Suspension NMR Spectroscopy of Phosphines and Carbonylnickel Complexes Immobilized on Silica

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Dedicated to Prof. H. P. Fritz on the occasion of his retirement

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³¹P Suspension NMR Spectra, Immobilized Bifunctional Phosphines, Immobilized Carbonylnickel Phosphine Complexes, Modified Silica, ³¹P CP/MAS NMR Spectra

The ³¹P suspension NMR spectra of silica-immobilized bifunctional phosphines and their di- and tricarbonylnickel complexes were recorded using conventional high resolution NMR equipment. The practical advantages of suspension NMR spectroscopy, as compared to ³¹P CP/MAS NMR spectroscopy, are discussed. General tendencies are demonstrated: The suspension NMR signals become broader with increasing solvent viscosity and decreasing solvent polarity. Phenyl groups as spacers lead to broader resonances than alkyl chains. The linewidths increase in the case of chelation.

Introduction

The immobilization of homogeneous catalysts on inert supports is of growing interest [1, 2], because the advantages of homogeneous and heterogeneous catalysis, like high selectivity and easy recycling, can in principle be combined. Since most metals form stable phosphine complexes, bifunctional phosphines like 1, 2, 3, or 4 [3, 4] are often used as linkers.

> $PPh_{2}(CH_{2})_{4}OH$ (1), $PPh_{2}(CH_{2})_{3}Si(OEt)_{3}$ (2), $PPh_{2}(C_{6}H_{4})SiMe_{2}OEt$ (3), $PPh_{2}(C_{6}H_{4})Si(OEt)_{3}$ (4).

Silica serves as a popular support, since it is cheap, inert against elevated temperatures and most organic solvents [5], and already well explored [5, 6]. The complexes can be preformed with the shown ligands and attached to the support subsequently [3]. Alternatively, the silica is modified with the phosphines 1 - 4 to form 1i to 4i [3, 4] *via* condensation reactions with surface silanol groups or addition reactions to surface siloxane groups [7] prior to the attachment of metal complexes. The latter procedure has the advantage that larger batches of modified silica with uniform quality can be prepared and reacted with different metal complexes.

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The most powerful and versatile technique to characterize phosphine-modified silica and surfacebound complexes is multinuclear solid-state NMR spectroscopy [8 - 10]. Usually, cross polarization (CP) and magic angle spinning (MAS) alone are applied for sensitivity and resolution enhancement, but there have also been described fruitful methods for line narrowing *via* adsorption [11] or sonication [12].

Alternatively, modified silicas have been investigated by NMR measurements of suspensions in order to elucidate chromatography mechanisms under realistic conditions [13 - 24]. Hereby, the silicas are most often coated by long alkyl chains of eight to eighteen carbon atoms. The mobility and ordering on the surface are probed by ¹³C [13 - 18, 20, 22 - 24] and ²H [19, 21] NMR spectroscopy in the presence of various solvents. Reports on ³¹P suspension NMR spectroscopy of immobilized phosphines and metal complexes thereof are rare [25 - 29] and mostly deal with solvent swollen polymers [25, 26, 28, 29] or phosphine moieties at the end of long alkyl chains [27].

In this contribution we demonstrate that ³¹ P NMR spectroscopy can successfully be applied to suspensions of **1i** to **4i** in different solvents. It is important to establish a correlation between solvent and mobility of surface species, because, as in the case of chromatography, the success of a catalytic

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Compound ^a	No.	Solvent	$\delta(^{31}\mathrm{P})^{\mathrm{b}}$	$\nu_{1/2}$ [Hz] ^c suspension	$\nu_{1/2}$ [Hz] solid-state
$PPh_2(CH_2)_4O-{SiO_2}$	1i		-16.8		420
		toluene	-16.1	860	
		hexane	-16.3	980	
		cyclohexane	-16.7	1760	
		nitromethane	-16.2	520	
$PPh_2(CH_2)_3Si(O-{SiO_2})_3$	2i		-16.3		550
		toluene	-16.5	290	
		hexane	-17.1	710	
		cyclohexane	-17.0	910	
		nitromethane	-17.1	170	
$PPh_2(C_6H_4)SiMe_2O-{SiO_2}$	3i		- 4.5		730
		toluene	- 5.2	1550	
		toluene (60 °C)	- 3.4	1200	
$PPh_2(C_6H_4)Si(O-{SiO_2})_3$	4i		- 4.5		750
		toluene	- 4.7	1300	
$(CO)_3NiPPh_2(CH_2)_4O-{SiO_2}$	5 i		23.5		400
		toluene	23.1	1540	
$(CO)_2Ni[PPh_2(CH_2)_3Si(O-{SiO_2})_3]_2$	6i		22.9		830
		toluene	22.5	3030	

Table I. Chemical shifts $\delta({}^{31}\text{P})$ and halfwidths $\nu_{1/2}$ of the ${}^{31}\text{P}$ NMR signals of suspensions of **1i** to **6i** in the indicated solvents at room temperature (298 K), if not stated otherwise. The $\delta({}^{31}\text{P})$ and $\nu_{1/2}$ values of the ${}^{31}\text{P}$ CP/MAS NMR signals are taken from refs. [3, 4]. Measurement conditions see Experimental.

^a {SiO₂} denotes the silica support, Ph a phenyl group (C₆H₅); compounds **2i**, **4i**, and **6i** are not necessarily bound to silica *via* three siloxane bridges (see text); ^b δ (³¹P) \pm 0.2 ppm and \pm 1 ppm (**5i**, **6i**); ^c $\nu_{1/2} \pm$ 10 Hz (**1i** - **4i**) and \pm 50 Hz (**1i** in cyclohexane, **3i**, **5i**, **6i**).

reaction depends on the proper choice of solvent. We also present here the first suspension NMR spectra of surface-bound di- and tricarbonylnickel complexes. The advantages and limitations of this method are discussed and compared to solid-state CP/MAS NMR spectroscopy.

2. Results

The dry, phosphine modified silica **1i** to **4i** [3, 4], as well as the immobilized carbonylnickel complexes $(CO)_3NiPPh_2(CH_2)_4O-{SiO_2}$ (**5i**) and $(CO)_2Ni[PPh_2(CH_2)_3Si(O-{SiO_2})_3]_2$ (**6i**) [4] can be characterized by their ³¹P CP/MAS NMR spectra. When these dry materials are subjected to ³¹P NMR spectroscopy under conditions of conventional high resolution (see 4.), no signal at all can be obtained. The same is true for CCl₄ suspensions. However, a plethora of other solvents gives reasonably narrow signals under the conditions described in 4. Table I gives the chemical shifts and linewidths of the ³¹P suspension signals of silica **1i** to **6i** in toluene. Additionally, the corresponding values of

hexane, cyclohexane, and nitromethane suspensions of **1i** and **2i** are given. A detailed study of a variety of other solvent/silica systems including T_1 values is under way [33].

The suspension ³¹P NMR spectra of **1i** in cyclohexane, hexane, and nitromethane are shown in Fig. 1, those of 5i and 6i in toluene in Fig. 2. It is known from silica esterification studies with butanol, that the Si-O-C group is easily hydrolyzed [31, 32]. Although siloxanes are more stable, the possibility of hydrolysis also exists for the Si-O-Si group. Therefore, in the cases of relatively narrow signals (1i/toluene; 1i/nitromethane; 2i/toluene; 2i/nitromethane) it was carefully checked in analogy to [13] that the resonances were not due to purely adsorbed species: The supernatant solution of the measured suspensions was subjected to ³¹P NMR separately; no ³¹P signals were detected in any case. Furthermore, a trace of the corresponding free phosphine was added to the suspensions and these were again measured after stirring for 1 h. A narrow resonance with about 30 to 50 Hz halfwidth was

always found in the suspension ³¹P NMR spectra, superimposed on the broad signals of the immobilized phosphines. The intensity of the latter did not change, as was checked by subtracting the spectra acquired before and after phosphine addition under identical NMR conditions with equal numbers of scans. As demonstrated in the pioneering works of Albert et al. [13] and Gilpin [17], the linewidths of suspension NMR signals increase with the surface coverage. Therefore, samples of 1i, 2i and 3i, 4i with similar surface coverages of about 5 % and 7 % carbon content, respectively, as determined by elemental analysis, were applied. For the measurements of 1i and 2i in different solvents, portions of the same batch of 1i and 2i, respectively, were used. The chemical shifts are in good agreement with the ones determined by ³¹P CP/MAS NMR (Table I) and by solution NMR spectroscopy of the dissolved compounds [4].



Fig. 1. 121.5 MHz suspension ³¹P NMR spectra of phosphine modified silica **Ii** in nitromethane (A), hexane (B), and cyclohexane (C). Measurement conditions and NMR data see Experimental and Table I, respectively. S denotes some oxidation products.

3. Discussion

The residual linewidths of the ³¹P CP/MAS NMR signals determined earlier [3, 4] are given in Table I. With the exception of the systems **2i**/toluene and **2i**/nitromethane, the suspension NMR resonances are broader than the solid-state ³¹P CP/MAS NMR lines of the dry samples. Even though there is the possibility to apply more favorable solvents (see below and [33]), even at this preliminary state suspension NMR spectroscopy offers some advantages as compared to ³¹P CP/MAS NMR:

1. The sample preparation is simple. The silica materials do not have to be dried before measurement. After the modification procedure [3] and washing with the appropriate solvent, the slurry can be filled into the NMR tube directly. Impurities (mostly from oxidation [3]) show up in the spectrum quite well (Fig. 1A), and if the silica does not meet the desired purity requirements, it can be discarded before a tedious work-up and drying procedure.

2. Quantitative data may be obtained conveniently. For simultaneous quantitative measurements of all the possible species present on the surface, the CP parameters have to be optimized carefully [3]. If one set of parameters does not give optimal signal intensity for all surface species, a multitude of spectra have to be recorded in order



Fig.2. 121.5 MHz suspension ³¹P NMR spectra of surface immobilized tri- and dicarbonylnickel complexes **5i** (A) and **6i** (B) in toluene. Measurment conditions and NMR data see Experimental and Table I, respectively.

to get quantitative information. Suspension NMR spectroscopy, however, gives quantitatively reliable signal intensities within one spectrum for oxidic species and phosphines under the (uncritical) measurement conditions applied (see 4.), as was checked by ³¹P CP/MAS NMR [3]. Furthermore, suspension NMR spectroscopy allows quantitative measurements of physically adsorbed species [13]. This is not easily done with CP/MAS NMR [7]. However, suspension NMR and CP/MAS NMR signals of adsorbed species have the same narrow linewidths. The latter distinguishes them from signals of chemically bound species [7].

3. There are no rotational sidebands that could lead to overlapping.

4. The measurement times are short. ³¹P CP/MAS NMR spectra of good S/N ratio of **1i** - **6i** require measurement times of about three to four hours [3, 4]. Suspension NMR spectra, on the other hand, are done in about 15 min. This is mostly due to the favorable T_1 times of these surface-attached, in the presence of solvents moderately mobile species ([34] and see below). Additionally, an approximately tenfold larger volume of silica can be used in a 10 mm glass tube than in a conventional 7 mm rotor.

5. No spinning gas is consumed. In an inorganic NMR laboratory, where air-sensitive compounds, diluted in a solid are mostly measured, nitrogen is best used as the drive- and bearing gas, because the otherwise useful airtight rotor inserts [35] need too much volume within the rotor at the expense of sample volume. With a large quantity of routine samples, this can become very expensive. However, suspension NMR spectroscopy does not need any nitrogen for spinning at all [30].

6. The catalysts are probed under realistic conditions. Suspension NMR spectroscopy provides information about the mobility of surface attached species in the presence of solvents, which is indispensable for a correlation of catalyst activity and applied solvent. This information can of course not be obtained from ³¹P CP/MAS NMR measurements of the dry samples.

From the present results the following trends for surface-bound species emerge: The suspension ³¹P NMR resonances of the immobilized phosphines **3i** and **4i** are substantially broader than those of **1i** and **2i** with the same solvent (Table I). Broader lines are indicative of restricted mobility, since then the chemical shift anisotropy and dipolar coupling

are reduced less effectively [8]. Therefore, we assume, that the phenyl spacer between phosphine moiety and silica surface leads to a more rigid arrangement of the phosphines on the surface than the alkyl chains with three and four segments. This is in line with refs. [25, 26]. Additionally, it was shown for alkyl modified silica *via* suspension ¹³C NMR measurements, that the signals are broader for less mobile and more rigid segments of the alkyl chains [13 - 21].

The ${}^{31}P$ NMR signals of phosphines 2i and 4i, which can be bound to the surface via up to three ethoxy groups, are narrower than the ones of 1i and 3i, which allow just one bond to the surface. At first sight this is in contrast to intuition, since a more stable "anchoring" should reduce the mobility. But the phosphorus nucleus is in every case presented here far away from the silica surface. Furthermore, as it was nicely demonstrated by the study of Albert et al. [14], small alkyl groups, adjacent to longer alkyl chains, reduce the mobility of the latter. Keeping in mind that ethoxysilane reagents preferentially add to surface siloxane groups of rigorously dried silica [7], the triethoxysilanes 2i and 4i would be expected to have more neighboring surface bound ethoxy groups and therefore display broader ³¹P suspension NMR lines than 1i and 3i. This is not the case. Therefore, we conclude that the effect of line broadening caused by adjacent small alkyl groups [14] is not dominant in the case of our phosphines with short alkyl and rigid phenyl spacers. We tentatively interpret the narrower linewidths of 2i and 4i as being the result of cross-linking and the formation of mobile, surface detached polysiloxane chains [36, 37]. This would also explain the broader resonances of 1i as compared to 2i in all solvents. But one has to be careful in the discussion of this case, because of the different alkyl spacer lengths of 1i and 2i. T₁ studies of terminal methyl resonances of long surface bound alkyl groups show that their rotational motion does not change with the chain length [17]. However, other systems with shorter *n*-alkyl ligands display a nonlinear change of mobility of terminal methyl groups with chain lengths and a maximal mobility for alkyl groups with six carbon atoms [38] in the solid state.

Regarding Table I, it is obvious that the solvent employed for the suspension NMR measurements plays a crucial role regarding linewidths. Nitromethane leads by far to the narrowest signals,

followed by toluene, hexane, and cyclohexane. As already described earlier [15, 16], solvent viscosity is one of the factors dominating the halfwidths of suspension NMR resonances. A comparison between the spectra obtained from cyclohexane ($\eta =$ 1.02 cP at 17 °C [39]) and hexane ($\eta = 0.33$ cP at 20 °C [39]) suspensions of 1i and 2i shows the dramatic effect of viscosity. The polarity of these solvents is similar. The linewidth increases with the viscosity of the solvent. If the solvent plays a crucial role for $\nu_{1/2}$ of the ³¹P NMR signals of immobilized phosphines, then $\nu_{1/2}$ should decrease with η at elevated temperatures for a given solvent. Indeed, when a toluene suspension ($\eta = 0.59$ cP at 20 °C [39]) of **3i** is measured at 60 °C ($\eta = 0.38$ cP at 60 °C [39]), the linewidth is reduced by 350 Hz (Table I). Another important factor governing the halfwidths of suspension NMR signals is the solvent polarity [21, 22, 24]. This can be demonstrated using the solvents toluene and nitromethane ($\eta = 0.62$ cP at 25 °C). Although their viscosities are similar, nitromethane leads to the narrowest lines. This might be due to the different polarities of toluene ($\varepsilon = 2.4$ at 25 °C [39]) and nitromethane ($\varepsilon = 38.6$ at 20 °C [39]). Since toluene and nitromethane dissolve the free phosphines 1 and 2 equally well, we suppose, in analogy to refs. [21, 22, 24], that nitromethane is better suited to adsorb at the polar silica surface and detach the phosphine moieties from there. This would enhance the mobility of the surface bound phosphines and decrease the linewidths of the suspension ³¹P NMR resonances.

The immobilized nickel complexes **5i** and **6i** give the largest linewidths. The lineshapes are somewhat unsymmetrical and resemble the overall signal shapes of the corresponding ³¹P CP/MAS NMR spectra [4], meaning that the chemical shift anisotropy of the signals in not removed by mobility of the bound complexes. Reduced mobility of immobilized phosphines after coordination of metals has already been reported for Rh [26 - 28] and Pt [25, 29] complexes. In the case of **6i**, chelation probably causes additional reduction of mobility. This chelation effect has for example been demonstrated for platinum complexes immobilized with chelating amine ligands [22].

With ³¹P CP/MAS NMR it is easily possible to distinguish the di- from the tricarbonylnickel complexes [4]. This is difficult using suspension NMR spectroscopy, due to the similar chemical shift and large linewidths (Fig. 2). Nevertheless, impurities and especially uncomplexed phosphines would show up in the suspension NMR spectra. Therefore, even here a "preselection" of samples for CP/MAS measurements can be made.

In conclusion, this work has shown that suspension ³¹P NMR spectroscopy is a useful method as a supplement to conventional ³¹P CP/MAS NMR spectroscopy. Its advantages lie mostly in the ease and convenience of application and in the saved time for routine measurements. It may help to understand why and how catalytic activity changes, if the metal complexes are immobilized. The above results show that the solvent plays a crucial role. For analytical purposes, there is some potential in suspension NMR spectroscopy in cases where paramagnetic or metallic impurities on the silica surface do not allow the recording of ³¹P CP/MAS NMR spectra. With the proper polar solvent it might be possible to move the immobilized complexes further away from the surface and to allow at least a suspension NMR spectrum to be recorded. A more detailed study of the mobility effects discussed above, including determination of T_1 values, is under way [33].

4. Experimental

For all the ³¹P suspension NMR measurements, a BRUKER MSL 300 NMR spectrometer, operating in the low power mode at 121.5 MHz and equipped with a conventional 10 mm broadband probehead, was applied. The dry modified silica of an approximate volume of 2 ml was filled under N₂ into 10 mm glass NMR tubes, equipped with ground glass joints, and stirred with an excess of the respective dried and oxygen free solvent (3 to 6 ml). After reversible sealing of the NMR tube with a glass stopper, the silica was allowed to settle down for about 1 h prior to the measurement. The following parameters are not optimized: The applied pulse width of 8 µs corresponds approximately to a 50° pulse. The dead time was 10 µs, the pulse delay could be as short as 200 ms. Usually, for a spectrum of a modified silica (5 % carbon content, as determined by elemental analysis) with good S/N ratio, 3000 scans was enough. This corresponds to a time requirement for the measurement of about a quarter of an hour. Chemical shifts are referenced with respect to external 85 % H_3PO_4 ($\delta(^{31}P) = 0$).

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