

Spin-Probe Study on the Dynamics and Distribution of Solution Molecules in the Nano-Channel of MCM-41

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The ESR spectrum of a spin-probe in 2-propanol, which was condensed into the nano-channel of MCM-41 from its vapor, showed three well-separated nitrogen hyperfine lines. This observation indicates that the system exists in the liquid state in the nano-channel, though the rotational diffusion of the spin probe molecule is considerably suppressed and anisotropic. In a mixed solvent composed of 2-propanol and cyclohexane, on the other hand, the ESR spectrum for the system prepared by the above procedure comprised two components, indicating that the solution is phase-separated in the nano-channel. When all of the space in the MCM-41 layer, including that among the granules, is filled with the solution, the molecules obtain a higher mobility and phase separation is suppressed even in the nano-channel. The distribution and dynamics of the solution molecules are discussed.

Mesoporous silica, such as MCM-41,[1] will become an important material in the chemical industry, since its nano-channel can be a nano-chemical factory,[2–5] a nano device,[6] etc. with suitable design of the system. To realize and utilize these fascinating functions, detailed information on molecular interactions as well as their dynamics in the nano-channel are indispensable. As for the probe of these molecular dynamics and interactions, the radical-pair intermediate in a photochemical reaction is sometimes very useful. For example, we observed a large magnetic field effect in a photoreaction in 2-propanol, which was allowed to flow in a column packed with MCM-41.[5,7,8] Since a large magnetic field effect occurs only for a system where the intermediate radical pair keeps pairing for a long period, e.g. more than a few μs, we proposed a model that the solution molecules in the nano-channel move collectively while preventing the intermediate free radicals to diffuse away. These interpretations are completely new, and thus we have to accumulate experimental results to build up systematic knowledge on the physical state of the molecules in the nano-space.

As for the flow of a solution, we already confirmed in a recent study that the solution actually "flows" in the nano-channel of MCM-41.[10] In a classical model, however, the Hagen–Poiseulle law[9] gives an extremely low velocity for a solution to flow through a nano-channel compared with the velocity typical in the flow experiment. On the other hand, several works have been made using the pulsed-field-gradient NMR (PFGNMR) method[11–13] to study the dynamics of the solution molecules in the nano-channel of MCM-41. Among others, Stallmach et al. observed that the rate of self-diffusion of benzene molecules in the nano-channel of MCM-41 exceeds that in the bulk, and presented a model that molecules diffuse through the gas-phase.[13] These studies also suggest that the classical fluid dynamics is not applicable to the fluid in the nano-space. In a previous study, we found that a mixture solution composed of cyclohexane and 2-propanol becomes inhomogeneous in the nano-channel with keeping the liquid character, though these are miscible with each other in the bulk.[10,14] In addition, evidences were obtained for the collective behavior of the solution molecules in the nano-channel, as mentioned above.[5,7,8]

In the present study, we investigated the physical state of the solution molecules in the nano-channel by means of the spin-probe method.[15] The spin-probe solution was transferred by condensing its vapor into an ESR cell packed with MCM-41 powder, by using a shielded glass apparatus. We could obtain the ESR spectra for the solution only in the nano-channel, which was prepared by stopping the condensation process before the MCM-41 particles became wet. On the other hand, when the solution was filled over the MCM-41 layer in the ESR cell by tilting the apparatus, the ESR spectrum should contain the responses from the spin-probe solution both among the MCM-41 particles and in the nano-channel. In the latter case, the dynamics of the solution molecules in the two regions referred above should be reflected in the ESR spectra. From the analysis of these spectral data, we could discuss on the molecular dynamics in the nano-channel, in the space among the MCM-41 particles, and over the two regions, etc.

Experimental

MCM-41 was synthesized by the template method, employing hexadecyltrimethyl ammonium bromide as the micellar component with referring to a procedure described in the literature.[16] The diameter of the nano-channel was calculated to be 3.4 nm from the X-ray diffraction data and the surface area of 1100 m^2/g which was measured by the one-point BET method (Flowsorb II 2300 of Micrometrics, Inc.).[8] Dimensions of the particles are distributed around 10 μm as shown in Fig. 1, which are SEM images of both MCM-41 and that trimethylsilylated. Trimethylsilylation was performed with trimethylsilyl chloride in hexamethyldisilane, as described in the literature.[17] Three spin probes (1. DTBN (di-*t*-butyl nitroxide), 2. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), and 3. TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl)) were purchased from Aldrich Chemicals and used as supplied. 2-

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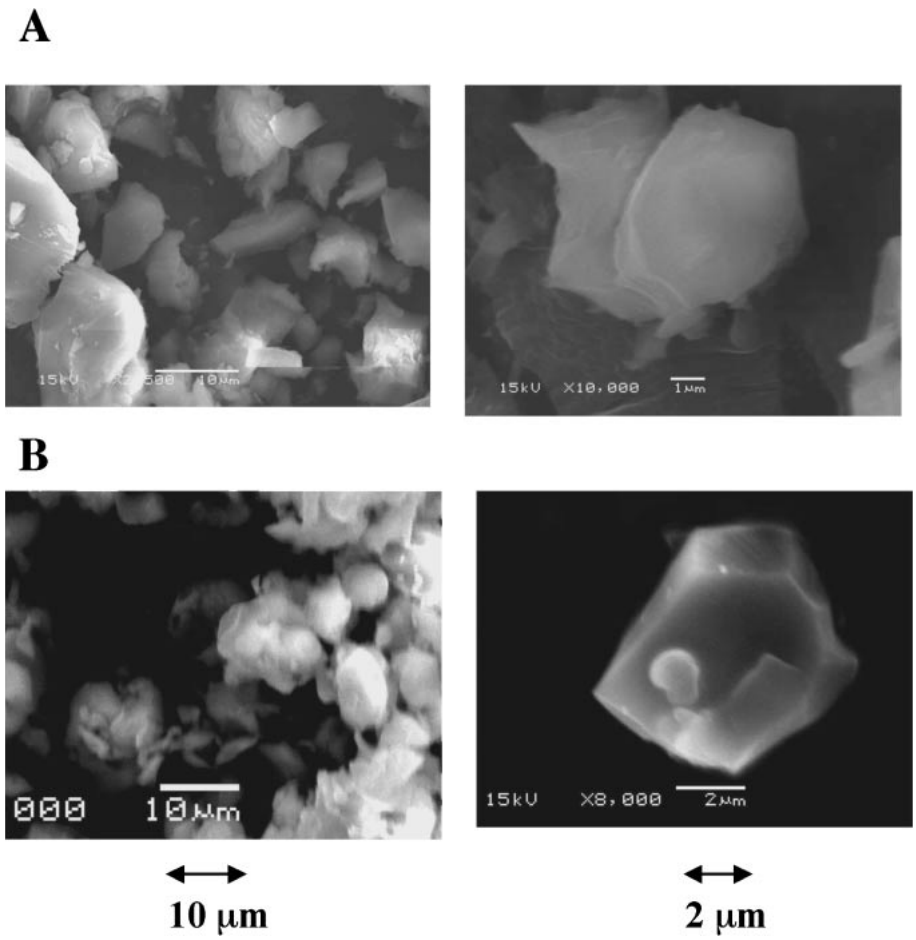

Fig. 1. SEM images of the MCM-41 particles synthesized with hexadecyl trimethylammonium bromide as the micellar component: A, MCM-41; B, trimethylsilylated MCM-41.

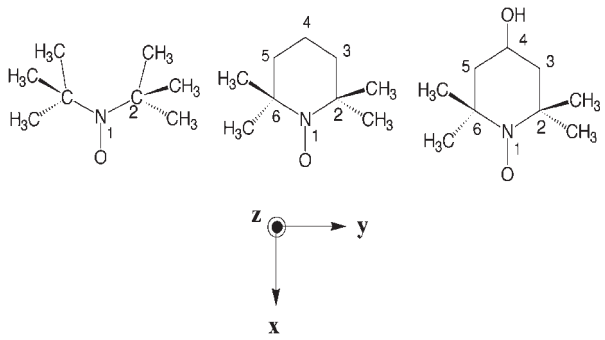

Chart 1.

Propanol and cyclohexane of guaranteed grade were purchased from Wako pure chemicals (Japan) and used after dehydration with molecular sieve 3A. The molecular structures of the spin probes and the definition of the molecular coordinate are shown as Chart 1. Shown in Fig. 2 is the experimental glass apparatus with which the sample treatment and the ESR observation were made. MCM-41, which dehydrated overnight at 400 K, was put into quartz ESR cell A and dehydrated further for an additional one hour in vacuo, and inlet S_1 was sealed off. Next, a spin-probe solution was introduced into the reservoir on the other side (B). After deoxygenation of the solution by pump-and-thaw cycles, inlet S_2 was sealed off. Cock C on the pyrex arm, which connected the two reserviors, A and B, was opened to allow the solution be evaporated and condensed into the nano-channel of MCM-41. Once the cock C was closed, the ESR spectrum was almost unchanged within 48 h: i.e. the radical did not decay rapidly.

ESR spectra were observed with a JEOL JES-RE1XM spectrometer at ambient temperature (ca. 298 K). The power of the microwave at 9.2 GHz was set below 1.0 mW so as to avoid saturation, and the amplitude of the field modulation was set to less than 0.01 mT to avoid modulaltion broadening.

Results and Discussion

1. ESR Spectra of DTBN in the Nano-Channel. Figure 3 shows the ESR spectra of a 2-propanol solution of DTBN transferred into ESR cell A (see Fig. 2) containing MCM-41 through various processes. Spectrum a) is of the DTBN solution, which was condensed into the MCM-41 nano-channel from its vapor. The apparatus, deaerated and sealed completely, was just left overnight at room temperature (ca. 298 K) to allow the vapor to go through cock C to condense into the nano-channel of MCM-41. Spectrum c) is for the MCM-41 layer filled with DTBN solution that was introduced directly by tilting the apparatus. Then, the DTBN solution in ESR cell A was evaporated and condensed into cell B gradually, which was cooled by liq. N_2. The spectrum changed to e) at the moment when the MCM-41 powder appeared to be dried. On further drying the MCM-41 layer, the spectrum changed to g), whose line shape appears

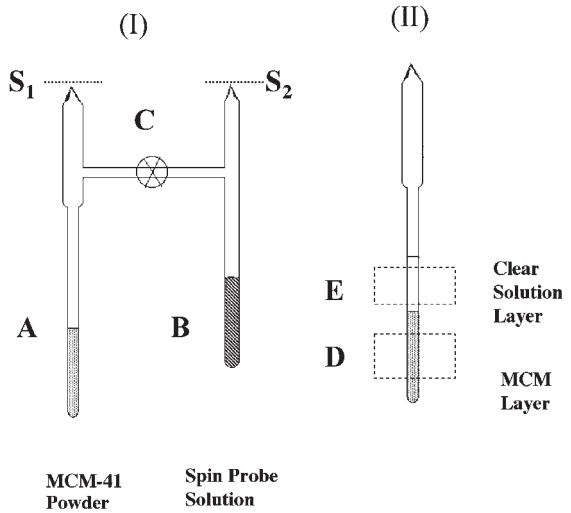

Fig. 2. Schematic diagram of the glass apparatus: (I) total view; (II) two positions for ESR observation. A, sample cell for ESR observation; B, reservoir for the spin probe solution; C, cock connecting the two regions. The two regions were degassed and sealed off at S_1 and S_2 separately to make the sample solution easily evaporated and transferred between the two regions. The two rectangles in (II) indicate the regions for ESR observation, lower: MCM-41 layer; upper, clear solution.

almost equal to that of a). Spectra b), d), and f) are the simulation spectra for a), c), and e), respectively. Here, h) is the ESR spectrum in the absence of MCM-41. Much larger signal intensities of spectra e) and g) compared with that for a) are mainly due to condensation of the DTBN radical by the evaporation of the solvent back to reservoir B.[18] The large difference in signal amplitude between a) and g) is also due to the much lower vapor pressure of DTBN compared with those of the solvents: i.e. it takes a long time to transfer DTBN from resirvor B to ESR cell A, and vice versa, through the evaporation processes.

The ESR spectra indicate that all of the systems were in the liquid state, since well-separated three-line spectra were observed. The broader linewidths of the spectra a)–g) compared with that of spectrum h) indicate that the spin probe molecules are a little immobilized in the MCM-41 nano-channel. It is remarked that the amplitude of the lower and higher-field lines of spectra a), e), and g) are considerably shorter than that of each central line. This spectral feature may be interpreted with the following models: one is that the rotational diffusion of the DTBN molecule is anisotropic and the preferred rotation axis is the *y*-axis, which is the longest molecular axis that spans between the two *t*-butyl groups.[19] Spectrum b), the simulation spectrum for a), was calculated by assuming that the rotational correlation time along its *y*-axis is 15-times shorter than those along the other axes.[19,20] Good agreement between these two spectra indicates that this model is basically correct. Another interpretation might be that it is due to overlapping of the ESR spectra with different hyperfine coupling constants (hfcc's) for the NO nitrogen (a_N). The fact that the high-field half of the high-field line appears slightly broader than the other half may indicate that the ESR line is composed of at least two components: the broader component has a little larger a_N. However, this is not the main mechanism for the observed relative

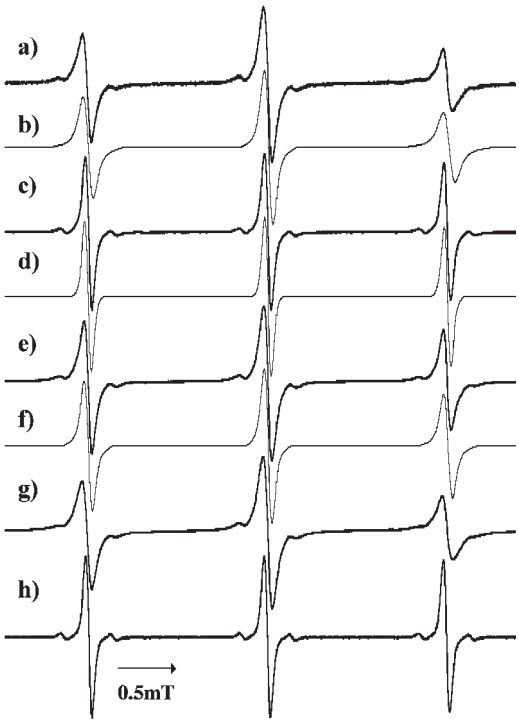

Fig. 3. ESR spectra of DTBN in 2-propanol transferred from reservoir B to ESR cell A (see Fig. 2) by: a) condensation from its vapor for ca. 24 h; c) pouring the solution into the cell. Spectra e) and g) are those observed after drying the surface of MCM-41 particles by cooling reservoir B (see text). Spectra b), d), and f) are the simulations for a), c), and e) respectively. Relative gain was set as 50, 3.0, 1.0, and 1.0 for spectra a), c), e), and g), respectively. Spectrum h) is of the 2-propanol solution of DTBN (0.1 mM) in the absence of MCM-41. Parameters for the simulations are listed in Table 1.

amplitudes, because the observed peak-to-peak linewidth of about 80 μT for the central line of spectrum a) is much larger than the difference between the a_N's of all the spectra in Fig. 3. The predominance of the anisotropic rotation model for the interpretation of the observed spectra a), e), and g) will become clearer later.

When the solution is introduced directly into the ESR cell containing MCM-41 by tilting the apparatus, the observed ESR spectrum c) is much sharper than that of a), indicating that the mobility in average of the spin probe molecules increases considerably. Since the ratio between the volume of nano-channels and that outside of the MCM-41 particles is about 1:1,[21] the signal from the solution outside the MCM-41 granules can not dominate that from the solution in the nano-channel. The sharp spectrum c) changes gradually as the solution is evaporated by cooling the other side B with liquid nitrogen, and spectrum e) is obtained when the MCM-41 powder appears to be dried. In this case, the point symmetry of the ESR absorption peaks is almost retained. Spectrum e) also shows that the DTBN molecule undergoes anisotropic rotational diffusion. Upon further drying, the spectrum is still broadened, as spectrum g), which is quite similar to spectrum a). This fact indicates that a decrease in the solvent quantity in the nano-channel causes a decrease in the space for the spin probe molecule, whose rotational diffu-

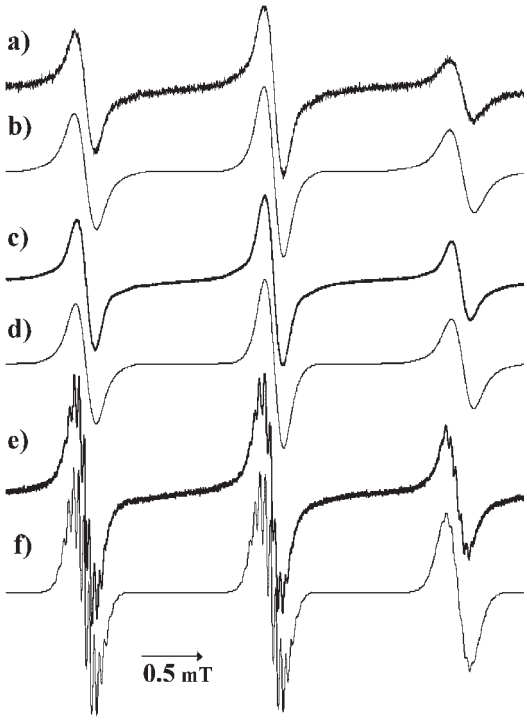

Fig. 4. ESR spectra of TEMPO, a) and c), and TEMPOL, e), in 2-propanol included in the MCM-41 nano-channel. The spin probe solution was condensed from the gas phase for 48 h (a) or introduced in the liquid state (c and e) to the ESR cell containing MCM-41 powder. In the latter cases, the solvent outside the nano-channel was evaporated (see Exp.). Relative gain was set as 3.6, 1.0, and 2.0 for spectra a), c), and e), respectively. Spectra b), d), and f) are the simulation for a), c), and e), respectively. The parameters used in the simulation are listed in Table 1.

sion becomes reduced and more anisotropic: i.e. preferred rotation along the *y*-axis of the DTBN molecule indicates that the molecule is in a narrowed tubular space.

Figures 4-a) and c) show the ESR spectra of the TEMPO radical in 2-propanol, which were observed after the same preparation procedures applyed to the DTBN system for spectra a) and e) of Fig. 3, respectively; b) and d) are the simulation spectra for a) and c), respectively. The relative peak heights of the three hyperfine components for the TEMPO radical are qualitatively similar to those of the corresponding spectra for DTBN. This means that the molecular dynamics of the TEMPO radical in the nano-channel of MCM-41 is similar to that of DTBN. The spectral difference between the two systems is due to a slightly larger linewidth for the TEMPO system, which is attributable to the larger hfcc for the γ-protons, a_H. On the other hand, TEMPOL showed a rather different spectral feature, as spectrum e), which corresponds to spectrum c) for TEMPO. The rotational diffusion rate is not largely reduced from that in the clear solution. Its anisotropy is considerably reduced and the preferred direction changes to *x*-axis (see Chart 1). We interpret this as being due to the OH group of TEMPOL, which makes the molecule miscible to the solvent 2-propanol, and allows the spin probe molecule to make the rotational diffusion almost isotropic. The parameters used in the spectral simulations are listed in Table 1.

2. Effect of Solvent Composition. In addition to the linewidths and the relative peak heights of the three lines, the nitrogen hfcc (a_N) gives another important information on the environment where the spin probe molecule exists, since hydrogen bonding on the NO oxygen of spin-probe molecule makes a_N larger.[22]

We observed the ESR spectrum of DTBN in a mixed solution composed of 2-propanol and cyclohexane to probe the physico-chemical state of the solution in the nano-channel of MCM-41. Figure 5 shows the a_N value of DTBN obtained for both the precipitated MCM layer (Fig. 2, II-D, open triangle) and the upper clear solution layer (Fig. 2, II-E, closed circle) as functions of F_{CHX}, the volume fraction of cyclohexane in the mixed solution. The ESR spectra in both regions were composed of three simple lines for all of the F_{CHX} values. The fact that the a_N value decreases steeply as the F_{CHX} value becomes larger, indicates that the DTBN molecule tends to make interactions preferably with the alcohol molecules. It should be emphasized that the a_N value obtained from the spectrum for the MCM-41 layer is close to the value for the corresponding clear

Table 1. ESR Simulation Parameters for the Spin-Probe Solutions in 2-Propanol[a)]

System	Simulated spectrum	τ_{av}/s averaged rotatonal correlation time	$\tau(//)/\tau(\perp)$ and preferred axis		ΔH/mT	a_N and a_H/mT
DTBN/MCM-41	Fig. 3, b)	2.0×10^{-10}	15	*Y*	0.015	$a_N = 1.591$, $a_H = 0.01$
	Fig. 3, d)	2.0×10^{-11}	7	*Y*	0.015	
	Fig. 3, h)	9.5×10^{-12}	1		0.015	
DTBN/methylated MCM-41	Fig. 7, b)	1.0×10^{-10}	15	*Y*	0.015	
	Fig. 7, d)	7.0×10^{-11}	15	*Y*	0.015	
TEMPO/MCM-41	Fig. 4, b)	3.75×10^{-10}	15	*Y*	0.015	$a_N = 1.621$, $a_H = 0.02$
	Fig. 4, d)	3.0×10^{-10}	15	*Y*	0.015	
TEMPOL/MCM-41	Fig. 4, f)	8.5×10^{-11}	3	*X*	0.015	$a_N = 1.605$, $a_H = 0.04$

a) A *g*-tensor (2.0089, 2.0061, 2.0027) is employed for the nitroxide radicals in all cases. A typical hyperfine coupling tensor (*Axx*, *Ayy*, *Azz*) = (0.76, 0.60, 3.18 mT) was used for the standard, from which a_N of 1.51 mT is obtained. The tensor components for each system were determined by multiplying the ratio of the observed a_N to 1.51 mT. ΔH is the width ($1/T_2$) of the component lines.

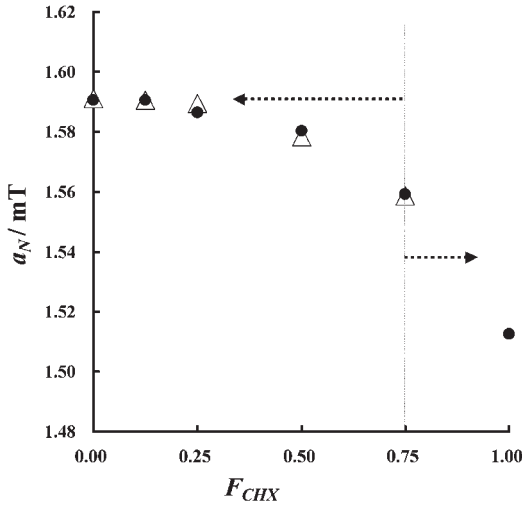

Fig. 5. Nitrogen hyperfine coupling constant (a_N) of DTBN as the function of volume fraction of cyclohexane (F_{CHX}) in the mixed solution composed of 2-propanol and cyclohexane. Closed circle, upper clear solution part; open triangle, in the MCM-41 layer (see Fig. 2); and the two dotted lines with arrows indicate the a_N's for the two component of spectrum c) in Fig. 6.

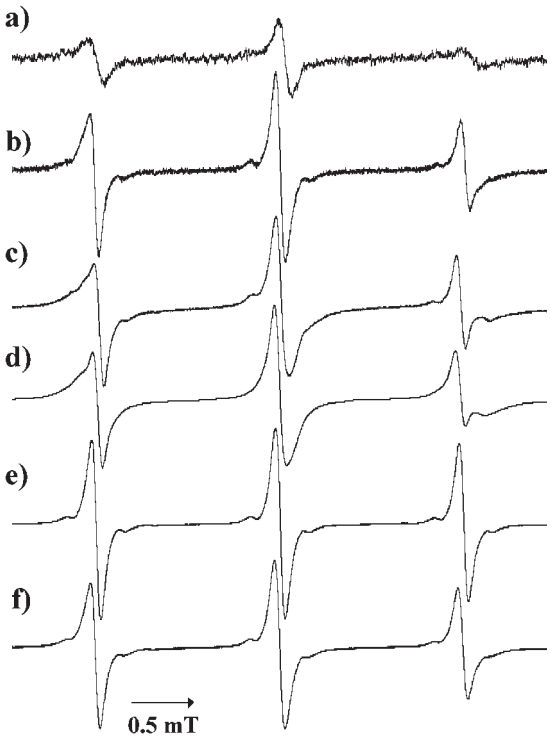

Fig. 6. ESR spectra of the DTBN solution transferred to the ESR cell containing MCM-41 powder. DTBN in a mixed solution composed of 2-propanol and cyclohexane at the volume ratio of 1:3 was transferred to the ESR cell from the gas state for 0.5 h, 1.0 h, and 21 h for a), b), and c), respectively. d) is the simulation spectrum for c) with the two components (see text). Spectrum e) is that observed for the solution directly introduced by tilting the sample cell to the ESR cell, and the last spectrum f) was observed after evaporating the solution until the powder appears dried. Relative gain were set as 400, 64, 16, 1.25, and 1.0 for spectra from a) through f), respectively.

solution. This indicates that the solution character in the MCM-41 layer is almost equal to that in the bulk solution. Thus, the solution molecules (and the spin probe molecules) may exchange their positions frequently from outside to inside, and vice versa, of the nano-channel.

When a mixed solution, in which DTBN is dissolved as the spin probe, was condensed in the nano-channel of MCM-41 via the gaseous state, the observed ESR spectrum changed bewilderingly with the transfer period, as shown in Fig. 6, where spectra a), b), and c) were observed after the condensation periods of 0.5 h, 1 h, and 21 h, respectively. Here, a mixture composed of cyclohexane and 2-propanol at the volume ratio of 3:1 was employed as the solution. Spectrum d) is a simulation for c) with the two components, whose a_N values are shown by dotted lines in Fig. 5. Spectrum e) was observed for the DTBN solution directly poured into the ESR cell containing MCM-41, and f) is that after evaporating the solution among the MCM-41 particles, as described above. The low S/N ratio of spectra a) and b) of Fig. 6, i.e. low DTBN concentration, is due to the relatively low vapor pressure of DTBN. In addition, without enough 2-propanol, the DTBN radicals strongly interact with the surface of the nano-channel, and its ESR spectrum is broadened out. Thus, the three-line ESR spectrum is not observed until the nano-channel surface is covered with 2-propanol. Besides, we have to pay attention to the difference between the vapor pressures of 2-propanol and cyclohexane to interpret the difference between spectra b) and c) of Fig. 6. The vapor pressure of 2-propanol is less than the half of that of cyclohexane at the temperature of the experiment; it takes a rather long time to reach the equilibrium composition in the ESR cell. That's why spectum b) is comprized of mainly a sharper component dut to the DTBN radical in the cyclohexane-rich region. After the solvent reached its equilibrium composition, the broad component due to the DTBN radical, which is in the 2-propanol rich region near the nano-channel surface, becomes considerable. A little larger a_N and the large linewidth of a) indicate that: 1) the spin probe molecule observable here exists mainly with the solvent 2-propanol molecules; 2) the content of 2-propanol in the nano-channel is small and those are immobilized considerably by having interactions with the surface oxygen of the nano-channel. With prolonged condensation of the mixed solution into the MCM-41 layer, the ESR spectrum becomes comprised of two components, as shown in spectra b) and c); one is the broad component similar to that observed initially in a), and the other is a sharper signal with a little smaller hfcc. Simulated spectrum d) proved this interpretation. The sharp comonent is undoubtedly due to the DTBN radical in the cyclohexane-rich environment. These observations clearly indicate that the solution is phase-separated in the nano-channel of MCM-41.[14] As referred above, the two arrows in Fig. 5 indicate the two a_N's for the DTBN radical in a mixed solution of $F_{CHX} = 0.75$ condensed into the nano-channel through evaporation.

When the spin-probe solution is added directly into the ESR cell by tilting the apparatus (Fig. 2, I) over the MCM-41 layer, the ESR spectrum changes into a single component as spectrum e) with the a_N value shown as a regular value in Fig. 5 at

$F_{CHX} = 0.75$. This observation indicates that the solution molecules move around freely, even over the boarder between the nano-channel and the space outside the MCM-41 particles, and phase separation of the solvent molecules is prevented. On the other hand, when a part of the solution is evaporated until the MCM-41 powder appears dried, the ESR spectrum changes to that with the two components as spectrum f). These observations indicate that without the solution filling the space among the MCM-41 particles, the solution in the nano-channel becomes phase-separated. We already proposed that a rapid "collective thermal movement (or flow)" of the solution molecules may occur through the nano-channel, when the intergranular space is filled with the solution.[8,10,14] We consider that the above observation is another evidence of this model.

3. Effect of the Channel Surface Structure. Similar experiments were conducted using a modified MCM-41, whose SiOH groups on the surface were trimethylsilylated with trimethylsilyl chloride. This modification reduces the Si-OH group on the surface of nano-channel to make it more hydrophobic.[23] The ESR spectra a) and c) of Fig. 7 are of DTBN in 2-propanol condensed into the nano-channel of trimethylsilylated MCM-41 for 17 and 41 h, respectively, by opening the cock between the ESR cell containing MCM-41 and the solution container (Fig. 2). Spectrum e) is that observed by introducing the solution directly to the ESR cell at a level well over the MCM-41 layer by tilting the whole apparatus. b) and d) are the simulations for a) and c), respectively.

Since the peak heights of both the M_n (Nuclear qauntum number) $= +1$ and -1 lines are much less than that of the central line, the anisotropy of the rotational diffusion is also large in this system. According to the simulation parameters, the anisotropy of rotational diffusion is large even if condensation of the DTBN/2-propanol vapor proceeds. In addition, the symmetry of both the $M_n = +1$ and -1 lines of spectrum a) of Fig. 7 is much better than those of spectrum a) of Fig. 3. Thus anisotropic rotational diffusion is the unique model for this line shape. These observations indicate that the solvent 2-propanol does not make strong interactions with the nano-channel surface of trimethylsilylated MCM-41, and the physical state of the solution molecules may be homogeneous. As a result, the dynamics of the DTBN molecules may also be homogeneous throughout the nano-channels in the MCM-41 layer.

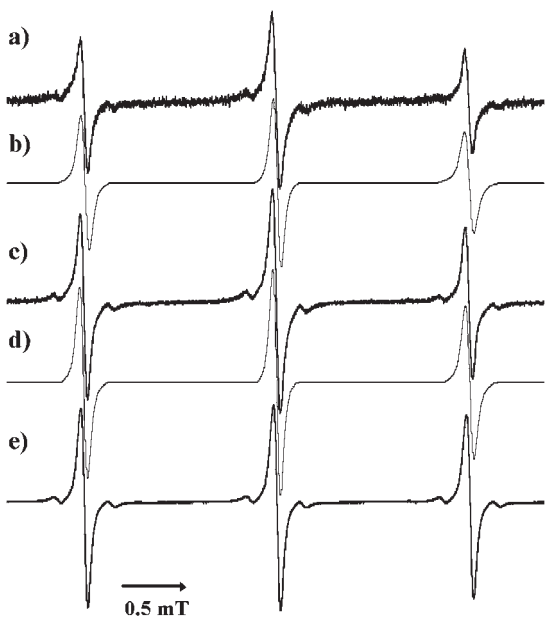

Fig. 7. ESR spectra a) and c) are of the DTBN solution in 2-propanol condensed into the ESR cell containing trimethylsilylated MCM-41 powder (Fig. 2) from the gaseous state for 17 and 41 h, respectively. The last spectrum e) is that observed for the DTBN solution which was directly introduced to the cell by tilting the apparatus. Relative gain was set as 20, 8, and 1.0 for spectra a), c), and e), respectively. Spectra b) and d) are the simulations for the observed spectra a) and c), respectively.

4. Physical State of the Solution Molecules. The MCM-41 powder in the ESR cell had no sticky appearance, even after condensation of the spin-probe solution into the cell for two days. Thus, these molecules should have been condensed into the nano-channel of MCM-41 and not on the surface of the particles. The physical state of the molecules in the nano-channel should be liquid, since the ESR spectrum of the spin probe is composed of three well-separated lines. As Figs. 3 and 7 show, the linewidth of the ESR spectrum becomes narrower as the condensation proceeds. This observation indicates that the rotational correlation time (averaged) becomes shorter as the condensation proceeds (after opening cock C): i.e. the fluidity of the solution increase during this process. This change in the fluidity of the solution indicates that the solution molecules condense on the surface of the nano-channel first and then gradually fill the whole space of the nano-channel.

The preferential rotational diffusion of the spin-probe molecules, DTBN and TEMPO, along the *y*-axis indicates that the NO group does not have a strong interaction with the channel surface, which has many SiOH groups. This means that the surface of nano-channel is covered with 2-propanol molecules, which separate the spin-probe molecules from the nano-channel surface.[24] Thus, the spin-probe molecules are accomodated in the soft core of the solution in the nano-channel, which has cylindrical symmetry. In short, an inhomogenuity exists in the fluidity of a solution in the nano-channel.

The ESR spectra of DTBN molecules in the mixed 2-propanol/cyclohexane solution condensed into the nano-channels of MCM-41 show two components after prolonged condensation: i.e. spectrum c) of Fig. 6 is comprized of both a rather sharp component and a broader component with a slightly larger hfcc. On the other hand, in the pure 2-propanol solvent, two components are not clearly observed, as shown in Fig. 3. The observations in the mixed-solvent system are easily explained as follows: a part of the DTBN molecules exist in the 2-propanol rich solution, which gives the broader ESR spectrum, and the other part of DTBN exists in the cyclohexane-rich region, which gives the sharper spectrum. In Fig. 5 the a_N values of DTBN are indicated with two dotted lines with arrows, from which we can estimate the compositions of the solutions in the nano-channel: the 2-propanol-rich and the cyclohexane-rich phases. This phenomenon on the mixed solution may be generallized that even a well-mixed solution in the bulk can be phase-separated in the nano-channel. This is a very important fact for the solution in the nano-space.

When the MCM-41 layer is filled with the solution, the solution molecules including the spin probe exchange their positions rapidly from inside to outside, and vice versa, of the nano-channel. Thus, a simple three-line spectrum is observed even when a mixed solvent is employed (spectrum e) of Fig. 6). Since the solution molecules can not diffuse in and out of the nano-channel frequently enough with the classical model, according to the Fick's law, it takes about 50–100 ms for the molecules to diffuse through the nano-channel of the MCM-41 particles employed here. The above-mentioned molecular dynamics through the nano-channel cannot be explained by the classical diffusion model. Therefore, the solution should diffuse through the nano-channel by another mechanism which is not common in the bulk. We consider that this type of movement of the molecules through the nano-channel may occur only as a collective one.[7,8,10] This is a newly observed phenomenon in the "nano-world".

According to the ESR simulation parameters in Table 1, the rotational correlation time of DTBN radical in 2-propanol is considerably long, around 2.0×10^{-10} s, and the rotational diffusion becomes anisotropic, if the solution is enclosed in the MCM-41 nano-channel. On the other hand, the correlation time becomes 10-times shorter when the MCM-41 layer is filled with the solution. This increase in the fluidity is understood to be related to rapid transmigration through the nano-channel of MCM-41; the solution (and also spin-probe) molecules get into and out of the nano-channel frequently when the space between the MCM-41 granules is also filled with the solution. We consider that this trans-nanochannel diffusion can be possible only as a collective movement (or flow) through the nano-channel, that is induced by the instantaneous pressure emerging between the inlet and outlet of the nano-channel as a thermal fluctuation.[10,14]

Conclusion

Spin-probe ESR observations were made for the solutions transferred through the vapor phase into the nano-channel of MCM-41, while leaving the inter-granular space vacant. In the case of a 2-propanol solution, molecules are in the solution state, but the dynamics is considerably surpressed and has a cylindrical inhomogenuity in the nano-channel. When a mixed solution composed of 2-propanol and cyclohexane is employed, phase-separation occurs in the nano-channel into an alcohol rich solution and a cyclohexane-rich solution. On the other hand, when the solution is poured directly to the ESR cell at a level well over the MCM-41 layer, the molecular mobility recovers considerably. Besides, phase-separation is suppressed for the 2-propanol/cyclohexane solution. We consider that molecules can go through the nano-channel frequently when the inter-granular space is filled with the solution. This high mobility prevents the solution molecules from being adsorbed on the surface of the nano-channel, and also from phase separation for a mixed solution.

Since the solution molecules can not diffuse in and out of the nano-channel frequently enough with the classical model, we have to consider a new model for the molecular dynamics in the present system. "Collective thermal movement (or flow)" through the nano-channel is our model.[7,8,10]

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24 We observed that the DTBN radical in the MCM-41 layer is immobilized, if pure cyclohexane is employed as the solvent.