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Layered Compounds

Interlayer Modification of a Layered Titanate with Two Kinds of Organic Functional Units for Molecule-Specific Adsorption**

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Layered materials have widely been used as adsorbents, catalysts, catalyst supports, and hosts for functional molecular species, owing to 1) their large surface areas derived from well-defined nanostructures composed of ultrathin sheets, 2) their chemical stability, and 3) the diversity of the materials.[1] The modification of interlayer nanospaces has been conducted through ion exchange[2] and grafting.[3] Though there have been several examples in which the adsorptive characteristics of layered materials have been tuned by organic modification,[4] the ability to strongly and specifically bind a particular molecular species is still a topic of interest.

We have reported that the organic derivative of a layered silicate that bears interlayer hydroxy groups and has been modified with controlled amounts of octyltrichlorosilane adsorbs *n*-alkyl alcohols and not *n*-alkanes.[5] This phenomenon was explained as the result of the cooperative effect of the chemical nature and geometry of the modified silicate, wherein the two functional units (alkyl and hydroxy groups) were spatially arranged to selectively bind *n*-alkyl alcohols. The immobilization of various kinds of organic functional units and the control of their spatial distribution in layered materials are worth further investigation to tailor guest-binding characteristics.

Herein we report the immobilization of two different organic functional units, alkyl and phenyl groups, in the interlayer space of a layered titanate to specifically adsorb 4-nonylphenol (NPh), a known contaminant of water, from aqueous solution. The adsorption of NPh onto activated carbon[6] or a mesoporous organosilica[7] from aqueous solution has been reported, while the adsorption selectivity and capacity of NPh were not documented. In the system reported in this work, alkyl and phenyl groups were immobilized in the interlayer space to interact with the nonyl and phenyl groups of NPh, respectively.

The adsorbent was synthesized as follows. Phenyltrimethoxysilane (PTMS) and *n*-octadecyltrimethoxysilane (C_{18}TMS) were allowed sequentially to react with $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (KTLO). The silylation of KTLO[8] was carried out by using the dodecyltrimethylammonium-exchanged form (C_{12}TMA-TLO) as the intermediate. The silylation with PTMS was carried out by dispersing C_{12}TMA-TLO (0.50 g) in a solution of PTMS (2.8 mL) in toluene (50 mL) and stirring the mixture for two days at 80 °C. The product was separated by centrifugation and washed with acetone. The phenylsilylated derivative (0.50 g) thus obtained (abbreviated as PTMS-TLO) was then dispersed in a solution of C_{18}TMS (3.0 mL) in toluene (40 mL), and the mixture was stirred for two days at 80 °C. The product was separated by centrifugation and washed with acetone, a mixture consisting of HCl_{aq} (0.1 M, 20 mL) and ethanol (20 mL) to remove the remaining C_{12}TMA, and finally a mixture of acetone (20 mL) and water (20 mL) to hydrolyze residual methoxy groups.[5] The silylated derivative thus obtained is abbreviated as PTMS-C_{18}TMS-TLO. To show the importance of the presence of the two functionalities, the organic derivatives of the titanate modified with one of the two silanes were also prepared, and the adsorption behavior of NPh for the three titanates from aqueous solution was compared in the presence or absence of competitive solutes, *n*-nonane and phenol.[9]

Figure 1 A shows the X-ray diffraction patterns of PTMS-TLO and PTMS-C_{18}TMS-TLO, together with those of KTLO and C_{12}TMA-TLO. The basal spacing changed from 2.8 nm for C_{12}TMA-TLO to 2.3 nm and then to 1.9 nm. In the infrared spectrum of PTMS-C_{18}TMS-TLO (Figure 1 B), the absorption bands of C_{18}TMS (e.g. ν(C-H) at about 2900 cm^{-1}) together with those of PTMS (e.g. δ(C-H) at 1160 cm^{-1}) were observed, and the intensity of the absorbance attributable to

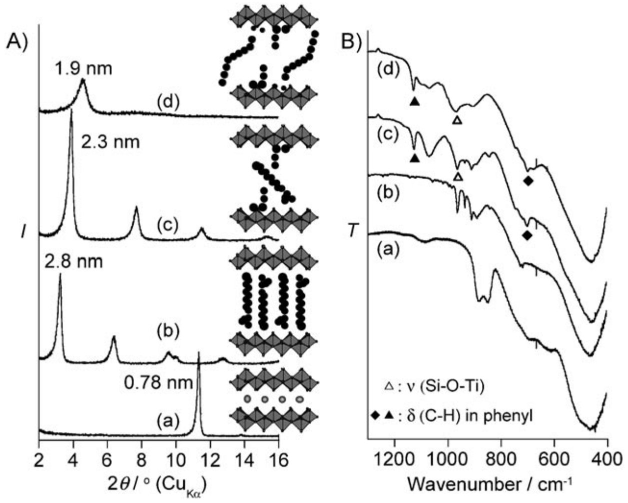

Figure 1. A) X-ray diffraction patterns and B) infrared spectra of KTLO (a), C_{12}TMA-TLO (b), PTMS-TLO (c), and PTMS-C_{18}TMS-TLO (d). *I* = intensity, *T* = transmittance. Inset: Schematic drawings of the corresponding interlayer structures.

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ν(Si-O-Ti) (969 cm^{-1}) increased upon reaction with C_{18}TMS. These results indicate that C_{18}TMS is intercalated into the interlayer space in which PTMS had been previously immobilized. The amounts of the attached PTMS and C_{18}TMS groups in PTMS-C_{18}TMS-TLO were determined—by subtracting the Si/TLO molar ratio of PTMS-TLO from that of PTMS-C_{18}TMS-TLO—to be 0.13 and 0.17 groups for a unit cell (equivalent to 0.55 and 0.72 mmol g^{-1}, respectively; Table 1). These values correspond to the distance of about 1.2 nm between adjacent PTMS or C_{18}TMS groups in PTMS-C_{18}TMS-TLO (Table 1). In light of the lateral size of the attached PTMS and C_{18}TMS groups (0.5 nm as $C_6H_5Si(OH)_2O$- or $CH_3(CH_2)_{17}Si(OH)_2O$-), the organosilyl groups are thought to cover the titanate surface almost fully such that the adsorbates cannot interact with the surface titanol (TiOH) groups. It should be noted here that two different functionalities resulted in "segregation", as observed for the adsorption of two cationic species in a smectite.[10] In PTMS-C_{18}TMS-TLO, the X-ray diffraction pattern of one crystalline compound reveals that the two functionalities (phenyl and octadecyl groups) are located in the same interlayer space and distributed homogeneously as schematically shown in the structures in Figure 1 A. The density of the two silyl groups in the interlayer space is controllable by changing the added amount of PTMS and C_{18}TMS.[5,11]

Table 1: Compositions and distributions of the silyl groups in the silylated derivatives.

	Mass %[a]		Molar ratio	Distance between adjacent silyl groups [nm][b]	
	Si	Ti	Si/TLO	PTMS	C_{18}TMS
PTMS-C_{18}TMS-TLO	3.9	38.4	0.30	1.3	1.2
PTMS-TLO[c]	2.1	52.6	0.13	1.3	–

[a] The composition of products was determined by ICP atomic emission spectrometry. [b] Calculated as $\sqrt{2\,a\,b/x}$ if the packing of the silyl groups is hexagonal closest packing (a, b, and x denote lattice constants of KTLO (0.38 and 0.30 nm)[8] and the Si/TLO ratio). [c] Washed with HCl_{aq}/ethanol.

Figure 2 shows the adsorption isotherms of NPh for PTMS-C_{18}TMS-TLO and KTLO. PTMS-C_{18}TMS-TLO adsorbed NPh from aqueous solution; however, KTLO hardly adsorbed NPh. The isotherm of NPh for PTMS-C_{18}TMS-TLO is type H, showing strong adsorbent–adsorbate interactions.[12] The maximum amount was more than 3.5 mmol g^{-1} (equivalent to 0.82 groups for a unit cell). Although the silylated derivatives in which one of the two functionalities are attached ($C_{18}TMS_{0.16}$-TLO and $PTMS_{0.22}$-TLO) also adsorbed NPh (the isotherms are type H and type L, respectively), the maximum adsorbed amounts (ca. 2.0 and 1.5 mmol g^{-1}, respectively) were much smaller than that of PTMS-C_{18}TMS-TLO. These results are explained by the cooperative effect with the two organic functional units. It is worth mentioning that the value of more than 3.5 mmol g^{-1} was larger than the maximum adsorbed amount of NPh (ca. 2.0 mmol g^{-1}) reported for activated carbon.[6] PTMS-C_{18}TMS-TLO accommodates NPh by expanding the interlayer space (Figure 2 inset).

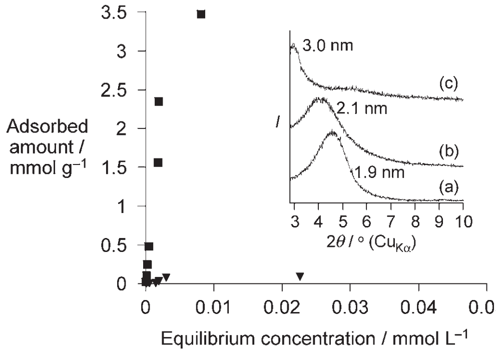

Figure 2. Adsorption isotherms of 4-nonylphenol from aqueous solution on PTMS-C_{18}TMS-TLO (■) and KTLO (▼). Inset: XRD patterns of PTMS-C_{18}TMS-TLO before adsorption (a), and after the adsorption of 0.106 (b) and 3.48 mmol g^{-1} 4-nonylphenol (c).

Figure 3 shows adsorption isotherms of NPh, n-nonane, and phenol for PTMS-C_{18}TMS-TLO from aqueous solutions containing the three solutes at the same concentration. The adsorption isotherms of n-nonane and phenol are type S or type L, corresponding to the relatively weak adsorbent–adsorbate interactions.[12] However, the isotherm of NPh is type H, thus showing the higher affinity of NPh toward PTMS-C_{18}TMS-TLO than those of n-nonane and phenol. The cooperative effect of the attached phenyl, octadecyl, and silanol groups (derived from the hydrolysis of methoxy groups) is thought to play an important role in the selective adsorption of NPh. From the fact that the swelling ability of alkylsilylated derivatives correlates to the alkyl chain length of the attached alkylsilanes,[11a] further variation in adsorption selectivity of alkylphenols with different alkyl chain length is expected from changing the chain length of the alkylsilanes.

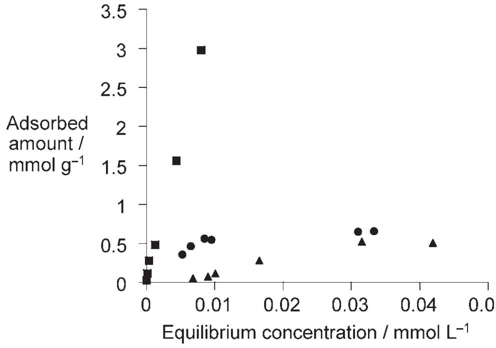

Figure 3. Adsorption isotherms of aqueous solutions of 4-nonylphenol (■), n-nonane (●), and phenol (▲) on PTMS-C_{18}TMS-TLO.

We have prepared an organically modified layered titanate with two organic functional units (phenyl and alkyl groups) to adsorb selectively and effectively NPh from aqueous solution. The immobilization of two kinds of functional units in a confined nanospace is a useful way to tailor

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materials with molecular recognition abilities for a wide variety of molecules.

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[9] The sample (1.0 mg) was dispersed in aqueous solutions of NPh (180 mL, 0.021–6.6 ppm), and the mixtures were stirred for two days at room temperature. After the mixtures were separated by centrifugation, the adsorbed amounts were determined from the concentrations of the adsorbate present in the supernatants by photoluminescence spectroscopy. As to the ternary system, the experiment was carried out by the procedure described above, except that aqueous solutions of 0.31–6.1 ppm NPh, *n*-nonane, and phenol were used, and the adsorbed amounts were determined from the remaining amounts in the supernatants by gas chromatography.

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