ACADEMIC PRESS

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Catalysis 217 (2003) 264–274

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Chiral catalysts confined in porous hosts 1. Synthesis

Heidi M. Hultman,[a,b] Martine de Lang,[a,b] Mathias Nowotny,[a] Isabel W.C.E. Arends,[b] Ulf Hanefeld,[a] Roger A. Sheldon,[b] and Thomas Maschmeyer [a,*]

[a] *Applied Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands*
[b] *Biocatalysis and Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands*

Received 11 July 2002; revised 8 November 2002; accepted 12 November 2002

Abstract

Chiral dirhodium carboxamide catalysts were immobilised inside the pores of MCM-41 and on a low-surface-area silica (Aerosil 200). The catalysts were immobilised via ligand exchange of one chiral ligand with a carboxylate tether group. In part 2 the catalytic activity of these catalysts is reported.

Keywords: Dirhodium catalyst; Immobilisation; MCM-41; Silica

1. Introduction

Currently, homogeneous metal complexes with chiral ligands are the most widely used and versatile enantioselective catalysts [1,2]. From an industrial point of view, however, heterogeneous catalysts are often of greater interest than homogeneous catalysts. An ideal catalyst combines the advantages of both types of catalysts. The first industrially successful types of heterogenised catalysts were the ion exchangers commercialised in the late forties and since then widely applied in acid–base catalysis. In the sixties the first examples of immobilised enzymes were reported and in the seventies heterogenised transition metal complexes were developed and increasingly studied [3].

Various attempts towards the immobilisation of organometallic complexes have been made previously, such as attachment to supporting materials by chemisorption, immobilisation by steric hindrance in zeolitic micropores (ship-in-a-bottle concept), or supported liquid-phase catalysts [4]. In recent reviews the potential of heterogeneous chiral catalysts has been evaluated [5–8].

The most frequently used inorganic support is silica. This material offers a wide variety of pore sizes, surfaces, and shapes of particles and it is also relatively cheap. A drawback is the broad pore size distribution. Even the so-called wide-pore silica contains substantial numbers of micropores, which form the main part of the specific surface area. An alternative carrier material is siliceous MCM-41 [9,10]. This is a mesoporous silica or aluminosilicate material. It has large channels ranging from 25 to 100 Å (depending on the synthesis method) which are ordered in a hexagonal array. It can be prepared with an almost uniform pore size [11]. Because of its well-defined and periodic mesopores, MCM-41 offers new opportunities for the encapsulation of large catalyst species. It is also suitable for the catalytic conversion of much larger substrates than those that can be converted by common zeolites [12].

Thus, by immobilising homogeneous chiral catalysts on the inner surfaces of porous solids, considerations such as separability, reuse, and selectivity may be addressed simultaneously [7]. In this study chiral dirhodium catalysts were immobilised with the aim of influencing their selectivity. It might be expected that the spatial constraints induced by a carrier, and especially by the pores of MCM-41, will increase the influence of the chiral ligands significantly. Earlier research showed that enantioselective reduction catalysed by a palladium complex immobilised inside the pores of MCM-41 can give a large increase in *ee* compared to the homogeneous palladium complex (*ee*'s increased from 43 to 96% [13] and from 6 to 17% [14]).

* Corresponding author.
E-mail address: t.maschmeyer@tnw.tudelft.nl (T. Maschmeyer).

0021-9517/03/$ – see front matter
doi:10.1016/S0021-9517(02)00154-9

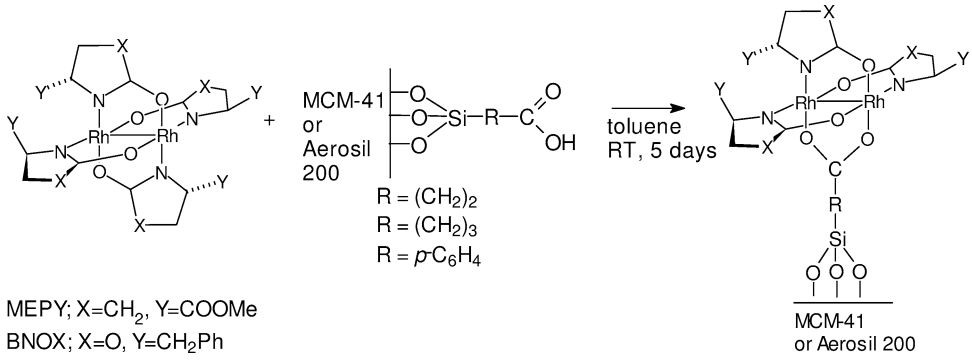

Fig. 1. Immobilisation of the dirhodium complexes on the carriers.

In order to immobilise the homogeneous catalyst on a surface, an organic linker group is needed. Organic functionalisation of a low-surface-area silica (Aerosil 200) or the internal mesopores of MCM-41 can be achieved, either by covalently grafting various organic species onto the surface, or (for MCM-41) by incorporating functionalities directly during the preparation [15]. In this study, covalent grafting was used to immobilise the dirhodium catalysts on both supports. Immobilisation proceeded via ligand exchange of surface-anchored carboxylic acid groups with one or possibly two chiral ligands per homogeneous chiral catalyst (Fig. 1). The number of organic linker groups limits the density of dirhodium complexes on the solid surface. A maximum of 10% of the surface silanol groups were derivatised with the tether group in order to minimise unwanted complex–complex interactions.

Upon immobilisation a steric constraint is created which might be expected to compensate for the loss of some of the chirality around the metal centers. In the case of the catalysts immobilised inside MCM-41, not only the constraint of the surface, but also of the pore itself has to be considered, potentially resulting in an even larger constraint.

Another factor that might influence the selectivity of the immobilised catalysts is the way in which they are attached to the carrier. Indeed, it has been shown that the length of the tether group does have an influence on the activity of the immobilised catalysts [3]. To investigate whether there is a significant difference between flexible linkers or more rigid ones, three different nonchiral carboxylate tether groups were used, comprising a $–(CH_2)_2COOH$, a $–(CH_2)_3COOH$, and a $–p\text{-}C_6H_4COOH$ linker (Fig. 2). The $–(CH_2)_2COOH$ and $–(CH_2)_3COOH$ linkers are flexible, allowing a catalyst–surface interaction. Protecting the surface silanol groups with dimethoxydimethylsilane or dichlorodimethylsilane changed the polarity of the carrier surface and narrowed the pores. Different types of surfaces (e.g., with protected or unprotected surface silanol groups) could have an influence on the performance of the catalysts (with the flexible linkers). With the $–p\text{-}C_6H_4COOH$ linker these types of interactions should be reduced significantly, because in that case the catalyst is relatively far removed from the carrier surface.

In this study the binuclear chiral $Rh_2(MEPY)_4$ and $Rh_2(BNOX)_4$ complexes, developed by Doyle et al. [16], were used as model catalysts. $Rh_2(MEPY)_4$ is a very selective catalyst in intramolecular cyclopropanation reactions. Both catalysts are less selective in intermolecular cyclopropanations using alkenes and diazoacetates. We choose this more difficult substrate/catalyst combination to prove the concept of selectivity improvement by confinement. By immobilising the catalyst inside the pores of the carrier via a tether of variable length, we intend to influence the catalyst (Fig. 3). In the homogeneous reaction only the chiral directing ligands and the catalytic centre have an influence on the transition state. In the heterogeneous reaction there is an additional parameter: The spatial confinement induced by the pore walls. It is expected to enhance the selectivity. Indeed, with the confinement we intend to simulate intramolecular conditions while performing an intermolecular reaction. A positive effect of the immobilisation is anticipated because the homogeneous catalysts show high selectivity in intramolecular reactions, the situation we mimic. This is

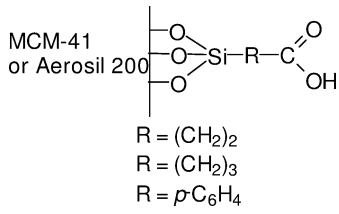

Fig. 2. Tether groups.

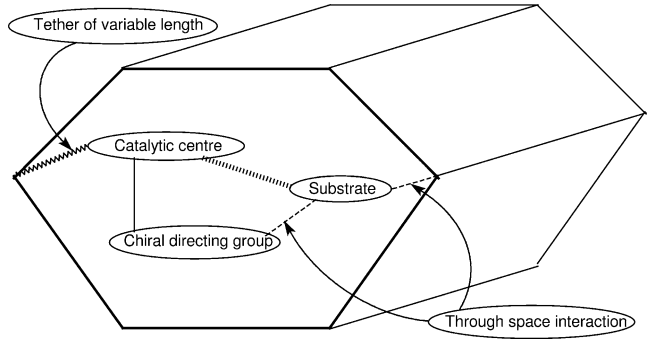

Fig. 3. Influence of the pore wall on the catalyst.

similar to the situation in enzyme catalysis, where reagents are brought close together so that they react in an intramolecular fashion while the noncatalytic reaction is intermolecular. The enzymatic selectivities are, therefore, much higher than in intermolecular reactions. In our case, the rhodium catalysts are between approximately 13 and 19 Å in size. The pores of the MCM-41 carrier can be prepared with different pore sizes, so we can create optimum conditions to test the influence of the confinement.

A second test reaction has been chosen on the basis that $Rh_2(MEPY)_4$ and $Rh_2(BNOX)_4$ are usually not used as catalysts for carbene insertions into the Si–H bond of organosilanes, because they are considered to be not very selective. With the immobilised catalysts an improvement in selectivity is anticipated.

2. Experimental section

All reactions and manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk-type techniques. Dry solvents were purchased from Aldrich and used without further purification. Silica sources for the MCM-41 synthesis were Cab-O-Sil M5 (fumed silica, Fluka) and a solution of sodium silicate (14% NaOH, 27% SiO_2, Aldrich). Templates for MCM-41 synthesis (cetyl trimethylammoniumbromide and tetramethylammoniumhydroxide) were obtained from Aldrich. All other reagents were purchased from Aldrich, Acros, or Baker and used without further purification. NMR spectra were obtained on a Varian Inova 300 MHz or a Varian VXR 400s spectrometer. FAB-MS analysis was performed using a VG 70 SE mass spectrometer and an 8-kV FAB gun using argon gas. Rhodium elemental analysis was performed using ICP-OES on a Perkin–Elmer Optima 4300DV, after the solid samples were dissolved in 1% v/v HF and 1.3% v/v H_2SO_4 in water. Silicon elemental analysis was performed using flame AAS on a Perkin–Elmer 2380(A), after the solid samples were dissolved in 1% v/v HF and 1.3% v/v H_2SO_4 in water. Loading of the aryl-COOH tether was determined via the mass balance. Loading of the alkyl-COOH tether was determined by C, H, N elemental analysis of the corresponding CN tether. Full conversion from CN to COOH was determined by IR analysis on a Perkin–Elmer Spectrum One FT-IR spectrometer in KBr from 4000–450 cm^{-1}. N_2 desorption analysis was performed at 77 K on a Quantachrome Autosorb-6B after the samples were dried at 200 °C in vacuo. Mesopore characteristics were calculated using the BJA model. X-ray powder diffraction (XRD) patterns were recorded using CuK_2 radiation on a Philips PW 1840 diffractometer equipped with a graphite monochromator. The samples were scanned in the range of 0.105° to 50.005° 2θ, with steps of 0.01°. All yields are isolated yields. The number of moles of silanol groups on the surface of Aerosil 200 and MCM-41 was calculated according to the literature [17] (gram solid × surface area (m^2/g) × 7.8×10^{-6} mol OH/m^2).

2.1. MCM-41 carrier preparation

2.1.1. MCM-41 (*I*)

A solution of Cab-O-Sil M5 silica (4.18 g) and tetramethylammoniumhydroxide (12.70 g of 25% wt solution in water) in water (26.15 g) was added with stirring to a solution of sodium silicate solution (20.21 g) in water (94.77 g). To this solution 14.81 g Cab-O-Sil M5 silica was added under stirring. The resulting solution was added to the template solution (cetyl trimethylammonium bromide (47.69 g) in water (319.32 g); heating was required to dissolve the template in water). After stirring for 1 h the polypropylene flask containing the suspension was sealed and placed in an oven at 100 °C for 2.5 days. The resulting suspension was filtered and the residue was washed extensively with water. After drying at 70 °C in vacuo for two days, the solid (**I**) was calcined in air (1 °C/min to 550 °C, 10 h at 550 °C, 1 °C/min to room temperature). Yield 21.12 g. ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −101.1 (Q3 Si), −110 (Q4 Si). XRD: $2\theta = 2.475°$, $d_{100} = 35.68$ Å.

2.1.2. MCM-41-$(CH_2)_3$CN (protected)(*II*) [18]

MCM-41 (**I**, 4.077 g, 0.032 mol OH) was activated at 200 °C in vacuo for 2 h. The outer surface silanol groups (10% of the total amount of silanol groups) were protected by reaction with dimethoxydimethylsilane (0.197 g, 1.63 mmol, 10.2% of the total amount of surface silanol groups) in refluxing toluene. After 3 h 4-(trichlorosilyl)butyronitrile (0.210 g, 1.04 mmol, 9.7% of the total amount of surface silanol groups) was added and refluxing was continued overnight. The remaining surface silanol groups were then protected with dimethoxydimethylsilane (2.304 g, 0.0192 mol, 119% of the total amount of surface silanol groups) and the mixture was refluxed for a further 3 h. The product was filtered off, washed with water and ethanol, and dried overnight at 70 °C in vacuo. Yield: 4.16 g. C, H, N analysis: C: 5.16, H: 1.28, N: 0.20, 0.143 mmol CN/g. XRD: $2\theta = 2.475°$, $d_{100} = 35.68$ Å.

2.1.3. MCM-41-$(CH_2)_3$COOH (protected) (*III*) [18]

The surface-protected MCM-41-$(CH_2)_3$CN (**II**, 2.117 g, 0.303 mmol CN) was hydrolysed by heating it at 160 °C for 3 h in 50% aqueous sulphuric acid (70 ml). The mixture was then stirred overnight at room temperature, filtered, and washed with water until the filtrate was neutral. The product (**III**) was dried overnight at 80 °C in vacuo. Yield: 2.02 g. ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −110.7 (Q4 Si), −15.7 (SiMe$_2$). ^{13}C CP MAS NMR (400 MHz, δ (ppm)): −1.4 ($(CH_3)_2$–Si), 12.2 (Si–CH_2), 18.4 (Si–CH_2–CH_2), 36.4 (Si–CH_2–CH_2–CH_2), 75.4 (Si–OCH_3), 105.2, 177.0 (C=O). XRD: $2\theta = 2.465°$, $d_{100} = 35.83$ Å.

*2.1.4. [4-(Dimethoxymethyl)phenyl]trimethoxysilane (**IV**)*

A mixture of 15 g (65 mmol) 4-bromobenzaldehyde dimethyl acetal, 20 ml (135 mmol) tetramethylorthosilicate, and 1.7 g (70 mmol) Mg turnings in 100 ml THF was heated under reflux for 9 h. Filtration and solvent removal in vacuo left a yellow oil that was subjected to vacuum distillation. Collection of the fraction boiling at 95–100 °C (10^{-2} mm) afforded (**IV**) as colourless liquid. Yield 9.27 g (52%). ^{1}H NMR (300 MHz, $CDCl_3$ δ (ppm)): 7.66 (d, $^3J = 8.24$ Hz, 2H, arom.-$H_{3,5}$), 7.49 (d, $^3J = 8.24$ Hz, 2H, arom.-$H_{2,6}$), 5.39 (s, 1H, CH(OCH$_3$)$_2$), 3.62 (s, 9H, Si(OCH_3)$_3$), 3.33 (s, 6H, CH(OCH_3)$_2$). ^{13}C NMR (300 MHz, $CDCl_3$ δ (ppm)): 140.50 (arom.-C_4), 134.76 (arom.-CH$_{2,6}$), 129.71 (arom.-C_1), 126.33 (arom.-CH$_{3,5}$), 103.02 (CH(OCH$_3$)$_2$), 52.77 (CH(OCH$_3$)$_2$), 50.86 (Si(OCH$_3$)$_3$). Anal. calcd. (found) for $C_{12}H_{20}SiO_5$: C, 52.92 (52.78); H, 7.40 (7.26).

*2.1.5. MCM-41-p-$C_6H_4CH(OCH_3)_2$ (only outside protected) (**V**)*

MCM-41 (unit cell size $a = 4.43$ Å, channel diameter ca. 30 Å, surface area $\geqslant 1100$ m^2 g^{-1}) 10 g (0.086 mol OH) was preactivated by heating at 100 °C in vacuo for 1 h. The outer surface silanol groups (10% of the total amount of silanol groups) were protected by reaction with dimethoxydimethylsilane (0.343 g, 2.86 mmol, 10% of the total amount of surface silanol groups) in refluxing toluene (50 ml). After 3 h 2.5 g (9.2 mmol, 11% of the total amount of silanol groups) [4-(dimethoxymethyl)-phenyl]trimethoxysilane (**IV**) was added in one portion and the mixture was heated to reflux under stirring for 24 h. The resulting solid (**V**) was separated by filtration, washed with CH_2Cl_2 and ether, and dried in vacuo. Yield 12.01 g. ^{13}C CP-MAS NMR (400 MHz, δ (ppm)): 141.07 (arom.-C_4), 133.78 (arom.-CH$_{2,6}$), 129.99 (arom.-C_1), 125.91 (arom.-CH$_{3,5}$), 102.44 (CH(OCH$_3$)$_2$), 49.67 (OCH$_3$). XRD $2\theta = 2.35°$, $d_{100} = 37.58$ Å.

*2.1.6. MCM-41-p-C_6H_4CHO (only outside protected) (**VI**)*

A slurry of 10 g MCM-41-p-$C_6H_4CH(OCH_3)_2$ (**V**) in a mixture of 40 ml $CHCl_3$ and 20 ml 5% aqueous CF_3COOH was vigorously stirred for 12 h at 20 °C. The title compound was collected by filtration, washed with 20-ml portions of water until the filtrate had pH 7, and subsequently washed with ethanol and ether, before being dried in vacuo at 70 °C for 10 h. Yield 9.45 g. IR: ν_{CO} 1713 cm^{-1}. ^{13}C CP-MAS NMR (400 MHz, δ (ppm)): 193.8 (CHO), 141.01 (arom.-C_1), 138.88 (arom.-C_4), 133.78 (arom.-CH$_{2,6}$), 126.06 (arom.-CH$_{3,5}$). XRD $2\theta = 2.35°$, $d_{100} = 37.56$ Å.

*2.1.7. MCM-41-p-C_6H_4COOH (only outside protected) (**VII**)*

MCM-41-p-C_6H_4CHO (**VI**), 5 g, was added with stirring to 50 ml of water containing 10 ml peracetic acid (32 wt% solution in acetic acid). Stirring was continued for 24 h at 20 °C; then the solid was isolated by filtration, washed with copious amounts of water to neutrality, then washed with ethanol and ether, and finally dried in vacuo at 70 °C for 12 h. Yield 4.83 g. IR: ν_{CO} 1714 cm^{-1}. ^{13}C CP-MAS NMR (400 MHz, δ (ppm)): 189.90 (COOH), 138.59 (arom.-C_1), 137.60 (arom.-C_4), 134.07 (arom.-CH$_{2,6}$), 128.24 (arom.-CH$_{3,5}$). ^{29}Si CP-MAS NMR (400 MHz, δ (ppm)): −110.8 (Q4 *Si*), −100.7 (Q3 *Si*), −68.8 (*Si*–OCH$_3$). XRD $2\theta = 2.39°$, $d_{100} = 36.86$ Å.

*2.1.8. MCM-41-$(CH_2)_2$CN (protected) (**VIII**)*

MCM-41 (**I**), 5.225 g (0.041 mol OH), was activated for 3 h at 200 °C in vacuo. Toluene (50 ml) and 0.165 g (1.28 mmol, 6% of the total amount of silanol groups) Cl_2SiMe_2 were added. This mixture was refluxed for 3 h. Then 0.269 g (1.24 mmol, 9% of the total amount of silanol groups) 3-(triethoxysilyl)propionitrile were added and the mixture was refluxed for another 12 h. Then 1.436 g (0.011 mol, 54% of the total amount of silanol groups) Cl_2SiMe_2 was added and the mixture was heated for another 3 h under reflux. The product was filtered, washed with water and ethanol, and dried overnight in vacuo at 100 °C. Yield: 2.499 g. C, H, N analysis: C: 2.49, H: 3.78, N: 1.14, 0.814 mmol CN/g.

*2.1.9. MCM-41-$(CH_2)_2$COOH (protected) (**IX**)*

To surface-protected MCM-41-$(CH_2)_2$CN (**VIII**, 2.056 g, 1.67 mmol CN), 30 ml of 50% aqueous sulphuric acid was added. This mixture was heated at 160 °C for 1 h. The product was filtered off and washed with water until the filtrate had pH 7. The product was dried overnight in vacuo at 80 °C. Yield: 1.614 g. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): 0.2 (Si–(CH$_3$)$_2$), 30.7 (CH$_2$–Si), 53.6 (CH$_2C$H$_2$CO). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −111.2 (Q4 *Si*).

*2.1.10. MCM-41-$(CH_2)_2$CN (only outer surface protected) (**X**)*

MCM-41 (**I**), 2.434 g (0.019 mol OH), was activated by heating for 3 h at 200 °C in vacuo. Toluene (30 ml) and 0.085 g (6.59×10^{-4} mol, 7% of the total amount of silanol groups) Cl_2SiMe_2 were added and this suspension was heated for 3 h under reflux. Then 0.163 g (7.50×10^{-4} mol, 12% of the total amount of silanol groups) 3-(triethoxysilyl)propionitrile were added and the mixture was refluxed for another 12 h. The product was filtered off and was washed with water and ethanol and dried overnight at 80 °C in vacuo. Yield: 0.868 g. C, H, N analysis: C: 19.05, H: 4.48, N: 1.70, 1.22 mmol CN/g.

*2.1.11. MCM-41-$(CH_2)_2$COOH (only outer surface protected) (**XI**)*

To MCM-41-$(CH_2)_2$CN (**X**, only outer surface silanol groups protected) (0.742 g, 9.05×10^{-4} mol CN), 20 ml of 50% aqueous sulphuric acid were added. This mixture was heated at 160 °C for 1 h. The product was filtered off and

washed with water until the filtrate had pH 7. The product was dried overnight in vacuo at 80 °C. Yield: 0.480 g. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): 30.3 (CH$_2$–Si), 53.9 (CH$_2$CH_2CO). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −111.3 (Q4 *Si*), −100 (Q3 Si). XRD: $2\theta = 2.165°$, $d_{100} =$ 40.79 Å.

2.2. Immobilisation via ligand exchange

2.2.1. MCM-41-(CH$_2$)$_3$CN-Rh$_2$(4*R*-BNOX)$_3$ (protected) (**XII**)

MCM-41-(CH$_2$)$_3$CN (protected, **II**) (0.894 g, 1.28×10^{-4} mol CN) and Rh$_2$(4*R*-BNOX)$_4$ (0.207 g, 2.27×10^{-4} mol) were stirred at room temperature for two days in toluene (16 ml). The resulting solid was Soxhlet extracted with dichloromethane (60 ml). The resulting pale blue solid was dried in vacuo. Rhodium content: 0.025 mmol/g.

2.2.2. MCM-41-(CH$_2$)$_3$COO-Rh$_2$(4*R*-BNOX)$_3$ (protected) (**XIII**)

MCM-41-(CH$_2$)$_3$COOH (protected, **III**) (0.886 g, 1.27×10^{-4} mol COOH) and Rh$_2$(4*R*-BNOX)$_4$ (0.205 g, 2.25×10^{-4} mol) were stirred at room temperature for 2 days in dichloromethane (16 ml). The resulting solid was Soxhlet extracted with dichloromethane (60 ml). The resulting pale green solid was dried in vacuo. Rhodium content: 0.045 mmol/g.

2.2.3. MCM-41-*p*-C$_6$H$_4$COO-Rh$_2$(5*S*-MEPY)$_3$ (only outside protected) (**XIV**)

MCM-41-*p*-C$_6$H$_4$-COOH (only outside protected, **VII**), 0.176 g (1.41×10^{-4} mol COOH) and Rh$_2$(5*S*-MEPY)$_4$ (0.129 g, 1.41×10^{-4} mol) were stirred for five days in toluene (10 ml) at room temperature. The solution was decanted and the solid residue was Soxhlet extracted with dichloromethane yielding a pale pink product. Yield: 0.15 g. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): 24.9 (CH$_2$CCOOCH$_3$), 30.7 (CH$_2$CORh), 50.1 (CH–COOCH$_3$), 67.3 (COOCH$_3$), 127.9 (Ar), 134.1 (Ar), 189.2 (C=O). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −109.6 (Q4 *Si*), −102.0 (Q3 *Si*), −68.0 (*Si*–CH$_3$).

2.3. Immobilisation via adsorption

2.3.1. Fully surface protected MCM-41 (**XV**)

MCM-41 (**I**, 1.294 g, 0.010 mol OH) was heated at 200 °C in vacuo for 2 h. Then 15 ml toluene and 1.4937 g (0.0124 mol) dimethoxydimethylsilane were added. After refluxing overnight, the mixture was filtered and the residue was washed with water and ethanol and dried overnight in vacuo (80 °C). Yield: 1.27 g. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): −2.7 (Si–(CH$_3$)$_2$), 48.9 (Si–(OCH$_3$)$_2$). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −109.7 (Q4 *Si*), −8.9 (*Si*–(OCH$_3$)$_2$). XRD: $2\theta = 2.435°$, $d_{100} = 36.27$ Å.

2.3.2. MCM-41-OH-Rh$_2$(4*R*-BNOX)$_4$ (not protected) (**XVI**)

To MCM-41 (**I**, 0.991 g, 7.81 mmol OH), toluene (10 ml) and 0.088 g (9.65×10^{-5} mol) Rh$_2$(4*R*-BNOX)$_4$ were added. After stirring at room temperature for 5 days, the solid was Soxhlet extracted with dichloromethane until the washings were colourless. The blue solid was dried in vacuo to yield 0.901 g immobilised complex. Rhodium content of (**XVI**): 0.053 mmol/g.

2.3.3. MCM-41-SiMe$_2$-Rh$_2$(4*R*-BNOX)$_4$ (surface fully protected) (**XVII**)

To fully surface-protected MCM-41 (**XV**, 0.991 g), toluene (10 ml) and 0.087 g (9.58×10^{-5} mol) Rh$_2$(4*R*-BNOX)$_4$ were added. After stirring for 5 days, the solid was Soxhlet extracted with dichloromethane until the washings were colourless. The solid was dried in vacuo to yield 0.842 g white solid. The washings were dried and gave a purple oily residue. Rhodium content of (**XVII**): below detection limit (0.00098 mmol Rh/g).

2.4. NMR experiments

2.4.1. Rh$_2$(5*S*-MEPY)$_3$(OAc) (**XVIII**)

Rh$_2$(5*S*-MEPY)$_4$ (20 mg, 2.58×10^{-5} mol) was dissolved in 0.5 ml CDCl$_3$. To this solution 7.2 µl (2.64×10^{-5} mol) acetic acid solution in CDCl$_3$ (220 mg acetic acid in 1 ml CDCl$_3$) was added. The reaction was performed at room temperature and was monitored by ^{1}H NMR; for results see Fig. 8.

2.4.2. Rh$_2$(5*S*-MEPY)$_3$(^{17}OAc) (**XIX**)

^{17}O-labelled acetic acid was prepared from a solution of 0.213 g (2.08×10^{-3} mol) acetic anhydride and 34 µl (1.79×10^{-3} mol) H$_2{}^{17}$O in 1 ml CDCl$_3$. Rh$_2$(5*S*-MEPY)$_4$ (0.050 g, 6.43×10^{-5} mol) was dissolved in 0.5 ml CDCl$_3$. To this solution 16 µl of the ^{17}O-labelled acetic acid solution in CDCl$_3$ was added (2.86×10^{-5} mol acetic acid and 2.86×10^{-5} mol ^{17}O-labelled acetic acid). The reaction was performed at 40 °C and was monitored by ^{1}H NMR and ^{17}O NMR. FAB-MS of the final product: m/z (%) 774 (42%, Rh$_2$(5*S*-MEPY)$_4$), 691 (14%, Rh$_2$(5*S*-MEPY)$_3$H^{17}OAc), 632 (48%, Rh$_2$(5*S*-MEPY)$_3$), 490 (27%, Rh$_2$(5*S*-MEPY)$_2$). The ^{1}H spectra gave results similar to the experiment described above. In the ^{17}O NMR spectra a shift of the peak of acetic acid was visible, indicating that first there was coordination to the axial position, followed by bidentate coordination. This proceeded on the same timescale as seen in the ^{1}H spectrum.

2.5. Aerosil 200 carrier preparation

2.5.1. SiO$_2$–(CH$_2$)$_2$CN (protected) (**XX**)

Aerosil 200 (surface area: 250 m^2/g) (3.769 g, 7.35 mmol OH) was activated at 200 °C in vacuo for 2 h. Toluene (35 ml) and 3-(triethoxysilyl)propionitrile (0.070 g,

3.22×10^{-4} mol, 13% of the total amount of surface silanol groups) were added and the mixture was refluxed overnight. The remaining surface silanol groups were protected with dimethoxydimethylsilane (0.709 g, 5.90 mmol, 160% of the total amount of silanol groups) and refluxing for 3 h more. The product was filtered off, washed with water and ethanol, and dried overnight at 100 °C in vacuo. Yield: 3.676 g. C, H, N analysis: C: 1.23, H: 0.40, N: 0.06, 0.043 mmol CN/g.

*2.5.2. SiO_2–$(CH_2)_2$COOH (protected) (**XXI**)*

SiO_2–$(CH_2)_2$CN (protected, **XX**) (3.250 g, 1.40×10^{-4} mol CN) was hydrolysed by heating it at 160 °C for 1 h in 50% sulphuric acid in water (32 ml). The product was then filtered off and washed with water until the filtrate was neutral. The product was dried overnight at 80 °C in vacuo. Yield: 3.208 g. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): −2.3 (Si–(CH$_3$)$_2$), 26.6 (CH$_2$, broad), 180, (C=O). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −108.5 (Q4 *Si*), −100.9 (Q3 *Si*), −17.0 (*Si*–(CH$_3$)$_2$).

*2.5.3. SiO_2–$(CH_2)_2$CN (not protected) (**XXII**)*

Aerosil 200 (surface area: 250 m^2/g) (2.501 g, 4.88×10^{-3} mol OH), was activated at 200 °C in vacuo for 2 h. Toluene (35 ml) and 3-(triethoxysilyl)propionitrile (0.058 g, 2.67×10^{-4} mol, 16% of the total amount of silanol groups) were added and the mixture was refluxed overnight. The product was filtered off, washed with water and ethanol, and dried overnight at 100 °C in vacuo. Yield: 1.784 g. C, H, N analysis: C: 0.76, H: 0.49, N: 0.06, 0.043 mmol CN/g.

*2.5.4. SiO_2–$(CH_2)_2$COOH (not protected) (**XXIII**)*

SiO_2–$(CH_2)_2$CN (not protected, **XXII**) (1.625 g, 6.99×10^{-5} mol CN) was hydrolysed by heating it at 160 °C for 1 h in 50% sulphuric acid in water (32 ml). The product was then filtered off and washed with water until the filtrate was neutral. The product was dried overnight at 80 °C in vacuo. Yield: 1.319 g. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): 30.4 (CH$_2$, broad). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −110 (Q4 *Si*), −100 (Q3 *Si*).

*2.5.5. SiO_2–$(CH_2)_3$CN (not protected) (**XXIV**)*

A mixture of 14.2 g vacuum-dried silica gel 60 (Merck, 530 m^2/g, 58.7 mmol SiOH) and 4.6 g (19.9 mmol, 102% of the total amount of silanol groups) 4-(triethoxysilyl)butyronitrile in 70 ml toluene was heated under reflux for 18 h. Filtration, washing with 100 ml methanol and 50 ml ether and drying in vacuo at 80 °C afforded 16.3 g of the functionalised material. IR: ν_{CN} 2257 cm^{-1}. C, H, N analysis: C: 5.82, H: 1.21, N: 0.68, 0.49 mmol CN/g.

*2.5.6. SiO_2–$(CH_2)_3$COOH (not protected) (**XXV**)*

SiO_2–$(CH_2)_3$CN (not protected, **XXIV**), 16 g, in 50 ml of H_2SO_4/ H_2O 1:1 was heated to 160 °C for 24 h. Filtration, washing with H_2O to neutrality and subsequently with methanol and ether, and drying in vacuo at 80 °C afforded 13.9 g of SiO_2–$(CH_2)_3$COOH. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): 178.2 (COOH), 35.968 (CH$_2$–COOH), 18.3 (Si–CH$_2$–CH$_2$), 11.3 (Si–CH$_2$), ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −112.1 (Q4 *Si*), −101.7 (Q3 *Si*), −64.8 (*Si*–CH$_2$). IR: ν_{COOH} 1715 cm^{-1}. C, H, N analysis: C: 3.52, H: 0.83, N: 0.00.

*2.5.7. SiO_2–$(CH_2)_3$CN (protected) (**XXVI**)*

Aerosil 200 (surface area: 250 m^2/g) (4.93 g, 9.62 mmol OH) was activated at 200 °C in vacuo for 3 h. Toluene (50 ml) and 4-(trichlorosilyl)butyronitrile (0.072 g, 3.55×10^{-4} mol, 11% of the total amount of silanol groups) were added and the mixture was refluxed for 12 h. The remaining surface silanol groups were protected by adding 0.35 g (2.7 mmol, 56% of the total amount of silanol groups) dichlorodimethylsilane and refluxing for 3 h. The product was filtered off, washed with water and ethanol, and dried overnight at 100 °C in vacuo. Yield: 2.895 g. C, H, N analysis: C: 1.60, H: 0.54, N: 0.08, 0.057 mmol CN/g.

*2.5.8. SiO_2–$(CH_2)_3$COOH (protected) (**XXVII**)*

SiO_2–$(CH_2)_3$CN (protected, **XXVI**) (2.895 g, 1.65×10^{-4} mol CN) was hydrolysed by heating it 160 °C for 1 h in 50% aqueous sulphuric acid (32 ml). The product was then filtered off and washed with water until the filtrate was neutral. The product was dried overnight at 80 °C in vacuo. Yield: 2.204 g. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): −3.0 (Si–(CH$_3$)$_2$), 35.8 (CH$_2$, broad). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −110.0 (Q4 *Si*), −100.9 (Q3 *Si*), −16.0 (*Si*–(CH$_3$)$_2$).

*2.5.9. SiO_2–p-C_6H_4COOH (not protected) (**XXVIII**)*

Synthesis analogous to the corresponding MCM-41 compound. ^{13}C CP MAS NMR (400 MHz, δ (ppm)): 179.7 (COOH), 134.1 (Ar), 129.1 (Ar). ^{29}Si CP MAS NMR (400 MHz, δ (ppm)): −112.1 (Q4 *Si*), −101.4 (Q3 *Si*).

2.6. Immobilisation via ligand exchange

*2.6.1. SiO_2–$(CH_2)_2$COO–Rh_2(4*S*-BNOX)$_3$ (protected) (**XXIX**)*

Surface-protected SiO_2–$(CH_2)_2$COOH (**XXI**) (0.889 g, 3.17×10^{-5} mol COOH) and Rh_2(4*S*-BNOX)$_4$ (0.070 g, 7.70×10^{-5} mol) were stirred at room temperature for 7 days in toluene (20 ml). The resulting solid was Soxhlet extracted with dichloromethane (60 ml). The resulting blue solid (0.671 g) was dried in vacuo. Rh content (**XXIX**): 0.0055 mmol/g.

*2.6.2. SiO_2–$(CH_2)_3$COO–Rh_2 (4*R*-BNOX)$_3$ (protected) (**XXX**)*

Surface-protected SiO_2–$(CH_2)_3$COOH (**XXVI**, 1.289 g, 7.35×10^{-5} mol COOH) and Rh_2(4*R*-BNOX)$_4$ (0.067 g, 7.36×10^{-5} mol) were stirred at room temperature for 5 days in toluene (20 ml). The resulting solid was Soxhlet extracted with dichloromethane (60 ml). The resulting blue

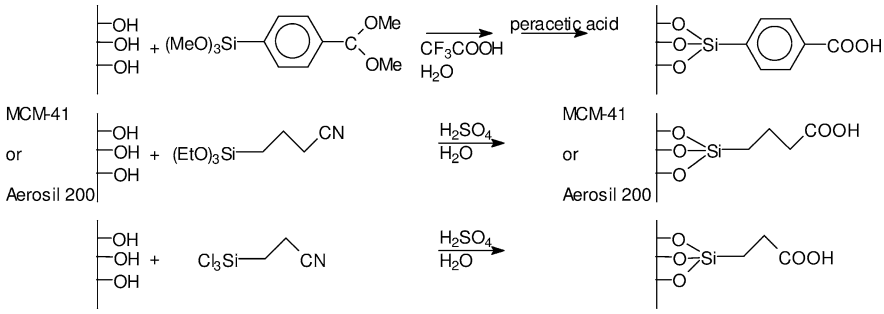

Fig. 4. Synthesis of functionalised carriers.

solid (1.060 g) was dried in vacuo. Rh content (**XXX**): 0.013 mmol/g.

*2.6.3. SiO_2–(C_6H_4)COO–Rh_2 (5*S*-MEPY)$_3$ (not protected) (**XXXI**)*

SiO_2–(C_6H_4)COOH (not protected, **XXVIII**) (0.553 g, 6.75×10^{-5} mol COOH) and Rh_2(5*S*-MEPY)$_4$ (0.022 g, 2.87×10^{-5} mol) were stirred at room temperature for four days in toluene (20 ml). The resulting solid was Soxhlet extracted with dichloromethane (60 ml). The resulting blue solid (0.429 g) was dried in vacuo. Rh content (**XXXI**): 0.205 mmol/g.

3. Results and discussion

3.1. Synthesis of functionalised carriers

The organically functionalised carriers needed for the immobilisation of the homogeneous catalysts were synthesised in different ways. The alkyl tether groups were attached to the surface by the reaction of 3-(triethoxysilyl)propionitrile or 4-(trichlorosilyl)butyronitrile with MCM-41 (**I**) or Aerosil 200. The nitrile function was then hydrolysed with 50% sulphuric acid in water. The phenyl tether group was prepared by the reaction of [4-(dimethoxymethyl)phenyl]trimethoxysilane (**IV**) with MCM-41 (**I**) or Aerosil 200. This acetal (**V**) was then hydrolysed with 5% aqueous trifluoroacetic acid to the aldehyde (**VI**), which was finally oxidised with peracetic acid to the acid (**VII**) (see Fig. 4). The homogeneous rhodium catalysts were immobilised by ligand exchange of the COOH functionalised carrier with the catalyst in dry toluene at room temperature. Additionally, the methodology developed by one of us (T.M.) [19] for the selective placement of tethers on the outside and/or inside of the MCM-41 surface has been employed to prepare a number of catalyst variations with tethered complexes only inside the pores of MCM-41.

3.2. Analysis of functionalised carriers with nitrogen desorption and XRD

The influence of the introduction of the tethers on the pore structure of the carriers was determined by nitrogen desorption measurements. These measurements show that the surface area, the total pore volume, and the pore size decrease, as expected, after attachment of the tether (Fig. 5, Table 1).

The XRD plots (Fig. 6) indicate, together with the N_2 desorption experiments, that the structure of MCM-41 remained intact when the CN-tether was introduced. The decrease in pore volume can be attributed to the presence of the tether inside the pore. After heating in aqueous sulphuric acid, in order to hydrolyse the nitrile groups, the pore structure was partially damaged. However, 50% of the channel structure remained intact (determined by the decrease of the

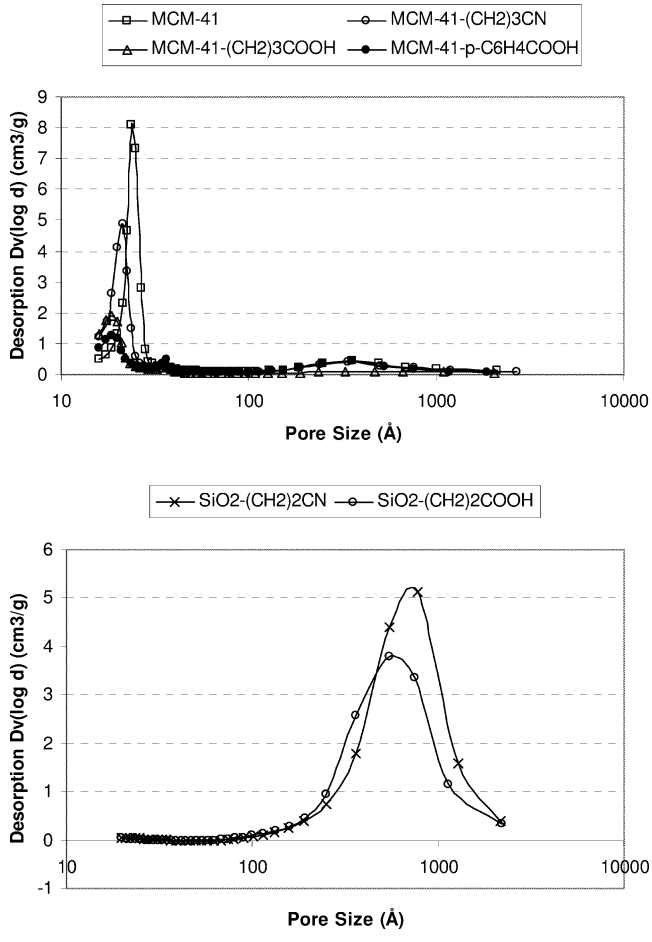

Fig. 5. Results of nitrogen desorption measurements.

Table 1
Results of N_2 desorption measurements

Entry	Sample	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Pore size (nm)
1	MCM-41 (**I**)	960 ± 13	1.01	2.4
2	MCM-41–$(CH_2)_3$–CN (**II**)	825 ± 21	0.78	2.1
3	MCM-41–$(CH_2)_3$–COOH (**III**)	566 ± 10	0.41	1.9
4	MCM-41–*p*-C_6H_4–COOH (**VII**)	528 ± 7	0.56	1.9
5	SiO_2–$(CH_2)_2$–CN (**XX**)	151 ± 18	1.38	80
6	SiO_2–$(CH_2)_2$–COOH (**XXI**)	147 ± 15	1.34	50

total pore volume; see Table 1, entries 2 and 3). This is in line with the observation that MCM-41 materials have only limited stability towards various treatments in boiling water [20]. This acid hydrolysis resulted in a gradual decrease in the surface area, broadening of pore size distribution towards the development of large pores, which is a result of the gradual removal of parts of the pore walls, however, without loss of the integrity of the solid particles, in terms of channel ordering.

3.3. NMR experiments

The analysis of the immobilised complexes by CP MAS NMR is hampered by the low loadings of the complexes on the carrier and the low sensitivity of the method in general. Only very broad peaks with low intensity are observed in the CP MAS spectra of the immobilised catalysts. In order to validate the exchange of ligand as a way of immobilisation, the reaction of $Rh_2(5S\text{-MEPY})_4$ with acetic acid (see Fig. 7) was followed by liquid phase ^1H NMR.

During the crystallisation of the dirhodium catalyst, *iso*propanol and acetonitrile are incorporated into the crystal as solvent ligands. They coordinate to the axial positions of the complexes. In the NMR experiment (Fig. 8), the singlets of the two different methyl esters in $Rh_2(5S\text{-MEPY})_4$ (around 3.7 ppm) broadened after addition of 1 equivalent of acetic acid. After some time the methyl ester signals split up into multiplets. The gradual broadening of the *iso*propanol peaks (around 1.2 ppm) is also clearly visible. Subsequently the *iso*propanol peaks regain their initial shape, while the methyl ester signals get even more complex.

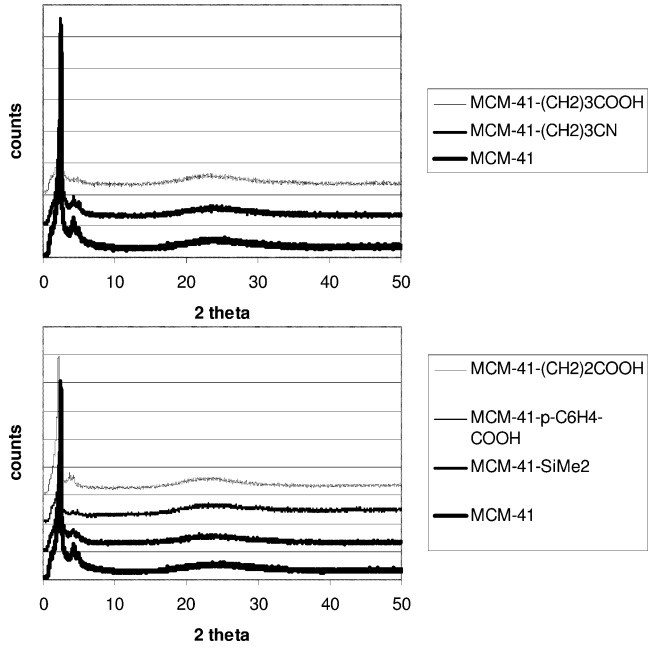

Fig. 6. Comparison XRD plots.

The initial broadening of the methyl ester and *iso*propanol signals indicates that in the first instance acetic acid exchanges with the axial ligands of the complex, thereby replacing the original acetonitrile and *iso*propanol ligands. The reconstitution of the initial shape of the *iso*propanol signals and the further splitting of the methyl ester signals indicates that the acetic acid starts to exchange with the MEPY ligands and, thus, forms a variety of different complexes. The initial axial coordination and subsequent ligand exchange of the acetic acid was also confirmed by NMR experiments with ^{17}O-labeled acetic acid.

FAB-MS of the product shows peaks at 774 ($Rh_2(5S\text{-MEPY})_4$), at 691 ($Rh_2(5S\text{-MEPY})_3OAc$), at 632 ($Rh_2(5S\text{-MEPY})_3$), and at 490 ($Rh_2(5S\text{-MEPY})_2$). These data indicate that more than one product is formed. The initial complex ($Rh_2(5S\text{-MEPY})_4$) is still detectable, and also the desired complex $Rh_2(5S\text{-MEPY})_3OAc$ is present. The other peaks show the usual decomposition products, which may originate from either of the two complexes. This shows that immobilisation takes place by exchange of one ligand with an acid function as was expected. It also shows that the exchange is not complete, since there is still unreacted complex present.

3.4. Immobilisation of the rhodium complexes

The exchange of acetonitrile to acetic acid and back to acetonitrile on the axial positions of the dirhodium complex in the NMR experiment shows that immobilisation is also possible via a nitrile function. Therefore, the immobilisation of $Rh_2(4R\text{-BNOX})_4$ on MCM-41-$(CH_2)_3$COOH in dichloromethane and on MCM-41-$(CH_2)_3$CN in toluene were compared. In both cases the resulting solids were coloured. The initial molar ratios between rhodium and tether were equal in these two experiments. However, the rhodium contents of the two resulting solids were different (as was determined by ICP-OES). The COOH carrier had a rhodium content of 0.045 mmol/g, while the CN carrier

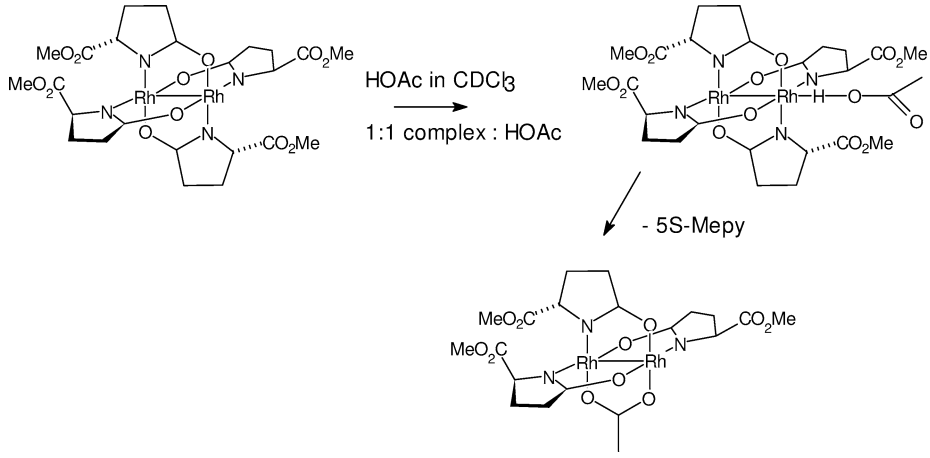

Fig. 7. Reaction of $Rh_2(5S\text{-MEPY})_4$ with acetic acid.

only had a rhodium content of 0.025 mmol/g. So, in order to have maximum loading of dirhodium complex, it is essential to validate that all of the nitrile tethers are indeed hydrolysed before the catalyst is immobilised.

With IR analysis it was proven that the conversion from CN tether to COOH tether was complete. For the CN tethers a small peak at 2261 cm^{-1} is visible for the CN vibration. After hydrolysis, this peak is not detectable any more and a new peak at 1731 cm^{-1} has appeared for the C=O vibration.

It was also attempted to immobilise $Rh_2(4R\text{-BNOX})_4$ via adsorption on MCM-41 either containing free silanol groups or being protected with dimethoxydimethylsilane. The immobilisation on unprotected MCM-41 gave a blue solid after Soxhlet extraction, while the immobilisation on protected MCM-41 (in line with expectation) was not successful, as the resulting solid was white. The rhodium contents of the two solids were determined by ICP-OES and were 0.053 mmol Rh/g for MCM-41 and less than 0.00098 mmol Rh/g for fully protected MCM-41 (below the detection limit). From these experiments it can be concluded that, if the surface of the carrier is protected, the complex is immobilised via the tether (CN or COOH), while in the case of unprotected carriers also adsorption can occur on the free silanol groups. Hölderich and co-workers [4] have shown that it is possible to immobilise complexes inside the pores of MCM-41 via ionic interactions and that no covalent bonding between the carrier and the catalyst is necessary.

In Table 2, representative examples of the immobilised catalysts are listed with the loadings of the tether and the dirhodium complex, respectively. For the alkyltethers the

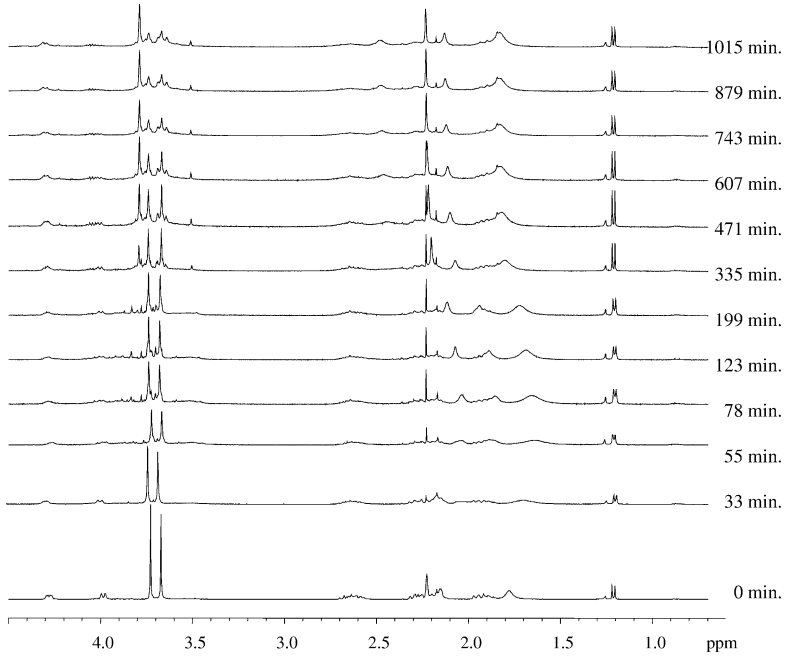

Fig. 8. ^1H NMR spectra of the reaction of $Rh_2(5S\text{-MEPY})_4$ with acetic acid.

Table 2
Immobilised catalysts with loading of CN tether and dirhodium complex

Catalyst	Protected	Loading tether (mmol tether/g)[a]	Loading Rh (mmol Rh/g)
1. SiO_2–*p*-C_6H_4COO–Rh_2(5*S*-MEPY)$_3$	no	0.12	0.090
2. SiO_2–*p*-C_6H_4COO–Rh_2(5*S*-MEPY)$_3$ (**XXXI**)	no	0.12	0.205
3. SiO_2–$(CH_2)_3COO$–Rh_2(5*S*-MEPY)$_3$	no	0.49	0.455
4. SiO_2–$(CH_2)_3COO$–Rh_2(4*S*-BNOX)$_3$	no	0.49	0.014
5. SiO_2–$(CH_2)_2COO$–Rh_2(4*S*-BNOX)$_3$ (**XXIX**)	yes	0.04	0.006
6. MCM-41–*p*-C_6H_4COO–Rh_2(4*R*-BNOX)$_3$	outer surface protected	0.80	0.022
7. MCM-41–$(CH_2)_2COO$–Rh_2(4*R*-BNOX)$_3$	yes	0.81	0.178
8. MCM-41–$(CH_2)_3COO$–Rh_2(4*R*-BNOX)$_3$ (**XIII**)	yes	0.14	0.045
9. MCM-41–$(CH_2)_3CN$–Rh_2(4*R*-BNOX)$_3$ (**XII**)	yes	0.14	0.025
10. SiO_2–*p*-C_6H_4COO–Rh_2(4*R*-BNOX)$_3$	no	0.12	0.048
11. SiO_2–$(CH_2)_2COO$–Rh_2(4*R*-BNOX)$_3$	yes	0.07	0.057
12. SiO_2–$(CH_2)_2COO$–Rh_2(4*R*-BNOX)$_3$	no	0.04	0.027
13. SiO_2–$(CH_2)_3COO$–Rh_2(4*R*-BNOX)$_3$ (**XXX**)	yes	0.06	0.013

[a] For the alkyl-COOH tethers, the amount of tether is determined via C, H, N elemental analysis of the corresponding CN tether. For the aryl-COOH tethers, the amount of tether is determined via the mass balance.

loading of the COOH tether was calculated from the C, H, N analysis of the corresponding CN tethers. With IR, we then checked if the conversion from CN to COOH was complete. For the aryl tethers this approach is not possible, because there is no CN intermediate. In this case the amount of [4-(dimethoxymethyl)-phenyl]trimethoxysilane that was added to the reaction mixture minus the amount that was recovered after washing was used for this calculation. We assume that the degradation of the pores due to the reaction conditions used in the hydrolysis of the CN tethers (vide supra) results in a lower loading of the COOH tether relative to the CN tether. The loading of the dirhodium complex will, therefore, always be lower than that of the CN tether (considering that ligand exchange with the COOH tether is taking place, rather than adsorption (vide supra)). The high rhodium loading of entry 2 could possibly be explained by the fact that the surface is not protected, allowing adsorption as an additional mechanism of immobilisation. Also in entries 1 and 3 the loading of the dirhodium complex is quite close to the loading of the CN tether, while in most other cases the loading of the dirhodium complex is much lower than the loading of the CN tether. For the MEPY complexes the rhodium loading is generally closer to the maximum loading than for the BNOX complexes. This can possibly be explained because of the difference in size of the complexes. The maximum size of $Rh_2(BNOX)_4$ is approximately 19 Å, and for $Rh_2(MEPY)_4$ approximately 13 Å. The fact that the BNOX complex is larger could be a reason why it is more difficult to immobilise.

In the immobilisation procedure we added only 10% of tethers relative to the amount of surface silanol groups. Therefore, we expect that the excess COOH groups on the surface cannot exchange with another ligand of the same catalyst molecule. We are currently investigating the influence of these groups on the performance of the catalyst.

4. Conclusion

Chiral dirhodium complexes can be immobilised via ligand exchange with surface-anchored carboxylic acid groups. When the surfaces of the carrier materials are fully protected, the immobilisation is solely due to this exchange and not to adsorption. The complexes were successfully immobilised inside the pores of MCM-41 and onto the Aerosil 200 surface. The pores of MCM-41 induce a spatial confinement around the complex. This enhances the enantio- and regioselectivity of the catalytic reactions (cf. [21]).

Acknowledgments

Dr. J.A. Peters is kindly acknowledged for his help with the NMR experiments. The Royal Netherlands Academy of Arts and Sciences (U.H.) and the Netherlands Research School Combination Catalysis (H.M.H.) are acknowledged for financial support.

References

[1] R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, Chichester, 1994.
[2] I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, Weinheim, 1993.
[3] M. Capka, Collect. Czech. Chem. Commun. 55 (1990) 2803–2839, and references cited therein.
[4] H.H. Wagner, H. Hausmann, W.F. Hölderich, J. Catal. 203 (2001) 150–156, and references cited therein.
[5] A. Baiker, Curr. Opin. Solid State Mater. Sci. 3 (1998) 86–93.
[6] T. Bein, Curr. Opin. Solid State Mater. Sci. 4 (1999) 85–96.
[7] J.M. Thomas, T. Maschmeyer, B.F.G. Johnson, D.S. Shephard, J. Mol. Catal. A, Chem. 141 (1999) 139–144.
[8] K. Fodor, S.G.A. Kolmschot, R.A. Sheldon, Enantiomer 4 (1999) 497–511.

[9] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartulli, J.S. Beck, Nature 359 (1992) 710–712.
[10] J.S. Beck, J.C. Vartulli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, D.H. Chu, C.T-W. Olsen, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834–10843.
[11] A. Corma, Chem. Rev. 97 (1997) 2373–2419.
[12] C. Huber, K. Moller, T. Bein, J. Chem. Soc. Chem. Commun. (1994) 2619–2620.
[13] B.F.G. Johnson, S.A. Raynor, D.S. Shephard, T. Maschmeyer, J.M. Thomas, G. Sankar, S. Bromley, R. Oldroyd, L. Gladden, M.D. Mantle, J. Chem. Soc. Chem. Commun. (1999) 1167–1168.
[14] S.A. Raynor, J.M. Thomas, R. Raja, B.F.G. Johnson, R.G. Bell, M.D. Mantle, J. Chem. Soc. Chem. Commun. (2000) 1925–1926.
[15] M.H. Lim, A. Stein, Chem. Mater. 11 (1999) 3285–3295.
[16] M.P. Doyle, W.R. Winchester, J.A.A. Hoorn, V. Lynch, S.H. Simonsen, R. Ghosh, J. Am. Chem. Soc. 115 (1993) 9968–9978.
[17] L.T. Zhuralev, Colloids Surf. 74 (1993) 71–90.
[18] M. Nowotny, L.N. Pedersen, U. Hanefeld, T. Maschmeyer, Chem. Eur. J. 8 (2002) 3724–3731.
[19] D.S. Shephard, W. Zhou, T. Maschmeyer, J.M. Matters, C.L. Roper, S. Parsons, B.F.G. Johnson, M.J. Duer, Angew. Chem. Int. Ed. Engl. 37 (1998) 2719–2723.
[20] M. Kruk, M. Jaroniec, A. Sayari, Micropor. Mesopor. Mater. 27 (1999) 217–229, and references cited therein.
[21] H.M. Hultman, M. de Lang, I.W.C.E. Arends, U. Hanefeld, R.A. Sheldon, T. Maschmeyer, J. Catal., in press.