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The Determination of the Absolute Parameters of Nuclear Magnetic Resonance Spectra of Surface Complexes of Benzene with Co^{2+} Ions on Aerosil

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We propose a method for the determination of the number of active surface sites and of the absolute values of paramagnetic ^1H-nmr-line shifts of coordinated molecules of surfaces containing paramagnetic ions. As an example the number of active Co^{2+} ions in the complex formation of benzene molecules with Co^{2+} ions on the Aerosil surface is determined. The paramagnetic ^1H-nmr shift of a benzene molecule in the coordination sphere of a Co^{2+} ion on Aerosil was found to be 150 ppm. Additional it was possible to detect the mechanism of exchange between coordinated and physically adsorbed molecules on the surface as a two particle substitution process.

INTRODUCTION

Nuclear magnetic resonance is a powerful tool for an investigation of complexes of organic molecules with paramagnetic metal ions in solutions. The method gives informations about the structure of complexes, their strengths, about the nature of metal–ligand bonds, about the reorientation time of complexes, the residence time of molecules in the solvation sphere a.o. (*1–7*). In (*8*) it was shown, that the nmr method together with adsorption measurements can be successful applied to study surface complexes of organic molecules with transition metal ions. Nuclear magnetic resonance spectra of adsorbed molecules on surfaces containing transition metal ions with short relaxation times show considerable paramagnetic shifts due to formation of surface complexes involving these ions. In the case of Co^{2+} and Ni^{2+} ions on SiO_2 surfaces this paramagnetic shift of ^1H-nmr lines is mainly caused by contact interaction of unpaired electrons of the ions with protons of coordinated molecules (*9*). Surface complexes of olefins and saturated hydrocarbons with Ni^{2+} and Co^{2+} ions on Aerosil were studied by ^1H-nmr in (*9*) and the structure and strength of the complexes with paramagnetic ions were discussed. ^1H-nmr studies of benzene adsorbed on Aerosil containing Co^{2+} ions were done in (*8, 10, 11*). ^{13}C-nmr gives additional information for these complex formation, as it were shown in (*11, 12*) in the case of Co^{2+}–benzene complexes on Aerosil and for Ni^{2+}–benzene complexes on SiO_2 surfaces in Ref. (*13*).

For understanding the nature of the bonds in such surface complexes the knowledge of the absolute parameters of nmr spectra of the coordinated molecules is very important. The first attempt in this direction was made by Hoffman (*11*) for surface complexes with Co^{2+} ions, which were

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TABLE 1

Temperature Dependence of the ^{1}H-nmr Resonance Line of Adsorbed Benzene on Aerosil/0.5% Co at the Coverage 4.6×10^{19} (molecules/g)

Temp t (°C)	Line shift (Hz)	Linewidth (Hz)
+10	1690	700
−20	1540	900
−30	1460	1100
−45	1370	1400

studied also in (*8*, *9*). He estimated the absolute values of the paramagnetic nmr line shifts in coordinated benzene for the ^{1}H and ^{13}C nuclei. From these data it followed, that all cobalt was active in complex formation. This conclusion does not agree with results reported in (*9*), where the amount of active cobalt was smaller than the amount of cobalt ions supported.

In this work we propose a method to determine the number of active surface sites in complex formation and the absolute values of paramagnetic ^{1}H-nmr line shifts of the coordinated molecules. We will use, for example, complexes of benzene with Co^{2+} ions on Aerosil.

EXPERIMENTAL METHODS

The sample was prepared as described in (*10*). After drying in air at room temperature the samples were activated *in vacuo* at 550°C for 1 h. The rate of heating to reach the final temperature was about 100 K/hr. The ^{1}H-nmr spectra were recorded using a Soviet made nmr spectrometer with an operating frequency at 60 MHz. This spectrometer and the apparatus for the simultaneous measurements of nmr spectra of the adsorbate and isotherms of adsorption were described in detail elsewhere (*9*, *10*). The nmr line shifts of the adsorbed benzene on the samples were measured with respect to the line position of adsorbed benzene on pure Aerosil with an accuracy of ±0.5 ppm. The accuracy of the adsorption measurements at low equilibrium pressure ($1.33 \times 10^1 \ldots 10^2$ Pa) was 5×10^{17} molecules/g of the adsorbent. Before adsorbing the benzene was purified by the freeze–pump–thaw method.

RESULTS AND DISCUSSION

The ^{1}H-nmr spectra of benzene adsorbed on Aerosil containing Co^{2+} ions showed a symmetrical line shifted to higher magnetic fields in comparison with the line position of benzene on pure Aerosil. Figure 1 gives the dependence of the measured line shifts of benzene on the samples with different contents of cobalt as a function of the inverse amount of adsorption. The curve is almost linear for the sample containing 0.75 wt% of cobalt but deviates greatly from the straight line for the samples with 0.25 and 1 wt% of cobalt. An analogous deviation was observed (*14*) for saturated hydrocarbons adsorbed on cobalt containing Aerosil and was explained by the formation of complexes of intermediate strength for these molecules with Co^{2+} ions. In our case this explanation cannot be applied, because the line shifts decrease and the linewidths increase with lowering the temperature for a constant amount of adsorbed benzene (cf. Table 1). It should be noticed, that in the case of "intermediate" complexes the increase of the number of surface complexes and the increasing paramagnetic shift due to Curie law lead to larger values of the observed shifts at lower temperatures (*14*).

The measured dependence of the shifts on the coverage and on the temperature obtained in this work can be explained if one assumes, that in the systems the exchange between benzene molecules in the coordination sphere of the Co^{2+} ions and physically adsorbed molecules is slightly restricted. Such a situation was observed earlier for cyclohexene adsorbed on cobalt containing Aerosil (*10*) and was theoretically examined in (*15*). As was shown in

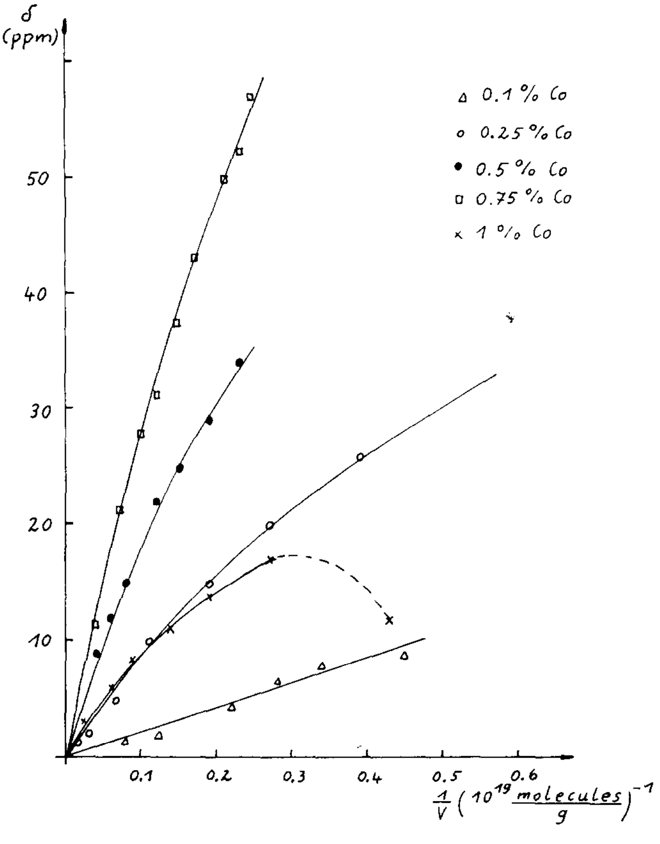

FIG. 1. ^{1}H-nmr shift of adsorbed benzene on Aerosil containing Co^{2+} ions at +10°C (with respect to benzene on pure Aerosil).

(*15*) the shifts of the observed resonance line in comparison to the line position of physically adsorbed molecules can be described as[1]

$$\delta = p_K\delta_K - 4\pi\tau_0 p_A p_K \delta_K \Delta H_K, \quad (1)$$

or for "strong" complexes

$$\delta = \frac{n\delta_K}{V}\left[1 - 4\pi\tau_0\Delta H_K\left(1 - \frac{n}{V}\right)\right] \quad (2)$$

where

δ	is the measured line shift (in comparison to the line positions of the physically adsorbed molecules)
$\delta_K, \Delta H_K$	paramagnetic shift and linewidth of a coordinated molecule
$p_K = n/V$	the mole fraction of coordinated molecules
$p_A = 1 - (n/V)$	the mole fraction of physically adsorbed molecules
n	the number of coordinated molecules (for a coordination number 1 equals to the

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[1] The derivation of Eq. (1) in (*15*) was based on the consideration of fast exchange of molecules between sites of physical adsorption and chemisorption. The nmr spectral line shape of physisorbed molecules was considered to be Lorentzian with linewidth ΔH_A. The spectrum of molecules in the chemisorbed state was approximated as a superposition of Lorentzian lines with linewidths ΔH_K and with distribution function $g(\omega)[\int_{-\infty}^{+\infty} g(\omega)d\omega = 1]$. Assuming that the mean lifetime of a molecule in any state with a given ω is equal to τ_0 the relaxation function $X(\tau)$ for a system of particles with spin $\frac{1}{2}$ was calculated using the kinetic equations of a density matrix. Eq. (1) then follows directly from $X(\tau)$. The applicability of Eq. (1) to the system under study was also discussed in (*15*) where the complete derivation may be found.

TABLE 2

Experimental Results for Benzene on Aerosil with Different Amount of Cobalt[a]

Sample		^{1}H-nmr results (10^{22} molecules Hz/g)	Adsorption isotherms			
Cobalt (wt %)	No. of Co^{2+} ions (10^{19} g^{-1})		n_c (10^{19} molecules/g)		n_{Co}; amount of active Co^{2+} ions	
			1	2	(10^{19} ions/g)	Relative amount (%)
0.1	1	1.3	0.5	0.67	0.15	15
0.25	2.5	5	0.9	1	0.55	22
0.5	5	13	2	1.9	1.55	30
0.75	7.5	18	2.5	2.4	2.05	27
1	10	6	1.2	1.3	0.85	10

[a] 1. values from the difference adsorption isotherms; 2. values from the adsorption isotherms.

number of active cobalt ions)

V the total amount of adsorbed molecules

τ_0 the characteristic time for the exchange process.

The characteristic time τ_0 depends on the exchange mechanism. There are two extreme cases of exchange (*15*):

1. Dissociative decomposition of the complex

$$[MA] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M + A. \qquad \text{(A)}$$

2. Two particle substitution exchange,

$$[MA] + A' \xrightarrow{k_{ex}} [MA'] + A. \qquad \text{(B)}$$

Here M denotes the adsorption center (Co^{2+} ion), A, A' the adsorbed molecules, and $[MA]$ the surface complex.

These two schemes of exchange lead to different dependences of the value τ_0 on the coverage, and using our data it is possible to detect the real mechanism of exchange between coordinated and physically adsorbed benzene molecules on cobalt containing Aerosil. Scheme (A) gives a value τ_0, which does not depend on the coverage. So the curves represented in Fig. 1 should be of convex curvature [cf. Eq. (2)] in contrast to the experimental result. On contrary, if the exchange in the system can be described by the scheme (B), the characteristic exchange time is

$$\tau_0 = \frac{1}{k_{ex} \cdot V}, \qquad (3)$$

and the dependence of the shift on the inverse coverage (for $p_A \gtrsim p_K$) should have the same character as shown in Fig. 1. Thus our data are in agreement with the proposition, that benzene molecules form strong complexes with the surface Co^{2+} ions, whereby the fast exchange between the coordinated and physically adsorbed molecules is slightly restricted and the mechanism of exchange is a two particle substitution process [cf. scheme (B)]. Now we can estimate some parameters characterizing the surface complexes and the exchange process.

Determination of the Absolute Value of the Paramagnetic Line Shift of the Benzene Molecules Coordinated with Co^{2+} Ions

The measured shift of the NMR line is an averaged value due to the exchange process in the system. If the exchange between coordinated and physically adsorbed molecules is fast, so the expression [Eq.

(1), (2)] for the shift is

$$\delta = \frac{n}{V} \delta_K. \tag{4}$$

Obviously fast exchange should occur at high coverage due to the decrease of the value τ_0 according to Eq. (3). Therefore the initial slopes of the curves in Fig. 1 give values for the product $n\delta_K$ [according to Eq. (4)], which are listed in Table 2. To calculate the absolute paramagnetic shift δ_K, the number of Co^{2+} ions which are active in complex formation must be determined. This can be done by a measurement of the adsorption isotherms of benzene at low equilibrium pressures. Figure 2 shows the isotherms of benzene adsorption for the samples, which were measured up to equilibrium pressures of 1.33×10^2 Pa. As can be seen from Fig. 2 the amount of benzene adsorbed on cobalt containing samples is significantly greater than that on pure Aerosil. This obviously is due to strong complex formation of the benzene molecules with Co^{2+} ions. The number of active cobalt ions was estimated in two ways assuming that only one benzene molecule interacts with a Co^{2+} ion and that this interaction is much stronger than the interaction of the physically adsorbed molecules with the surface.

In the first way the adsorption isotherm of benzene on pure Aerosil is subtracted from the isotherms of the cobalt containing samples. An example for this procedure is shown in Fig. 3.

In the second way the number of strongly adsorbed benzene molecules is determined directly from the isotherms assuming that the experimental isotherms can be described by a sum of two Langmuir-type equations, where the adsorption constant for the physically adsorbed molecules does not change after impregnation of cobalt on Aerosil. Both of these methods give similar results, which are listed in Table 2. From the data listed in Table 2 one can see, that only a part of impregnated cobalt on Aerosil is active in the complex formation with benzene.

Figure 4 shows the dependence of the product $n\delta_K$ determined from NMR measurements on the amount of the excess (n_e) of the benzene adsorption on the different samples. The linear relation indicates, that the shift of the coordinated benzene molecules does not depend on the amount of the cobalt on Aerosil and hence the Co^{2+} ions which are active in complex formation are identically. The slope of this line (cf. Fig. 4) gives a value $\delta_K = 150$ ppm, which is by a factor of 2.5 larger than that reported by Hoffmann (*11*). The value δ_K

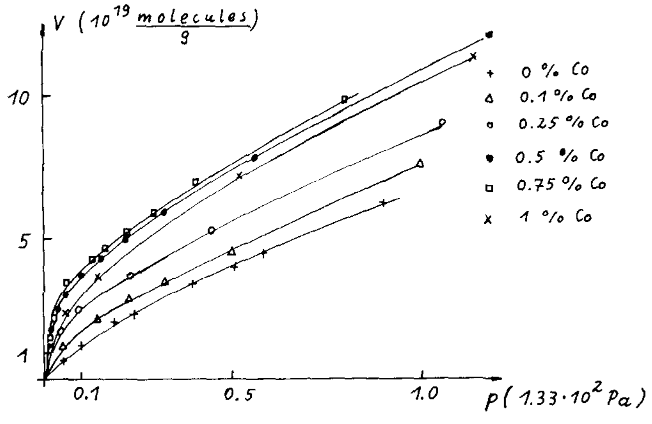

FIG. 2. Adsorption isotherms of benzene on Aerosil with various amount of Co^{2+} ions (at +10°C).

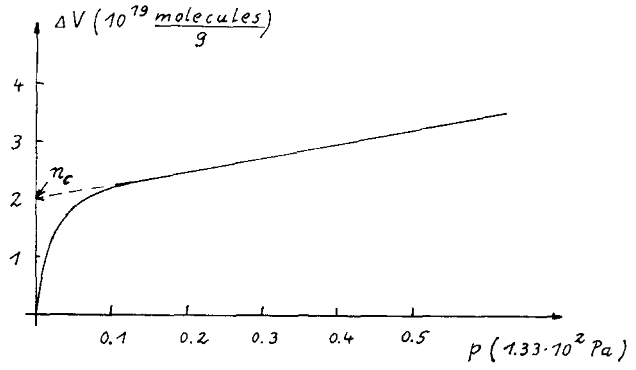

FIG. 3. Difference of the adsorbed amount of benzene on Aerosil with 0.5% of cobalt and on pure Aerosil.

given by Hoffmann (*11*) is too small, since our measurements on the 0.75 wt% sample [which is similar to that in (*10*)] show a monotonic increase of the shift down to the lowest measured coverage (3.8 × 10^{19} molecules/g), which is about 50% of the total amount of cobalt on this sample. The scheme proposed in (*11*) for the dependence of the shift from the inverse coverage does not agree with the observed dependence in this work and especially it does not explain the lowering of the shift for the lowest measured coverage on the sample with 1 wt% of cobalt (cf. Fig. 1). In (*11*) the linearity of the shift was observed down to a coverage of about $\frac{1}{3}$ monolayer, which corresponds to 1.7 × 10^{20} molecules/g in our case, and we found also a linear dependence of the shift in this range (cf. Fig. 1). The shift of the lowest measured coverage in (*11*) is in agreement with our values but the extrapolated curve in (*11*) does not agree with the observed monotonic increase of the shift on this sample in our measurements.

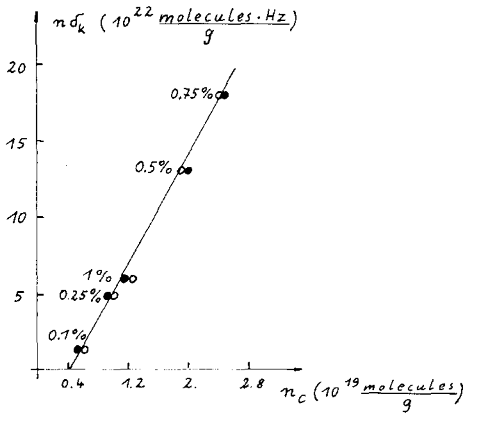

FIG. 4. Correlation between $n\delta_K$ and the number n_c of coordinated benzene molecules on Aerosil with various amount of Co^{2+} ions: (●) from the difference adsorption isotherms; (○) from the adsorption isotherms.

The intercept on the abscissa of the straight line in Fig. 4 may be an indication for the existence of diamagnetic sites of strong benzene adsorption after impregnation of cobalt on Aerosil. In column 6 of Table 2 the numbers of active Co^{2+} ions are given. These values were obtained as the difference of the number of strong adsorbed benzene molecules (n_c) and the number of diamagnetic sites (4 × 10^{18} molecules/g) on the surface. The last column of Table 2 shows the relative amount of active cobalt (%). The maximum number of active cobalt ions on Aerosil in the complex formation with benzene was found to be at the samples with 0.5 ... 0.75 wt% of cobalt. It should be noticed, that the number of active cobalt ions on the surface depends on the conditions of the sample pretreatment, which influence the state and the distribution of the impregnated Co^{2+} ions.

In this work it was shown, that for benzene adsorbed on Aerosil containing Co^{2+} ions exists a slightly restricted fast exchange (at +10°C) between coordinated and physically adsorbed molecules by a two particle substitution process. Only a part of the impregnated cobalt is active in complex formation with benzene and the maximum number of active Co^{2+} ions was found on the samples with 0.5 ... 0.75 wt% of cobalt.

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