

Studies of Adsorption of 2,2'-Bipyridyl on the Surface of Highly Regulated Silica Matrix of the MCM-41 Type by Means of ^{15}N NMR Spectroscopy

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Abstract—The study of 2,2'-bipyridyl adsorption on the surface of highly regular MCM-41 silica at 300 and 130 K was carried out by the ^{15}N NMR spectroscopy. It was shown that at 300 K the adsorbed molecules were involved in the processes of isotropic reorientation accompanied by the formation and rupture of hydrogen bonds with the surface-located hydroxy groups. Each molecule of 2,2'-bipyridyl forms no more than one hydrogen bond at a time, and their surface density is about one molecule per 1 nm^2 of the surface. At 130 K 2,2'-bipyridyl forms a monolayer on the surface of silica including about 1.6 molecule per 1 nm^2 . In this monolayer each molecule forms a hydrogen bond with one hydroxy group and prevents the interaction of the other bipyridyl molecules with one more hydroxy group.

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The structure, chemical, and the adsorption properties of nano-porous materials present great interest from the scientific as well as from the practical point of view [1–5]. From the scientific point of view such structures can be regarded as the ideal test systems permitting to study indirectly the processes of self-organization of complex organic molecules because the above-mentioned matrices are their replicas [6, 7]. From the practical point of view the use of such materials opens the possibilities of performing selective synthesis and controlled polymerization inside the strictly regular nano-pores permitting the creation of molecular structures with the initially desired properties [8]. In particular, there appears a possibility not only of the simple control of the primary structure of complex polymer chains, but of their two- and three-dimensional spatial arrangement.

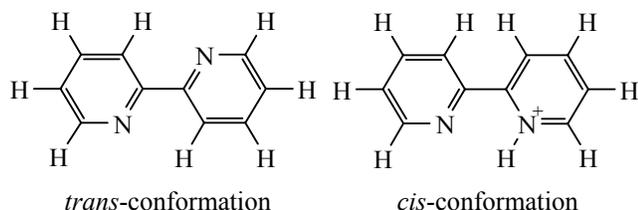
Most widespread are the matrices on the basis of silicon dioxide. Up to now a large number of various procedures is developed permitting to carry out selective modification of physicochemical properties of such matrices. For example, introduction of functional groups or metal ions into their structure can be carried out either directly in the course of synthesis

[9] or by the subsequent modification [10], by ion exchange [11, 12], or by adsorption [13, 14]. Besides, the possibilities of regulated alteration of the surface morphology of the silica matrix are studied [15]. Nevertheless, in realizing processes taking place on the internal surface of pores the main role is played by the structure of the starting matrix.

The surface of any silica is covered with hydroxy groups. Their density depends on the morphology of the sample, on the method of its synthesis, and on the history of its treatment. The density of the hydroxy groups usually varies from 1.2 to 4.5 groups per a square nanometer [16, 17]. Some types of silica contain strongly adsorbed water which leaves the surface slowly at the evacuation even at the temperatures above 500 K [18]. Contrary to the expectations the amount of the chemisorbed water does not correlate either with the specific surface area of the silica sample or with the density of hydroxy groups on its surface [17, 19]. At the temperatures above 500 K adjacent surface hydroxy groups may form covalent bonds by the dehydration reaction. Hence, an attempt of removing the chemisorbed water may be accompanied by the alteration in the morpho-

logy of the sample. While using silica of MCM-41 and SBA-15 types this problem does not appear. It was shown previously that drying these matrices at 400–420 K and the residual pressure 10^{-8} bar for 12 h permits to remove completely the traces of water from their surface without the change in the matrix structure [20, 21]. This fact and also a large specific surface area (about $1000 \text{ m}^2 \text{ g}^{-1}$) significantly simplifies the problem of investigation of the dynamics of simple molecules on the surface of these silica by NMR spectroscopy [22, 23]. The structure and surface properties of mesoporous silica of the MCM-41 and SBA-15 types were studied using pyridine enriched with the ^{15}N isotope as the probe molecule [20]. It was shown that pyridine molecules form the $\text{N}\cdots\text{HO}$ hydrogen bonds with the surface hydroxy groups. Their length is close to that of H-bond in the water-pyridine complex [24]. The formation of hydrogen bond causes significant increase in the value of the ^{15}N isotropic chemical shift [25]. Analysis of these spectral variations permits several important conclusions [20]. The surface density of hydroxy groups of the matrices of MCM-41 and SBA-15 types and their proton-donating ability were evaluated experimentally. Detailed description of behavior of the pyridine molecules inside the pores at room temperature was also performed. But as the most important result may be considered the fact that in the best species of MCM-41 no measureable amount of structural defects was found. It makes MCM-41 silica an ideal matrix for investigating the behavior of complex molecules on the inner surface of pores because the results obtained can be generalized on the other types of mesoporous silica.

For better understanding the distribution of hydroxy groups on the surface of highly ordered silica matrices and with the aim of practical use of these materials it seems important to study their interaction with the molecules containing several proton-acceptor centers. In this work the 2,2'-bipyridyl enriched with ^{15}N isotope was chosen as a probe molecule.



The bipyridyl can be regarded as two pyridine molecules bound with the covalent bond in the position 2. It was shown previously that in the gas phase [26] as

well as in crystal [27] in the absence of specific interactions bipyridyl acquires the almost planar trans-conformation [28]. The protonation of bipyridyl is accompanied by the transition to the *cis*-conformation [29]. At the same time bipyridyl always crystallizes as the monoprotonated base. The formation of the twice-protonated form becomes possible only in the strongly acidic media [30]. Though the electronic density redistribution caused by protonation of one of the nitrogen atoms is accompanied by a considerable decrease in the proton-acceptor ability of the second nitrogen atom, in some cases it does not prevent the formation of the sufficiently strong intramolecular hydrogen bond [30]. It is known also that bipyridyl can change conformation while forming chelates with the transition metals [31] and during the interaction with surface in zeolites [32].

The aim of this work was the evaluation of the number of hydrogen bonds formed by bipyridyl adsorbed on the surface of MCM-41 silica, establishing of the highest possible density of the adsorbed molecules, and also the investigation of the effect of temperature on the density of the adsorbed molecules. For the solution of these problems it was necessary to obtain ^{15}N NMR spectra of the compound under study at room temperature and at the temperature when the diffusion and reorientation of molecules inside the pores becomes impossible.

In Fig. 1 ^{15}N NMR spectrum of the polycrystalline sample of bipyridyl is presented.

This spectrum contains only one signal at 268 ppm showing the magnetic equivalence of nitrogen atoms in the molecule of bipyridyl. The value of the chemical shift of the bipyridyl nitrogen atom is by 7 ppm higher than in pyridine [20, 25].

In Fig. 2 ^{15}N NMR spectra of the samples 1, 2 of bipyridyl adsorbed on MCM-41 obtained at 130 K are presented. These spectra contain signals at 268 and 246 ppm.

It is evident that the signal at 246 ppm belongs to the nitrogen atom forming the H-bond with the surface hydroxy group. Formation of the $\text{N}\cdots\text{OH}$ bond causes the decrease in ^{15}N isotropic chemical shift by 22 ppm. In the case of pyridine the formation of H-bond with the surface hydroxy groups caused the decrease in the ^{15}N chemical shift value by 24 ppm [20]. Note that the formation of hydrogen bond by one of the aromatic rings of the bipyridyl must lead to the decrease in the electronic density of the second ring, and hence to the

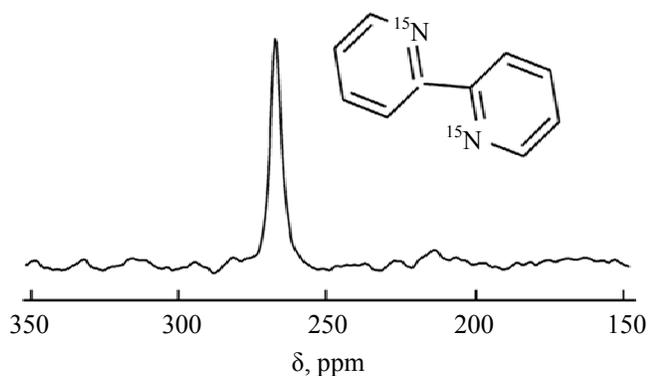


Fig. 1. $\{^1\text{H}\}$ - ^{15}N CPMAS NMR spectrum of polycrystalline sample of ^{15}N 2,2'-bipyridyl at 300 K.

decrease in the chemical shift of the signal related to the free nitrogen atom. But the value of this effect does not exceed 2 ppm even in the case of the complete protonation of the neighboring ring. It is not noticeable at the formation of the comparatively long $\text{N}\cdots\text{HO}$ bond in the case under consideration. The presence of two signals unambiguously indicates that at least some part of the bipyridyl molecules is adsorbed on the surface of MCM-41 silica according to the mechanism of formation of $\text{N}\cdots\text{HO}$ hydrogen bond with the surface hydroxy groups.

Unlike pyridine bipyridyl can form one as well as two hydrogen bonds. The ratio of the integral intensities of the signals at 268 and 246 ppm is 1.2:1 for the sample 1 and 1:1 for the sample 2. On the assumption that bipyridyl is adsorbed on surface with the formation of the conjugated H-bonds (structure **B**) the ratio of integral intensities obtained for the sample 2 would mean that for the formation of monolayer of the adsorbed bipyridyl 0.45 molecule per 1 nm^2 of surface must be sufficient. It follows then that in the case of sample 1 the ratio of signal intensities should be 3:1. The ratio equal to 1.2 :1 observed in the experiment shows evidently that bipyridyl is adsorbed on surface with the formation of only one hydrogen

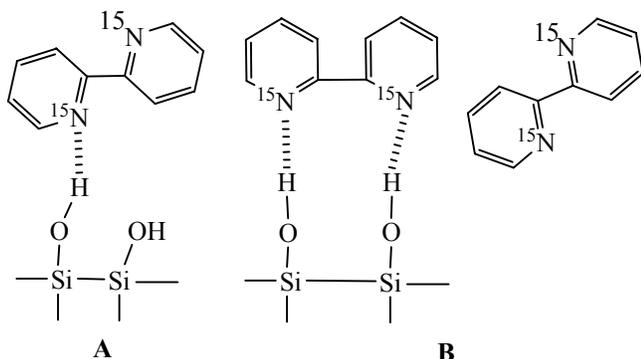


Fig. 2. $\{^1\text{H}\}$ - ^{15}N CPMAS NMR spectrum of 2,2'-bipyridyl adsorbed on MCM-41 at 130 K. Samples (a) 1 and (b) 2.

bond (structure **A**). In the case of sample 1 about 10% of bipyridyl molecules did not form H-bond with hydroxy groups. Therefore the highest density of bipyridyl molecules in the first surface layer is 1.6 molecules per 1 nm^2 . Note that for pyridine this value is about 3 molecules per 1 nm^2 . Hence, each molecule of bipyridyl in the first subsurface layer forms H-bond with one hydroxy group and blocks the interaction of the other molecules with one more hydroxy group.

The melting point of bipyridyl crystal is about 70°C . But on the surface of silica bipyridyl molecules remain mobile at room temperature even if the amount of the adsorbed molecules is larger than it is necessary for the formation of the monolayer. Static and MAS ^{15}N NMR spectra obtained for the sample 1 at 300 K are presented in Fig. 3.

Both spectra contain one signal at 262 ppm. Consequently all the molecules of bipyridyl are located in the subsurface layer and are engaged in the fast (in the NMR time scale) reorientation accompanied by the formation and rupture of hydrogen bonds with the surface-located hydroxy groups. Fast isotropic reorientation of bipyridyl molecules is averaging the anisotropy of the ^{15}N chemical shift in the static spectrum (Fig. 3a). The chemical shift value of the averaged signal permits to establish the surface density of bipyridyl molecules forming complexes with hydroxy groups at 300 K. The total amount of bipyridyl in the sample 1 is about 1.8 molecule per 1 nm^2 , that means 3.6 nitrogen atoms per 1 nm^2 . The chemical

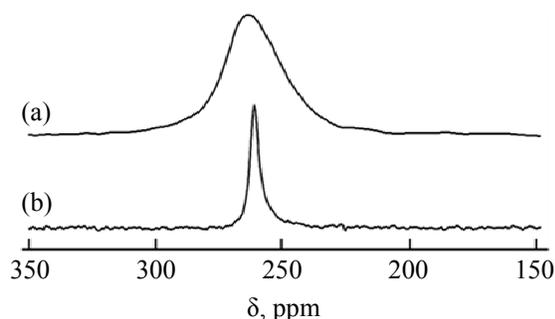


Fig. 3. $\{^1\text{H}\}\text{-}^{15}\text{N}$ NMR spectrum of the sample 1 at 300 K. (a) Static and (b) MAS spectra.

shift of the nitrogen atoms taking part in the interaction with hydroxy groups is 246 ppm, while the shift of those free from H-bond formation is 268 ppm. Since even at low temperature the bipyridyl forms single H-bonds on the surface of MCM-41 matrix, it can be suggested that the situation at room temperature is the same. Then the surface density of bipyridyl molecules forming H-bonds with hydroxy groups at 300 K is determined by the equation $\sigma = 3.6(268 - 262)/(268 - 246) \approx 1 \text{ nm}^{-2}$.

Hence, in this work the study of adsorption of bipyridyl molecules on the surface of the highly regular MCM-41 silica was carried out. The process of sample formation excluded the presence of adsorbed water on the matrix surface. It is shown that the interaction with surface prevents the formation of bipyridyl crystals. At room temperature adsorbed molecules are involved in the processes of fast isotropic reorientation accompanied by the formation and rupture of hydrogen bonds with the surface hydroxy groups. Each molecule of bipyridyl forms no more than one hydrogen bond at a time. The surface density of such molecules at room temperature is about 1 molecule per 1 nm^2 of surface of the MCM-41 matrix. At the decrease in temperature to 130 K bipyridyl molecules form a monolayer on the surface of silica including about 1.6 molecules per 1 nm^2 . At the same time the surface density of hydroxy groups for the MCM-41 silica is about 3 per 1 nm^2 . Therefore only one half of the surface-located hydroxy groups takes part in the formation of hydrogen bonds with bipyridyl. The orientation of bipyridyl in the first subsurface layer provides the formation of H-bond between one molecule and one hydroxy group and prevents the interaction of the other bipyridyl molecules with one more hydroxy group.

EXPERIMENTAL

Solvents and reagents for the synthesis and MCM-41 silica from Sigma-Aldrich were used without the additional purification. 2,2'-Bipyridyl enriched with ^{15}N isotope was synthesized according to the procedure described in [34–36].

NMR studies. Measurements were carried out on a Varian 300 CMX spectrometer (300 MHz) equipped with a probe for the 6 mm rotor and designed for the measurements at the temperatures above 120 K. The spinning of samples was carried out at the Magic Angle (MAS) at a 6 kHz rate. Low-temperature ^{15}N NMR spectra were obtained by the cross-polarization (CP) method. Time of contact 5 μs , relaxation time 20 s. ^{15}N chemical shifts are presented in the scale of crystalline $^{15}\text{NH}_4\text{Cl}$ (0 ppm).

In the work presented two samples differing in the MCM-41 – bipyridyl ratio were studied. Both of them were prepared according to the following procedure. Starting materials, MCM-41 and ^{15}N -bipyridyl were dried in a high vacuum (10^{-8} bar) for a day to remove the adsorbed water. MCM-41 was dried at 420 K, and bipyridyl, at room temperature. MCM-41, 34 mg, and 16 mg (sample 1) or 8 mg (sample 2) of ^{15}N -bipyridyl were placed in a standard 6 mm rotor under argon. After that the rotor was kept under argon for 12 h at 400 K.

Calculated density of bipyridyl molecules was 1.8 and 0.9 molecules per 1 nm^2 for the samples 1 and 2 respectively.

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