Sealing Effect of Magic-Angle-Spinning Rotors in Solid-State NMR

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Several methods are proposed to check the sealing of a magic-angle-spinning (MAS) rotor. The intrusion of moisture into the MAS rotor is checked by trimethylphosphine oxide, which is highly hygroscopic. Its hydrated form is separately observed in ^{31}P MAS NMR spectra from the crystalline (anhydrous) form. ^1H MAS NMR can monitor the hydrated form, the crystalline form, and adsorbed water independently. Gas leakage from the MAS rotor is monitored by measuring ^{129}Xe MAS NMR spectra of xenon (Xe) confined in zeolites as well as ^3He MAS NMR spectra of ^3He gas. The sealing effect of MAS rotors has been checked quantitatively using the above methods.

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Introduction

High-resolution solid-state NMR is a powerful method widely used in a number of research fields. Magic-angle spinning (MAS) of a sample is commonly used to obtain high resolution. Samples are packed into MAS rotors made of ceramics and polymers, which are spun by compressed gas. Some samples are reactive to H_2O and O_2 . Those samples might react with H_2O and O_2 in the driving gas during measurements, because MAS rotors cannot prevent the intrusion of the outer atmosphere completely. In order to measure MAS NMR spectra of moisture- and air-sensitive materials, several techniques have been proposed: a magic-angle spinner for vacuum-sealed glass samples,^{1,2} a sealed MAS rotor insert made of polychlorotrifluoroethylene (Kel-F),³ an O-ring end-plug,⁴ a glass insert sealed after packing the sample,⁵ and so on. The use of inert gases, such as N_2 and He , as a driving gas instead of compressed air also protects any sensitive materials, but the consumed gas is expensive. The leakage of samples from the rotor can also be prevented by the above techniques. We have successfully utilized a sealed rotor insert to measure the MAS NMR spectra of liquid samples including low boiling points, such as tetramethylsilane (TMS).^{6,7} The techniques described above work very excellently, showing no effects of the outer atmosphere, and no leakage of the inner materials. On the other hand, they need careful preparation of the samples for NMR measurements.

In practical experiments, one wishes to avoid any troublesome preparation procedures if the sealing of the MAS rotor is sufficient for the experiments. However, the sealing of MAS rotors has not been checked quantitatively so far.

We propose here several methods to check the sealing of the MAS rotor. We have evaluated the intrusion of moisture from air and the leakage of gaseous materials from the rotor.

Experimental

Materials

Trimethylphosphine oxide (TMPO) was obtained from Alfa Aesar (USA). Y-type zeolite, coded as JRC-Z-Y5.3, was supplied by the Catalysis Society of Japan. This zeolite was in the Na^+ form, and the nominal $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was 5.3. In this work, this zeolite is expressed as NaY5.3. Xenon gas contained ^{129}Xe with the natural abundance (26.4%). ^3He gas was obtained from Isotec Inc. (Miamisburg, USA), whose purity was at least 99.95 atom%.

Apparatus

^{31}P and ^1H MAS NMR spectra were measured at room temperature with a Bruker ASX400 spectrometer at Larmor frequencies of 161.98 and 400.13 MHz, respectively. A Bruker MAS probehead was used with a zirconia rotor of a 4.0-mm outer diameter. The pulse sequences for ^{31}P measurements were a single-pulse sequence with ^1H high-power decoupling during acquisition (HD) and a cross polarization pulse sequence with ^1H high-power decoupling during acquisition (CP). The ordinary single-pulse sequence was used for ^1H measurements. The spin-lattice relaxation times, T_1 , of ^{31}P were also measured at room temperature by an inversion recovery method.

^{129}Xe MAS spectra were traced at room temperature with a Bruker ASX400 spectrometer at 110.68 MHz. A Bruker MAS probehead was used with a zirconia rotor having a 4.0-mm outer diameter. The ordinary single-pulse sequence was used. The pressure dependence of the ^{129}Xe shift was measured at room temperature with a Bruker ASX400 spectrometer, using a Bruker probehead for a solution with a sample tube having a 10-mm diameter. A special sample tube was used, which was similar to that previously used for ^3He NMR measurements,⁸ but the inner tube was not necessary. The sample tube was connected with a system of evacuation and gas supply through an adapter and a 1/8-inch plastic tube, which was also similar to that used for ^3He NMR measurements.⁸

^3He MAS NMR spectra were measured at room temperature with a Bruker ASX200 spectrometer at 152.46 MHz. A Bruker

Fig. 1 ^{31}P HD/MAS NMR spectra of trimethylphosphine oxide (TMPO). The spinning rate of the sample was fixed at 8.0 kHz. (A) A partially hydrated sample, (B) a dried sample, and (C) a sample kept in a rotor for 48 days after packing the dried sample. The marks * show spinning sidebands. The accumulations are (A) 128, (B) 32, and (C) 64.

MAS probehead for ASX400 was used with a zirconia rotor having a 4.0-mm outer diameter. The ordinary single-pulse sequence was used, in which the pulse width was set at 5.0 μs , corresponding to a $\pi/2$ pulse; the repetition time was 10 s and the number of accumulation was 4.

The frequency scale of the ^{31}P spectrum was expressed with respect to an 85% H_3PO_4 aqueous solution by adjusting the signal of $(\text{NH}_4)_2\text{HPO}_4$ to 1.33 ppm.⁹ The ^1H spectrum was expressed with respect to neat tetramethylsilane (TMS) by adjusting the signal of adamantane spinning at 8.0 kHz to 1.87 ppm.¹⁰ The ^{129}Xe spectrum was expressed with respect to Xe gas at 0 atm by setting Xe gas at 1 atm to 0.50 ppm.¹¹ Gaseous ^3He at a pressure of 100 kPa was set at 0 ppm in the ^3He spectrum.

A hygroscopic substance was packed into the MAS rotor under a N_2 atmosphere in a glove bag. We introduced Xe gas and ^3He gas into the MAS rotor, and then capped the rotor, using a home-made special tool similar to the CAVERN apparatus.¹²

Results and Discussion

Hygroscopic substances

The intrusion of moisture in an air atmosphere into the MAS rotor was checked by measuring the MAS NMR spectra of moisture-sensitive materials. Hygroscopic substances are very useful for this purpose, although they are not suitable for routine measurements. Trimethylphosphine oxide (TMPO) is highly hygroscopic. This compound is suitable, because ^{31}P is easily

Fig. 2 Expanded plots of the isotropic region in the ^{31}P MAS NMR spectra of TMPO. The pulse sequences were (A), (B) HD and (C) CP. The spinning rate of the sample was fixed at 8.0 kHz. (A) A dried sample and (B), (C) a sample kept in a rotor for 48 days after packing the dried sample.

detected by NMR.

Figure 1 shows ^{31}P MAS NMR spectra of TMPO. The spectrum in Fig. 1A consists of two components, even though we tried to pack the compound under an ambient atmosphere as quickly as possible. The 44.9-ppm peak has negligible spinning sidebands, being ascribed to hydrated TMPO molecules. On the other hand, the 42.0-ppm peak is accompanied by strong spinning sidebands, which are assigned to crystalline TMPO molecules without hydration. When the compound was dried under a vacuum by placing the sample bottle in a vacuum oven at room temperature for 4 h, the peak of hydrated TMPO became negligibly small, while crystalline TMPO remained, as shown in Fig. 1B. The isotropic region is expanded in Fig. 2A. A very small amount of hydrated TMPO was detected at 45.0 ppm. Figure 1C is a spectrum measured 48 days after the packing, and the isotropic region is expanded in Fig. 2B. The MAS rotor packed with the sample was left in an ambient atmosphere for 15 days, and then kept in a glass bottle for 33 days. No increase was found in the fraction of hydrated TMPO.

The use of cross polarization (CP) could not detect hydrated TMPO, as shown in Fig. 2C. Hydration enhanced the motion of TMPO molecules. The negligible intensities of the spinning sidebands also demonstrate the mobile state of hydrated TMPO. The spin-lattice relaxation times, T_1 , of ^{31}P were 6.3 and 1.7 s for crystalline TMPO and hydrated TMPO, respectively. Thus, quantitative analysis could be performed by using the HD pulse sequence with a sufficiently long repetition time.

^1H MAS NMR spectra were measured in parallel to the ^{31}P MAS NMR measurements. The conditions of the sample drying and keeping were the same as those for the ^{31}P MAS NMR. Figure 3A shows the spectrum of a compound packed under an ambient atmosphere. Two sharp peaks were observed at 4.6 and 1.6 ppm from TMS. The 4.6-ppm peak is ascribed to H_2O ,^{6,7} while the 1.6-ppm peak is to CH_3 in hydrated TMPO. A very broad hump was observed on the baseline, which is ascribed to

Fig. 3 ^1H MAS NMR spectra of TMPO. The spinning rates of the sample were (A) 4 kHz and (B), (C) 8.0 kHz. (A) A partially hydrated sample, (B) a dried sample, and (C) a sample kept in a rotor for 48 days after packing the dried sample. The small 0.2-ppm peak is a background signal. The marks * show spinning sidebands.

CH_3 in crystalline TMPO. The signal intensities of H_2O (4.6 ppm) and hydrated TMPO (1.6 ppm) were reduced by drying under a vacuum, as shown in Fig. 3B. Instead, the signal of crystalline TMPO increases relatively, which is centered at 1.6 ppm and has a broad line width as well as considerably large spinning sidebands. The broad line width of crystalline TMPO indicates the rigid property of TMPO molecules in the crystalline state. Figure 3C is a spectrum measured 48 days after the packing. The H_2O peak at 4.9 ppm increases slightly.

The ^1H signal intensities are proportional to the hydrogen concentrations. Consequently, the contents of H_2O and hydrated TMPO could be estimated by measuring each signal area including the spinning sidebands. The spin-lattice relaxation time, T_1 , of ^1H was about 0.4 s for the dried sample.

Gaseous substances

Air-sensitive materials usually react with O_2 . Xenon gas was used instead of O_2 gas to check the sealing of the MAS rotor against gaseous substances, because it is very difficult to detect O_2 by NMR. One can observe Xe in the gas state by ^{129}Xe NMR. However, the pressure dependence of the ^{129}Xe chemical shift is very small in the gas state.¹¹ The shift difference between 0 and 1 atm is only 0.50 ppm. On the other hand, it is well known that Xe adsorbed in zeolites has a chemical shift that is largely dependent on the pressure in the gas phase.^{13,14}

Figures 4A and 4B show the ^{129}Xe MAS NMR spectra of NaY5.3 zeolite, measured at 0.5 – 14 h after Xe loading and capping. The zeolite sample was heated at 573 K for 3.1 h under N_2 flow, and then evacuated at room temperature before Xe loading. After introducing Xe gas, the MAS rotor was capped under Xe gas at a pressure of 102.1 kPa. Xe confined in the micropores of NaY5.3 has a peak at 101.6 ppm from Xe gas

Fig. 4 ^{129}Xe MAS NMR spectra of NaY5.3 zeolite loaded with Xe gas; measured at (A), (B) 0.5 – 14 h and (C) 19 days after the capping. The MAS rotor was capped under Xe gas at a pressure of 102.1 kPa. The spinning rate of the sample was set at 4.0 kHz. The signal of the gas phase was set at 0.50 ppm. The mark * shows a spinning sideband.

at 0 atm. The line shape is the same as that for a static sample. The NMR measurements were continued, and the peak position reached 101.5 ppm after 2 days. Thereafter, the MAS rotor packed with the sample was kept in a glass bottle. Figure 2C shows the ^{129}Xe MAS NMR spectrum of the same sample, measured after 19 days. The peak is located at 100.5 ppm. This small shift originated from the escape of Xe gas from the rotor, because the ^{129}Xe shift decreased with a decrease in the Xe pressure in the gas phase.

The Xe pressure could be estimated from the ^{129}Xe chemical shift. The pressure dependence of the ^{129}Xe chemical shift of Xe confined in NaY5.3 zeolite was measured by an NMR probehead for a solution. Xe gas was introduced in the NaY5.3 sample after evacuation at 590 K for 1.2 h. The pressure of the gas phase was monitored with a pressure sensor during ^{129}Xe NMR measurements. The ^{129}Xe chemical shift shows a linear dependence on the pressure, which is expressed as

$$\delta_{\text{Xe}} = 55.88 + 0.42p_{\text{Xe}}, \quad (1)$$

where δ_{Xe} is the ^{129}Xe chemical shift in ppm units and p_{Xe} is the pressure in kPa units. Using the relation in Eq. (1), the Xe pressure in the MAS rotor could be estimated as 108.4 and 106.0 kPa at the initial time and after 19 days. Consequently, the Xe pressure decreased by 2.4 kPa per 19 days. Although the MAS rotor was capped under Xe gas at a pressure of 102.1 kPa, the inside pressure was increased up to 108.4 kPa. The capping process slightly compressed the gas.

The ^{129}Xe signal intensity might be monitored to check the sealing. There is equilibrium between Xe confined in zeolites

and Xe gas. Therefore, the total signal intensity should be monitored. However, one should be careful of a long ^{129}Xe spin-lattice relaxation time in the gas phase.¹⁵ The advantage of using the ^{129}Xe chemical shift is that one can estimate the pressure of the gas phase from the calibration curve expressed by Eq. (1). The second advantage is that the chemical shift is determined much more accurately than the signal intensity. The signal intensity might be changed by the instrumental status.

The invasion of O_2 into a rotor can be monitored by using Xe gas as a probe. The ^{129}Xe spin-lattice relaxation time, T_1 , of Xe gas is shortened by O_2 . The relaxation rate, T_1^{-1} , is proportional to the pressure of O_2 .¹⁵

Helium is a light atom, which easily escapes from a confined space. ^3He spins have a high sensitivity in NMR detection.⁸ However, the ^3He chemical shift of gaseous ^3He is almost independent of the pressure.⁸ Therefore, the signal intensity in the ^3He MAS NMR spectra is monitored as a function of time. The MAS rotor was capped under ^3He gas at 103.1 kPa. The signal intensity decreased 10% during 2 days, demonstrating that 10% of the ^3He gas escaped from the rotor. It is reasonable that helium gas leaked much more easily than Xe gas.

Conclusions

We have proposed several methods to check the sealing of the MAS rotor.

(1) The intrusion of moisture in an air atmosphere into the MAS rotor is checked by measuring the MAS NMR spectra of moisture-sensitive materials. Trimethylphosphine oxide (TMPO) is highly hygroscopic, and its hydrated form can be separately observed in the ^{31}P MAS NMR spectra from the crystalline (anhydrous) form. The quantity of the hydrated form can be evaluated from its signal intensity in the ^{31}P HD/MAS NMR spectra. ^1H MAS NMR can also monitor the hydrated form, the crystalline form, and adsorbed water.

(2) Gas leakage from the MAS rotor is monitored by measuring the ^{129}Xe MAS NMR spectra of Xe confined in zeolites. The Xe pressure in the gas phase is estimated from the ^{129}Xe chemical shift of Xe in zeolites. The pressure change, *i.e.*, the gas leakage, is evaluated quantitatively and non-destructively.

(3) The leakage of helium gas is monitored by tracing ^3He MAS NMR spectra of ^3He gas loaded in the MAS rotor. The signal intensity is monitored as a function of time, and a signal decrease is observed due to leakage.

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