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Solid-State NMR Characterization of Wilkinson's Catalyst Immobilized in Mesoporous SBA-3 Silica

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Abstract: The Wilkinson's catalyst [$RhCl(PPh_3)_3$] has been immobilized inside the pores of amine functionalized mesoporous silica material SBA-3 and The structure of the modified silica surface and the immobilized rhodium complex was determined by a combination of different solid-state NMR methods. The successful modification of the silica surface was confirmed by ^{29}Si CP-MAS NMR experiments. The presence of the T_n peaks confirms the successful functionalization of the support and shows the way of binding the organic groups to the surface of the mesopores. ^{31}P-^{31}P *J*-resolved 2D MAS NMR experiments were conducted in order to characterize the binding of the immobilized catalyst to the amine groups of the linkers attached to the silica surface. The pure catalyst exhibits a considerable ^{31}P-^{31}P *J*-coupling, well resolvable in 2D MAS NMR experiments. This *J*-coupling was utilized to determine the binding mode of the catalyst to the linkers on the silica surface and the number of triphenylphosphine ligands that are replaced by coordination bonds to the amine groups. From the absence of any resolvable ^{31}P-^{31}P *J*-coupling in off-magic-angle-spinning experiments, as well as slow-spinning MAS experiments, it is concluded, that two triphenylphosphine ligands are replaced and that the catalyst is bonded to the silica surface through two linker molecules.

Keywords: heterogeneous catalysis · NMR spectroscopy · phosphorus · Wilkinson's catalyst

Introduction

Organometallic catalysts are widely used in organic synthesis, as for example in pharmaceutical and natural products chemistry and fine synthesis. Owing to the favorable properties of heterogeneous catalysts many attempts to produce catalytically active organic–inorganic hybrid materials have been done in recent years.[1–23] In these so-called immobilized catalysts, the organic or organometallic functional groups are immobilized on a solid inorganic support by binding, for example, to the outer surface of nanoparticles or the inner surfaces of micro- or mesoporous materials. Depending on the intended application, the functional group is immobilized on the surface by various techniques.[24–26] Recent examples of immobilized catalysts contain metals such as Zn, Cu, Ru, Rh, and Pt.[27] Their successful applications were reported in asymmetric synthesis, hydrogenation, oxidation, and many other reactions.[1–4,6,8–9,12,15,19,21,28–30] Their catalytic efficiency depends strongly on the transport properties inside the pores.[31]

While the separation of the catalyst from the reactants is always a problem in a homogeneous reaction, immobilized catalysts can be very easily separated and reused. Furthermore, by using immobilized catalysts, less heavy metal is employed, which is in agreement with the principles of green chemistry.[27]

Inorganic oxides, especially periodic mesoporous silicas, are a class of materials that combine all of these qualities. Since the discovery of the M41S structure by Mobil Oil Corporation in 1992[32], the family of mesoporous silica material is expanding continuously. In the last years intensive scientific efforts have been devoted to synthesis, characterization, and application of ordered mesoporous materials in catalysis, sorption, separation, delivery, sensors, and electronics.[33–41]

Since the pore structure of the support material prevents the swelling or aggregation of the active site of the catalysts on the large inner surface, the active surface area of the catalyst can be increased dramatically. As a result, the efficiency of the catalyst can be enhanced by immobilization the active part of a homogeneous catalyst into mesoporous materials.[20,27]

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MCM- and SBA-type materials are prominent representatives of periodic mesoporous silica materials. They possess large pore spaces, ordered and tunable pore sizes, and have a relatively homogenous and large surface area. Since the physical properties of their inner surface, such as the surface acidity, can be chemically modified, mesoporous silica materials open up a new possibility for the construction of advanced catalytic materials with selective and efficient applications.

The functionalization of the surface silanol groups provides stable binding sites for metal complexes inside mesopores. In general there are two synthetic routes of surface functionalization, the grafting method known also as post-synthesis (silylation) and the direct synthesis or co-condensation .[42] Grafting is the most commonly used method in performing surface modification by covalently linking organosilane species with surface silanol groups.[43]

Recently we presented the immobilization and solid-state NMR characterization of a ruthenium catalyst in mesoporous silica SBA-3.[44] Herein we report the incorporation of Wilkinson's catalyst $[RhCl(PPh_3)_3]$ (see Figure 1) on amine-functionalized mesoporous silica SBA-3.

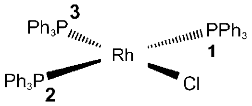

Figure 1. Schematic structure of the Wilkinson's catalyst

The $[RhCl(PPh_3)_3]$ complex is the most widely investigated of all known homogenous hydrogenation catalysts.[45] Its applications in many organic reactions have induced a strong demand for the efficient separation of catalyst from the product stream.[46] Various attempts towards catalytic applications of the immobilized Wilkinson's catalyst and its analogues have been undertaken previously.[7,47–50] Although $[RhCl(PPh_3)_3]$ tethered to the inorganic support has shown high activity and stability during catalytic processes, the structure of the heterogenized catalyst is still under discussion.[51]

The immobilization of the catalyst on an inorganic support combines molecular chemistry with surface science and solid-state chemistry. However, characterization of the molecules incorporated into the silica surface is difficult if only classical methods of organometallic chemistry are applied. Therefore, there is need to rely on an advanced spectroscopic technique such as solid-state NMR, which is able to study the structures of fairly disordered bulk samples. Owing to these favorable properties several studies of immobilized species on surfaces employing modern techniques of solid-state NMR are reported in the literature.[23,52–54]

In this work we use a combination of ^{29}Si and advanced ^{31}P solid-state NMR methods to investigate and characterize modified surface of mesoporous silica and to study the exact binding of Wilkinson's complex to the modified silica surface. We demonstrate that the ^{31}P *J*-resolved 2D slow-spinning magic-angle-spinning (MAS) and Off-MAS ^{31}P NMR techniques are efficient tools to reveal the detailed binding situation of the supported $[RhCl(PPh_3)_3]$ molecule.[55]

Experimental Section

Materials: All chemicals used for the synthesis were commercially purchased from Sigma–Aldrich, Carl ROTH GmbH and STREM Chemicals and they were used as received, except of solvents. The solvents were dried by performing standard purifying procedures. All reactions were carried out under an argon atmosphere, using Schlenk techniques.

Synthesis of $[RhCl(PPh_3)_3]$: The Wilkinson's catalyst was prepared according to the procedure described elsewhere.[56–57] A solution rhodium trichloride trihydrate (2 g) in hot ethanol (70 mL) was added to a solution triphenylphosphine (12 g) in hot ethanol (350 mL). The resulting solution was heated to reflux for 30 min, and the red crystals were filtered from the hot solution. The crystals were washed with ether and dried under vacuum. Yield: 5.71 g (78 %).

Synthesis of mesoporous SBA-3 silica: Mesoporous silica SBA-3 was prepared based on the reported procedures.[58–59] Cetyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) were used as surfactant and silica source, respectively. An aqueous solution of 37 % HCl was used to adjust the pH value of the reaction. The surfactant was mixed with water and hydrochloric acid for 30 min and then TEOS was added dropwise to this solution. The mixture was stirred at room temperature for 3 h and the obtained white precipitate was aged for 12 h. The sample was recovered by filtration, washed with water. After drying at ambient temperature the product was calcined at 550 °C for 8 h in order to remove the surfactant.

Functionalization of SBA-3: The modification of SBA-3 with 3-aminopropyltriethoxysilane (APTES) was performed following the procedure described elsewhere.[10] Before functionalization, the silica material was activated at 423 K in the vacuum for 10 h. Then freshly activated SBA-3 (3 g) was heated to reflux in toluene (50 mL) with APTES (3 g) for 3 h under argon atmosphere. The resulting solid was washed with diethyl ether and Soxhlet extracted with anhydrous dichloromethane. Finally it was dried in vacuum for 24 h.

Immobilization of Wilkinson's catalyst: A solution of $[RhCl(PPh_3)_3]$ (0.1 g) in anhydrous toluene (10 mL) was added to a suspension of freshly activated modified silica (1 g) in dry toluene (40 mL). The resulting solution was refluxed for 3 h and the obtained solid was Soxhlet extracted with anhydrous toluene and dried under vacuum for 24 h.

Solid-state NMR experiments: All NMR experiments were carried out on a Bruker AVANCE II$^+$ spectrometer at 400 MHz proton resonance frequency, employing a Bruker 4 mm double resonance probe at various spinning rates at room temperature. ^{29}Si, ^{13}C (not shown), and ^{31}P spectra were recorded utilizing ramped CP-MAS sequences at spinning rates of 5 kHz and 10 kHz, respectively. Contact times were set to 4 ms and tppm[60] decoupling with a 20° phase jump was applied during data acquisition. ^{29}Si and ^{13}C spectra were referenced with respect to TMS (tetramethylsilane) and ^{31}P spectra were recorded using H_3PO_4 as standard. ^{31}P *J*-resolved spectra were recorded establishing ^{31}P polarization by means of CP with contact times of 5 ms followed by a rotor synchronized π pulse after n rotor periods ($n = 1,2,3\ldots$) and recording the spin echo. In order to detect obscured ^{31}P-^{31}P *J*-couplings in 2D experiments in the case of immobilized Wilkinson's catalyst, *J*-resolved spectra were recorded under slow-spinning and Off-MAS conditions. For the off-MAS *J*-resolved spectra, the spinning angle was set to approximately 46.7°. All 2D experiments were processed in magnitude mode.

Results and Discussion

^{29}Si CP-MAS experiments: In order to characterize the surface of mesoporous SBA-3 material before and after the modification with APTES, ^{29}Si CP-MAS NMR experiments were performed. Figure 2 shows the ^{29}Si CP-MAS NMR spectrum of the mesoporous silica material SBA-3. Three signals at −94, −102, and −110 ppm are assigned by spectral

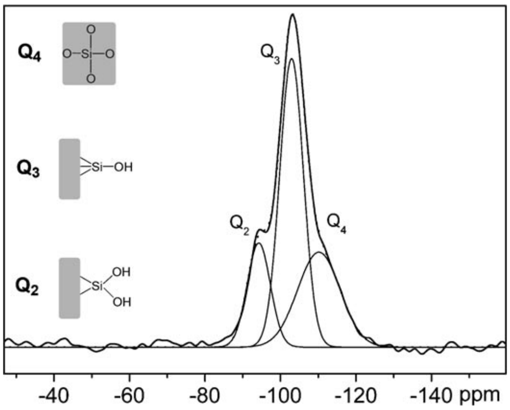

Figure 2. The ^{29}Si CP-MAS NMR spectrum of the mesoporous silica SBA-3 displays the silicon groups Q_n present at the surface.

deconvolution to the silicon atoms of silanol groups present at the surface, labeled as Q_n (see Figure 2).

The structural changes of the silica surface after the process of modification with APTES are visible in the ^{29}Si CP-MAS spectrum presented in Figure 3. This spectrum exhibits not only lines of the Q_n-type groups but also an additional set of signals which are denoted as T_n-type groups visible between −50 and −70 ppm. These peaks are attributed to the silicon atoms of the organic linker 3-aminopropyltriethoxysilane attached covalently to the silica surface. The appearance of T_n-groups and the significant decrease of the intensity of the Q_3 and Q_2 lines with respect to the Q_4 line in the spectrum depicted in Figure 2, confirm that the successful functionalization of the surface silanol groups is achieved through chemical bonds and not by adsorption at the surface.

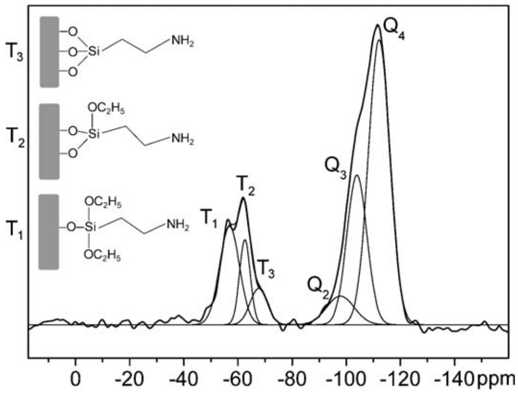

Figure 3. The ^{29}Si CP-MAS NMR spectrum of the mesoporous silica SBA-3 after functionalization with 3-aminopropyltriethoxysilane reveals the three different types of binding of the organic linker (T_n groups) to the surface.

The subsequent immobilization of $[RhCl(PPh_3)_3]$ on the surface of functionalized SBA-3 does not create any noticeable changes in the ^{29}Si CP-MAS spectrum in the lines attributed to the T_n and Q_n groups (spectrum not shown).

^{31}P solid-state NMR spectroscopy

^{31}P CP-MAS experiments: Since the metallic rhodium core of the Wilkinson's catalyst is ligated to three phosphine ligands, the phosphorus atoms of which are directly coordinated to the rhodium, ^{31}P solid-state NMR is an ideal tool to monitor the changes of the coordination sphere of the rhodium due to the immobilization. The first step in the characterization of the structure of Wilkinson's catalyst after the process of immobilization is the comparison of the ^{31}P CP-MAS NMR measurements of the bulk catalyst before and after incorporation inside the mesoporous SBA-3.

The spectrum of the neat catalyst shows a large number of spinning side bands. They demonstrate the existence of large ^{31}P chemical shift anisotropy.[61] The presented spectrum (Figure 4) shows only the center bands and can be divided into three parts, with isotropic chemical shifts of 47.5, 30, and 21 ppm. These peaks are attributed to the three nonequivalent phosphorus atoms in the catalyst molecule (see Figure 1).

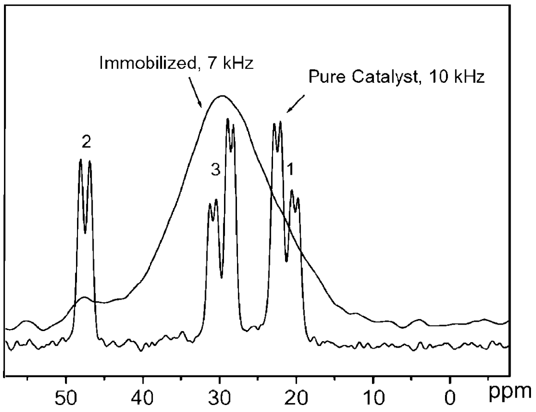

Figure 4. ^{31}P CP-MAS spectrum of the neat Wilkinson's catalyst and after its immobilization on the mesoporous silica (only the center bands are shown).

The low-field doublet at 47.5 ppm results from the *J*-coupling between the phosphorus P2 and the central rhodium atom, with the coupling constant $J(\text{Rh-P}) = 194$ Hz. The multiplet observed at the higher field corresponds to the two magnetically nonequivalent phosphorus atoms labeled as P1 and P3, with isotropic chemical shifts of 21 and 32 ppm, respectively. Both lines are split into a doublet of doublets; the inner splitting is 140 Hz for the line at 32 ppm and 144 Hz for the line at 21 ppm. The outer splitting of the two high-field doublets is 394 Hz. This last value is characteristic for a homonuclear $^2J(^{31}P\text{-}^{31}P)_{trans}$ coupling, which it is usually much larger than $^2J(^{31}P\text{-}^{31}P)_{cis}$ coupling, which is in the range 0–50 Hz[61] and thus not resolvable in our linewidth. This interpretation is in accord with the SSNMR results published by Wasylishen et al.[62–63] and with liquid-state NMR data of the complex.

The ^{31}P CP-MAS spectrum of the Wilkinson's catalyst immobilized on the amine functionalized SBA-3 material differs significantly from that of the pure [RhCl(PPh$_3$)$_3$]. Its main intensity is concentrated in a single broad asymmetric peak at 32 ppm, which in comparison with the spectrum of the pure catalyst can be related to the phosphorus atom labeled as P3. In addition there is a weak broad signal at the position of the former P2 signal, which corresponds to less than 5 % of the integral intensity and most probably can be assigned to a small amount of not immobilized Wilkinson's catalyst. These results show that P2 has evidently been replaced by an amine group of the linker grafted on the surface.

This raises the question about the exact binding of the catalyst through the linkers. The broadening of the main signal does not allow for a direct attribution of the signal to the remaining phosphorus atom P3. The observed peak may also consist of two coalescent ^{31}P chemical shifts related to phosphorus atoms labeled as P3 and P1. Thus, the results of ^{31}P CP-MAS experiment suggest two possible scenarios of immobilization of Wilkinson's catalyst.

In the first case the catalyst is attached to the surface through one coordination bond with one organic group of linker molecule, resulting from substitution of one phosphine ligand by an amine group of APTES (see Figure 5a). The two remaining *trans* phosphines may be chemically equivalent now, which could explain the broad signal in the spectrum.

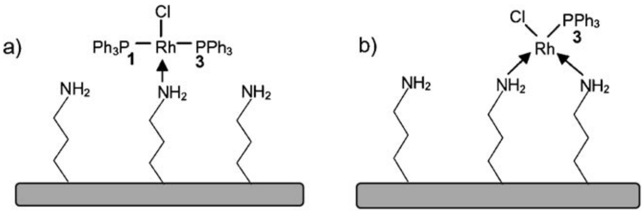

Figure 5. Two possibilities of the immobilization of the Wilkinson's catalyst at the surface of amine modified silica material SBA-3

Alternatively, two phosphine ligands P1 and P2 are substituted by amine groups and the resulting anchored catalyst is immobilized on the silica surface through two linker molecules (see Figure 5 b). The immobilized catalyst possesses now one phosphine ligand with a corresponding signal at 32 ppm in the ^{31}P CP-MAS spectrum. It is impossible to distinguish between these both binding situations by means of 1-D ^{31}P CP-MAS NMR results.

^{31}P 2D *J*-resolved experiments: Since the structure of the heterogenized Wilkinson's catalyst is not only of principal scientific interest, but also of great importance for the further application of this material in catalysis, it is necessary to apply more advanced ^{31}P solid-state NMR methods. For this reason 2D *J*-resolved ^{31}P NMR experiments were applied, which allow the determination of the number of phosphine ligands in the investigated sample, based on spin–spin interactions in the molecule.

The 2D *J*-resolved ^{31}P NMR spectrum of the pure [RhCl(PPh$_3$)$_3$] is depicted in Figure 6. It confirms the results of the 1D ^{31}P CP-MAS experiments. The well-resolved pattern of *J*-coupling due to the heteronuclear ^{1}J(Rh-P) coupling remains along the f_2 dimension, while the characteristic large homonuclear *J*-coupling due to interaction between P1 and P3 nuclei, appears along the f_1 dimension.

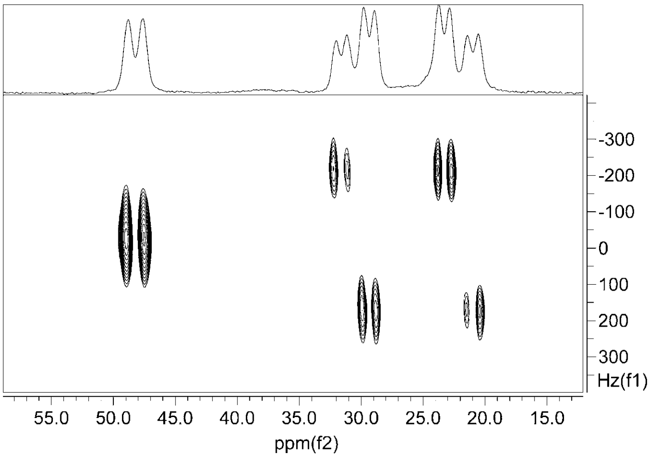

Figure 6. Two-dimensional ^{31}P *J*-resolved NMR spectrum of the pure [RhCl(PPh$_3$)$_3$], spinning speed 10 kHz.

Fast-spinning MAS spectra, even in the case of *J*-resolved 2D experiments, do not allow us to distinguish between the presences of one or two chemically equivalent nuclei, since under fast-spinning MAS conditions, the situation is comparable to liquid-state NMR; that is, chemical shift anisotropies are averaged out. However, under static conditions, the chemical shift tensors of two chemically equivalent nuclei do not coincide and both nuclei have, in general, different chemical shifts at certain orientations of the molecules with respect to the magnetic field axis. That is, the spin system may be described as an AB system, instead of an A$_2$ spin system. Slowly spinning the molecule at the magic angle will give rise to a modulated AB spin system that is no longer describable by simple averaged Hamiltonian theory. Instead, higher order correction terms have to be taken into account, effectively reintroducing the *J*-coupling into the spectra. A comprehensive theoretical description of the Hamiltonian under slow spinning conditions, validated by experimental investigations is given in reference [64] and references therein.

Therefore a slow-spinning ^{31}P 2D *J*-resolved experiment was performed for the immobilized Wilkinson's catalyst. Under these conditions the chemical shift anisotropy is modulated rather than completely averaged out and the transition probability between *J*-coupled levels becomes considerably larger than zero. Under these conditions the *J*-coupling interactions may be observed in solid-state *J*-resolved MAS NMR spectra. The slow-spinning ^{31}P 2D *J*-resolved spectrum of $[RhCl(PPh_3)_3]$ after the process of immobilization is presented in Figure 7.

This spectrum does not reveal any ^{31}P-^{31}P *J*-couplings within the spectral resolution. This suggests the presence of only a single P3 phosphorus atom in the catalyst molecule attached to the silica surface. Owing to the partial overlap of the center band with the spinning side bands, the broad base of the center band is not visible. Since the slow-spinning region depends on chemical shift anisotropy, direct dipolar- and *J*-coupling, which all are unknown in the case of immobilized catalyst, the absence of resolved *J*-couplings at 2.5 kHz does not unequivocally prove the presence of only one phosphine ligand. To confirm the result obtained by the slow-spinning experiment, the *J*-resolved measurement was performed under Off-MAS conditions, which are more relaxed regarding the detection of *J*-couplings.[65]

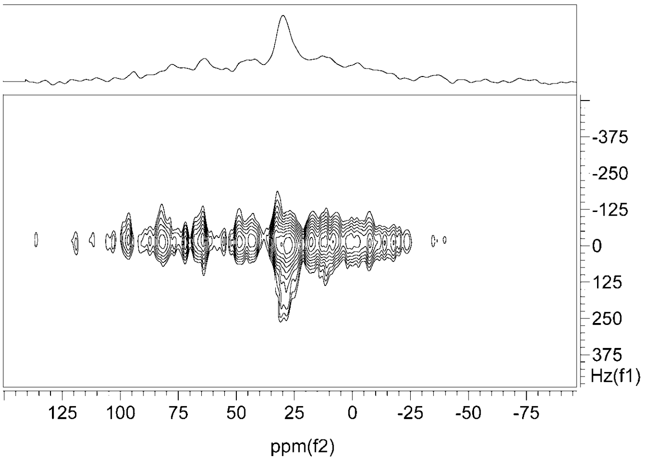

Figure 7. Two-dimensional ^{31}P *J*-resolved MAS slow spinning (2.5 kHz) spectrum of the $[RhCl(PPh_3)_3]$, immobilized on mesoporous silica.

Wu and Wasylishen[65] showed that the averaged Hamiltonian under fast-spinning off-magic-angle conditions resembles a two spin AB system in liquid-state NMR spectra. That is, the anisotropic parts of the chemical shift tensors of both nuclei are not completely averaged out under off-magic-angle conditions. These anisotropic parts render the different nuclei magnetically inequivalent. As a result of this inequivalency the *J*-coupling between the nuclei becomes visible in the spectrum, similar to the transition from an A_2 to an AB or AX spin system. Details are given in reference [65] and references therein. Furthermore, fast-spinning under off-magic-angle conditions offers higher spectral resolution, considerably increased signal-to-noise ratios, and drastically reduced experimental times, with respect to slow spinning conditions.[65]

The ^{31}P 2D J-resolved Off-MAS spectrum of the immobilized Wilkinson's catalyst is shown in Figure 8. In the spectrum there is evidently no visible *J*-coupling. This confirms not only the results of the slow-spinning measurements, but also proves the presence of only a single remaining phosphorus atom, P3. The presence of one phosphine ligand in the molecule of heterogenized catalyst proves the assumption deduced from the 1D spectrum that during the immobilization process two phosphine ligands are substituted by amine groups of organic linker. The phosphine with phosphorus atom labeled as P3 remains in the molecule.

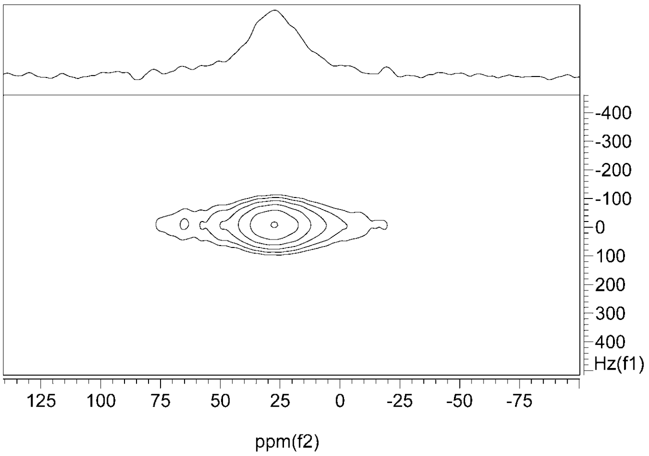

Figure 8. Two-dimensional ^{31}P *J*-resolved Off-MAS spectrum of the immobilized Wilkinson's catalyst.

The question now arises about the exact mode of coordination of the linker to the catalyst. In principal this question can be answered by ^{15}N labeling of the linker, which however is beyond the scope of the current paper.

Conclusions

Mesoporous silica material SBA-3 was synthesized and modified with the organic linker 3-aminopropyltriethoxysilane. Employing ^{29}Si CP-MAS solid-state NMR techniques we demonstrated successful functionalization of the silica surface. Next, Wilkinson's catalyst was immobilized on the surface of amine modified silica. The exact binding of $[RhCl(PPh_3)_3]$ to the organic linker was studied by different ^{31}P NMR techniques. The results of ^{31}P CP-MAS experiment confirmed the attachment of the catalyst to the organic linker, but do not allow us to distinguish whether the catalyst is coordinated by one or two amine groups of the modifying agent. This problem was solved by 2D ^{31}P *J*-resolved experiments, which allowed us to determine the number of linking phosphine groups.

The experiments provide clear evidence that after the process of immobilization only a single phosphine ligand remains in the catalysts. It shows that Wilkinson's catalyst is immobilized on the silica surface through a coordination to the two amine ligands in the form of $SiO_2(NH_2)_2RhClPPh_3$. In conclusion we demonstrate that employing advanced ^{31}P solid-state NMR techniques, we are able to gain the insight into the immobilization of the Wilkinson's catalyst on the surface of mesoporous silica SBA-3 and determine the type of binding of the catalyst.

Acknowledgements

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