Stationary phases composed of sol–gel processed organometallic complexes functionalized with polyethylene glycol†

Joachim Büchele, Michael Marzini and Hermann A. Mayer *

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany. E-mail: hermann.mayer@uni-tuebingen.de

A tripodal phosphine molybdenum tricarbonyl complex has been functionalized with polyethylene glycol spacers of average chain lengths ranging from 0 to 90. Hydrolysable end groups were attached to the spacers *via* a platinum catalysed hydrosilylation, a Williamson ether synthesis $Cl(CH_2)_3Si(OEt)_3$ and an addition reaction of $OCN(CH_2)_3Si(OEt)_3$. The resulting complexes were sol–gel processed by two different methods with varying amounts of $Si(OMe)_4$ and $Si(OEt)_4$ as cocondensation agents. This generated organometallic/inorganic hybrid materials with characteristic features depending on the spacer length and the amount of cocondensation agent. A detailed multinuclear NMR spectroscopic investigation established the structure of the metal complexes in the polymer and revealed the cross-linking and degree of condensation of the materials. Furthermore, relaxation studies gave insight into the dynamics of the metal complexes, within the hybrid polymers. Chemistry in the interphase was performed with selected materials. The molybdenum tricarbonyl fragments were removed by a combined photochemical/oxidative method leaving the tripodal phosphine in the polymer. These polymerised phosphines served as starting materials for new rhodium and iridium complexes as reactive centres in stationary phases.

Introduction

Concepts to recover catalysts are attracting increasing attention as they may offer an important contribution to sustainability.[1] Therefore transition metal catalysts anchored onto insoluble supports are of great interest.[2–5] They allow easy purification as well as catalyst recycling and thus play an important role with respect to ecological and economic aspects.[6] On the other hand the immobilisation of a transition metal complex affects the homogeneity as a result of the diminished mobility which causes minor changes in the structure of the active centres. This leads to a reduced reactivity and selectivity of immobilised catalysts.[7] Furthermore the influence of the support on the catalytic properties such as activity and selectivity is unknown due to the lack of knowledge about the active structure of the catalysts and the matrix.[8] In contrast, in solution homogeneous catalysts possess uniform and well defined reactive centres, which are responsible for the high and reproducible selectivity.[9] A further disadvantage of immobilized catalysts is their short lifetime caused by leaching. To prevent leaching and circumvent the reduced reactivity which supported metal complexes suffer from, we introduced the concept of chemistry in interphases.[10,11] Interphases are special regions within a material where a stationary and a mobile component penetrate one another on a molecular level. In these regions a reactive centre becomes highly mobile with properties close to those in solution. Therefore optimal productivity of the supported catalysts should be obtained because the reactive centre is in an environment which is similar to homogeneous reaction conditions.[10]

The simultaneous cocondensation of various types of alkoxysilanes with functionalized metal complexes using sol–gel processes leads to highly cross-linked polymers as stationary phases.[12] Thus the covalent attachment of the catalysts to the matrix prevents leaching. At the same time sufficient swellability and permeability, respectively, needs to guarantee the accessibility and the mobility of the metal complexes in interphase conditions.

The sol–gel approach to prepare stationary phases permits infinite variation of the composition, structure and properties of the matrices.[13–17] In particular it can be used to introduce metal complexes into the polymer network under mild conditions. As hydrolysable end groups have to be attached to transition metal complexes the most popular method for such complexes to be prepared is the reaction of an appropriate metal precursor with a silylated ligand.[11,12,18]

In this work stationary phases consist of metalla-phosphaadamantanes as reactive centres, polyethylene glycol as mobile spacers and a silica support.[19] Metalla-phospha-adamantanes are transition metal complexes of a tripodal phosphine ligand with three diphenylphosphine groups stereospecifically bound *cis,cis* to the 1,3,5-positions of the cyclohexane ring.[20] The functionalization of this ligand can be only achieved by the assistance of an organometallic protecting group.[21]

Results and discussion

Polyethylene glycol spacer

The linkage of the reactive centre with the support is accomplished by flexible polyethylene glycol chains which, in spite of areas with zigzag like secondary and partially crystalline structures, have an inner mobility.[22] With a proper length of the chain it is assumed that the reactive centres become mobile as well and thus a situation similar of a solution should be possible in the interphase. Variation in assembling the matrix by different cocondensation agents changes the mobility of the active centre. As demonstrated, the functionalisation of the cyclohexane backbone of the tripodal phosphine **1** is achieved after protecting the phosphine groups by coordination to the $Mo(CO)_3$ fragment and converting the methoxycarbonyl functions into hydroxymethyl groups (Scheme 1).[23] A base-catalysed polyaddition reaction of oxirane to the trialcoholate of **2** allows control of the chain length of the polyethylene glycol spacer by simply weighing the appropriate amounts of oxirane.[23] In Table 1 the degrees of polymerisation P and the calculated average molecular weight M_P together with some characteristic features of the resulting homologous polymers $3_{(P)}$ are listed. The physical and chemical properties of the hydroxy(polyethoxymethyl)

† Based on the presentation given at Dalton Discussion No. 6, 9–11th September 2003, University of York, UK.

Electronic supplementary information (ESI) available: Tables of the ^{29}Si (Table 1S and Table 5S) and ^{31}P (Table 2S) NMR data as well as synthesis (Table 3S and Table 4S) of the hybrid polymers. See http://www.rsc.org/suppdata/dt/b3/b304205g/

Table 1 Polyethylene glycol spacered complexes $3_{(P)}$

Degree of polymerisation P^a	Molecular weight $M_P{}^a$/g mol^{-1}	Consistency	Colour	Melting area/°C	Solubility
0	906	Powder	Colourless	$-^b$	DMF
3	1038	Powder	Off white	$-^b$	Acetone
6	1170	Powder	Off white	$-^b$	Acetone
9	1302	Powder	Yellow	$-^b$	THF
48	3224	Highly viscous	Yellow	$-^b$	DMF
90	4870	Highly viscous	Off white	$-^c$	MeOH, CH$_2$Cl$_2$, CHCl$_3$, THF, toluene, H$_2$O
120	6190	Waxy	Yellow	42–50	
150	7510	Waxy	Yellow	50–53	
230	11030	Brittle	Amber	54–57	
270	12790	Brittle	Amber	57–60	

^{a} Calculated from the relative integration of the ethoxy and phenyl protons in the ^{1}H NMR spectra: $P = (30I_{ethoxy}/4I_{phenyl}) - 3/2$; $M_p = PM_o + M_e$ (M_o: molecular weight of oxirane; M_e: molecular weight of **2**) ^{b} Not melting, decomposition. ^{c} Oil at room temperature.
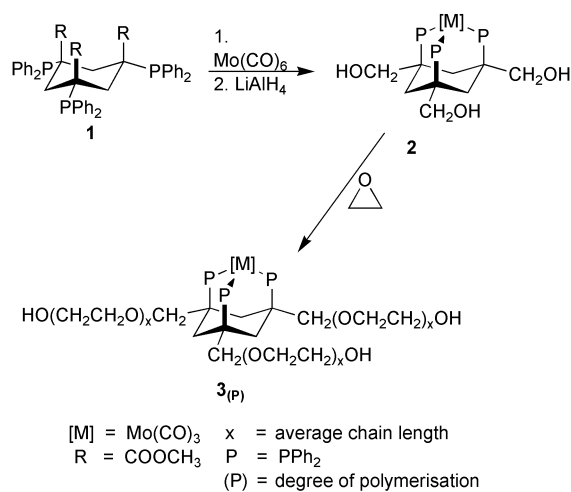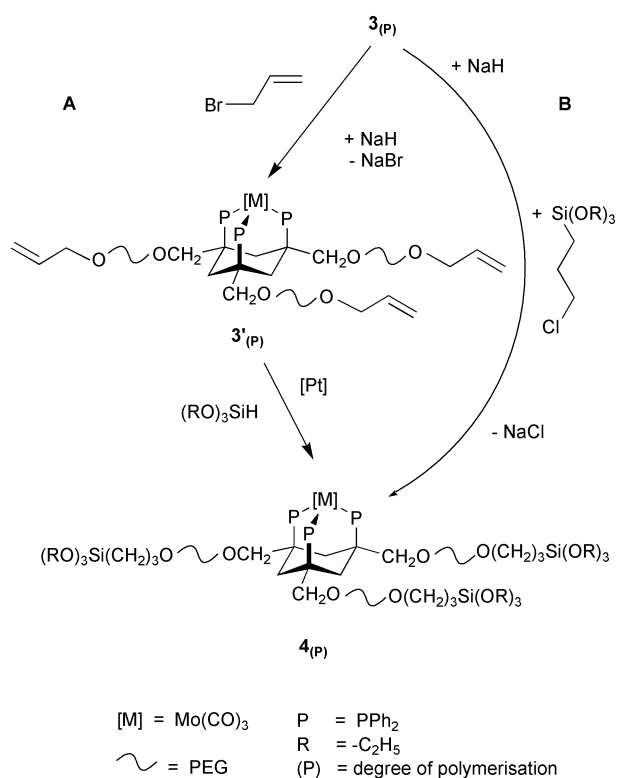

Scheme 1

adamantanes $3_{(P)}$ depend mainly on the chain length. The materials with long chains are dominated by the characteristics of the PEG part. Yellow–brownish substances are obtained with melting points between room temperature and 60 °C. Accordingly at room temperature $3_{(270)}$ is brittle, $3_{(250)}$ waxy and $3_{(48)}$ a highly viscous oil. They are soluble in organic solvents such as methanol, dichloromethane, chloroform, THF as well as toluene, and swell in diethyl ether. At degrees of polymerisation of 90 and higher they are miscible in water in any ratio. The properties of the materials with short chains are determined by the metal complex. Thus yellow powders are obtained which decompose at higher temperatures and dissolve in polar solvents.

Introduction of the hydrolysable end group

To support the PEG complexes $3_{(P)}$ in a sol–gel process the hydroxyethyl groups have to be converted into hydrolysable alkoxy silanes. A common procedure to generate alkoxy silanes is the platinum-catalysed hydrosilylation of terminal olefins.[24–26] Hence $3'_{(P)}$, which are easily obtained by a Williamson ether synthesis of $3_{(P)}$ with allylbromide, were treated with triethoxysilane in the presence of a platinum catalyst (Scheme 2(A)). Unfortunately this way turned out to be unfavourable for several reasons. The incomplete hydrosilylation leads to side products which are statistically distributed over the PEG functions and a separation of the main product by distillation or chromatography is not possible. Furthermore, due to the colloidal platinum which cannot be separated from the PEG functionalized metal complexes, a later use of these materials for catalysis can not be considered.

Therefore the polymers $3_{(P)}$ were treated with Cl(CH$_2$)$_3$-Si(OEt)$_3$ under Williamson ether synthesis conditions at 60 °C in THF assisted by NaH as a base to give compounds $4_{(P)}$

Scheme 2

(Scheme 2(B)). According to the integration of the ^{1}H NMR signals of the Si–CH$_2$–CH$_2$– protons the conversion succeeds quantitatively. Unfortunately the reaction conditions create a strong basic ambience which causes an untimely hydrolysis and condensation by a nucleophilic attack of the OH$^-$ at silicon. The hydrolysis and condensation already takes place during the 20 h of the ether synthesis and thus is like an uncontrolled sol–gel process which continues even after neutralisation and during removal of the solvent THF. According to ^{29}Si CP/MAS NMR spectroscopy of such materials a preferred condensation to Si–O–Si dimers takes place. Although due to the reversibilty of the Si–O–Si formation these materials can still be used in a sol–gel process (see below) a third strategy to connect the PEG functions with a hydrolysable end group has been explored. The addition of an isocyanate to an amine or alcohol generating an urethane is a well-known reaction in polymer chemistry.[22] Consequently treatment of $3_{(P)}$ with stoichiometric amounts of 3-(trialkylsilyl)propylisocyanate in DMF at 120 °C gave the materials $5_{(P)}$ (Scheme 3) in quantitative yields. The advantages of this reaction are the neutral conditions which prevent an early hydrolysis and condensation, the uniform reaction which produces no side products and the stability of the urethane group. The reaction can be followed via IR spectroscopy by the

Scheme 3

disappearance of the O=C=N valence vibration and by the emerging amide bands at 1699 cm^{-1} (O=C valence vibration) and 1525 cm^{-1} (N–H deformation vibration) of the urethane groups. In the ^{1}H NMR spectra characteristic patterns due to the propylsilyl groups at 0.32–0.62 and 1.40–1.60 ppm are observed. Furthermore the resonances and the proper integration ratios of the ethoxy protons at δ 1.10 and 3.72 show that no hydrolysis took place.

Sol–gel process

The support of the PEG functionalized organometal complexes $4_{(P)}$ and $5_{(P)}$ is achieved *via* the silyl functions in a sol–gel process. In contrast to the anchoring of metal complexes on a surface like silica, in this procedure the matrix is built up in consecutive steps of hydrolysis and condensation reactions under integration of the organometal functionalized silane. It is assumed that the specific properties of the PEG functionalized precursors $4_{(P)}$ and $5_{(P)}$ can be conferred to the matrix. While in other examples of interphase chemistry the mobility of the metal complexes is obtained *via* flexible inorganic–organic cocondensation agents,[27,28] according to this approach the PEG functions are considered to be responsible for a high swelling ability of the materials. This should result in a high mobility and uniform accessibility of the active centres. The inorganic part of the matrix which is introduced *via* the sol–gel process into the hybrid polymer serves only to connect the end groups of the PEG functions in order to effect the insolubility of the matrix.

In *method A* the polymers $4_{(P)}$ with $P = 3$–150 were mixed with 0–15 equivalents of tetraethoxyorthosilicate (TEOS), an excess of water, and di-*n*-butyltindiacetate as a Lewis acid catalyst (Scheme 4). If only small quantities of TEOS are used ethanol has to be added to provide homogeneous reaction

Scheme 4

conditions. Larger amounts of TEOS produce enough alcohol during the hydrolysis which homogenise the reaction mixture within minutes. The hybrid materials $6_{(P)}$a–d were characterised by ^{29}Si and ^{31}P solid-state NMR spectroscopy (Table 2). In spite of the high degree of condensation for both types of silicon groups (>85% T-, 75% Q-groups) it is obvious that the real stoichiometry does not match the expected stoichiometry.[29] In the residue of the polar solvents after solvent processing condensed silicate structures were found which indicate a disassembly of the materials. Furthermore the observation of several resonances in the ^{31}P NMR spectra indicate that parts of the molybda-phospha-adamantane complexes decomposed. This might be due to the strong Lewis acid di-*n*-butyltindiacetate which acts as a catalyst for the hydrolysis and condensation in the sol–gel process. While the cyclohexane cage resists strong Brønsted acids and bases it is attacked by Lewis acids at higher temperatures.[21] After the raw materials are washed several times with solvents of decreasing polarity (solvent processing), the oligomers which are not integrated in the network were removed. This leads to clean and stable materials which are well suitable for further chemistry (see below).

According to *method B* an *in-situ* sol–gel process is initiated after the addition reaction of the isocyanate to $4_{(P)}$ in DMF is complete (Scheme 5). Without isolating $5_{(P)}$, HCl as a catalyst and double stoichiometric amounts of water are added. For kinetic reasons the cocondensation agent tetramethylorthosilicate (TMOS) is applied. The solvent DMF proved to be advantageous over methanol or ethanol as cosolvents. According to ^{31}P NMR spectroscopy the materials $7_{(P)}$a–c are obtained pure, no further washing procedures are necessary. Thus the application of HCl as catalyst assures a non-destructive support of the molybdenum complexes.

Scheme 5

The consistency of the materials $6_{(P)}$a–d and $7_{(P)}$a–c depends on the amount of added cocondensation agent. When small amounts of TEOS and TMOS, respectively, are used the properties of the materials are dominated by the PEG groups. They do not melt any more but remain waxy. Increasing cocondensation agent content changes the characteristics of the substances from rubber to powder. The ability to swell decreases with increasing amount of silicon content. In the ^{31}P CP/MAS NMR spectra of all samples ($6_{(P)}$a–d and $7_{(P)}$a–c) each a singlet is observed between 43.5 and 45.2 ppm which agree well with those found for the soluble polymers $3_{(P)}$, $4_{(P)}$ and $5_{(P)}$. The IR spectra of the sol–gel processed complexes $6_{(P)}$a–d and $7_{(P)}$a–c display the A$_1$ and E modes of the CO vibration at 1936 and 1864 cm^{-1} which confirms that the C_{3v} symmetry of the molybdenum carbonyl complex fragments is preserved.

Chemistry in interphase – replacement of the Mo(CO)$_3$ group with M(COD) fragments

After the successful support of the molybdenum–phospha-adamantane complexes the Mo(CO)$_3$ fragment has to be

Table 2

Table 2 Hybrid materials prepared according to method A

Compound	Degree of condensation (%) T/Q[a]	Real stoichiometry (T : Q)[a]	$\delta(^{31}P)$[b]/ppm	Linewidth $v_{1/2}(^{31}P)$/Hz
$6_{(3)}a$	88.5/79.4	1 : 6.7	44.8	759
$6_{(6)}b$	96.8/–	1 : 0.0	44.8	727
$6_{(90)}a$	92.3/78.5	1 : 4.3	45.0	613
$6_{(120)}c$	90.3/79.4	1 : 2.4	45.0	337
$6_{(120)}d$	89.7/75.3	1 : 9.8	45.2	178
$6_{(150)}a$	95.1/87.9	1 : 1.7	45.1	430
$6_{(150)}d$	86.3/77.2	1 : 10.5	44.9	538

[a] Obtained according to ref. 32. [b] Singlet after solvent processing.

separated from the ligand to generate the non-coordinated tripodal phosphine within the matrix for further use. A smooth method to remove the $Mo(CO)_3$ protection group from polymerised complexes is a combined photochemical oxidative pathway.[21] After activation of the metal carbonyl bond with UV light the oxygen transferring agent N_2O is able to selectively oxidise the $Mo(CO)_3$ fragment to MoO_3. As has been demonstrated in solution this method works without oxidation of the phosphine ligand.[21] Thus if a suspension of the polysiloxanes $6_{(P)}a,d$ in THF is irradiated with UV light in the presence of N_2O the supported ligands $8_{(P)}a,d$ are generated quantitatively (Scheme 6). This was shown by a shift of the ^{31}P resonance to lower frequencies (δ 29) in the ^{31}P CP/MAS spectra of $8_{(P)}a,d$ and confirmed by the absence of the $v(CO)$ absorptions due to the $Mo(CO)_3$ fragment in the IR spectra. After conversion of MoO_3 into MoO_4^- with K_2CO_3 the molybdate is extracted by washing procedures. The disappearance of the Mo-K_α and Mo-K_β lines in the EDX spectra indicates that the molybdate is washed out completely. This demonstrates that all reactive centers are easily accessible by diffusion of the N_2O molecule and that the polymer matrices are transparent for UV-light. Thus penetration of the stationary phase by the mobile phase is complete. While a number of functionalized phosphine monomers was accessible in this way in homogenous solution,[21] a partial oxidation of the supported phosphine ligand $8_{(P)}a,d$ is observed in the interphase. This was attributed to the high oxophilicity of the polyethylene glycol groups and is prevented by adding reducing agents such as nBu_3P to the suspension

during the reaction. It is noteworthy that the linewidth of the ^{31}P resonances are strongly reduced (up to 480 Hz) compared to the supported molybdenum complexes.

Rhodium carbonyl hydrido complexes of the tripodal phosphine ligand **1** and the PEG functionalized counterparts have been successfully applied in the hydroformylation of 1-hexene in mono and biphasic environments.[23] Consequently the stationary phases $8_{(P)}a,d$ were treated with appropriate complex precursors of iridium and rhodium to generate the corresponding tripodal phosphine complexes (Scheme 6). This also served as a further test to study the accessibility of the active centres. When the supported tripodal phosphine ligands $8_{(P)}a,d$ are treated with Vaska's complex no reaction is observed. This is in contrast to the results found in homogeneous phase.[21] Several attempts with various reaction conditions failed as well. Obviously the $Ir(PPh_3)_2(CO)Cl$ complex is too large to enter the interphase and react with the tripodal phosphine. If the dimers $[M(COD)Cl]_2$ (M = Rh, Ir) are stirred in a suspension of $8_{(P)}a,d$ in toluene at room temperature for 20 h no conversion is detected by ^{31}P CP/MAS NMR spectroscopy. Only after the dimers are split by the addition of $NaBPh_4$ do the new anchored rhodium and iridium complexes $9_{(P)}d$ and $10_{(P)}a$ form. The characteristic ^{31}P NMR signals are shifted to δ 38.4 ($9_{(P)}d$) and -7 ($10_{(P)}a$), respectively.

^{29}Si Solid-state NMR spectroscopy based characterisation of the matrices $7_{(P)}a–c$

To allow a comparison of the different materials, stoichiometry as well as degrees of hydrolysis and condensation of the polysiloxane containing parts of the hybrid polymers have to be known and should be similar in size. Fig. 1 displays the ^{29}Si CP/MAS NMR spectra of compounds $7_{(0)}a–c$. The typical patterns due to T and Q groups which arise when the condensation is incomplete are observed. Therefore substructures of different average chemical shift can be distinguished at δ -44.1 (T^0), -52.0 (T^1), -58.9 (T^2), -66.8 (T^3) as well as -90.5 (Q^2), -100.1 (Q^3) and -109.1 (Q^4). Increasing degree of condensation results in a decreasing chemical shift for both T and Q groups.
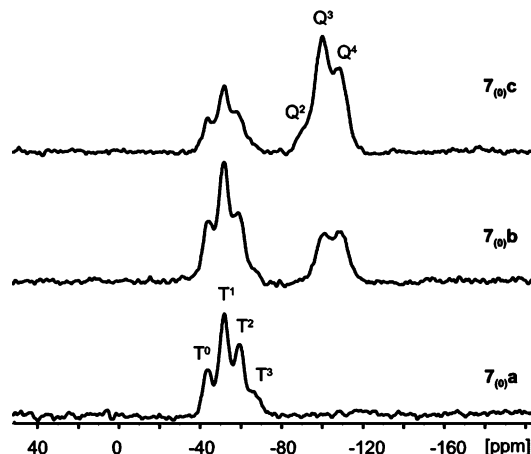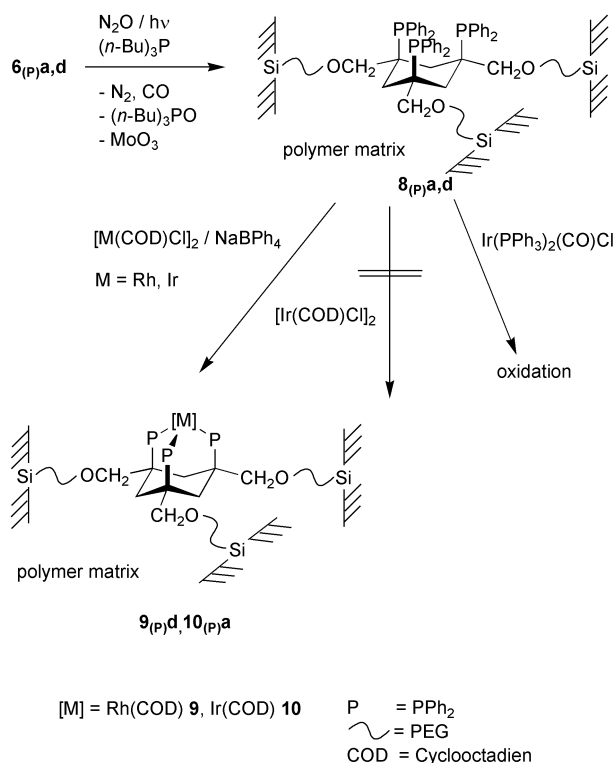

Scheme 6

Fig. 1 ^{29}Si CP/MAS NMR spectra of the hybrid polymers $7_{(0)}a–c$.

All kinds of silicon atoms embedded in the polysiloxane matrices of the synthesised materials are surrounded by hydrogen atoms at distances which allow an efficient Hartmann–Hahn transfer of magnetic polarisation. Thus all silicon atoms are accessible by ^{29}Si CP/MAS NMR spectroscopy. In general it is possible to analyse the spectra by deconvolution and line-fitting procedures, and careful considerations of the cross-polarisation dynamics in CP/MAS experiments [30] or time consuming MAS spectra allow the evaluation of the relative populations (quantification) of the different silicon groups. Thus the real ratio of T to Q groups, as well as the resulting degrees of condensation were determined by a combination of experiments as high-power-decoupling single-pulse-excitation (HPDEC SPE), variation of the contact time in cross-polarisation (CP) experiments and spin-lock–τ–CP sequence with fixed contact time and variable τ.[31–34] The latter experiment offers the advantage that a simple fitting procedure for the data evaluation leads to numbers with higher accuracy. The degrees of condensation of the synthesised copolymers ranged from 42.3 to 100% for T groups and 83.7 to 94.8% for Q groups, respectively (Table 1S†). While the degree of condensation for Q groups hardly varies with the PEG chain length, the degrees of cross-linking for T groups strongly depend on the chain length. In addition, unlinked chains could be detected *via* chemical shifts of T^0 groups in materials with $P = 0$ or 9. As the functionalized adamantanes offer three linkable chain ends per molecule, cross-linking with the matrix is still likely. As is shown in Fig. 2 the longer the PEG chain, the higher the degree of polymerisation of the T groups. Complete condensation is observed for materials which have a degree of polymerisation equal to or higher than 230. A dependence of the degree of cross-linking on the amount of cocondensation agent is not found for any of the PEG chains. ^{13}C CP/MAS NMR spectra of the compounds with $P = 0$ and 9, respectively, show signals at 58.2 and 17.9 ppm which are assigned to the ethoxy functions of non-hydrolysed T groups. As ^{29}Si CP/MAS NMR spectra report a complete condensation for $P = 230$ or higher, there are no signals
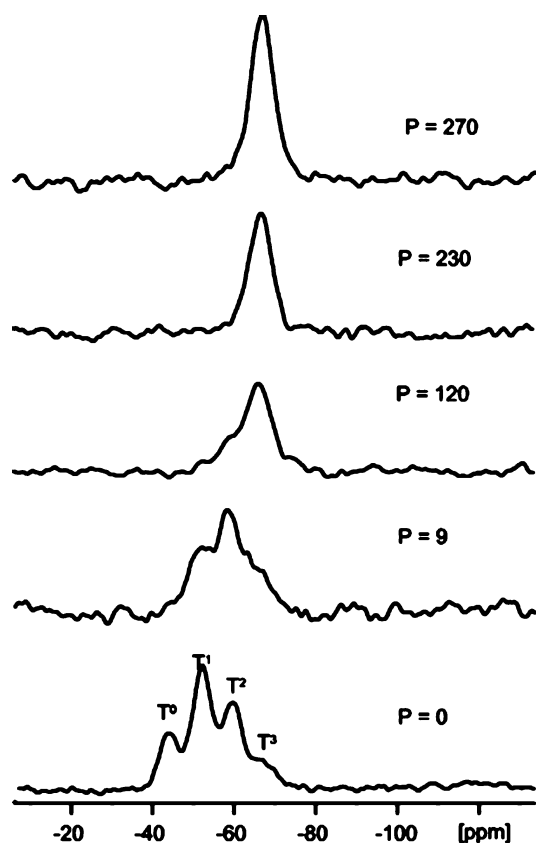
due to ethoxy groups in the corresponding ^{13}C CP/MAS NMR spectra of these materials. Furthermore there are no signals showing the presence of sterically less demanding methoxy remainders with respect to Q groups. Thus in the hybrid polymers with small PEG chains, the steric influence of the large phosphine complex reduces hydrolysis as well as condensation. The complex is thought to shield the linkable groups against the nucleophilic attack of the water molecules in a very efficient way. In materials of longer chain length the reaction centres have, on average, a larger distance to the metalla-phosphine centres and thus are easier accessible for the reagent.

It is remarkable that short polymers retain the physical properties of the educts after self condensation. They do not melt, although the degree of cross-linking is low. On the other hand, if no further linking groups are added, materials with $P = 120$, 230 and 270, respectively, melt although condensation of the silyl species is complete. The inorganic parts of these materials are obviously not able to compensate the small forces of cohesion between the PEG chains, due to their small mass contribution (1.2–2.4%). After small amounts of TMOS are added and processed, the materials do not melt any more. The relaxation times $T_{1\rho H}$ allow the conclusion that the added TMOS groups are homogeneously distributed within the material (Table 1S†). All samples show for T and Q groups, respectively, uniform relaxation times in the rotating frame ($T_{1\rho H}$) with respect to the protons. This indicates, that the inorganic silica like areas are homogeneously structured and that no domains are formed for TMOS equivalents $y = 3$ and 12. If y becomes higher, comparable systems show an inhomogeneous distribution of the T and Q groups.[27,33] $T_{1\rho H}$ values decrease slightly while the amounts of cocondensation agent increase with respect to the same chain length. They are comparable to $T_{1\rho H}$ of immobilised transition metal catalysts. The corresponding values of longer chains are lower than those of short chains, namely 1.46–2.49 ms compared to 2.18–5.53 ms. As in these cases the precondition of a short contact time compared to $T_{1\rho H}$ is not met an evaluation of contact time variation experiments was not possible. SPE experiments confirm, that the real amounts of compounds only differ 15% at the maximum from the applied stoichiometry. Hence, the matrices are comparable with each other.

^{31}P Solid-state NMR spectroscopic characterisation of the matrices

The knowledge of dynamics in detail with respect to the stationary components is of great interest, as interphases are actually designed to imitate homogeneous types of reaction. Higher degrees of mobility in the catalytic materials are assumed to improve the accessibility of the reactive centres as well as their uniformity, thus enhancing the activity and selectivity of the catalyst. Motions belonging to different dimensions on the time scale can be scanned using a set of parameters, namely T_{PH}, T_{1P} and $T_{1\rho H}$ as well as linewidth, evaluated from NMR spectroscopic investigations (Table 2S†).[32,35–38]

Corresponding to the results from ^{29}Si CP/MAS NMR spectra, investigations made by ^{31}P NMR show large differences between materials containing long PEG chains and those with short chains. While linewidth ranges from 430 to 495 Hz for $P = 0$ and 9, respectively, a reduced width from 308–358 Hz is observed for $P = 120$, 230 and 270 (measured at 22 °C). Decreasing linewidth indicates increasing mobility of the phosphine groups in analogy to $T_{1\rho H}$. Values for the latter range from 5.10 to 6.91 ms in the case of short chains, and 1.21 to 1.99 ms for long chains, respectively. All of these $T_{1\rho H}$ relaxation times decrease with increasing temperature and thus belong to the slow motion regime in the "correlation time curve".[39] Hence, shorter times represent increased mobility in the kHz range. The $T_{1\rho H}$ relaxation times determined by ^{31}P NMR investigations correspond well with those obtained *via* [29]Si. There

Fig. 2 ^{29}Si CP/MAS NMR spectra of the hybrid polymers **7$_{(P)}$a** with $P = 0$–270.

exists only one reservoir of protons, which wraps all different parts of the molecules by an efficient spin diffusion. Yet, this excludes an investigation in detail with respect to the motion of a specific part which uses the relaxation time of protons in the rotating coordination system. In fact there is no phase boundary or domain established by the inorganic parts within the organic polymer matrix.[27]

A different dependence on the spin–lattice relaxation time T_{1P} on the temperature is observed. Whereas materials containing short chains show increasing T_{1P} while temperature increases, values for T_{1P} of long chains are found on the opposite branch of the correlation time curve. Hence, short chain lengths generate long relaxation times (T_{1P}, 38.2 and 54.8 s) as well as high mobilities in the MHz range which corresponds to a decreased transfer of magnetic polarisation. As different kinds of motion have to be considered, each contributing differently to several ways of relaxation, no contradiction is evoked by a comparison of these results with those gained by evaluation of linewidths or $T_{1\rho H}$ measurements. This distinction cannot be made with respect to the cross-polarisation constants T_{PH} which display a narrow range from 0.37 to 0.95 ms for all investigated copolymers. Numbers and distances of the nearest protons with respect to the phosphorus atoms do not vary for all synthesised materials. Therefore no significant differences in T_{PH} are obtained, as the nearest protons have the strongest influence on the phosphorus atoms. Comparing samples of short chains with those of long chains, only a slight dependence on the chain length can be observed.

It is remarkable that doubling the degree of polymerisation, namely $P = 120$ to $P = 230$ and 270, respectively, does not lead to an improved mobility of the centres. There is a certain maximum of mobility which cannot be enhanced by increasing the number of PEG units per chain. Measurements at constant chain length show, that materials synthesised without co-condensing agent, possess the highest mobility and therefore the smallest linewidths. Samples of a degree $P = 120$ and 230, respectively, show decreasing mobility in all ranges of frequency for increasing amounts of Q groups in the materials.

Conclusion

The concept of an organometallic protecting group has been successfully transmitted to the chemistry in interphases and offers access to new supported transition metal complexes. The required functionalization, the assembly of the spacer, the introduction of the hydrolysable end group and the sol–gel process are only possible in a straight forward way if the tripodal phosphine ligand is protected. The application of PEG groups as mobile spacers results in stable materials which allow to control the mobility of interphase by their length. Moreover sterically hindered reactants are still able to penetrate the matrix which is a precondition for applications in catalysis.

Experimental

General

All reactions were performed under an atmosphere of dry argon using Schlenk type glassware. Solvents were distilled from CaH_2 (dichloromethane), sodium/benzophenone ketyl (THF, toluene, diethyl ether), CaO (DMF), $CaCl_2$ (acetone), Mg (methanol), molecular sieves (ethanol, isopropanol), $LiAlH_4$ (n-pentane, n-hexane) under argon prior to use. The reagents $Si(OEt)_4$, $Si(OMe)_4$ und $Cl(CH_2)_3Si(OEt)_3$, OCN-$(CH_2)_3Si(OEt)_3$ as well as di-n-butyltindiacetate were also distilled under argon. Water, acids and bases were degassed and stored under an argon atmosphere. A Heraeus TQ 150 W (Orginal Hanau) high-pressure mercury lamp was applied for the irradiation of the reaction mixtures. $Si(OEt)_4$, $Cl(CH_2)_3$-$Si(OEt)_3$, $Cl(CH_2)_3Si(OMe)_3$, (n-Bu)$_3$P and di-n-butyltindi-

acetate were purchased from Merck, $OCN(CH_2)_3Si(OEt)_3$, from Aldrich, oxirane and $Si(OMe)_4$ from Fluka. N_2O was used as supplied by Messer-Griesheim.

Tricarbonyl[cis,cis-1,3,5-tris(diphenylphosphine)-1,3,5-tris-(hydroxymethyl)cyclohexane]molybdenum (2),[21] [Ir(COD)-Cl]$_2$[40] and [Rh(COD)Cl]$_2$[41] were prepared according to literature procedures. Molybdenum hexacarbonyl was donated by BASF AG.

Solution ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer operating at 250.13, 62.90, 101.26 MHz, respectively. ^1H chemical shifts were referenced to the residual protons of the solvents versus TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplet vs. TMS. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken positive.

Solid-state NMR spectra were obtained on Bruker multi-nuclei spectrometer equipped with wide-bore magnets (DSX 200, 4.7 T; ASX 300, 7.1 T). 100–400 mg of the samples were packed into double-bearing rotors made from ZrO_2. Magic Angle Spinning was applied at spinning frequencies of 4 and 10 kHz (^{13}C), 4 kHz (^{29}Si) as well as 5 and 10 kHz (^{31}P) and at 294 K. The FIDs were accumulated with cross-polarisation (^{13}C, ^{29}Si, ^{31}P) or single pulse excitation (^{29}Si, ^{31}P) using high-power-decoupling in all cases. Frequencies, standards and parameters: ^{13}C: 50.29 and 75.47 MHz [TMS, signal of the carbonyl group of glycin (δ 170.09) as second standard], contact time 2 ms, recycle-delay 2–4 s, typical $\pi/2$ pulse: 3.25 and 5.0 μs, respectively. The cross-polarisation constants T_{PH} were determined by variation of the contact time [ca. 20 experiments]. The relaxation times of the protons in the rotating co-ordination system $T_{1\rho H}$ were measured by direct spin lock–τ–CP experiments.[32] The $T_{1\rho H}$ values were calculated using the Bruker Spectrospin Software SIMFIT. Deconvolution of the NMR spectra resulted from the Bruker-Spectrospin-Software XNMR or WIN-NMR (Gauss line form). The corrected relative intensities of the single species were calculated according to known methods.[31,34] ^{29}Si: 39.75 and 59.60 MHz [Q_8M_8], $\pi/2$ pulse: 3.7 and 5.5 μs, respectively, contact time 3 ms, recycle delay 2 s (CP/MAS) and 30 s (MAS). ^{31}P: 81.00 and 121.49 MHz [85% H_3PO_4, $NH_4H_2PO_4$ (δ 0.8) second standard], $\pi/2$ pulse: 3.7 and 5.6 μs, respectively, contact time 1 ms, recycle delay 2 s (CP/MAS), 5 s (MAS). T_{1P} times were measured according to Torchia.[42] Due to the imperfect measurement conditions as well as inaccuracy of calculations and fits the general error for any value obtained by NMR spectroscopy is reasonably estimated to about 15% at the maximum. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyser.

Preparation of the polyethylene glycol spacers

The synthesis of the polyethylene glycol spacers of compounds $\mathbf{3}_{(P)}$ with degrees of polymerisation $P > 6$ was described earlier.[23] The molybdenum complexes $\mathbf{3}_{(P)}$ where $P = 3$ and 6, respectively, only differ in the work up procedures. After the reaction was completed excess oxirane was removed under reduced pressure. The white precipitate was separated from the reaction mixture, dissolved again in acetone and passed over a short column containing NH_4Cl. The solvent was removed and the residue was dried in vacuo at 60 °C.

$\mathbf{3}_{(3)}$: 907 mg (1.0 mmol) of $\mathbf{2}$, 72 mg (3.0 mmol) of NaH, 1.32 g (30.0 mmol) oxirane. Yield: 0.81 g (78.2%). Number of PEG protons (^1H NMR): 12.

$\mathbf{3}_{(6)}$: 907 mg (1.0 mmol) of $\mathbf{2}$, 72 mg (3.0 mmol) of NaH, 1.98 g (45.0 mmol) oxirane. Yield: 0.87 g (74.1%). Number of PEG protons (^1H NMR): 24.

Introduction of the hydrolysable end groups

Method A (general procedure). After a suspension of $\mathbf{3}_{(P)}$ (258 mg, 0.249 mmol) and NaH (54 mg, 2.241 mmol) in 70 mL

of THF was stirred for 2 h at 80 °C, 357 μL (1.494 mmol) of Cl(CH$_2$)$_3$Si(OEt)$_3$ were added dropwise at room temperature and stirred for 20 h at 60 °C. The reaction mixture was allowed to warm to room temperature, neutralised and separated from precipitated salts by passing the suspension over a column of dry NH$_4$Cl (3 cm). The solvent was removed under vacuum and the oily residue treated with 30 mL of *n*-pentane. The yellow precipitate was separated and washed with *n*-pentane three times and dried under vacuum. Characteristic data for **4$_{(3)}$**: yield: 288 mg (70.0%). IR (KBr, cm^{-1}): 1938, 1849 *v*(CO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 46.7. ^{1}H NMR (acetone-d$_6$): δ 0.54–0.60 [m, SiCH$_2$], 1.17 [t, $^3J_{HH}$ = 7.2 Hz, OCH$_2$C*H$_3$*], 1.55–1.75 [m, SiCH$_2$C*H$_2$*], 1.77–1.93 [m, CH*H*$_e$], 2.44–2.79 [m, CH*H*$_a$], 3.30–3.62 [m, OCH$_2$CH$_2$OCH$_2$CH$_2$], 3.75 [q, $^3J_{HH}$ = 7.2 Hz, OC*H$_2$*CH$_3$], 7.05–7.39 [m, C$_6$H$_5$]. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 7.1 [s, SiCH$_2$], 17.5 [s, OCH$_2$C*H$_3$*], 23.3 [s, SiCH$_2$C*H$_2$*], 30.3 [m, CH$_2$], 39.3 [br s, CP], 57.3 [s, OC*H$_2$*CH$_3$], 67.4–76.7 [m, OCH$_2$-CH$_2$OCH$_2$CH$_2$], 127.5 [s, *meta*-C$_6$H$_5$], 128.9 [s, *para*-C$_6$H$_5$], 136.3 [m, *ipso*-, *o*-C$_6$H$_5$].

Method B (general procedure). A specified amount of **3$_{(P)}$** was dissolved in 10 mL of dry DMF. After stoichiometric amounts (3 equivalents) of 3-(triethoxysilyl)propylisocyanate were added to the yellow solution, the reaction mixture was stirred at 120 °C for 10 h. The reaction mixture was allowed to warm to room temperature. This solution was used for the sol–gel process (see below) or isolated for structural studies. For this the products of the reaction mixture was poured into 50 mL of *n*-hexane. A brownish precipitate formed which was separated from the solution and washed three times with 5 mL of *n*-hexane each.

Characteristic data for **5$_{(0)}$**: 157 mg (0.173 mmol) of 28 μL (0.519 mmol) OCN(CH$_2$)$_3$Si(OEt)$_3$. Yield: 244 mg (85.4%), off white powder. IR (KBr, cm^{-1}): 1938, 1849, 1699 *v*(CO), 1525 *v*(NH). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 46.7. ^{1}H NMR (acetone-d$_6$): δ 0.39–0.62 [m, SiCH$_2$], 1.10 [t, $^3J_{HH}$ = 7.2 Hz, OCH$_2$C*H$_3$*], 1.40–1.60 [m, SiCH$_2$C*H$_2$*], 1.63–1.93 [m, CH*H*$_e$], 2.57–2.88 [m, CH*H*$_a$], 2.95–3.08 [m, NCH$_2$], 3.72 [q, $^3J_{HH}$ = 7.2 Hz, OC*H$_2$*-CH$_3$], 3.81–3.95 [m, CH$_2$O], 6.12 [br s, NH], 6.92–7.52 [m, C$_6$H$_5$]. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 7.9 [s, SiCH$_2$], 18.3 [s, OCH$_2$C*H$_3$*], 23.6 [s, SiCH$_2$C*H$_2$*], 28.3 [m, CH$_2$], 38.9 [br s, CP], 43.7 [s, NCH$_2$], 58.4 [s, OC*H$_2$*CH$_3$], 66.5 [m, CH$_2$O], 127.8 [s, *meta*-C$_6$H$_5$], 129.0 [s, *para*-C$_6$H$_5$], 136.2 [m, *ipso*-, *o*-C$_6$H$_5$], 158.7 [s, CONH]. ^{29}Si CP/MAS-NMR: δ −44.3 (T^0). Calc. for C$_{78}$H$_{108}$MoN$_3$O$_{18}$P$_3$Si$_3$: C 56.82, H 6.60, N 2.55. Found: C 56.54, H 6.71, N 2.55%.

Preparation of the sol–gel processed materials 6$_{(P)}$a–d

Method A (general procedure). Specified amounts (Table 3S†) of **4$_{(P)}$**, Si(OEt)$_4$ and water were dissolved in a minimum of ethanol. The mixture was homogenised by stirring for 30 min in a closed Schlenk tube at room temperature. After a drop of (*n*-Bu)$_2$Sn(OAc)$_2$ had been added the reaction mixtures were heated for 4 h to 60 °C and dried for another 4 h at 60 °C. The accumulated inhomogeneous gel-particles were stirred in *n*-hexane (3 × 3 h in 50 mL) and after drying *in vacuo* (1 h) washed with ethanol, acetone and *n*-hexane (each three times, 10 mL). Finally the products **6$_{(P)}$a–d** were dried for 8 h *in vacuo* at 60 °C. Characteristic spectroscopic data: IR (KBr, cm^{-1}): 1936, 1846 *v*(CO). ^{31}P CP/MAS NMR: δ 45.0 [s]. ^{29}Si CP/MAS NMR (Si substructure): δ −59.7 (T^2), −67.2 (T^3), −92.1 (Q^2), −100.8 (Q^3), −109.2 (Q^4).

Method B (general procedure). To the reaction mixture containing the coupled products **5$_{(0)}$** (see above) specified amounts (0, 3 and 12 equivalents) of tetramethylorthosilicate (TMOS) were added at room temperature under vigorous stirring. The hydrolysis and condensation processes were started by adding the double stoichiometric amount of HCl/water (pH 3) (18, 42

and 114 equivalents). After 2 d stirring the viscosity gradually increased until the gel point was reached. The solvent was removed *in vacuo* and the materials dried at 100 °C. Further condensation steps were initiated by heating the materials to 120 °C *in vacuo* for 12 h. The inhomogeneous compounds were crushed mechanically to powders giving very good yields (Table 4S†). Typical spectroscopic data: IR (KBr, cm^{-1}): 1938, 1849, 1700 *v*(CO), 1525 *v*(NH). ^{31}P CP/MAS NMR: δ 43.9 [s]. ^{13}C CP/MAS NMR: δ 9.0 [CH$_2$Si], 24.3 [*C*H$_2$CH$_2$Si], 27.8 [CH$_2$], 38.8 [CP], 43.0 [NCH$_2$], 62.0, 71.4 [PEG] (66.4 [CH$_2$O] for *P* = 0), 127.9 [*m*-, *p*-C$_6$H$_5$], 137.1 [*ipso*-, *o*-C$_6$H$_5$], 158.7 [CONH] as well as 17.9 [OCH$_2$C*H$_3$*], 58.2 [O*C*H$_2$CH$_3$] for *P* = 0, 9, 120. ^{29}Si CP/MAS NMR: see Table 5S†.

General procedure for formation of polymers 8$_{(P)}$ from 6$_{(P)}$. Suspensions of **6$_{(P)}$a,d** in 50 mL acetone placed in a double-walled Duran Schlenk tube were degassed and 5 ml of (*n*-Bu)$_3$P were added under N$_2$O atmosphere. The vigorously stirred suspensions were cooled to 10 °C and N$_2$O was added (1.3–1.5 bar). The reaction mixtures were irradiated for 30 min with the light of a TQ 150 W (Original Hanau) high-pressure mercury lamp, which was located 5 cm from the Schlenk tube. After complete conversion of the educt (monitored by ^{31}P CP/MAS NMR spectroscopy) the red solution was filtered off and the yellow powder was washed twice with 5 mL of an aqueous solution of K$_2$CO$_3$ (0.05 mmol) and three times each with 10 mL of acetone and *n*-pentane. The material was dried under vacuum. ^{31}P CP/MAS NMR: δ 29.8 [s].

8$_{(90)}$a. A 321 mg (0.059 mmol) sample of **6$_{(90)}$a** was used. Yield: 294 mg (92.0%). ^{31}P CP/MAS NMR: δ; 29.8 [s], $v_{1/2}$ = 134 Hz.

8$_{(150)}$a. A 307 mg (0.039 mmol) sample of **6$_{(150)}$a** was used. Yield: 277 mg (90.1%). ^{31}P CP/MAS NMR: δ; 29.8 [s], $v_{1/2}$ = 170 Hz.

8$_{(150)}$d. A 225 mg (0.026 mmol) sample of **6$_{(150)}$d** was used. Yield: 204 mg (92.3%). ^{31}P CP/MAS NMR: δ; 29.5 [s], $v_{1/2}$ = 86 Hz.

Procedure for 9$_{(150)}$d and 10$_{(150)}$a. To 227 mg (0.035 mmol) of **8$_{(150)}$a** suspended in 35 mL of dichloromethane were added 21.9 mg (0.035 mmol) of [Ir(COD)Cl]$_2$. The yellow suspension was stirred for 30 min and 24 mg (0.07 mmol) of NaBPh$_4$ in 4 mL of dichloromethane was added to the reaction mixture. After stirring for 20 h the product was separated from the solution, washed with acetone and *n*-hexane (each three times, 5 mL) and dried under vacuum. IR (KBr, cm^{-1}): 1415 *v*(C=C). ^{31}P CP/MAS NMR: δ; −7.3 [br s].

Material **9$_{(150)}$d** was prepared according to the same procedure except that the suspension of **8$_{(150)}$d** was added to the solution of [Rh(COD)Cl]$_2$ in dichloromethane. IR (KBr, cm^{-1}): 1462 *v*(C=C). ^{31}P CP/MAS NMR: δ; 38.4 [br s].

Acknowledgements

References

1 H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.*, 2001, **101**, 953.
2 A. J. Sandee, D. G. I. Petra, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Chem. Eur. J.*, 2001, **7**, 1202.

3 N. E. Leadbeater and M. Marco, *Chem. Rev.*, 2002, **102**, 3217.
4 C. E. Song and S. G. Lee, *Chem. Rev.*, 2002, **102**, 3495.
5 A. P. Wight and M. E. Davis, *Chem. Rev.*, 2002, **102**, 3589.
6 P. M. Price, J. H. Clark and D. J. Macquarrie, *J. Chem. Soc., Dalton Trans.*, 2000, 101.
7 F. R. Hartley, *Supported Metal Complexes. A New Generation of Catalysts*, D. Reidel Publishing Company, Dordrecht, 1985.
8 D. Rechavi and M. Lemaire, *Chem. Rev.*, 2002, **102**, 3467.
9 *Applied Honogeneous Catalysis With Organometallic Compounds – A Comprehensive Handbook in Two Volumes*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 1996.
10 E. Lindner, M. Kemmler, T. Schneller and H. A. Mayer, *Inorg. Chem.*, 1995, **34**, 5489.
11 E. Lindner, T. Schneller, F. Auer and H. A. Mayer, *Angew. Chem., Int. Ed.*, 1999, **38**, 2154.
12 Z. L. Lu, E. Lindner and H. A. Mayer, *Chem. Rev.*, 2002, **102**, 3543.
13 A. Baiker, J. D. Grunwaldt, C. A. Muller and L. Schmid, *Chimia*, 1998, **52**, 517.
14 N. Huesing and U. Schubert, *Angew. Chem., Int. Ed.*, 1998, **37**, 23.
15 J. J. E. Moreau and M. W. C. Man, *Coord. Chem. Rev.*, 1998, **180**, 1073.
16 U. Schubert, C. Egger, K. Rose and C. Alt, *J. Mol. Catal.*, 1989, **55**, 330.
17 U. Schubert, *New J. Chem.*, 1994, **18**, 1049.
18 S. P. Watton, C. M. Taylor, G. M. Kloster and S. C. Bowman, *Prog. Inorg. Chem.*, 2003, **51**, 333.
19 J. Büchele and H. A. Mayer, *Chem. Commun.*, 1999, 2165.
20 P. Stößel, W. Heins, H. A. Mayer, R. Fawzi and M. Steimann, *Organometallics*, 1996, **15**, 3393.
21 P. Stößel, H. A. Mayer, C. Maichle-Mössmer, R. Fawzi and M. Steimann, *Inorg. Chem.*, 1996, **35**, 5860.
22 H.-G. Elias, *Makromoleküle*, Hüthig & Wepf, Heidelberg, 1981.
23 P. Stößel, H. A. Mayer and F. Auer, *Eur. J. Inorg. Chem.*, 1998, 37.
24 J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. Chem. Soc.*, 1957, **79**, 974.
25 L. Giraud and T. Jenny, *Organometallics*, 1998, **17**, 4267.
26 S. Sakaki, N. Mizoe and M. Sugimoto, *Organometallics*, 1998, **17**, 2510.
27 E. Lindner, M. Kemmler, H. A. Mayer and P. Wegner, *J. Am. Chem. Soc.*, 1994, **116**, 348.
28 F. Hoehn, E. Lindner, H. A. Mayer, T. Hermle and W. Rosenstiel, *J. Chem. Inf. Comput. Sci.*, 2002, **42**, 36.
29 As the polycondensation of the silanol groups generally does not proceed quantitatively there is always a deviation from the ideal stoichiometric composition. This is expressed in the labelling scheme of the silicon atoms. Capital letters are used to characterise silicon atoms and refer to the number of reactive hydrolysable groups, *e.g.* T stands for trifunctional and Q for quadrifunctional silicon. Thus T and Q type silicons are bound to three and four, respectively, hydrolysable alkoxy groups without considering the degree of hydrolysis. After condensation the number of Si–O–Si bonds formed is indicated by superscripts *n*, ranging in integers from zero (no condensation) to the number of alkoxy groups originally attached to the observed atom (complete condensation). E. Lippmaa, M. Mägi, A. Samson, G. Engelhardt and A.-R. Grimmer, *J. Am. Chem. Soc.*, 1980, **102**, 4889.
30 W. Kolodziejski and J. Klinowski, *Chem. Rev.*, 2002, **102**, 613.
31 R. K. Harris, *Analyst*, 1985, **110**, 649.
32 M. Alla and E. Lippmaa, *Chem. Phys. Lett.*, 1976, **37**, 260.
33 R. A. Komoroski, A. J. Magistro and P. P. Nicholas, *Inorg. Chem.*, 1986, **25**, 3917.
34 R. Voelkel, *Angew. Chem.*, 1988, **100**, 1525.
35 G. Engelhardt and D. Michel, *High Resolution Solid State NMR of Silica and Zeolites*, John Wiley & Sons, New York, 1987.
36 J. Schaefer, E. O. Stejskal and R. Buchdahl, *Macromolecules*, 1977, **10**, 384.
37 W. S. Veeman, E. M. Menger, W. Ritchey and E. de Boer, *Macromolecules*, 1979, **12**, 924.
38 M. J. Sullivan and G. E. Maciel, *Anal. Chem.*, 1982, **54**, 1606.
39 C. A. Fyfe, *Solid State NMR for Chemists*, CRC Press, Guelph, ON, 1984.
40 J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg. Synth.*, 1974, **73**, 18.
41 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1979, **19**, 218.
42 A. D. Torchia, *J. Magn. Reson.*, 1978, **30**, 613.