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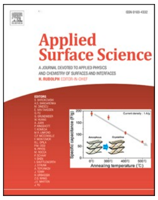

Full Length Article

Creating Well-Defined monolayers of phosphine linkers incorporating ethoxysilyl groups on silica surfaces for superior immobilized catalysts

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ABSTRACT

Many applications of catalysts immobilized on solid supports like silica via bifunctional phosphine linkers are still hampered by their decomposition, leaching, agglomeration, and uncontrolled nanoparticle formation, all of which change their activities and selectivities. In general, the success of an immobilized catalyst is crucially dependent on the linker and its attachment to the oxide support. In this contribution, an improved method for covalently binding phosphine linkers to silica via ethoxysilane groups is described. This method leads to well-defined sub-monolayers of linkers on silica surfaces without cross-linking of the linkers, which typically leads to clogged pores and metal agglomeration during catalysis, thus entailing less active and selective catalysts. The novel immobilization method has been supported by multinuclear classical CP/MAS solid-state NMR spectroscopy, as well as suspension NMR of slurries. It has been demonstrated by TEM that nickel complexes coordinated by immobilized phosphine linkers in a well-defined sub-monolayer coverage do not form larger aggregates or nanoparticles during the catalytic cyclotrimerization of phenylacetylene under various conditions, in contrast to analogous complexes in homogeneous catalytic runs.

1. Introduction

Alkoxysilanes are important chemicals for industrial scale use, and for applications in academia. [1–3] They can be found in such far-ranging areas as restoration and surface protection of sculptures, [1,2] sol–gel processes, [1,2] degradable polymers, [3] and for immobilizing diverse species on solid supports. [4] In particular, immobilized catalysts make ample use of linkers featuring an intramolecular ethoxysilane group for anchoring. [5–9] The metal centers are most often coordinated by phosphine groups within the linkers. [10–16] The ethoxysilane and phosphine groups are typically separated by methylene chains $(CH_2)_n$ of variable length. [6,9,14] In this study, the linkers $(EtO)_3Si(CH_2)_{2,3}PPh_2$ have been employed. Linker-immobilized catalysts are of enormous interest because they can be recovered easily by settling from reaction mixtures and reused, while remaining as active and selective as their homogeneous analogs. [10–15] However, their activity, selectivity, and longevity crucially depend on the surface coverage [17] and the quality of anchoring. [6] The goal is a well-defined distance between the metal centers on the surface to prevent premature deactivation by dimerization and to have a durable anchoring to the surface to curb leaching of the linker and catalyst. Therefore, reactions of ethoxysilane groups with solid oxide supports, in particular with silica [1–4] surfaces, have been investigated previously. [18,19].

Silica offers many advantages. For example, in organic solvents it is chemically and thermally inert. Silica is mechanically stable and robust and can be stirred in a Schlenk flask for days without being ground into smaller particles. This is important regarding the separation and reuse of the support after the reaction by settling and decanting the supernatant. In case the support particles become too small they will remain suspended in the solvent and not settle. Ultracentrifugation is an option in such cases, but renders the separation of the support from the reaction mixture tedious. [20] The particle size distribution that is most favorable for immobilized catalysts is 0.063–0.200 mm, corresponding to large grains that settle within minutes from organic solvents. The large particle size also allows for easy handling of the materials in a nitrogen stream or a glovebox, and filling rotors for solid-state NMR analysis poses no problem, as compared to powders of small particles like aerosil that are hard to contain. Suppliers also offer a large variety of well-defined silica with different pore sizes and specific surface areas. Regarding the pore sizes, it is important that they are large enough to allow for catalysts and substrates to enter and reaction products to exit without substantial diffusion delays. Since the most powerful method applied in the presented study is the moderately sensitive solid-state NMR, [11,21–23] the largest possible specific surface area that allows for maximal loading with a reactive species and minimal bulk is desired. Silica with an average pore size of 40 Å and a specific surface area of 750 m^2/g has proven to be a favorable combination of large pores and surface area while retaining the mechanical stability. In order to create reproducible surface characteristics, all silica batches have been dried at 200 °C for 12 h to remove adsorbed water and condense vicinal silanol

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groups. [24].

Over the years, we have obtained, characterized, and studied many superior silica-immobilized catalysts with unprecedented lifetimes and activities. Based on a deeper understanding of fundamental processes taking place at the liquid/solid interface, numerous crucial improvements could already be implemented. [9–15] However, many applications of immobilized catalysts are still hampered by their decomposition, [25,26] leaching, [6] agglomeration, and uncontrolled nanoparticle formation, [14,27,28] all of which change their activities and selectivities. [12] In general, the success of an immobilized catalyst is crucially dependent on the linker and its attachment to the oxide support. One catalytic reaction that is particularly sensitive with respect to metal aggregation and nanoparticle formation is the nickel-catalyzed cyclotrimerization of phenylacetylene. [12,28–31] However, this reaction is an important C—C bond formation reaction that was also the focus of increased attention recently. [29] Therefore, and because there is already expertise in our group, [10,12,28] this reaction has been chosen as a sensitive model system for the improved linker attachment procedure described in the following.

One particular problem arises when triethoxysilyl groups cross-link and form oligomeric strings that detach from the surface (Fig. 1). This surface-detached growth typically leads to clogged pores and metal agglomeration during catalysis, thus entailing less active and selective catalysts. The cross-linking of the ethoxysilanes tends to occur when the immobilization of triethoxysilanes is performed in solvents that are not dried rigorously. In academic settings, solvents are usually dried by boiling them over Na or Na/K alloys in distills. While in a university laboratory this is a standard procedure, due to safety issues on a larger scale in industry, this is not appropriate. An additional issue arises for commercial products when cyclic siloxanes might form due to cross-linking during the immobilization process because they have recently been banned from large scale products due to their endocrine disrupting properties. [32] In general, a procedure is needed that prevents the cross-linking of ethoxysilanes on silica surfaces and produces well-defined monolayers.

Therefore, an improved method for covalently binding ethoxysilanes to mesoporous silica has been investigated. Supporting this endeavor, the phosphine groups in the linkers $(EtO)_3Si(CH_2)_3PPh_2$ (**1**) and $(EtO)_3Si(CH_2)_2PPh_2$ (**2**) conveniently serve as tags facilitating the characterization of the materials. The novel approach described here is based on an adsorption step, followed by heating of the adsorbed linker in the absence of a solvent. This method leads to well-defined mono- or, if desired, sub-monolayers of the linkers on silica surfaces without decomposition or cross-linking of the linkers.

The novel immobilization method has been supported by characterizing the solid materials with multinuclear classical CP/MAS (cross-polarization with magic angle spinning) and MAS NMR spectroscopy, [11,18,21–23] and wideline NMR of static samples of slurries in solvents. [33,34].

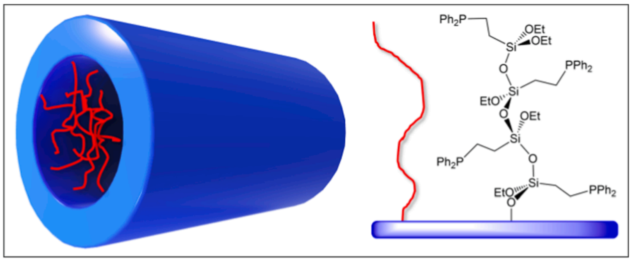

Fig. 1. Clogged pore due to surface-detached cross-linking.

2. Results and discussion

2.1. *Ethoxysilanes incorporating phosphine groups*

Previous studies of the reactions of ethoxysilanes with oxide supports made use of Me_3SiOEt [18] and $(EtO)_3SiCH{=}CH_2$. [19] Therefore, only ^{29}Si and ^{13}C NMR could be employed for characterizing the surface-bound species. Both nuclei have intrinsic low abundance and the dilution on the silica surface additionally exacerbates the measurement challenge. While the recently developed DNP (dynamic nuclear polarization) techniques improve this situation, [35,36] the required instrumentation is not available in all NMR facilities. Fortunately, by using ethoxysilanes incorporating a phosphine group, the favorable nucleus ^{31}P can additionally be used for characterization. ^{31}P NMR spectroscopy also allows the study of dynamic effects in the presence of a solvent.

In this contribution, we demonstrate how to prevent cross-linking and linear growth that detaches from the surface (Fig. 1). In principle, this can be achieved by using monoethoxysilanes, such as $EtOMe_2$-$SiC_6H_4PPh_2$ [37] or $EtOSi(CH_2PPh_2)_3$. [8] However, the former is not trivial to synthesize and purify, [37] while the latter suffers hydrolysis of one Si-C bond during immobilization. [8] Therefore, more conventional and robust ethoxysilanes have been used. The linker $(EtO)_3Si(CH_2)_3PPh_2$ (**1**) has been synthesized from Ph_2PCl by reaction with Li to obtain Ph_2PLi and subsequent quenching with $Cl(CH_2)_3Si(OEt)_3$ in high yields. [6] Linker $(EtO)_3Si(CH_2)_2PPh_2$ (**2**) is commercially available and has been used as obtained.

With respect to immobilized homogeneous catalysts, the reaction of the ethoxysilane groups with silica is crucial for irreversibly immobilizing the phosphine linkers and therewith the catalysts. Therefore, this reaction has been studied earlier. [18,19] The two main outcomes of these studies are that in polar, strongly adsorbing solvents ethoxysilanes cannot reach the surface and are consequently not bound irreversibly in a covalent manner, even at high temperatures. Subsequent leaching of the metal complex together with the linker is inevitable. [19] This outcome can be prevented by immobilizing the linkers using toluene or heptane as the solvent. Another well-known problem arises when ethoxysilanes are reacted with silica in the presence of traces of moisture. In this case, the ethoxysilanes can cross-link and form siloxane growth that is detached from the silica surface ("snotting", Fig. 1). This scenario entails a cohort of problems during catalysis, like clogged pores that slow the diffusion of the substrate to the catalyst, or fast agglomeration and deactivation of the metal complexes. Therefore, in this contribution the emphasis will be on improving and controlling the reaction of the ethoxysilane groups of the linkers **1** and **2** with a silica surface.

2.2. *Characterization of Surface-Bound species*

While molecular species can be fully characterized by established methods, including single crystal X-ray structures, the most powerful method for characterizing surface-bound species is solid-state NMR spectroscopy using the techniques mentioned above. An additional technique, suspension NMR spectroscopy [6] of the modified silica in a slurry with a solvent, but without sample spinning, can also be applied. The advantage of this method is that it allows to distinguish between adsorbed and covalently bound species. [6] Most importantly, all phosphine linkers and catalysts can be investigated by ^{31}P suspension NMR with respect to their structures and possible dynamic effects. Additionally ^{29}Si CP/MAS is applied, for example, to prove that the linker remains intact during immobilization, coordination and catalysis. [19,37] Importantly, it also gives insight into the number of Si-O-Si bonds formed between the ethoxysilanes and the silica surface. [6,19] ^{31}P CP/MAS indicates any oxidation of the phosphines and confirms the expected loss of the PPh_3 ligand when creating the immobilized Ni catalyst by ligand exchange with $(CO)_2Ni(PPh_3)_2$. Both methods will also prove the coordination of all metal complexes, and their potential migration across the surface, as described previously for Pd(II) complexes. [15,16] Although nanoparticles themselves are not amenable to solid-state NMR measurements, ^{31}P CP/MAS detects uncoordinated, surface-bound phosphines that are generated in case the metals agglomerate. All catalysts have been monitored with TEM images before, during, and after catalysis runs. This method allows to determine the presence and size distribution of nanoparticles and clusters, even though they reside within the silica pores. [14,27,28].

2.3. Immobilization and mobilities of Surface-Bound linkers

The linkers **1** and **2** have been immobilized on silica to give **1i** and **2i** using toluene as the solvent according to the established method. [6,19] The structure determination and check for side-products like phosphine oxides has been performed with the classical CP/MAS technique using dry samples. Hereby, the mobility of linker-bound surface species is limited. However, in the presence of a solvent, HRMAS (high-resolution magic angle spinning in the presence of a solvent) techniques allow the investigation of mobilities, such as metal migration over a phosphine linker "lawn". [15,16] In addition, the measurement of linker-modified silica without MAS, but in the presence of a solvent is often beneficial. [6] Most importantly, suspension NMR spectroscopy of static samples, wetted by a favorable solvent like toluene or acetone, can easily distinguish merely adsorbed or dissolved linkers from those covalently bound. In the following, suspension NMR measurements are described that have been performed on a routine solution NMR spectrometer using acetone as the suspension medium.

In order to obtain precise data, spectrum processing parameters like linebroadening factors and phase correction routines have been optimized for high-quality Lorentz fits of the broad signals. This is important because the halfwidths of the signals are in the kHz range and deviations can be large in case the fitting procedure is performed in an imprecise manner. A representative example of a deconvolution and line fitting procedure is displayed in Fig. 2. The narrow ^{31}P suspension NMR signal of translationally mobile, surface-adsorbed phosphine linker **1** (Fig. 3, top) is overlapping with the resonance of the covalently bound linker **1i** (Fig. 3, bottom). Such analyses are important to determine the degree of linker leaching and to confirm that all linker molecules are bound in a covalent manner. Furthermore, due to the mobility of adsorbed phosphine linkers, their signal intensity is reduced substantially when applying CP/MAS methods.[18] Therefore, wideline ^{31}P suspension NMR of static samples is an indispensable tool to investigate the status of linker immobilization.

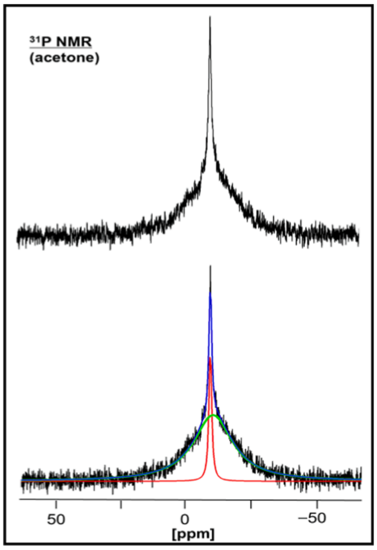

Fig. 2. Deconvolution of overlapping NMR signals from a suspension of linker-modified silica in acetone (top). A narrow signal is found for a translationally mobile adsorbed linker **1** (bottom, red line) overlapping with the broad resonance of the less mobile covalently bound phosphine **1i** (bottom, green line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

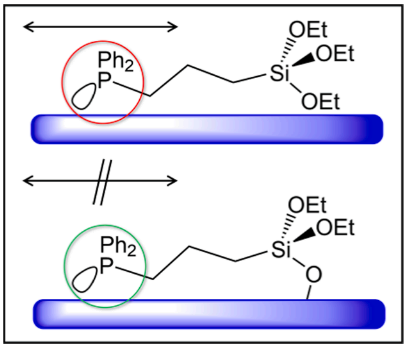

Fig. 3. Surface-adsorbed, translationally mobile phosphine **1** (top) and covalently bound, immobilized linker **1i** (bottom).

Next, the halfwidths of the ^{31}P suspension NMR signals of the immobilized linkers **1i** and **2i** were studied and correlated with their surface coverage and linker length (Table 1, Fig. 4). Hereby, crucial results have been obtained. First, the longer the linker chain, the less mobile the phosphines are in the presence of a solvent, as manifested by the larger signal halfwidths. This result contradicts earlier HRMAS NMR studies of phosphine linkers incorporating very long (C_{4-11}) methylene chains, where longer linkers showed narrower NMR signals. [14,27] It should also be noted that by using ^{31}P suspension NMR of static samples, for **1i** and **2i** the effect of the different mobilities is visible for all surface coverages, even though the difference in chain length is only one methylene group (Fig. 4).

Furthermore, in contrast to anticipation, diluting the linker molecules on the surface, from maximal surface coverage M to one tenth of M, leads to a broadening of the signals (Fig. 4). In principle, the additional space between the linkers on the surface should lead to their increased mobility and, therefore, narrower signals. However, this effect is obviously overridden by the enhanced probability of the phosphine groups to strongly interact with the silica surface via the free electron pair when the linkers are arranged in a blanket- instead of a brush-type manner (Fig. 3, bottom). This adsorption of the phosphines also explains why **1i** is less mobile than **2i**. The latter is too short and rigid to allow for "bending down" of the phosphine group to the surface and in this way retains higher mobility.

In order to prove this hypothesis, the phosphine groups of **1i** and **2i** were transformed into the borane adducts **1i•BH$_3$** and **2i•BH$_3$** by reaction with $H_3B{\cdot}SMe_2$. All immobilized linkers are accessible to the borane, as the ^{31}P NMR spectra before and after complete reaction with the protecting group prove (Fig. 5). The free electron pairs at phosphorus are now masked and can no longer interact with the surface. Indeed, contemplating M/2 to M/10 for the borane adducts of the surface-bound linkers, the linewidths of the ^{31}P suspension NMR signals show a much weaker correlation with the surface coverage (Table 1,

Table 1
^{31}P Suspension NMR signal halfwidths $\Delta\nu_{1/2}$ (kHz) of **1i**, **2i**, **1i•BH$_3$**, and **2i•BH$_3$** in acetone. M denotes the maximal surface coverage, as described in the Experimental Section. A linebroadening value of 100 Hz was applied prior to the line fitting procedure.

^{31}P NMR	$\Delta\nu_{1/2}$ (kHz)			
Surface Coverage	1i	2i	1i•BH$_3$	2i•BH$_3$
M	2.90	2.83	3.00	3.30
M/2	3.17	2.93	2.79	3.58
M/4	3.39	3.34	2.89	3.73
M/10	3.69	3.50	2.99	3.72

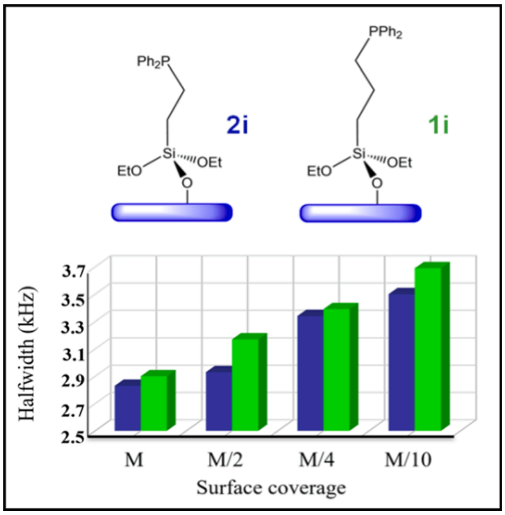

Fig. 4. ^{31}P Suspension NMR signal halfwidths of static samples of the immobilized linker phosphines **1i** and **2i** in the presence of acetone. M stands for maximal surface coverage.

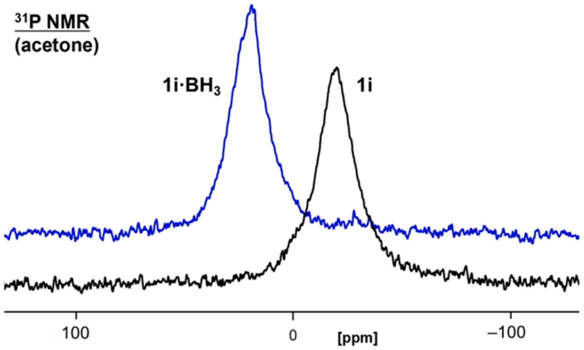

Fig. 5. ^{31}P Suspension NMR signals of static samples containing immobilized **1i** (-19.2 ppm) and its borane adduct **1i•BH$_3$** (21.6 ppm) in the presence of acetone.

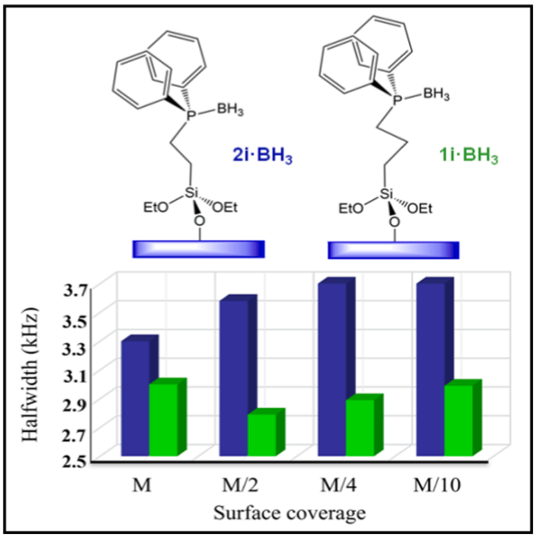

Fig. 6. ^{31}P Suspension NMR signal halfwidths of static samples containing the borane adducts of the immobilized phosphines **1i•BH$_3$** and **2i•BH$_3$** in the presence of acetone. M stands for maximal surface coverage.

Fig. 6). Additionally, the longer linker chain of **1i•BH$_3$** now results in substantially smaller halfwidths than **2i•BH$_3$** for all surface coverages. The borane adduct formation prevents the phosphine from interacting with the surface and the longer alkyl chain of the linker **1i•BH$_3$** allows for increased mobility in the suspension medium.

Contemplating the ^{31}P suspension NMR halfwidths for the maximal surface coverage M, they deviate from the trend observed for M/2 to M/10 for both borane-masked linkers **1i•BH$_3$** and **2i•BH$_3$** (Fig. 6). Furthermore, the T_1 relaxation time values for the surface-bound linkers with maximal surface coverage M assume a broad range from milliseconds to several seconds. This means that each signal is composed of resonances from an infinite number of similar species. These species display starkly different degrees of mobilities for both **1i•BH$_3$** and **2i•BH$_3$**, which results in vastly different T_1 times. This observation is independent of the chain length and therefore has to originate from the silane moiety of the linkers. Most probably, cross-linking prior or during immobilization with off-surface growth is the culprit (Fig. 7). Since maximal surface coverage is often preferred, e.g. for immobilized catalysts, in order to have minimal bulk of the support material, next a method for reducing this off-surface cross-linking is described.

2.4. *Solvent-Free immobilization to prevent Cross-Linking*

The conventional way of immobilization by heating ethoxysilanes with silica in a solvent typically leads to some degree of cross-linking of the triethoxysilanes. Cross-linking does not only occur among covalently surface-bound ethoxysilanes, but also between surface-bound silanes and molecules in solution, leading to surface-detached growth (Fig. 7). The cross-linking is due to traces of water in the used solvent that may also stem from the silica surface. Furthermore, the hydrolysis/condensation can already take place in solution, and the growth can continue after a covalent bond is formed with the surface. The solvent enables this growth by allowing the ethoxysilanes to move to the off-surface cross-linking site and "pile on". Besides the described dimerization and deactivation of bound catalysts, one direct indicator that such cross-linking takes place is the fact that a broad range of different T_1 relaxation times is found in ^{31}P suspension NMR, indicating nuclei with very

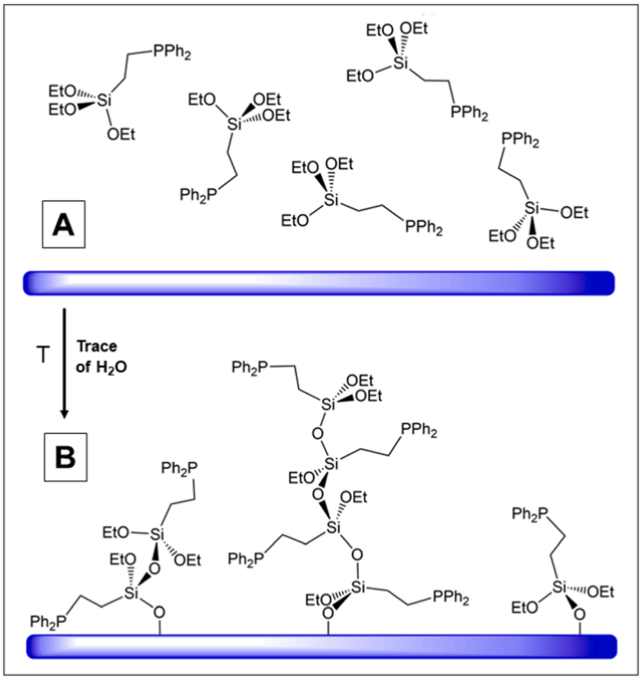

Fig. 7. When ethoxysilanes are heated with silica in a solvent (**A**), due to traces of water, surface-detached cross-linked ethoxysilanes form (**B**).

different mobilities, as discussed for the borane adducts above. Furthermore, the ^{31}P suspension NMR signals do no longer allow a clear deconvolution (Fig. 2) when the signals are composed with contributions of many phosphines with various mobilities.

In order to prevent the described cross-linking scenario of the linkers that is detrimental, for example, to any future immobilized catalysts, a new method has been employed. This method makes use of the fact that at ambient temperature ethoxysilanes do not react with the silica surface, but only get adsorbed (Fig. 8, top). [18,19] This can also be proven by mixing the ethoxysilanes with silica in the absence of a solvent. The ethoxysilanes spread out on the surface, as previously described for phosphine oxides, [38–40] alkanes, [41] and metallocenes. [41–46] Furthermore, merely adsorbed linker molecules can quantitatively be washed off of the silica surface with a polar solvent like THF. However, the solvent-free adsorption process is slow, and therefore the linkers **1** and **2** have been dissolved in sub-monolayer amounts in toluene and combined with silica. After removal of the solvent, the linkers are spread out on the surface, as displayed in Fig. 8. The linkers do not stack on top of each other due to the strong interactions with the surface. Besides the previously described interactions of the lone pair at phosphorus with the surface, methylene chains are bound to silica via van der Waals interactions, as demonstrated for cyclododecane earlier. [41] Ethoxy groups can also adsorb on silica surfaces via hydrogen bonding, as shown for ethanol previously. [18].

When the silica with adsorbed linkers is heated to 70 °C for 42 h, the adsorbed ethoxysilanes form covalent bonds with the surface (Fig. 9). Since the adsorbed linker molecules are spread out across the dry surface and cannot float on top of each other during the heating phase, a well-defined sub-monolayer of covalently surface-bound linkers is obtained (Fig. 9).

The solid-state NMR spectra of dry samples of silica with adsorbed and covalently bound linker prove that this method works as described (Fig. 10). The adsorbed linker **2** shows the typical narrow ^{31}P NMR signal with a halfwidth of only 270 Hz, mostly due to its translational mobility across the silica surface. [38–46] The mobility partially averages out anisotropic interactions present in the solid state. Upon heating the sample in the absence of a solvent, the linewidth increases to 540 Hz because there is no longer any translational mobility of the covalently bound linker on the surface. At the same time, the Chemical Shift Anisotropy (CSA) increases, as the emerging rotational sidebands indicate (Fig. 10, top). The isotropic ^{31}P chemical shift changes from −10.4 to −9.6 ppm. It is noteworthy that, as an additional bonus of the method, no phosphine oxides [38–40] or phosphonium salts [26] form during the solvent-free heating of the sample. Ethylphosphonium salts come into existence when phosphines take up an ethyl group from the ethoxysilane group of another linker molecule. [26] Spreading out the linker phosphines on the surface prior to heating the sample efficiently prevents this detrimental side-reaction from taking place.

Further proof for the adsorption/covalent binding sequence has been derived from the ^{29}Si MAS spectra of surface-adsorbed **2** and covalently bound linker **2i** (Fig. 11). The adsorbed linker shows one narrow signal at −43 ppm, which lies in the $\delta(^{29}\text{Si})$ region for triethoxyalkylsilanes in solution. The small halfwidth of 120 Hz again originates from the translational mobility of the adsorbed silanes. After heating the dry material to 70 °C for 42 h, one siloxane bond to the silica surface forms (Fig. 11). The characteristic chemical shift of about −49 ppm proves the presence of one Si-O-Si bridge. [6,19] Heating the dry sample to 180 °C for an additional 12 h leads to the selective formation of two siloxane bridges to the support. The characteristic $\delta(^{29}\text{Si})$ for this species of about −60 ppm is found in the ^{29}Si MAS spectrum. [6,19] In contrast to this, immobilizing linker **2** in the conventional way with toluene as the solvent results in the typical random distribution of linkers bound by one, two, or three siloxane bridges. [6,19] Hereby, the latter most probably stems from cross-linking between ethoxysilane groups. Regarding the ^{29}Si MAS measurement technique combined with ^{1}H high-power decoupling, applied for both spectra in Fig. 11, it is noteworthy that mobile species do not profit from cross-polarization (CP) and their signals suffer substantial intensity loss. This has been demonstrated earlier for ^{13}C MAS and CP/MAS spectra of silica-adsorbed, mobile ethanol. [18] Accordingly, recording the spectrum of adsorbed **2** with ^{29}Si CP/MAS did not result in a convincing signal, while the resonance of covalently bound **2i** was enhanced substantially. In order to achieve comparability of both samples, we recorded both spectra displayed in Fig. 11 with MAS only.

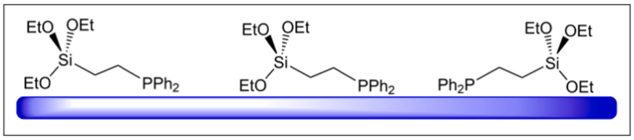

Fig. 8. Linker **2**, surface-adsorbed in a sub-monolayer.

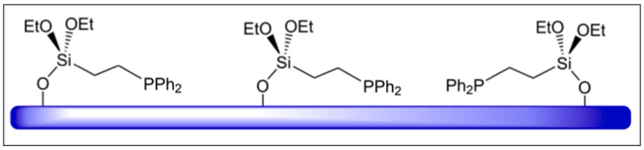

Fig. 9. Well-defined sub-monolayer of covalently bound linker **2i**.

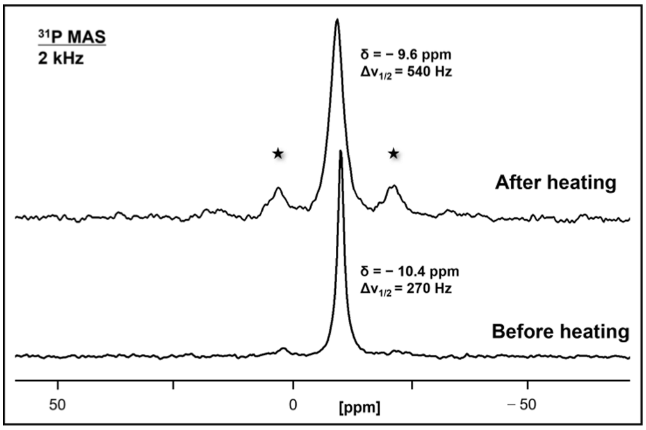

Fig. 10. ^{31}P MAS spectra of **2** adsorbed on the silica surface (bottom) and covalently bound linker **2i** (top). Asterisks denote rotational sidebands of the signal.

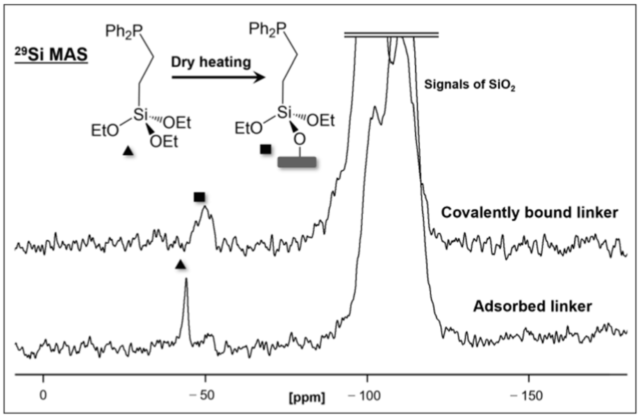

Fig. 11. ^{29}Si MAS spectra of adsorbed **2** (bottom) and covalently bound linker **2i** (top). The broad signals between −100 and −120 ppm stem from the silica support.

The solvent-free immobilization after adsorption and solid-state

NMR characterization of the obtained material has also been performed for linker **1** and the results show that the method is generally applicable to various phosphine linkers incorporating ethoxysilane groups. It also allows the creation of monolayers without surface-detached cross-linking. The well-defined mono- and sub-monolayers of phosphine linkers on silica surfaces are now ready to coordinate to metal complexes and keep them at a distance that prevents dimerization or agglomeration. Furthermore, the catalysis results will be more meaningful because the rate limiting step is no longer diffusion of the substrate through a clogged pore (Fig. 12).

2.5. Nickel catalysts for the cyclotrimerization of alkynes

As a probe to test the superior linker-modified silica, the nickel-catalyzed cyclotrimerization of phenylacetylene has been investigated. This reaction offers many advantages. It proceeds at moderate temperatures and ambient pressure, while only one substrate and no base or co-catalyst are needed. [10,12,28–31] Furthermore, the Ni catalysts are inexpensive compared to Rh or Pd catalysts and no gases and ensuing diffusion effects are involved, as e.g. in hydrogenation. [13,14,17,27] The linker-immobilized Ni catalysts are diamagnetic and CP/MAS analysis is easy due to the narrow lines. [10,12,28–31] Furthermore, the reaction products can be quantified for all species, molecular catalysts, Ni SACs, [31,47–50] and nanoparticles. [28,31,51] Immobilized nickel carbonyl catalysts have been chosen for the purpose of testing whether the well-defined linker arrangement on the surface prevents metal aggregation because they are prone to nanoparticle formation. [12,28,31] The creation of nickel nanoparticles during the cyclotrimerization of phenylacetylene was expected to be diminished when using linkers bound to the surface by the new adsorption-dry heating process. Nanoparticle formation has previously been detected by the loss of selectivity in the course of several hours during the first catalytic run and in consecutive recycling steps. [12] While pristine homogeneous and molecular immobilized nickel catalysts yield 1,2,4- and 1,3,5-triphenylbenzene in a molar ratio of approximatelty 5: 1, aged catalyst, composed mainly of nanoparticles, produce a 1: 1 ratio of the cyclotrimers. [12] The nanoparticle formation originating from $(Ph_3P)_2Ni(CO)_2$ in homogeneous catalytic runs has also been proven by TEM. [28].

In order to check whether the well-defined monolayer of linkers without cross-linking can prevent nanoparticle formation, a nickel carbonyl complex has been immobilized by ligand exchange of **2i** with $(Ph_3P)_2Ni(CO)_2$ as described earlier. [12,37] The complete exchange is proven by the change of $\delta(^{31}P)$ from −9 ppm for **2i** to 31 ppm for **2i-Ni** $\mathbf{(PPh_3)(CO)_2}$ in the CP/MAS spectrum. During the cyclotrimerization of phenylacetylene that was carried out according to the standard procedure, [12] potential nanoparticle formation was monitored by TEM during the first and consecutive runs. No nickel nanoparticles or aggregates larger than 1 nm have been detected in any of the TEM images. Fig. 13 displays two representative images from different catalyst samples.

Since the silica background of the measurement leads to a “grainy” appearance of the image, a standard sample has been prepared to demonstrate that nanoparticles would indeed be well visible in the images. For this purpose, commercially obtained nickel nanoparticles with 20 nm diameter were suspended in toluene and applied to silica. After removal of the solvent the TEM image clearly showed the nanoparticles (Fig. 14). Therefore, it can be concluded that creating well-defined mono- and sub-monolayers of phosphine linkers on silica surfaces without off-surface cross-linking successfully prevents nickel nanoparticle formation.

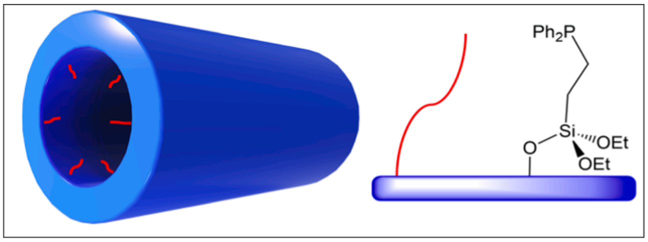

Fig. 12. Well-defined sub-monolayer of phosphine linker **2i** within an open pore of silica.

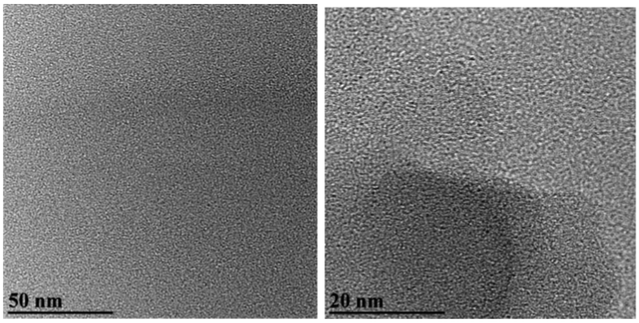

Fig. 13. Representative TEM image of an immobilized nickel catalyst using **2i** with a well-defined monolayer of phosphine linkers.

3. Conclusion

It has been demonstrated in this contribution that propagation of alkoxysilane cross-linking away from the surface of silica can be prevented by an improved immobilization strategy. By first adsorbing the ethoxysilanes and allowing them to spread out on the surface prior to heating to form the covalent linkage to the support, a well-defined monolayer, or sub-monolayers if desired, can be created. The adsorption process followed by heating to create the covalent bond to the surface has been proven by classical multinuclear CP/MAS, MAS, and suspension NMR techniques. A nickel catalyst has been bound to the well-defined immobilized phosphine linkers and monitored for nanoparticle formation during the catalytic cyclotrimerization of phenylacetylene. The TEM images obtained after multiple catalytic runs under various conditions proved that no nanoparticles or larger nickel aggregates formed when phosphine linkers on silica in well-defined mono- and submonolayers without off-surface cross-linking were applied. Detailed studies including turnover rates, yields, and selectivities for homogeneous, dry-immobilized, and conventionally solvent-immobilized nickel catalysts will be communicated in a future contribution. Successfully preventing nanoparticle formation due to the homogeneous linker distribution on the support surface without cross-linking represents the most beneficial step into the direction of recyclable immobilized catalysts with improved long-term selectivity and longevity.

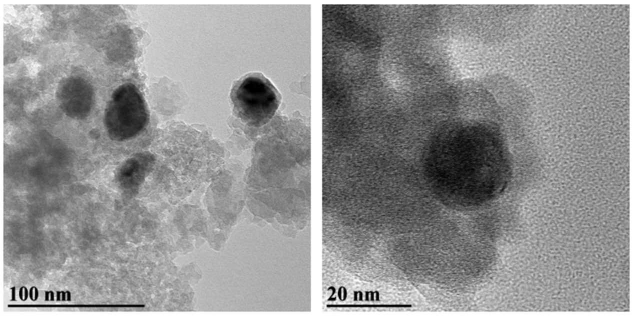

Fig. 14. TEM image of a standard sample generated applying 20 nm nickel particles to silica.

4. Experimental Section

4.1. Materials

The silica (Silicycle, 40 Å average pore diameter, 0.06–0.2 mm average particle size, specific surface area 750 m^2/g) was dried *in vacuo* at 200° C for 12 h to remove adsorbed water and condense vicinal surface silanol groups. [15,43].

4.2. Instrumentation and measurements

The ^{31}P wideline NMR spectra of static samples in the presence of acetone were recorded on a Bruker Avance NEO 400 instrument with a recycle delay of 200 ms. Neat Ph_2PCl ($\delta(^{31}P) = +81.92$ ppm) in a capillary centered in the 5 mm NMR tubes was used for referencing the ^{31}P NMR chemical shifts.

MAS NMR spectra were measured with a Bruker Avance 400 solid-state NMR spectrometer equipped with a two-channel 4 mm MAS probehead. $(Me_3Si)_4Si$ ($\delta(^{29}Si) = -9.9$ ppm) and $NH_4H_2PO_4$ ($\delta(^{31}P) = +0.81$ ppm) were used as external standards for ^{29}Si and ^{31}P chemical shift references and to adjust the Hartmann-Hahn condition.

The materials were loosely filled into the rotors. All ^{31}P MAS spectra were recorded using a single pulse program with high-power decoupling and a 10 s repetition time. For ^{29}Si MAS measurements, a repetition time of 5 s was used with a single pulse program and high-power decoupling. ^{29}Si CP/MAS spectra were recorded with a contact time of 6 ms and a pulse repetition time of 4 s. Deconvolution of signals and processing of the spectra were accomplished using the software Origin pro.

4.3. Immobilization of 1 and 2 on silica

Ethoxysilane **1** has been prepared as described previously. [6] Silane **2** was purchased from Gelest and used as obtained.

For immobilization in toluene, ligand and silica were heated to 70 °C in toluene and stirred for 42 h as described previously. [12] Maximal surface coverage M was obtained by weighing back the residual ligand in the supernatant solution after solvent removal. M has been determined as 160 mg (0.410 mmol) per g of silica for **1** and 114 mg (0.303 mmol) per g of silica for **2**.

4.4. Preparation of the borane adducts 1i•BH_3 and 2i•BH_3

Modified silica (**1i**, **2i**, 0.5–1 g) was suspended in toluene (10 ml) and an excess of $Me_2S{\cdot}BH_3$ (three drops of 10 M THF solution) was added. The reaction mixture was stirred for 30 min, then the modified silica was allowed to settle and toluene was decanted. The borane-protected linker on silica was washed for one minute with 10 ml of acetone under stirring. After decanting the supernatant the solid was dried *in vacuo*.

4.5. Dry immobilization

Dry immobilization was carried out by removing toluene *in vacuo* prior to heating the adsorbed ligand on silica to 70 °C for 42 h under inert atmosphere.

4.6. Catalytic cyclotrimerization

The catalytic cyclotrimerization was performed as described previously for nickel complexes tethered to silica via phosphine linkers. [12].

4.7. Nickel nanoparticle standard

The standard Ni nanoparticle sample for TEM was prepared by suspending commercially obtained nickel nanoparticles (20 nm diameter, 17 mg) in THF (3 ml) using ultrasonication for fifteen minutes. Silica (1.2 g) was added to the stirred suspension. Ultrasonication was applied for another fifteen minutes before THF was removed *in vacuo* to yield a dry sample.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Dr. Janet Bluemel reports financial support was provided by National Science Foundation].

Data availability

Data will be made available on request.

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