Adsorption of Trimethylphosphine Oxide Molecules
from the Gas Phase to Probe Surface Acidity by Solid-state NMR

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Trimethylphosphine oxide (TMPO) molecules were adsorbed on H-type mordenite to probe the surface acidity by solid-state NMR. We found that dichloromethane was coadsorbed when it was used as a solvent. To avoid the effect of the solvent, TMPO was adsorbed from the gas phase, and we have obtained ^{1}H and ^{31}P magic-angle-spinning (MAS) NMR spectra of TMPO-adsorbed H-type mordenite without the effect of the solvent.

Solid acid catalysts have intensively been studied, which can replace liquid acid catalysts.[1,2] Evaluation of the acid properties is important for developing new acid catalysts. The acidic properties have been probed by several techniques such as ammonia temperature-programmed desorption (NH$_3$-TPD), FT-IR, and solid-state NMR. In the field of solid-state NMR, trimethylphosphine oxide (TMPO) has been used to probe surface acidity,[3–14] because the ^{31}P chemical shift of TMPO is sensitive to acidity. TMPO is a solid substance at room temperature, whose melting point is about 140 °C. Anhydrous tetrahydrofuran and dichloromethane were used as a solvent when TMPO was adsorbed. After adsorption of TMPO the solvents were removed by evacuation.

We have studied the surface acidity of several porous materials using TMPO as a probe molecule. During the course of those studies, we found that some samples adsorbed the solvent molecules as strongly as TMPO. Consequently, the solvent molecules could not be removed without desorption of TMPO. The previous work reported in the literature did not check whether the solvent molecules were removed or not.

In this work, first we present results showing that H-type mordenite adsorbs dichloromethane (CH$_2$Cl$_2$) as strongly as TMPO. Mordenite framework has one-dimensional channels with a size of 0.74×0.65 nm^2.[15] Next, we propose a method to avoid the effect of the solvents. TMPO is successfully adsorbed from the gas phase for the first time, although it is a solid substance. The adsorption of TMPO has been confirmed by ^{1}H and ^{31}P magic-angle-spinning (MAS) NMR.

TMPO was obtained from Alfa Aesar (USA). H-type mordenite was supplied by The Catalysis Society of Japan, which was coded as JRC-Z-HM20. The number is a nominal SiO$_2$/Al$_2$O$_3$ molar ratio. The prepared samples were carefully handled without exposure to air atmosphere because they easily adsorb moisture in air.

^{31}P and ^{1}H MAS NMR spectra were measured at room temperature with Bruker MSL400 and ASX400 spectrometers at Larmor frequencies of 161.98 and 400.13 MHz, respectively. Bruker MAS probe heads were used with a zirconia rotor of a 4.0-mm outer diameter. The pulse sequence for ^{31}P measurements was a single-pulse sequence with ^{1}H high-power decou-

pling during acquisition. An ordinary single-pulse sequence was used for ^{1}H measurements. The frequency scale of the ^{31}P spectrum was expressed with respect to 85% aqueous H$_3$PO$_4$ solution by adjusting the signal of (NH$_4$)$_2$HPO$_4$ to 1.33 ppm.[16] The ^{1}H spectrum was expressed with respect to neat tetramethylsilane (TMS) by adjusting the signal of adamantane spinning at 8.0 kHz to 1.87 ppm.[17] All the samples were packed into the MAS rotors under an N$_2$ atmosphere. The sealing of the 4-mm MAS rotors was rather good.[18]

The as-supplied sample contained NH$_4$$^+$ ions, which was confirmed by a 6.6-ppm signal in ^{1}H MAS NMR spectra (The spectrum is not shown). Therefore, the sample was calcined at 808 K under an air atmosphere to convert to H$^+$ form. Figure 1A shows the ^{1}H MAS NMR spectrum of the calcined sample. The main broad peak is centered at 6.7 ppm, being ascribed mostly to Brønsted acid sites. The chemical shift reflects the acid strength. The large line width means a large distribution of acid strength. Three small peaks were observed additionally at 8.9, 1.8, and 1.4 ppm. The 1.8- and 1.4-ppm peaks are ascribed to
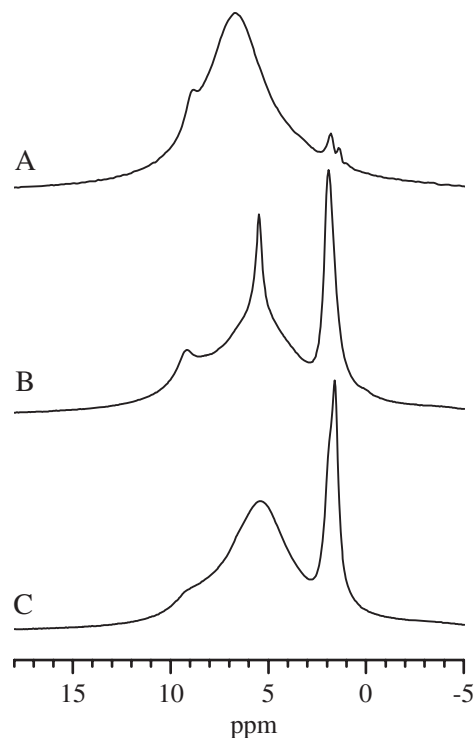

Figure 1. ^{1}H MAS NMR spectra of H-type mordenites (A) without any adsorption, (B) with TMPO adsorbed from a CH$_2$Cl$_2$ solution, and (C) with TMPO adsorbed from the gas phase. The spinning rates were (A) 12 and (B, C) 10 kHz.

isolated Si–OH, while the 8.9-ppm peak is attributed to strongly hydrogen-bonded Si–OH tentatively.

TMPO was adsorbed from a CH_2Cl_2 solution as follows: The host sample was dried at 673 K for 3 h in an air atmosphere. The dried sample was sealed in a vial, and a measured amount of TMPO in an anhydrous CH_2Cl_2 solution was added through a gas-tight syringe. After contact with the solution for 3 d, the sample was evacuated at room temperature to remove the solvent. Figure 1B shows the ^{1}H MAS NMR spectrum. The 1.9-ppm peak is ascribed to methyl groups in TMPO. The 5.5-ppm peak is due to CH_2Cl_2, as the chemical shift of neat CH_2Cl_2 is 5.443 ppm.[19] The other signals come from H-type mordenite. The broad signal attributed mostly to Brønsted acid sites is centered at about 5.5 ppm. Thermogravimetric and differential thermal analyses (TG/DTA) could not differentiate mass losses due to desorption of TMPO and CH_2Cl_2. Thus, it is impossible to remove CH_2Cl_2 without desorption of TMPO. Coadsorption of the solvent molecules might take place in other host materials too.

Next, TMPO was adsorbed from the gas phase as follows: The host sample was dried at 673 K for 3 h in an air atmosphere. The dried sample was transferred to a vacuum desiccator under an N_2 atmosphere. TMPO previously dried under vacuum was placed in the same desiccator. The desiccator was evacuated, and then the static vacuum was kept for 1 day. Figure 1C shows the ^{1}H MAS NMR spectrum. The relatively sharp peak at 1.6 ppm is ascribed to methyl groups of TMPO. The main peak mostly due to Brønsted acid sites is observed at 5.4 ppm. The 8.9-ppm peak remains unchanged. Note that the peak due to CH_2Cl_2 is missing.

Figure 2 shows the ^{31}P MAS NMR spectra of the TMPO-adsorbed samples. The signals between 80 and 50 ppm are ascribed to TMPO adsorbed on Brønsted acid sites. The acid strength is stronger as the chemical shift is larger. The signal at 46 ppm is ascribed to physisorbed TMPO. This signal is strong in the sample adsorbing TMPO from the gas phase under static vacuum. For the sample adsorbing TMPO from a CH_2Cl_2 solution, partial
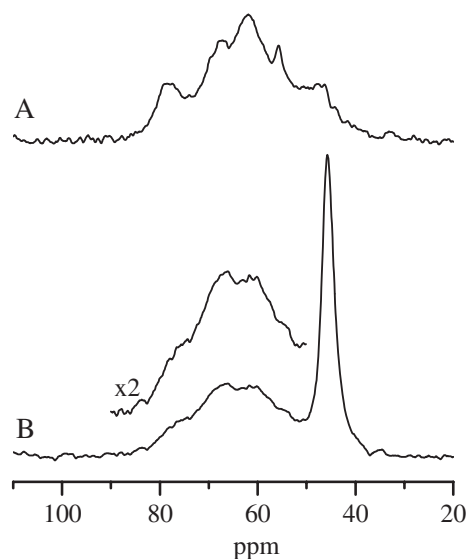
removal of TMPO might take place by evacuation, although a measured amount of TMPO was introduced. The adsorption of TMPO from the gas phase results from sublimation of TMPO. In an air atmosphere it is difficult to observe sublimation of TMPO because it is highly hygroscopic.[18]

In summary, TMPO molecules were adsorbed on H-type mordenite to probe the surface acidity by solid-state NMR. We found that dichloromethane was coadsorbed when it was used as a solvent. To avoid the effect of the solvent, TMPO was adsorbed from the gas phase, and we have obtained ^{1}H and ^{31}P MAS NMR spectra of TMPO-adsorbed H-type mordenite without the effect of the solvent. We can apply the proposed method to various materials. Quantitative analysis of the spectra is now in progress.

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Figure 2. ^{31}P MAS NMR spectra of H-type mordenites (A) with TMPO adsorbed from a CH_2Cl_2 solution and (B) with TMPO adsorbed from the gas phase. The spinning rates were 10 kHz. The intensity is arbitrary.