



The adsorption of chromocene and ferrocene on silica: A solid-state NMR study



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ABSTRACT

Ferrocene and chromocene can be adsorbed on silica surfaces by impregnation or by grinding powders of the metallocenes with silica. The vanishing crystal lattice and formation of mobile surface species can in both cases be proven by diminished Chemical Shift Anisotropies and reduced residual linewidths as well as changes in the chemical shifts of the ¹H and ¹³C MAS NMR signals. In contrast to adsorbed ferrocene, the surface-adsorbed chromocene is highly air-sensitive and continues to react with the silica surface within an hour.

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1. Introduction

Metallocenes and ferrocene in particular represent classic organometallic compounds. Their derivatives are ubiquitous in such important fields as catalysis and stereoselective synthesis. Therefore, it seems surprising that the knowledge about their surface chemistry on common oxides, such as silicas, which are often used for their chromatographic purification, is rather limited.

While ferrocene is comparatively robust, chromocene, for example, reacts with silica to result in the Union Carbide polymerization catalyst [1,2]. However, prior to the potential reaction the first step is always an interaction with the surface, namely adsorption. The research results described here for the two representative metallocenes chromocene and ferrocene provide new insights into surface adsorption processes and the dynamics of the adsorbed molecules. It will be demonstrated for the first time that ferrocene and chromocene can be brought onto a silica surface in

the form of a monolayer. Interestingly, this can not only be achieved by the impregnation method but also by dry grinding of the metallocenes with silica. Using the fast and straightforward ¹H and ¹³C MAS NMR measurements, we will describe how the adsorption and mobilities of the surface species manifest themselves in a chemical shift change of the signals, as well as reduced Chemical Shift Anisotropy (CSA) and residual linewidths in the ¹H and ¹³C MAS NMR spectra, as compared to the spectra of polycrystalline ferrocene and chromocene. The results should have far reaching implications, e.g., for studying mechanisms in surface catalysis and for an improved insight into solid–solid interactions in general.

Many of the surface techniques applied in academic studies are either invasive in nature, deal with model systems with planar surfaces, give only limited insight, like IR, or are simply not practical for quick measurements of large numbers of samples. In recent years, solid-state NMR spectroscopy [3] has increasingly and successfully been used to study adsorption phenomena. From the pioneering work by Günther [4,5] it is obvious that the narrowing of the ¹³C MAS signals is a general phenomenon for adsorbed polycyclic aromatic hydrocarbons (PAH), and a variety of PAH derivatives have been measured [4,5]. If adsorption takes place, the

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^{13}C chemical shift changes, and the residual linewidth and Chemical Shift Anisotropy (CSA) [3a] of the ^{13}C and ^1H MAS signals will be reduced [4,5].

Besides these pioneering works, nearly all adsorption studies are based on volatile adsorbates and/or metal surfaces. This literature is extensive and cannot be discussed here because it would exceed the scope of the paper. Instead, representative cases of adsorption studies from the literature in relevant fields will be described.

- (a) Phosphine oxides [6] and phosphines [7] have been used in many studies to probe acidic sites on surfaces. Solid-state NMR has been applied because ^{31}P is a spin-1/2 nucleus with 100% natural abundance, and its chemical shift is sensitive to the surrounding electron density, which is lowered by interactions with acidic surface sites. Most of the adsorbed phosphines [7] are highly mobile on oxide surfaces, which manifests itself, for example, in the cross-polarization (CP) characteristics determined by the ^{31}P solid-state NMR measurements.
- (b) Adsorbed hydrocarbons, even PAH with higher melting points can display substantial mobility on various oxide surfaces, as the pioneering papers show [4,5,8]. It has been demonstrated that the NMR analysis of adsorbed PAH can be more revealing than that of phosphines. For example, not only are there significant ^{13}C chemical shift changes as compared to the polycrystalline state, but also their huge intrinsic CSA [3a] is reduced substantially due to their increased mobility in the adsorbed state. More recently it has been found that fullerenes are adsorbed on the mesoporous silica MCM-41, even after dry grinding [9]. Interestingly, the adsorption process with its ensuing high mobility of the adsorbates tolerates diverse halide substituents, as in 1,4-dibromonaphthalene, and even keto functionalities, as in benzophenone. Since the ^{13}C signals shift with the adsorption [4,5], it is obvious that this process is based on some sort of interaction of the delocalized electrons with the surface. Hence, it is of interest to investigate whether metals sandwiched between the aromatic Cp ligands have a measurable effect on their adsorption.

Therefore, in this contribution we want to study whether the adsorption phenomena found for PAH on surfaces [4,5,8] of mesoporous oxide materials will also be present in the model organometallic compounds chromocene (**1**) and ferrocene (**2**) once they are adsorbed on silica to form **1a** and **2a**. The interest in surface-adsorbed chromocene is based on its potential to evolve into the attractive Union Carbide Catalyst for olefin polymerization over time [1,2]. As paramagnetic metallocene its signals are also shifted out of the diamagnetic region, this way avoiding diverse background signals of silica and rotor inserts. Furthermore, the solid-state NMR measurement parameters for chromocene have already been optimized in previous work [10]. Ferrocene is chosen not only because it represents a prominent cornerstone in organometallic chemistry, but because it is robust and only proceeds to generate ferrocenium salts after the adsorption when it is exposed to oxygen for several days [11]. Therefore, the sampling of data can take place over extended periods of time. Finally, being diamagnetic in nature, the chemical shifts of **2** versus **2a** are expected to be more straightforward to interpret than the chemical shift changes of the paramagnetic **1**.

Chromocene and ferrocene will constitute an instructive pair of adsorbates because they have high and nearly the same melting points (ferrocene: 172–174 °C, chromocene: 168–170 °C) and similar crystal packing. Hence, only electronic factors should play a role in the adsorption process and mobilities across the surfaces. ^1H and ^{13}C solid-state NMR techniques are used in order to probe

the potential change in mobility on going from the crystal lattice to a monolayer on the surface and to develop a better understanding of adsorption phenomena in general.

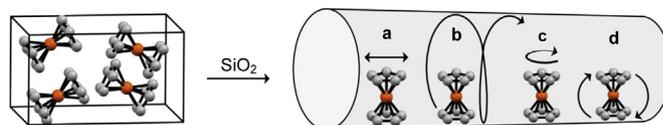
2. Results and discussion

The polycrystalline compounds chromocene (**1**) and ferrocene (**2**) have been adsorbed on silica to form **1a** and **2a** as described in the experimental section. For **2**, the impregnation method results in the same material **2a** as the dry grinding of the components. The amounts have been calculated to result in a sub-monolayer coverage with metallocene, so that the molecules have enough space for traveling freely on the surface. For the calculation of the footprint of **1** and **2** we assume that in analogy to adsorbed PAH [4,5,8], the aromatic ligands are oriented parallel to the surface (Scheme 1). This means that the metallocenes are “standing upright” on the surface.

Although at this point it will not be possible to disentangle specific modes of mobility, several considerations can be discussed, as depicted for ferrocene in Scheme 1. Translational mobility (a) is an indispensable prerequisite for forming a monolayer of molecules by direct interaction of polycrystalline ferrocene with silica. There has to be sort of a “melting process”, which overcomes the packing forces of the crystal lattice, and enables the ferrocene molecules to glide away from the crystal and make space for successor molecules. It should be reasonable to assume that the translational mobility persists also at a later point after consumption of the crystals and formation of the monolayer and is not just present in the initial contact phase.

Next, it is important to consider that the surface of the amorphous silica used is not planar but consists mostly of concave surface within the pores. Therefore, as depicted in Scheme 1, scenario (b), the adsorbed molecules can cruise inside the pores like skaters in a halfpipe, which overall leads to isotropic reorientation of the molecules in space. This isotropic reorientation should be mostly responsible for the reduction of the CSA and residual linewidths of the signals of adsorbed molecules. It should be pointed out that practically all the surface of the silica used is surface inside the pores because the average particle size is very large, between 0.063 and 0.2 mm in diameters. Taking into account that 1 cm³ of the silica used weighs 0.515 g and that spheres can only fill 74.048% of space, one can calculate that even in the case of the smallest particle diameter of 0.063 mm only about 2% of the whole surface area of 750 m²/g is contributed by surface outside of the pores. For the application presented in this manuscript this is negligible, and we can assume that practically all metallocene molecules are adsorbed on the surface inside the pores.

It is well-known that the Cp rings in metallocenes rotate even in the solid materials [3b], therefore we can also assume this ring rotation for the adsorbed molecules. Beyond that, the whole molecules can most probably rotate in their place, as depicted in (c) of Scheme 1. Since this mode of mobility is already present in the polycrystalline material, if both rings rotate in parallel, it is not



Scheme 1. When polycrystalline ferrocene (**2**) is ground with silica, the crystal lattice breaks up and the molecules are adsorbed on the surface within the pores. They can undergo various modes of translational and rotational mobility. The scheme is not according to scale, the pore diameter would be about sixfold the depicted one.

assumed to contribute to the reduction of the residual linewidths or CSA for **2a** in a substantial manner. The rotation of the whole molecule around its metal center, as shown in scenario (d) of Scheme 1, however, represents isotropic reorientation of the molecule, rolling on the surface like a tumbleweed. Therefore, this mode of mobility would in principle reduce the residual linewidths and CSA of **2a** signals as compared to those of **2**. However, taking into account that the interaction of a Cp ring with the surface is strong enough to break down the crystal lattice, this mode of mobility seems rather unlikely. Equally unlikely would be the rolling of the metallocene with the Cp rings oriented perpendicular to the surface, like the wheels on a car axle, as pointed out above.

Finally it should be noted that the drawing in Scheme 1 is not according to scale. The average pore diameter of the silica used is 40 Å, while the height of ferrocene, including the Van Der Waals radii of the carbon atoms is about 6.7 Å. Therefore, if one ferrocene molecule is attached to the “bottom” of a pore, and another one to its “ceiling”, this still leaves an open gap of 26.6 Å between the ferrocene molecules. Since ferrocene travels on the inner surface of the pores, and its crystals “melt” onto the surface, it cannot get stuck in the pores and block them.

The following results demonstrate that both chromocene and ferrocene are adsorbed on the surface of rigorously dried silica. Both the chemical shift and the CSA [3a] change upon adsorption. The CSA becomes substantially smaller in all cases, due to the increased mobility of the surface species as compared to the molecules confined to their places in the crystal lattice. The mobility reduces anisotropic interactions in general, and therefore the residual halfwidths of the isotropic lines are also substantially smaller. Table 1 summarizes all halfwidth data.

It should be mentioned that no indication for stacking of chromocene or ferrocene on the surface is found in the spectra. For adsorbed phosphines this is a trivial point because their free electron pair is consumed by the interaction with the surface. However, aromatic compounds and metallocenes have “two sides” and could in principle offer themselves for stacking, as surface-adsorbed phosphine oxides do [12].

In Fig. 1 the ^1H MAS spectra of polycrystalline (**1**) and adsorbed chromocene (**1a**) are compared at 13 kHz spinning speed. The chemical shift of the signal of polycrystalline **1** changes from $\delta(^1\text{H}) = 315$ ppm to $\delta(^1\text{H}) = 298$ ppm for the adsorbed species **1a**. Since the overall chemical shift range of paramagnetic metallocenes is large, the difference between the signal shifts of polycrystalline versus adsorbed chromocene is not too surprising. Especially because, together with mobility effects, the adsorption is also expected to change the electronic state of the organometallic complex.

Most obvious in Fig. 1 is the reduction of the CSA of the ^1H signal in **1a** compared to **1**. For the latter, all rotational sidebands are much more intensive, for example, the first order rotational sidebands reach nearly half the height of the isotropic line. In contrast, for **1a** the rotational sidebands barely emerge from the baseline and might even be due to traces of residual polycrystalline material **1**.

Upon adsorption, the residual halfwidth of the isotropic signal is also reduced from about 4.9 kHz in **1** to 2.9 kHz in **1a**. Regarding the spectrum of **1a** in Fig. 1 it is also noteworthy that once it is adsorbed

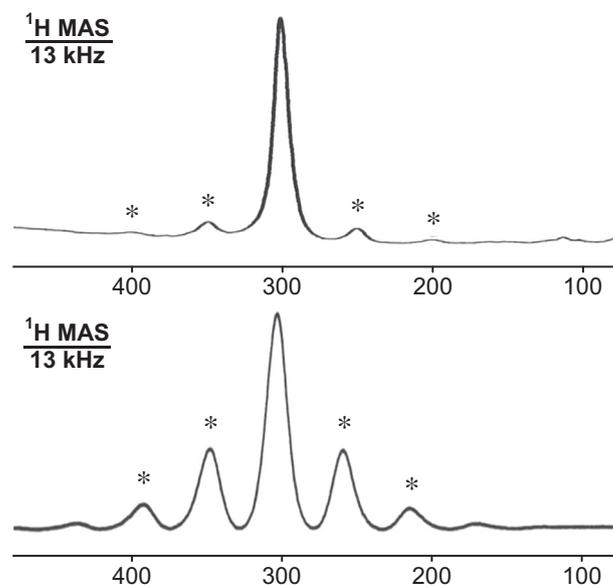


Fig. 1. ^1H MAS NMR spectra of polycrystalline chromocene (**1**, bottom) and chromocene adsorbed on silica (**1a**, top, proton background signal of silica not shown). The asterisks denote rotational sidebands.

on the surface, chromocene starts to react with silica within an hour, losing one Cp ligand as cyclopentadiene and forming various half sandwich and dimeric species, as outlined in previous work [2]. Some of these reaction products contribute to the background signal in the diamagnetic region of the spectrum around 0 ppm.

Regarding the spectra displayed in Fig. 2, the carbon chemical shift of polycrystalline **1** changes from $\delta(^{13}\text{C}) = -258$ ppm (10 kHz) to $\delta(^{13}\text{C}) = -222$ ppm (15 kHz) upon adsorption and formation of **1a**. About 20 ppm of this signal migration into the diamagnetic region might be attributed to the higher spinning speed for **1a** and the heating due to friction effects [10]. However, about 16 ppm of chemical shift difference remain which can again be explained by changes in the shielding of the Cp rings upon adsorption on the silica surface.

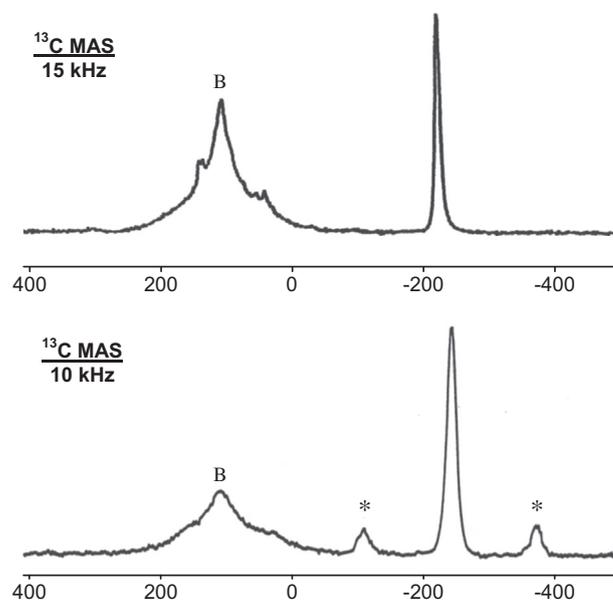


Fig. 2. ^{13}C MAS NMR spectra of polycrystalline chromocene (**1**, bottom) and chromocene adsorbed on silica (**1a**, top). The asterisks denote rotational sidebands, B the signal of the carbon background of a teflon spacer in the rotor.

Table 1

Residual linewidths $\Delta\nu_{1/2}$ [kHz] of the ^1H and ^{13}C solid-state NMR signals of polycrystalline chromocene (**1**) and ferrocene (**2**) and their adsorbed forms on silica (**1a**, **2a**). Single-pulse experiments at the MAS frequencies [kHz]: ^a13, ^b15, ^c10, ^d2.

$\Delta\nu_{1/2}$ [kHz]	Chromocene		Ferrocene		
	$^1\text{H}^a$	$^{13}\text{C}^b$	$^1\text{H}^c$	$^1\text{H}_{\text{linewidth}}$	$^{13}\text{C}^d$
Adsorbed	2.90	0.65	0.24	0.94	0.43
Polycrystalline	4.90	1.20 ^c	0.75	14.25	0.93

The residual halfwidth of the isotropic ^{13}C line is reduced to nearly half its original value on going from **1** (1.20 kHz) to **1a** (0.65 kHz) (Table 1). Again, this “slimming” effect can be attributed to the increased mobility of the molecules on the surface. The very narrow line of **1a** even implies that the motion might be fully isotropic with translational in addition to rotational movements. Probably the adsorbed molecules in **1a** can even cruise along the walls and “ceiling” of the irregularly oriented pores of the silica like a skateboarder in a halfpipe, thus mimicking isotropic, solution-like mobility, as discussed above and depicted in Scheme 1.

The CSA of the ^{13}C MAS signals is reduced substantially when adsorbing **1** on silica to generate **1a**. This can again be deduced from the disappearance of the first order rotational sidebands (Fig. 2).

The ^1H MAS spectrum of polycrystalline ferrocene (**2**) shows one isotropic line (Fig. 3), as expected from the similar crystal packing compared to chromocene. The CSA pattern also looks symmetric and is composed of two sets of rotational sidebands in addition to the isotropic line. When **2** is adsorbed on silica to form **2a**, its chemical shift changes from $\delta(^1\text{H}) = 4.4$ ppm to $\delta(^1\text{H}) = 4.6$ ppm for **2a** at 10 kHz rotational frequency. This, albeit small, downfield shift is a typical trend for adsorbed species, e.g. phosphines [7f] or phosphine oxides [12]. At the same time the residual linewidth of the isotropic line is reduced from 750 Hz for the signal of **2** to less than half that value, 240 Hz for the resonance of **2a** (Table 1).

The background signal in the ^1H MAS spectrum of **2a** (Fig. 3) stems mainly from the protons in silica. When a rotor is filled with silica and a ^1H MAS spectrum is recorded using the same measurement conditions and parameters, including the receiver gain, the small background signal is observed. It can be subtracted from the ^1H MAS spectrum of **2a** without distortions of the baseline, yielding a clean spectrum with symmetric center line (not shown).

As in the case of chromocene, the CSA is reduced substantially, and the two miniscule first order rotational sidebands might stem from trace amounts of residual polycrystalline material **2**.

The ^1H MAS signal of polycrystalline **2** is already rather narrow, and both the CSA and dipolar interactions are small. This is most probably due to the fast rotation of the Cp ring which takes place even in the solid state, because the activation barrier of this process is comparatively low with about 9 kJ/mol [3b]. In order to better see the difference between the signals of **2** and **2a**, the ^1H wide-line NMR spectra without rotation have been recorded in order to allow maximal CSA and dipolar interactions for static protons. This trick

has been used recently to distinguish between backbone protons and included mobile water molecules in polymers [13]. Indeed, as Fig. 4 shows, the difference between the ^1H wide-line spectra of **2** and **2a** is substantial. After deconvolution of the spectrum of **2a** the linewidth of the narrow signal sitting on the background hump can be determined to be 0.94 kHz (Table 1). In contrast, the signal of polycrystalline ferrocene has a large halfwidth of 14.25 kHz. Again, this scenario can only be interpreted based on a fast isotropic motion of the adsorbed ferrocene molecules across the silica surface in the pores (Scheme 1, a and b).

The ^{13}C solid-state NMR data (Fig. 5, Table 1) corroborate the assumption that ferrocene is adsorbed on the silica surface and rather mobile. The chemical shift of the signal of polycrystalline **2** changes from $\delta(^{13}\text{C}) = 69.9$ ppm to $\delta(^{13}\text{C}) = 71.2$ ppm for **2a** at 2 kHz rotational frequency. This is in accordance with the downfield shifts observed for adsorbed phosphines and phosphine oxides [7f,12]. The comparatively small CSA for polycrystalline **2** [3a] leads to the absence of rotational sidebands at high MAS spinning speeds. Therefore, slow spinning with 2 kHz has been chosen for most experiments on **2** and **2a** (Fig. 5). Upon adsorption the CSA is further reduced and at 2 kHz there are no longer sidebands present in the ^{13}C MAS spectrum of **2a**, only the isotropic line. Again, this can be attributed to the fast isotropic mobility of the adsorbed ferrocene across the support surface.

The ^{13}C linewidths of **2** and **2a** deserve some more detailed analysis. They are not directly comparable as shown in Fig. 5 because different pulse programs have been used to record the spectra with optimal signal to noise (S/N) ratio. As demonstrated for adsorbed molecules in previous work, CP/MAS is no longer efficient because the dipolar interactions are reduced due to the mobility of the molecules [14]. Only the polycrystalline **2** gives good S/N with CP/MAS (Fig. 5), and the residual linewidth has been determined as 88 Hz. An approximate halfwidth of 290 Hz has been estimated from the ^{13}C CP/MAS spectrum of **2a** with poor S/N. Simple high-power decoupling leads in both cases to the narrowest signals at 2 kHz spinning speed, with 53 Hz for **2** and 264 Hz for **2a**. It is known from previous work on chromocenes that high-power decoupling can lead to a broadening of the signals of non-quaternary carbon nuclei when the decoupling frequency matches approximately the frequency of the Cp ring rotation [10]. In order to avoid this complication, as well as interferences of the Cp ring rotation with the MAS frequency [15] and splitting of the

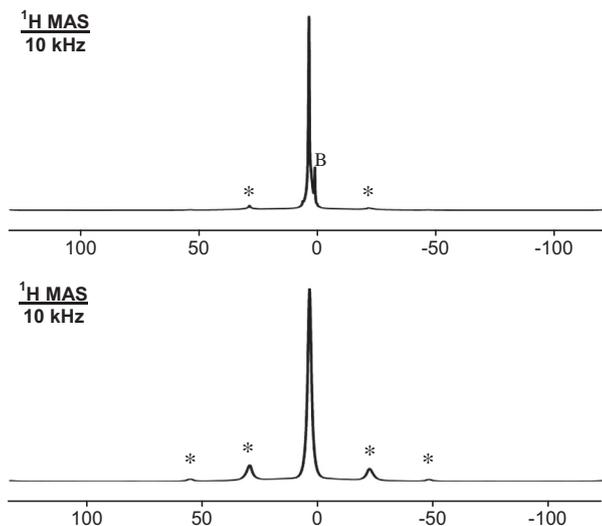


Fig. 3. ^1H MAS NMR spectra of polycrystalline ferrocene (**2**, bottom) and ferrocene adsorbed on silica (**2a**, top) at 10 kHz spinning speed. The asterisks denote rotational sidebands, B the signal of the proton background of the silica.

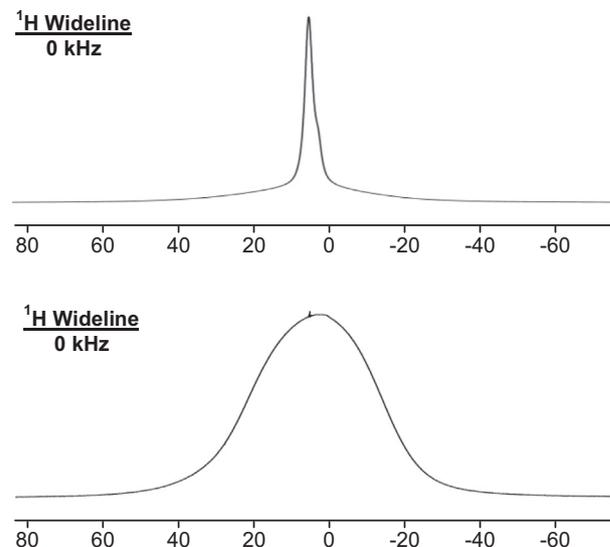


Fig. 4. ^1H wide-line NMR spectra of polycrystalline ferrocene (**2**, bottom) and ferrocene adsorbed on silica (**2a**, top).

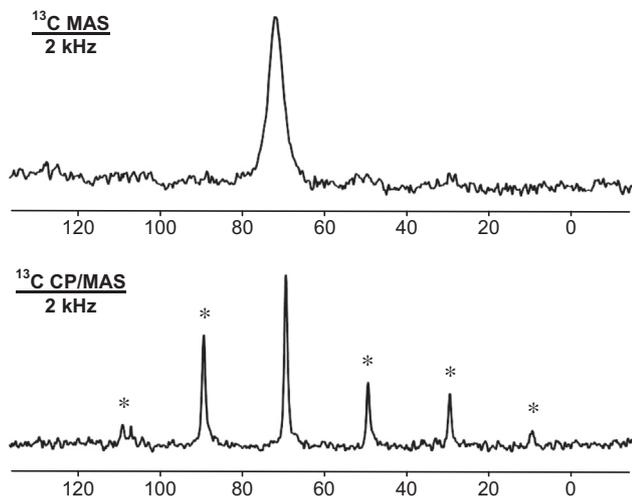


Fig. 5. ^{13}C CP/MAS NMR spectrum of polycrystalline ferrocene (**2**, bottom) and ^{13}C MAS NMR of ferrocene adsorbed on silica (**2a**, top) at 2 kHz rotational speed. The asterisks denote rotational sidebands.

Hartmann-Hahn matching profile at higher MAS rates [16], we have recorded the ^{13}C MAS spectra of **2** and **2a** (Fig. 5) with single-pulse excitation at 2 kHz rotational frequency. This results in the half-widths of ca. 930 Hz for **2** and 430 Hz for **2a** (Table 1), fulfilling the expectation of a line-narrowing effect due to the extra mobility of ferrocene molecules in **2a**. The finding that adsorbed ferrocene is mobile on silica surfaces is also in accordance with earlier results obtained by photochemical techniques [17]. Lowering the spinning speed for **2a** to 0 kHz and recording the ^{13}C wideline spectrum still gives a signal with respectable S/N ratio, and the linewidth increases only to 517 Hz. In contrast to this, the wideline spectrum of polycrystalline **2**, recorded with single-pulse excitation results in a broad hump that merges into the baseline. Faster spinning with a rotational frequency of 12 kHz reduces the linewidth of the single-pulse spectrum of **2** to 398 Hz, but unfortunately all rotational sidebands are spun out of existence in this case and herewith the CSA information is lost.

The residual linewidths for ^{13}C MAS signals of **1a** and **2a** (Table 1) are still larger by a factor of about 10 as compared with the spectacular results seen for adsorbed PAH [4,5,8]. The residual linewidth should be very sensitive with respect to the electron density in the aromatic system because this is one factor determining the strength of surface adsorption and thus the mobility. The electron density is different for aromatic systems bound to metal centers as compared to the uncoordinated aromatic rings in the PAH, like naphthalene and biphenyl [4,5,8], and therefore the residual linewidths of the Cp signals in the metallocenes cannot be compared with the linewidths of those PAH. Additionally, in the case of chromocene, the paramagnetism leads to an increased residual linewidth. Besides the electron density in the Cp rings, the pre-treatment of the support plays a role because the degree of wetness also influences the mobilities of the species on the surface and in turn the residual linewidth. This has been investigated by the authors in a parallel project about adsorbed phosphines [12].

At this point one might also contemplate whether the presence of two different Cp signals, one for the ring interacting with the surface and one for the ring without surface contact, can be seen in the spectra of **2a**. Unfortunately, the chemical shift difference between polycrystalline and adsorbed ferrocene is rather small. Therefore, it will not be possible to discern two different signals stemming from one adsorbed molecule. However, one can conclude that, in case two overlapping signals were present in principle, both their CSA is diminished. If one signal would retain the original CSA,

all sidebands in the spectrum of adsorbed ferrocene would be half as intense as those in the spectrum of polycrystalline **2**, because the ratio of adsorbed to non-adsorbed Cp rings is 1:1.

However, since there are basically no rotational sidebands left in the spectra of adsorbed ferrocene, we conclude that the CSA is diminished due to the mobility of the ferrocene molecules on the surface, which has to be the same for adsorbed and non-adsorbed Cp rings. So, in contrast to adsorbed phosphines, where partial phosphonium formation might reduce the CSA, the CSA reduction of adsorbed metallocenes is entirely due to the mobility and not any interaction with the surface.

To summarize this section, although ^{13}C solid-state NMR spectra need extra consideration with respect to linebroadening effects due to the Cp ring rotation which can interfere with any high-power decoupling, the assembly of applied techniques still unequivocally supports the results from the ^1H spectra. Ferrocene is adsorbed on the silica surface and shows substantial mobility, mostly due to translational movement across the surface.

3. Conclusion

It has been demonstrated unequivocally by ^1H and ^{13}C solid-state NMR techniques that chromocene and ferrocene are strongly adsorbed on a silica surface and then display translational mobility. In the case of ferrocene, the adsorption process can take place by impregnation when a solution of it is mixed with a slurry of silica in the solvent and subsequent removal of the solvent. Additionally, for both chromocene and ferrocene, the adsorption can be achieved at room temperature by grinding the dry components, metallocene and silica. In this case, obviously the forces that drive the surface adsorption are able to break down the crystal lattices of chromocene and ferrocene. The scenario can be described as sort of a melting process although the melting points of both metallocenes are much higher than room temperature with 172–174 °C for ferrocene and 168–170 °C for chromocene. The fact that the crystalline material “melts” onto the surface and the molecules spread out to produce a sub-monolayer corroborates the findings by solid-state NMR that the molecules must be translationally mobile. No indication for stacking of the metallocene molecules on the surface has been found.

In future studies the mode of the mobility will be defined and its extent quantified for both ferrocene and chromocene. The $^{13}\text{C}T_1$ and $^1\text{H}T_2$ relaxation times [13], as well as CSA values will be measured at different temperatures. Furthermore, ^2H NMR [18] of perdeuterated material [10] will be used in combination with ^2H NMR lineshape simulations to determine the mode of the mobility and quantify its extent [18]. Since the subsequent reaction of the adsorbed chromocene with the bare silica surface complicates the investigation of the mobility, an end-capped, e.g. Me_3Si -modified surface [14a] can be used for prolonging the lifetime of adsorbed molecular chromocene. The diamagnetic and robust ferrocene will be employed to obtain complementary information. For chromocene, the reaction products will be identified by fast ^1H MAS and ^{13}C CP/MAS NMR.

4. Experimental section

The ^1H and ^{13}C solid-state NMR spectra were measured with Bruker MSL 300 and Avance 400 widebore NMR spectrometers equipped with 4 mm MAS probeheads. For the measurements of the polycrystalline and adsorbed chromocene teflon inserts were used in the rotors to protect the samples from moisture and oxygen. Ferrocene-containing samples were measured without teflon spacers by filling the whole rotors. For the ^{13}C MAS measurements ^1H high-power decoupling was turned off or applied as detailed in the text. Cross-polarization was only applied in the case of polycrystalline ferrocene. The chromocene-containing samples were

spun with dry N₂ as the bearing and drive gas, for the ferrocene samples purified compressed air was used. The recycle delays were 10 s for the ¹³C NMR spectra with high-power decoupling and 3 s for the CP/MAS spectra. The ¹³C single-pulse experiments were run with a pulse delay of 10 s while for all ¹H spectra 2 s were applied. Typically 64 transients were accumulated for ¹H and 2400 for ¹³C measurements. For adsorbed and polycrystalline chromocene the parameters given in Ref. [10] were used.

All adsorption experiments were carried out in a glove-box or using standard Schlenk techniques and a purified N₂ atmosphere, if not stated otherwise. The pentane was dried by boiling over Na, distilled, and stored under N₂. The silica (Merck, 40 Å average pore diameter, 0.063–0.2 mm average particle size, specific surface area 750 m²/g) was rigorously dried *in vacuo* at 400 °C for 4 days to remove adsorbed water and condense surface silanol groups.

The footprint of ferrocene, standing upright on the surface, was calculated based on the distance between the center of the Cp ring and an H atom (2.3 Å) and taking the Van Der Waals radius of H into account to give an overall radius of 3.5 Å. Assuming hexagonal packing of these circles on the surface, about 201 ferrocene molecules can maximally occupy 100 nm² of surface area in a monolayer, corresponding to 2.50 mmol of ferrocene per g of silica. Accordingly, in order to achieve about 85% of the theoretically possible maximum surface coverage (2.125 mmol ferrocene per g of silica), 139.8 mg of ferrocene (0.7515 mmol) was ground for about 1 min with silica (300.6 mg). The mixture was transferred to a vial and sealed. Then the mixture was allowed to sit undisturbed for two days before the measurements were started. In the course of the two days the color changed from orange to yellow. Alternatively, the corresponding amount of ferrocene was dissolved in pentane and added to a slurry of silica in pentane. Then the solvent was removed *in vacuo*. Both methods of preparation, dry grinding and impregnation, led to the same material with surface-adsorbed ferrocene.

Assuming the same footprint for chromocene, 421 mg of chromocene (2.31 mmol) were ground in a glove-box with 1 g of silica to result in a surface coverage of 92% of the theoretically possible maximal surface coverage. The sample was transferred to the rotor within 10 min, and the NMR spectra were recorded immediately.

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