = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$ for MCM-48.

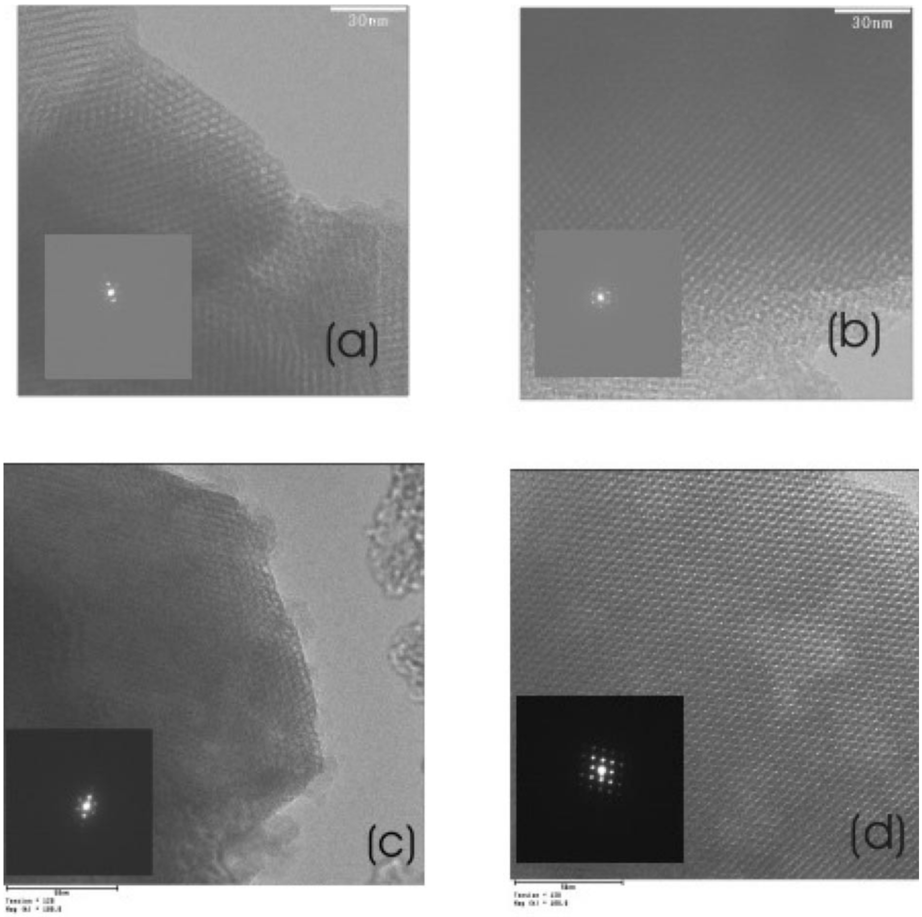


Figure 3. Transmission electron micrograph images of (a) Al-MCM-41-OReO$_3$ (b) Al-MCM-48-OReO$_3$ (c) MCM-41-OReO$_3$ and (d) MCM-48-OReO$_3$.

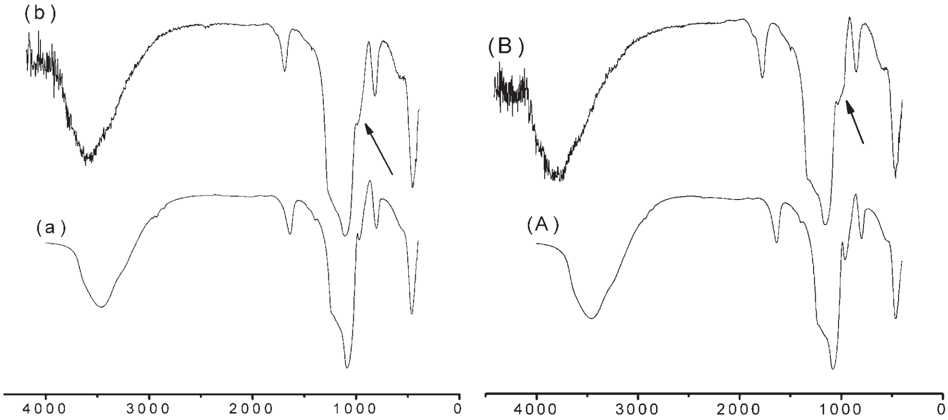
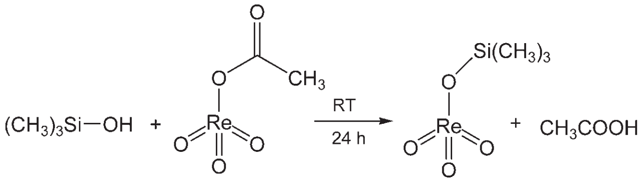


Figure 4. FT-IR spectra of (a) Al-MCM-41, (b) Al-MCM-41-OReO$_3$, (A) Al-MCM-48, (B) Al-MCM-48-OReO$_3$.

Catalytic Applications

The grafted samples are applied for olefin epoxidation with cyclooctene being the substrate and H_2O_2 as the oxidizing agent. The results are summarised in Table 2. The kinetic curves of the reaction with all catalysts are shown in Figure 6 a. In all cases the initial activity is high (see Table 3 and Figure 6 a) and slows down as the reaction proceeds, which is due to the consumption of substrate and possibly enhanced



Scheme 2. Synthesis of trimethylsilyl perrhenate from trimethylsilanol and acylperrhenate.

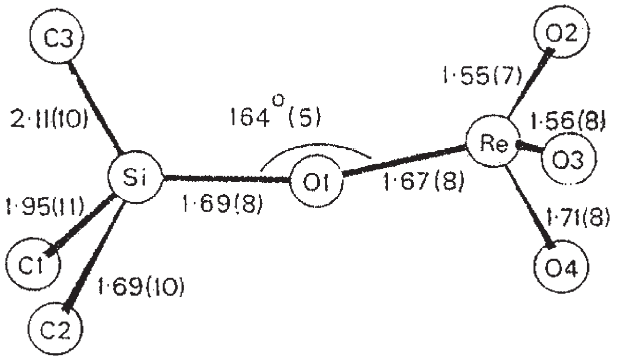


Figure 5. The molecular structure of trimethylsilyl perrhenate.[28]

by the formation of H_2O (as by-product from consumed H_2O_2) thus lowering the concentration of the catalytic active species by partial hydrolytic decomposition.[27] When using a 30% H_2O_2 solution in water as oxidising agent for conducting the olefin epoxidation (Table 3) no reaction could be observed. This observation supports the assumption of negative effects of the formed water on the catalyst.

Furthermore, the catalysts grafted on surfaces without aluminium show much higher reactivity (82% conversion after 24 h, for MCM-41-$OReO_3$ and 86% for MCM-48-$OReO_3$) than the catalysts on surfaces containing aluminium (59% conversion after 24 h, for Al-MCM-41-$OReO_3$ and 70% for Al-MCM-48-$OReO_3$); see Table 2. A probable cause is the stronger electron-donating capability of the aluminium-containing surfaces thus reducing the Lewis acidity of the metal centre as well as the catalytic activity. Whilst the reaction time to reach high conversion is relatively long, the selectivity towards epoxides is high (the amount of the only detectable other product, the diol, is never higher than 10%). When using other, less reactive substrates, such as styrene the reaction times increase again considerably. In the case

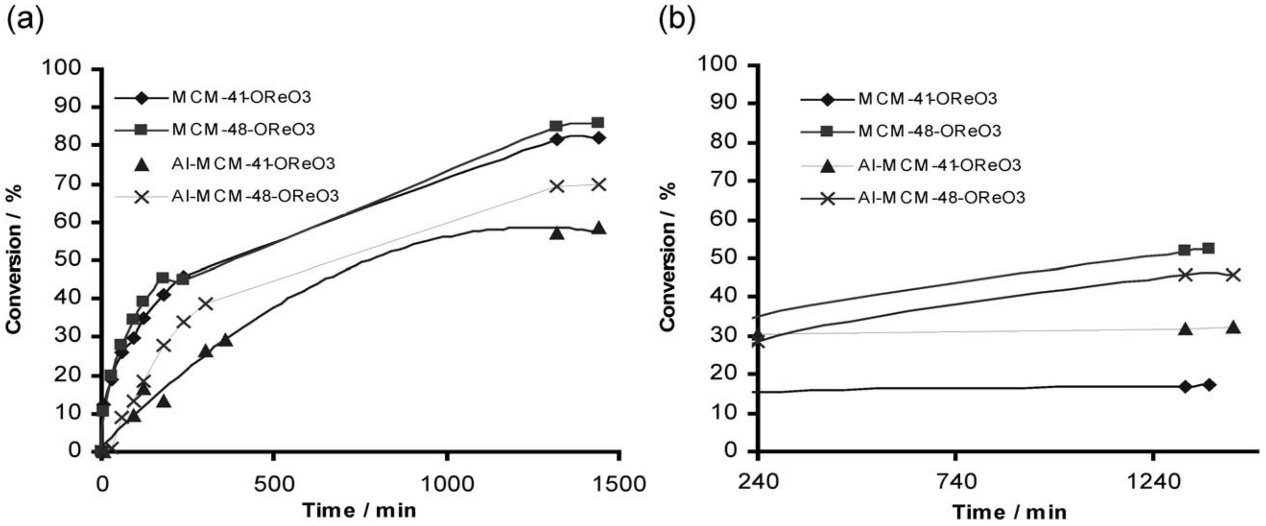


Figure 6. Epoxidation of cyclooctene over (a) various catalysts and (b) leaching test over various catalysts. [*Reaction conditions:* 7 mmol cyclooctene, 7 mmol hydrogen peroxide (23.8 ethyl acetate), 0.014 mmol catalyst and 1 g mesitylene (GC standard); reaction temperature is 323 K]. The TOF was determined after 90 min for each catalyst.

Table 2. Cyclooctene oxidation with peroxorhenium catalyst grafted on mesoporous materials.

Sample	Time				TOF [h^{-1}]
	4 h		24 h		
	Conversion [%]	Selectivity[a] [%]	Conversion [%]	Selectivity[a] [%]	
MCM-41-$OReO_3$	46	100	82	84	63
MCM-48-$OReO_3$	45	94	86	72	86
Al-MCM-41-$OReO_3$	20	79	59	73	37
Al-MCM-48-$OReO_3$	34	90	70	73	51

[a] The only detectable by-product by GC-MS is the diol.

Table 3. Recycling experiments with MCM-41-$OReO_3$ as a catalyst, and different oxidising agents.

Catalyst	Oxidising agent	Time			
		4 h		24 h	
		Conversion [%]	Selectivity [%]	Conversion [%]	Selectivity [%]
MCM-41-$OReO_3$	H_2O_2 in H_2O	0	0	0	0
	H_2O_2 in EtOAc	41	86	78	77
	Second run	20	84	39	78
	Third run	6	88	19	74
	TBHP[a]	13	87	19	86
	Second run	2	61	15	62
	Third run	3	57	10	40

[a] 5–6 M solution in decane, used as purchased from Sigma–Aldrich.

of cyclohexene the selectivity is reversed and the diol is obtained as main product.

In order to examine the extent of leaching, the catalytic reaction was interrupted after a conversion of 50% had been reached. The solution was filtered off and the filtrate examined for its remaining catalytic activity. This activity for the solution obtained from a catalyst on a MCM-41 type surface (hexagonal structure) is negligible (<2%) but the solutions originating from molecules immobilised on a MCM-48 surface (cubic structure) show relatively high activity (15%) originating clearly from a more pronounced leaching of the catalytically active species in the latter case. The three-dimensional pore structures of these surfaces render the active sites obviously more sensitive, resulting in a higher extent of leaching.

Recycling experiments have been carried out with MCM-41-$OReO_3$, as the most active and the most stable catalyst, under the conditions applied. After the reaction the catalyst was filtered, washed with dichloromethane, dried under vacuum and reused under the same reaction conditions as previously applied. The catalytic activity decreases somewhat during the first three runs, as can be seen in Table 3, the selectivity, however is largely maintained. Such an activity loss, however, is not necessarily accompanied by a concomitant leaching. The results presented above indicate that water, as a product of the epoxidation, partially coordinates to the catalytically active species on the surface, which results in activity loss. Only after some runs is a saturation level reached, leading to more stable results, with respect to the obtained epoxide yields, although requiring long reaction times to reach good yields.

In order to minimise the influence of water in these experiments the epoxidation reactions were attempted additionally with *tert*-butyl hydroperoxide (TBHP) as oxidising agent. TBHP lowers the reactivity of this catalytic system considerably, but it improves its recycling ability to a certain degree. The lower initial activity in the second and the third run of the recycling experiments might indicate that as the reaction proceeds, the adsorption of the organic compounds (*tert*-butyl alcohol, and TBHP) on the surface (hydrogen bonding on the remaining surface silanol groups) hinders the diffusion to and away from the catalytically active centres. As a result a notable decrease of the initial activity of the catalyst can be observed. Furthermore, the selectivity losses are more pronounced than in the presence of H_2O_2 being the oxidant.

Conclusions

Acylperrhenate was successfully grafted onto the surface of MCM-48, MCM-41, Al-MCM-48 and Al-MCM-41 molecular sieves. The experiments with trimethylsilanol as a model for the MCM surface show that a $-Si-O-Re$ moiety is formed on the surface and $-SiOReO_3$ is most likely the precursor of the catalytic active species. The grafted samples are active and highly selective catalysts for the epoxidation of cyclooctene with H_2O_2 as oxidising agent. Catalyst deactivation and leaching, however, are problems for most of the grafted catalysts. MCM-41 surfaces proved to be the best carrier materials, when applied together with the oxidant TBHP. The conversions, however, are low in this case, even after 24 h. The highest selectivities, however, are obtained with H_2O_2 as the oxidising agent. Under such conditions higher conversions are reached as well.

Experimental Section

Materials and General Methods

Mesoporous molecular sieves were synthesised following the procedures described earlier,[18,22] with molar gel compositions of 1.0 SiO_2 : 0.2 NaOH : 0.27 TMAOH : 0.27 CtABR : 60 H_2O : x Al_2O_3 ($x=0$ for MCM-41 and $x=0.005$ Al-MCM-41); and 5.0 SiO_2 : 0.85 CTABr : 0.15 Brij 30 : 2.46 NaOH : 400 H_2O : x Al_2O_3 (x=0 for MCM-48 and $x=0.025$ for Al-MCM-48). Acetonitrile was taken from an MBraun solvent purification system. All other solvents were used as received without further purification. All preparations were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. Acylperrhenate was synthesised as described in the literature,[20] and used as obtained.

The grafting experiments were carried out under an argon atmosphere using standard Schlenk techniques. The procedures began with pre-activation of the mesoporous materials at 473 K under vacuum (10^{-3} bar) for 4 h to remove the physisorbed water. After cooling the materials to room temperature 2 mmol of acylperrhenate were added, dissolved in 30 mL of acetonitrile. After 24 h at 298 K the grafting process was completed. The substrate was filtered off and washed several times with acetonitrile until the physisorbed complex was removed from the surface. After this the obtained material was dried carefully under oil pump vacuum at room temperature.

Trimethylsilyl perrhenate was synthesised from trimethylsilanol and acylperrhenate at room temperature in acetonitrile. Acylperrhenate was prepared as described above and trimethylsilanol was synthesised from trimethylchlorosilane applying the two-phase hydrolysis described earlier.[23] The reaction requires 24 h and the product crystallises at 253 K.

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). IR spectra were measured with a JASCO FT-IR-460Plus spectrometer using KBr pellets. NMR spectra were measured on a JEOL 400 spectrometer. Power XRD data were collected using a Philips X′pert diffractometer with Cu-Kα radiation. Nitrogen adsorption-desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2M5 microbalance and an Edwards Barocel pressure sensor. Prior to analysis, parent and grafted samples were degassed at 723 K overnight, resulting in a residual pressure of *ca.* 10–24 mbar. The specific surface area (SBET) was determined by the BET method. The total pore volume (VP) was estimated from the N_2 uptake at $p/p_0 = 0.95$, using a liquid nitrogen density of 0.8081 $g\,cm^{-3}$. The pore size distribution curves (PSD, the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron microscopy (TEM) data were recorded on a JEOL JEM2010 operating at 120 kV.

Epoxidation of Cyclooctene

The catalytic reactions were performed without moisture and oxygen precautions. The anhydrous hydrogen peroxide in ethyl acetate was prepared from 30% hydrogen peroxide under Dean–Stark conditions.

Cyclooctene (770 mg, 7 mmol), 23.8% hydrogen peroxide in ethyl acetate (236 mg, 7 mmol), mesitylene (1 g, 8.3 mmol, internal standard) and 7 mL of ethyl acetate as a solvent were first stirred at 353 K for one hour. After cooling to 323 K, the catalytic reactions were started by adding 0.014 mmol of catalyst (based on the rhenium content). The reactions were monitored with a Hewlett Packard 5890 Series II gas chromatograph equipped with a Supelco Alpha Dex^{TM} 120 column and using an FID detector. Samples were taken every 30 min in the first 2 h and every hour for the following 3 h. The reaction was terminated after 24 h.

Acknowledgements

A. S. is grateful to the Bayerische Forschungsstiftung for financial support. The authors also thank Prof. Dr. J. A. Lercher and his co-workers, Mr. Franz-Xaver Hecht, Dr. Marianne Hanzlik and Dr. G. Raudaschl-Sieber for experimental support. The Leonhard-Lorenz-Stiftung is also acknowledged for financial support and the Fonds der Chemischen Industrie for support of WAH and FEK.

References

[1] R. A. Sheldon, in: *Applied Homogeneous Catalysis with Organometallic Compounds*, (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, **2002**, Vol. 1, p 412.

[2] E. G. E. Hawkins, *J. Chem. Soc.,* **1950**, 2169.

[3] J. Kollar, (to Halcon), US Patent 3,350,422, **1967**; *US Patent* 3,351,635, **1967**.

[4] M. N. Sheng, J. G. Zajacek, (to ARCO), British Patent 1,136,923, **1968**.

[5] M. N. Sheng, J. G. Zajacek, *ACS Advan. Chem. Ser.* **1968**, *76*, 418.

[6] a) C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* **1983**,*48*, 3831; b) C. Venturello, R. D′Aloisio, *J. Org. Chem.* **1988**, *53*, 1553.

[7] a) D. De Vos, T. Bein, *J. Chem. Soc., Chem. Commun.* **1996**, 917; b) D. De Vos, T. Bein, *J. Organomet. Chem.* **1996**, *520*, 195; c) D. De Vos, J. L. Meinershagen, T. Bein, *Angew. Chem. Int. Ed.* **1996**, *35*, 2211.

[8] a) F. E. Kühn, A. M. Santos, W. A. Herrmann, *J. Chem. Soc., Dalton Trans.* **2005**, 2483; b) W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* **1997**, *30*, 169; c) C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.* **1997**, *97*, 3197; d) A. K. Yudin, K. B. Sharpless, *J. Am. Chem. Soc.* **1997**, *119*, 11536.

[9] a) W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem. Int. Ed.* **1991**, *30*, 1638; b) W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. Scherer, *J. Mol. Catal.* **1994**, *86*, 243; c) W. A. Herrmann, D. W. Marz, J. G. Kuchler, G. Weichselbaumer, R. W. Fischer, (to Hoechst AG), German Patent DE 3,902,357, **1989**; d) A. Al-Ajlouni, J. H. Espenson, *J. Am. Chem. Soc.* **1995**, *117*, 9234; e) F. E. Kühn, A. M. Santos, P. W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I. V. Yudahov, C. Di Valentin, N. Rösch, *Chem. Eur. J.* **1999**, *5*, 3603.

[10] a) W. A. Herrmann, M. Wang, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1641; b) W. A. Herrmann, P. W. Roesky, M. Wang, W. Scherer, *Organometallics* **1994**, *13*, 4531; c) A. M. Santos, C. C. Romão, F. E. Kühn, *J. Am. Chem. Soc.* **2003**, *125*, 2414; d) J. C. Mol, A. Andeini, *J. Mol. Catal.* **1988**, *46*, 151; e) J. C. Mol, *Catal. Today* **1999**, *51*, 289; f) A. M. Santos, F. M. Pedro, A. A. Yogalekar, Isabel S. Lucas. C. C. Romão, F. E. Kühn, *Chem. Eur. J.* **2004**, *10*, 6313; g) F. E. Kühn, A. M. Santos, *Mini-Rev. Org. Chem.* **2004**, *1*, 55.

[11] a) Ref.[10d] b) ref.[10e] c) P. Ferreira, W. M. Xue, E. Bencze, E. Herdtweck, F. E. Kühn, *Inorg. Chem.* **2001**, *40*, 5834.

[12] a) F. E. Kühn, A. Scherbaum, W. A. Herrmann, *J. Organomet. Chem.* **2004**, *689*, 4149; b) G. S. Owens, J. Arias, M. M. Abu-Omar, *Catal. Today* **2000**, *55*, 317.

[13] a) D. Mandelli, M. C. A. van Vliet, U. Arnold, R. A. Sheldon, U. Schuchardt, *J. Mol. Catal. A.* **2001**, *168*, 165; b) T. Bein, C. Huber, K. Moller, C. G. Wu, L. Xu, *Chem. Matter.* **1997**, *9*, 2252; c) W. Adam, C. R. Saha-Möller, O. Weichold, *J. Org. Chem.* **2000**, *65*, 2897; d) N. A. Caplan, F. E. Hancock, P. C. Bulman Page, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2004**, *43*, 1685.

[14] a) R. Saladino, V. Neri, A. R. Pelliccia, E. Mincione, *Tetrahedron* **2003**, *59*, 7403; b) R. Bernini, E. Mincione, M. Cortese, R. Saladino, G. Gualandi, M. C. Belfiore, *Tetrahedron Lett.* **2003**, *44*, 4823; c) G. Bianchini, M. Crucianelli, F. De Angelis, V. Neri, R. Saladino; *Tetrahedron Lett.* **2004**, *45*, 2351; **2005**; 46, 2427; d) L. M. R. Gonzàles, A. L. Villa de P. , C. Montes de C. , G. Geldard, *Reactive & Functional Polymers* **2005**, *65*, 169.

[15] a) M. Li, J. H. Espenson, *J. Mol. Catal. A: Chem.* **2004**, *208*, 123; b) R. Bernini, A. Coratti, G. Fabrizi, A. Goggiamani; *Tetrahedron Lett.* **2003**, *44*, 8991; c) R. Bernini, A. Coratti, G. Provenzano, G. Fabrizi, D. Tofani, *Tetrahedron* **2005**, *61*, 1821; d) G. S. Owen, M. M. Abu-Omar, *J. Chem. Soc., Chem. Commun.* **2000**, 1165.

[16] A. Sakthivel, G. Raudaschl-Sieber, F. E. Kühn, *Dalton Trans.* **2006**, 468–472.

[17] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.

[18] a) A. Sakthivel, P. Selvam, *J. Catal.* **2002**, *211,* 134; b) A. Sakthivel, S. E. Dapurkar, P. Selvam, *Appl. Catal. A* **2003**, *246*, 283; c) A. Sakthivel, P. Selvam, *Catal. Lett.* **2002**, *84*, 37.

[19] P. Edwards, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1984**, 2695.

[20] a) W. A. Herrmann, W. R. Thiel, F. E. Kühn, R. W. Fischer, M. Kleine, E. Herdtweck, W. Scherer, *Inorg. Chem.* **1993**, *32*, 5188; b) W. A. Herrmann, P. W. Roesky, F. E. Kühn, W. Scherer, M. Kleine, *Angew. Chem. Int. Ed.* **1993**, *32*, 1714; c) W. A. Herrmann, P. W. Roesky, F. E. Kühn, M. Elison, G. Artus, W. Scherer, C. C. Romão, A. Lopes, J.-M. Basset, *Inorg. Chem.* **1995**, *34*, 4701.

[21] T. B. Towne, F. E. McDonald, *J. Am. Chem. Soc.* **1997**, *119*, 6022.

[22] a) A. Corma, H. Garcia, *Chem. Rev.* **2002**, *102*, 3837; b) L. Cunha-Silva, I. S. Gonçalves, M. Pillinger, W. M. Xue, J. Rocha, J. J. C. Teixeira-Dias, F. E. Kühn, *J.Organomet. Chem.* **2002**, *656*, 281; c) A. Sakthivel, J. Zhao, M. Hanzlik, F. Kühn, *Dalton Trans.* **2004**, 3338; d) M. J. Jia, A. Seifert, M. Berger, H. Giegengack, S. Schulze, W. R. Thiel, *Chem. Mater.* **2004**, *16*, 877; e) A. Sakthivel, J. Zhao, M. Hanzlik, A. S. T. Chiang, W. A. Herrmann, F. E. Kühn, *Adv. Synth. Catal.* **2005**, *347*, 473; f) A. Sakthivel, J. Zhao, M. Hanzlik, A. S. T. Chiang, G. Raudaschl-Sieber, F. E. Kühn, *App. Catal. A: Gen.* **2005**, *281*, 267.

[23] a) J. A. Cella, J. C. Carpenter, *J. Organomet. Chem.* **1994**, *480*, 23; b) B. Marciniec, P. Blazejewska-Chadyniak, M. Kubicki, *Can. J. Chem.* **2003**, *81*, 1292; c) E. Popowski, N. Holst, H. Kelling, *Z. anorg. allg. Chem.* **1982**, *494*, 166.

[24] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscow, R. A. Pierotti, T. Rouquerol, T. Siemienewska, *Pure Appl. Chem.* **1985**, *57*, 603.

[25] a) D. C. Calabro, E. W. Valyocsik, F. X. Ryan, *Mesoporous Materials* **1996**, 7, 243; b) S. M. Holmes, V. L. Zholobenko, A. Thursfield, R. J. Plaisted, C. S. Cundy, J. Dwyer, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2025.

[26] M. Schmidt, H. Schmidbaur, *Inorg. Synth.* **1967**, *9*, 149.

[27] A. Omar Bouh, J. H. Espenson, *J. Mol. Catal. A: Chem.* **2003**, *200*, 43.

[28] G. M. Sheldrick, W. S. Sheldrick, *J. Chem. Soc. (A)* **1969**, 2160.