NMR of Hectorite Ion-exchanged by Trimethyltin and Dimethyltin Cations

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(Received August 16, 1995)

^{119}Sn high resolution solid state NMR of hectorite ion-exchanged by trimethyltin (TMT) and dimethyltin (DMT) cations has shown that under dry atmosphere TMT loses coordinated water molecules to give an abnormally high chemical shift δ= 300.

Interaction of organotin cation with clays may play an important role in the behavior of organotin compounds in environment,[1a,b] especially in relation to its retention in sediment and soil. Chemistry of organometallic compounds in the characteristic structural spaces of clay minerals is by itself interesting subject which has not been studied so far. In this report we describe ^{119}Sn magic angle spinning (MAS) NMR of trimethyltin and dimethyltin cations intercalated in a synthetic hectorite. Although much has been reported of NMR of tin compounds,[2] there has been no report on the MAS NMR of tin compounds adsorbed on or intercalated into clay minerals.

Synthetic hectorite $Na_{1/3}Mg_{8/3}Li_{1/3}SiO_4(OH, F)_2$ supplied from Topy Ind. was purified by sedimentation-separation method. Commercial trimethyltin chloride (TMTCl, Aldrich Chemical Company Inc.) and dimethyltin dichloride ($DMTCl_2$, Wako Pure Chemical Ind.) were used without further purification. To exchange Na^+ in hectorite to the organotin cations, 300 mg of Na-hectorite was suspended in aqueous solution of the organotin chlorides including organotin cations equivalent to 2.5-3 times of cation exchange capacity of hectorite and stirred for 45 h. The extent of the exchange was determined from the concentrations of Na and Sn in aqueous phase measured by ICP spectrometry(JY-48PVH) before and after the exchange and from the elemental composition of the hectorites measured by X-ray photoelectron spectroscopy (XPS, Vacuum Generator ESCALAB 5).

Magic angle spinning (MAS) NMR spectra were recorded on a Bruker MSL400 spectrometer at frequency of 149.214 MHz for ^{119}Sn and 400.137 MHz for ^{1}H.[3] Chemical shifts were determined relative to tetramethyltin (intact) for ^{119}Sn and tetramethylsilane (intact) for ^{1}H.

In the case of TMT/hectorite, 65% Na was leached into the solution and 35% of the leached Na was replaced by Sn. With DMT/hectorite, of 95% Na leached, 80% was replaced by equivalent Sn. The residual amount of the leached Na, 30% and 15% for TMT/hectorite and DMT/hectorite respectively, were considered to be exchanged by H^+, because the aqueous solution of TMTCl and $DMTCl_2$ was acidic. The larger extent of the exchange of Na by DMT than by TMT is attributable to preference of the higher valent cation in the exchange reaction.

For TMT-hectorite and DMT-hectorite kept in the ambient atmosphere, ^{1}H, ^{13}C and ^{119}Sn MAS NMR were observable. The results of ^{119}Sn and ^{1}H NMR under different moisture conditions are summarized in Table 1. ^{119}Sn MAS NMR of TMT-hectorite kept under saturated water vapor and spun at 4.0 kHz exhibited single line at 50 ppm (Figure 1a). This value is close to the chemical shift for TMTCl aqueous solution.[4a,b] Under ambient atmosphere the line shifted to δ = 75-80 (Figure 1b; the line

Table 1. ^{119}Sn and ^{1}H NMR of hectorite ion-exchanged by trimethyltin and dimethyltin cations

Sample and atmosphere	δ(^{119}Sn)	δ(^{1}H)	^{1}H(H_2O)[b] / ^{1}H(CH_3)	H_2O[c] / Sn
Me_3Sn/hectorite				
Ambient	75-81	4.7 (H_2O) 0.8 (CH_3)	2.5-3.0	11.3-13.5
H_2O saturated	50	4.8 (H_2O) 0.7 (CH_3)	8.0	36
Vacuum	308	6.2 (H_2O) 4.5 (H_2O) 1.1 (CH_3)	0.73	3.3
Me_2Sn/hectorite				
Ambient	-300	5.2 (H_2O) 1.2(CH_3)	9.7	29.1
Vacuum	n.d.[a]	5.8(H_2O) 1.1 (CH_3)	5.4	16.2

a Not detected; b Ratio of ^{1}H signal intensities due to interlayer H_2O and to methyl attached to Sn; c Molecular ratio of interlayer H_2O and Sn calculated from b.

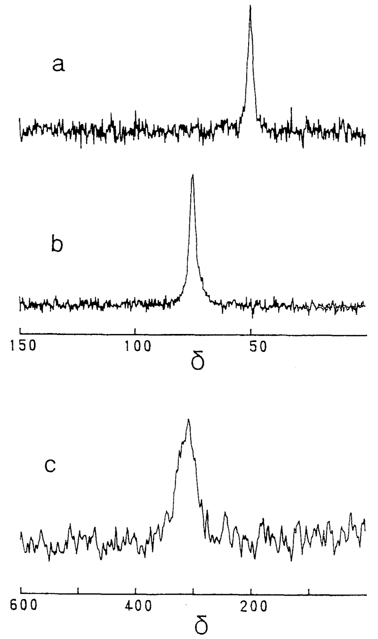

Figure 1. ^{119}Sn NMR of hectorite ion-exchanged by TMT cation, under H_2O saturated atmosphere (a), ambient atmosphere (b), and vacuum (c).

position is slightly variable, see below). When the sample was evacuated, the line shifted significantly to about δ = 300 and broadened (Figure 1c). The MAS spectrum of DMT-hectorite under ambient condition showed a broad peak at δ = -300. The chemical shift is comparable with that of ^{1}H-decoupled MAS spectrum of $DMTCl_2$ aqueous solution, δ = -285. While the spectrum of DMT-hectorite was much broader than that of aqueous solution, the spectrum of DMT-hectorite became unobservable when evacuated, presumably because of further line broadening.

^{1}H MAS spectrum of TMT-hectorite under saturated water vapor pressure had two peaks at δ = 0.7 and 4.8. The former was assigned to methyl-^{1}H and the latter to the interlayer water. When the sample was evacuated the intensity of the peak due to the interlayer water relative to that of methyl diminished and the peak splitted into two components of which the component with the higher chemical shift appeared as a shoulder. The relevant informations are tabulated in the table. From the measured intensity ratio of interlayer water ^{1}H to methyl ^{1}H, the ratio of interlayer water to Sn can be calculated, which is included in the table. Not all of interlayer water necessarily coordinate to Sn even under vacuum. Interlayer proton which was considered to exchange partly leached Na can contribute to the binding of interlayer water. In general retention of interlayer water in DMT-hectorite was higher than in TMT-hectorite. This is consistent with the higher charge on Sn in DMT.

Let us consider the possible coordination condition of Sn in TMT- and DMT-hectorite from the above observations in light of existing informations on chemical shifts in ^{119}Sn NMR of various Sn compounds with known coordination numbers. Several reports concern NMR of Sn compounds with coordination of $(CH_3)_xSnO_{n-x}$ type where n is coordination number (n = 4, 5, 6) and have shown that the ^{119}Sn chemical shift depends on both x and n.[5a-h] For x = 3 and n = 4, the chemical shift ranges from δ = +130 to +110, and +95 to -62 for x = 3 and n = 5. 5-fold coordination for trimethyltin cation in aqueous solution has been proposed,[4b] where two water molecules coordinates to Sn from both side of $(CH_3)_3Sn$ plane, making a trigonal bipyramidal structure, with reference to the crystallographic evidence for 5-fold coordinated tin compound with two coordinated water molecules.[6] The observed chemical shift of TMT in hectorite under saturated water vapor suggests that it has a coordination condition similar to that in aqueous solution. As for the characteristically large positive chemical shift of TMT-hectorite in vacuum, among 4-fold coordinated Sn(IV) compounds such range of chemical shifts have been reported only for alkyltin compounds with multiple coordination by transition metal carbonyls.[7] TMT in hectorite is unlikely to have coordination comparable to those compounds. Considering the substantial loss of interlayer water molecule upon evacuation, 3-fold coordination with three methyls and without coordinated water molecules can be assumed to TMT-hectorite in vacuum.

The variable chemical shift of TMT-hectorite in the ambient atmosphere is attributable to the rapid exchange of coordinated water molecule between the different coordination states. TMT-hectorites kept over silica gel and P_2O_5 gave the same ^{119}Sn chemical shift as in vacuum, although the amount of interlayer water given by the ^{1}H NMR were different. This indicates a stable intermediate coordination condition is unlikely to exist.

The ^{119}Sn chemical shift of DMT-hectorite in the ambient condition, close to that in aqueous solution, is consistent with the structure in which two methyl group and Sn are linearly arranged and possibly 4 water molecules occupying remaining coordination sphere of Sn (x = 2, n = 6).[8] Disappearance of ^{119}Sn line under vacuum is due to slow exchange between several coordination states of Sn with reduced numbers of coordinated water molecules.

The present study has demonstrated that organotin cations in the interlayer of smectite clay mineral are coordinatively unsaturated under reduced water vapor pressure, which is effectively probed by solid state NMR spectroscopy.

References and Notes

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3 The measurement conditions for ^{119}Sn NMR in Figure 1 are: pulse sequence, single pulse sequence with ^{1}H decoupling and with $\pi/4$ pulse for (a, b) and $\pi/6$ pulse for (c); spinning rate, 4.00 kHz (a, b) and 8.00 kHz (c); repetition time, 5.0 s (a), 10.0 s (b) and 20.0 s (c); number of transients, 980 (a), 1400 (b) and 2700 (c). For ^{1}H: pulse sequence, single pulse sequence with $\pi/4$ pulse; spinning rate, 4.00 kHz for ambient and H_2O-saturated samples and 9.00 kHz for vacuum-dried samples; repetition time, 1.0 s; number of transients, 16 for ambient and H_2O-saturated samples and 128 for vacuum-dried samples.

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