Microporous cesium salts of tetravalent Keggin-type polyoxotungstates

\[ \text{Cs}_4[	ext{SiW}_{12}\text{O}_{40}], \text{Cs}_4[\text{PW}_{11}\text{O}_{39}\text{(Sn-}n\text{-C}_4\text{H}_9)] \text{, and Cs}_4[\text{PW}_{11}\text{O}_{39}\text{(Sn-OH)}] \]

and their adsorption properties

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ABSTRACT

Microporous cesium salts of modified and unmodified tetravalent Keggin-type polyoxometalates, including Cs$_4$[SiW$_{12}$O$_{40}$], Cs$_4$[PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)], and Cs$_4$[PW$_{11}$O$_{39}$(Sn-OH)], were synthesized. The crystalline structures, which had body-centered cubic (bcc) arrangements, the lattice constants, and the pore-size distributions of the three Cs salts were similar, regardless of the presence or absence and types of functional groups introduced. The Cs salts had only micropores and no mesopores. The micropore size distributions were determined from adsorption isotherms of Ar, which showed a sharp peak at 0.59 nm and a shoulder at 0.62 nm. The fractions of the external surface areas to the total surface areas of the Cs salts were less than 6%. It is plausible that the micropores originate from the heteropoly anion defects in the crystallite, which form to avoid mismatches in the Cs$^+$/heteropoly anion) ratio required for charge balance (= 4) and for a bcc structure (= 3). The surface of the Cs salt introduced with $n$-butyl groups was hydrophobic, although the surface density of the $n$-butyl groups was low. On the other hand, the hydroxyl groups present on the surface of Cs$_4$[PW$_{11}$O$_{39}$(Sn-OH)] had little effect on the adsorption of water, methanol, ethanol, and hexane but a great impact on that for benzene due to the interactions between the -OH groups and the aromatic rings (-OH···π).
Keywords: Heteropoly acid; Hydrophobicity; Microporous material; Adsorption property; Anion defect
1. Introduction

Ionic crystals, which are important families of crystalline materials, have been attracting considerable interest because of their unique chemical and physical properties, which depend on their crystalline structures and constituent ions [1–9]. Normally, cations and anions are densely packed in the crystal lattice, with the coordination numbers determined by the relative sizes and charges of the constituent ions since the Coulombic forces are strong and directionless. Therefore, most ionic crystals do not have structural micropores caused by the crystal structure, unlike crystalline aluminosilicates, and thus, they only have low surface areas. However, by using the proper sizes, charges, and compositions of the constituent ions as well as precise control of the preparation conditions, some ionic crystals become porous [10,11].

An example of porous ionic crystals is a series of polyoxometalate salts with macrocations [2,6,12–15]. Polyoxometalates with a Keggin structure ([XW_{12}O_{40}]^{n−}, abbreviated as Keggin-POM) are nano-sized metal-oxide multivalent anions with well-defined molecular structures. Although the salts of Keggin-POMs normally do not have intrinsic micropores in the crystal lattice, like conventional ionic crystals, Keggin-POM salts with macrocations, such as oxo-bridged trinuclear chromium carboxylate ([Cr_3O(OOCR)]^{n+}), have intrinsic pores in the crystal lattice and show unique adsorption properties, which depend on the types of organic groups on the
macrocation and the residual counter cations [16–18].

On the other hand, in some cases, *Keggin-POM* salts form microporous solids even when relatively small cations, like Cs⁺ and NH₄⁺, are used as counter cations [19–25]. Among them, the crystal and pore structures of acidic and neutral Cs salts of a trivalent *Keggin-POM* (Cs₃H₃⁺[PW₁₂O₄₀]) have been extensively studied [26–28]. The pore structures of Cs₃H₃⁺[PW₁₂O₄₀] are very sensitive to the Cs⁺ ion content [29]. It has been reported that Cs₂.¹H₀.⁹[PW₁₂O₄₀] is microporous. This *Keggin-POM* salt acts as a size-selective catalyst for acid-catalyzed reactions [30], whereas the pores of Cs₃H₃⁺[PW₁₂O₄₀] with x ≥ 2.₃ show bimodal distributions, ranging from microporous to mesoporous [29].

In contrast to Cs₃H₃⁺[PW₁₂O₄₀], there are only a few reports involving Cs salts of tetravalent *Keggin-POMs* like [SiW₁₂O₄₀]⁴⁻, although the molecular structure of [SiW₁₂O₄₀]⁴⁻ is similar to that of [PW₁₂O₄₀]³⁻. The major difference between [PW₁₂O₄₀]³⁻ and [SiW₁₂O₄₀]⁴⁻ is the electronic charges, which are −3 and −4, respectively. Moffat et al. have reported that the neutral Cs salt Cs₄[SiW₁₂O₄₀] has micropores and a high surface area (150 m² g⁻¹) [31]. However, the size of the micropores is uncertain. Pizzio and Blanco have reported the synthesis of acidic Cs salts, C₅H₄⁺H₀.₆[SiW₁₂O₄₀] and Cs₃H₁.₂[H₀.₂][SiW₁₂O₄₀], and that they act as acid catalysts towards phenol tetrahydropyranylation [32]. However, these microporous Cs salts also have well-developed
mesopores.

The hydrophobicity of the solid surface is a critical factor affecting the adsorption properties of solid materials. Modification of the surface with alkyl groups and fluorine enhances the hydrophobicity, leading to unique adsorption properties [33–36]. Kuwahara et al. have demonstrated that the hydrophobicities of Y-type zeolites significantly increase upon modification with triethoxyfluorosilane [37]. Inumaru et al. have reported that mesoporous silica MCM-41, whose mesopore walls were grafted with n-octyl groups, selectively incorporates 4-nonylphenol and 4-n-heptylaniline into its mesopores from aqueous phases due to strong interactions between the hydrophobic surface and the substrates [38].

In our previous communication [39], we have reported that microporous Cs₅H₄₄[SiW₁₂O₄₀] with highly developed micropores forms when \( x > 2 \) and the titration speed of an aqueous Cs₂CO₃ solution to an aqueous H₄SiW₁₂O₄₀ solution is carefully controlled. In addition, the acidic Cs salt Cs₃H[SiW₁₂O₄₀] acts as a size-selective catalyst towards acid-catalyzed reactions in the liquid phase due to its uniform micropores and small external surface area.

Here we expand on our previous findings that Cs salts of the tetravalent Keggin-POM [SiW₁₂O₄₀]⁺ formed microporous ionic crystals with the Cs salts of other tetravalent Keggin-POMs modified with n-butyl and hydroxyl groups, [PW₁₁O₃₉(Sn-n-C₄H₉)]⁺ and [PW₁₁O₃₉(Sn-OH)]⁺ (Fig.
1). In the present study, we investigated the molecular and crystalline structures of the neutral Cs salts of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{PW}_{11}\text{O}_{39}(\text{Sn-n-C}_4\text{H}_9)]^{4-}$, and $[\text{PW}_{11}\text{O}_{39}(\text{Sn-OH})]^{4-}$. In addition, the pore size distributions, which ranged from the microporous to mesoporous, and the external surface areas were determined by combining Ar porosimetry with conventional mesopore analysis using N$_2$ adsorption-desorption isotherms. These Cs salts had highly developed micropores with small external surface areas, regardless of the presence or absence of functional groups ($n$-butyl and hydroxyl). We discuss the mechanism for the formation of micropores in terms of the crystal structures and morphology of the particles and in comparison with that for Cs$_3$[PW$_{12}$O$_{40}$]. In addition, the effects of $n$-butyl and hydroxyl groups on the adsorption properties were investigated by measuring the adsorption isotherms of various adsorbates.

(Fig. 1)

2. Experimental

2.1 Synthesis of Cs and K salts of polyoxotungstates

2.1.1 Materials

Dodecatungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$) and dodecatungstosilicic acid
(H₄SiW₁₂O₄₀·nH₂O) were supplied by Nippon Inorganic Color and Chemical Co. After H₃PW₁₂O₄₀·nH₂O was recrystallized from water several times, H₃PW₁₂O₄₀·nH₂O was dried at 338 K in a vacuum to obtain H₃PW₁₂O₄₀·6H₂O. H₄SiW₁₂O₄₀·nH₂O was dried in a similar manner to H₃PW₁₂O₄₀·6H₂O, but recrystallization was not conducted before drying.

n-C₄H₉SnCl₃ (Aldrich), SnCl₂·2H₂O (Wako Pure Chemical Co., Ltd.), CsCl (Wako Pure Chemical Co., Ltd.), Cs₂CO₃ (Aldrich), KHCO₃ (Wako Pure Chemical Co., Ltd.), KCl (Wako Pure Chemical Co., Ltd.), and bromine water (Wako Pure Chemical Co., Ltd.) were used as received.

2.1.2 Synthesis of a Cs salt of [PW₁₁O₃₉(Sn-n-C₄H₉)]⁴⁺ (Cs₄-PW11(Sn-n-Bu))

To an aqueous solution of H₃PW₁₂O₄₀ (6.0 × 10⁻² mol dm⁻³, 100 cm³), 1 g of KCl was added, and the pH of the solution was adjusted to 5.4 with an aqueous solution of KHCO₃ (1 mol dm⁻³). The insoluble matter was filtered off. The filtrate was concentrated under vacuum until a solid just started to form and then was allowed to stand overnight. The resulting white solid (K₇[PW₁₁O₃₉]-15H₂O, K₇-PW11) was recovered by filtration and dried at room temperature overnight.

[PW₁₁O₃₉(Sn-n-C₄H₉)]⁺ was prepared according to the method in [40] with some modifications. Liquid n-C₄H₉SnCl₃ (300 μL, 1.756 mmol) was added to an aqueous solution (100
cm$^3$) of 1.55 mmol of K$_7$-PW11 with stirring. The solution was stirred at room temperature for 1 h to yield [PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)]$^{4+}$ in solution. Incorporation of $n$-C$_4$H$_9$ group was confirmed from $^1$H NMR spectrum of [PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)]$^{4+}$ in D$_2$O (see Fig. S1, Supplementary information). After the insoluble matter was filtered off, an aqueous solution of CsCl (0.5 mol dm$^{-3}$, 15 cm$^3$) was added to the resulting filtrate. The clear solution changed to a white colloidal suspension just after the addition of the CsCl solution. The suspension was then allowed to stand overnight at room temperature. The resulting white solid was recovered by filtration and dried at room temperature overnight. The solid was suspended in water (100 cm$^3$), and the suspension was heated at 368 K until most of the solid dissolved. After the insoluble matter was filtered off at 368 K, the filtrate was cooled and allowed to stand at room temperature overnight, during which time a solid precipitated. The solid was collected by filtration and dried under ambient conditions, yielding Cs$_4$[PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)]·8H$_2$O, hereafter referred to as Cs$_4$-PW11(Sn-$n$-Bu). Yield: 59%.  $^{31}$P MAS NMR: $\delta$ (ppm) –12.4. IR (KBr, cm$^{-1}$): $\nu$ 2960 (w), 2931 (w), 2871 (w), 1069 (m), 971 (s), 879 (m), 798 (s). Elemental analysis for Cs$_4$[PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)]·8H$_2$O (%): calcd P 0.88; W 57.3; Sn 3.36; Cs 15.1; C 1.36; H 0.71; found P 0.79; W 57.6; Sn 3.06; Cs 14.8; C 1.40; H 0.68.

2.1.3 Synthesis of a Cs salt of [PW$_{11}$O$_{39}$(Sn-OH)]$^{4+}$ (Cs$_4$-PW11(Sn-OH))
K₅[PW₁₁O₉Sn]·4H₂O was prepared by a similar manner to [41], but using SnCl₂·2H₂O and water as a tin compound and solvent, respectively, instead of SnSO₄ and an aqueous solution of acetic acid. K₇-PW11 (10 g, 3.13 mmol) was suspended in water (80 cm³), and then the suspension was heated at 353 K until all of the solid dissolved. Nitrogen gas was bubbled into the solution at 353 K for 1 h, and then SnCl₂·2H₂O (0.73 g, 3.15 mmol) was added. The solution was stirred at 353 K overnight with the continuous N₂ bubbling. After the insoluble matter was filtered off, the resulting dark-green solution was concentrated in a vacuum at 318 K until a solid began to form. The solution containing a small amount of the solid was allowed to stand at room temperature overnight. The resulting yellow solid (K₅[PW₁₁O₉Sn]·4H₂O) was collected by filtration, washed with water, and then dried at 333 K overnight.

The powder of K₅[PW₁₁O₉Sn]·4H₂O (5.0 g, 1.63 mmol) was dissolved in water (50 cm³). To the solution, bromine water (10 cm³) was added [41], during which time the color of the solution momentarily changed from light yellow to clear, affording [PW₁₁O₉(Sn-OH)]⁴⁺. Air was bubbled into the solution for 1 h to remove unreacted Br₂. An aqueous solution of CsCl (1 mol dm⁻³, 9.97 cm³) was added dropwise to the solution. The resulting suspension was allowed to stand at room temperature for 24 h. The white solid was collected by filtration, washed with water, and dried at 373 K overnight to afford Cs₃.₆K₄.₆[PW₁₁O₉(Sn-OH)]·8H₂O, hereafter referred to as
Cs$_3$-PW$_{11}$(Sn-OH).  Yield: 91%.  $^{31}$P MAS NMR: $\delta$(ppm) –12.2.  IR (KBr, cm$^{-1}$): v 1083 (m), 1055 (m), 982 (s), 883 (m), 800 (s).  Elemental analysis for Cs$_{3.6}$K$_{0.4}$PW$_{11}$O$_{39}$(Sn-OH)-8H$_2$O (%): calcd P 0.90; W 58.6; Sn 3.44; Cs 13.9; K 0.45; found P 0.91; W 58.6; Sn 3.57; Cs 13.9; K 0.45.

2.1.4 Synthesis of Cs$_3$[PW$_{12}$O$_{40}$]($\text{Cs}_3$-PW$_{12}$) and Cs$_4$[SiW$_{12}$O$_{40}$] ($\text{Cs}_4$-SiW$_{12}$)

An aqueous solution of Cs$_2$CO$_3$ (0.10 mol dm$^{-3}$, 24 cm$^3$) was added dropwise to an aqueous solution of H$_3$[PW$_{12}$O$_{40}$] (8.0 $\times$ 10$^{-2}$ mol dm$^{-3}$, 20 cm$^3$) with stirring. A white suspension formed. After the suspension was stirred for 30 min, it was allowed to stand for 48 h at room temperature. The suspension was completely dried at 313 K in a vacuum to afford a white solid. Finally, the white solid was dried in a vacuum at room temperature to obtain Cs$_3$[PW$_{12}$O$_{40}$]·6H$_2$O (Cs$_3$-PW$_{12}$). Yield: 100%.  $^{31}$P MAS NMR: $\delta$(ppm) –15.0.  IR (KBr, cm$^{-1}$): v 1080 (m), 985 (s), 890 (m), 804 (s).  Elemental analysis for Cs$_3$[PW$_{12}$O$_{40}$]·6H$_2$O (%): calcd P 0.92; W 65.2; Cs 11.8; found P 0.92; W 65.1; Cs 11.6.

Cs$_4$[SiW$_{12}$O$_{40}$]·9H$_2$O (Cs$_4$-SiW$_{12}$) was prepared in a similar manner to that for Cs$_3$-PW$_{12}$ using an aqueous solution of H$_3$[SiW$_{12}$O$_{40}$] instead of H$_3$[PW$_{12}$O$_{40}$]. Yield: 100%.  IR (KBr, cm$^{-1}$): v 980 (m), 926 (s), 878 (w), 779 (s).  Elemental analysis for Cs$_4$[SiW$_{12}$O$_{40}$]·9H$_2$O (%): calcd Si 0.80; W 61.8; Cs 14.9; found Si 0.86; W 61.6; Cs 14.8.
2.2 Characterization

$^{31}$P nuclear magnetic resonance (NMR) spectra were acquired at ambient temperature on a JEOL EX-400 NMR spectrometer. The samples were dissolved into H$_2$O/D$_2$O (5:1 v/v). Chemical shifts were referenced to the external standard 85% H$_3$PO$_4$ (0 ppm). Solid-state $^{31}$P magic angle spinning (MAS) NMR spectra were acquired on a JEOL ECA-400 spectrometer. The spinning rate of the sample was 7.0 kHz. A $\pi/2$ pulse width of 5.5 μs and a pulse delay of 5 s were used. 85% H$_3$PO$_4$ was used as a reference.

Thermogravimetric/differential thermal analysis (TG/DTA) was conducted in air on a Rigaku Thermo plus 8120. Temperature of the sample was increased at a rate of 10 K min$^{-1}$. Infrared (IR) spectra of the samples were recorded on an IR spectrometer (FT-IR/230, JASCO) as KBr (Merck) pellets diluted to 0.5 wt%. Powder X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku Mini Flex) with Cu Kα radiation ($\lambda = 0.154$ nm).

Adsorption-desorption isotherms of N$_2$ at 77 K were acquired on a Belsorp-mini instrument (BEL Japan Inc.) after the samples were pretreated at 473 K in a N$_2$ flow for 1 h. Specific surface areas were estimated from the slopes of the $t$-plots derived from the N$_2$ adsorption isotherms. Mesopore-size distributions were calculated by using the Dollimore-Heal (DH) method on the
desorption isotherms of N₂. Micropore-size distributions were determined by using the Saito-Foley method on Ar adsorption isotherms at 87 K measured on an automatic apparatus (Belsorp 28SA, BEL Japan Inc.). Before measurement, the samples were pretreated at 473 K in a vacuum for 3 h.

Elemental analyses of the compounds were performed on an atomic absorption spectrometer (HITACHI A-2000) for Cs and K and inductively coupled plasma-atomic emission spectrometer (Shimadzu ICPS-7000) for P, W, and Sn. The amounts of C and H of the compounds were determined by the Center for Instrumental Analysis at Hokkaido University (Sapporo, Japan).

Adsorption isotherms of H₂O, methanol, ethanol, 1-propanol, n-hexane, and benzene were obtained at 298 K on an automatic apparatus (Belsorp 18, BEL Japan Inc.) after the samples were pretreated at 473 K in a vacuum for 3 h.

3. Results and discussion

3.1 Structures of Keggin-POMs in solution and of their Cs salts

We investigated the formation of the heteropoly anions [PW₁₁O₃₉(Sn-n-C₄H₉)]⁴⁻ and [PW₁₁O₃₉(Sn-OH)]⁴⁺ in solution. Figure 2A shows ³¹P NMR spectra of [PW₁₂O₄₀]⁵⁻, [PW₁₁O₃₉]⁷⁻, [PW₁₁O₃₉(Sn-n-C₄H₉)]⁴⁺, and [PW₁₁O₃₉(Sn-OH)]⁴⁺ in H₂O/D₂O. In the ³¹P NMR spectrum of
[\text{PW}_{12}\text{O}_{40}]^{3–}, there was a peak at –14.7 ppm (Fig. 2A(a)), which is the same as the value previously reported [42]. When one \([\text{W}=\text{O}]^{4+}\) was eliminated from \([\text{PW}_{12}\text{O}_{40}]^{3–}\) to form a mono-lacunary \([\text{PW}_{11}\text{O}_{39}]^{7–}\), the \(31^\text{P}\) NMR peak shifted to –10.5 ppm (Fig. 2A(b)), which is also consistent with the previously reported chemical shift [42]. For the \textit{Keggin-POM} with an \(n\)-butyl group ([\text{PW}_{11}\text{O}_{39}(\text{Sn}-n\text{-C}_4\text{H}_9)]^{5–}), only one peak was observed, indicating that there was no phosphorus-containing impurities (Fig. 2A(c)). The \(31^\text{P}\) NMR chemical shift for \([\text{PW}_{11}\text{O}_{39}(\text{Sn}-n\text{-C}_4\text{H}_9)]^{5–}\) (Fig. 2A(b)) is the same as that for \([\text{PW}_{11}\text{O}_{39}\text{Sn}]^{5–}\) (see Fig. S2(A) in Supplementary information), in which \(\text{Sn}^{2+}\) was incorporated into the lacunal sites of \([\text{PW}_{11}\text{O}_{39}]^{7–}\) [41]. In other words, \([\text{Sn}-n\text{-C}_4\text{H}_9]^3{+}\) could be incorporated into the lacunal sites of \([\text{PW}_{11}\text{O}_{39}]^{7–}\) to form \([\text{PW}_{11}\text{O}_{39}(\text{Sn}-n\text{-C}_4\text{H}_9)]^{5–}\). The incorporation of \(\text{Sn}-n\text{-C}_4\text{H}_9\) was also confirmed from 1H NMR spectrum of \([\text{PW}_{11}\text{O}_{39}(\text{Sn}-n\text{-C}_4\text{H}_9)]^{5–}\) in \(\text{D}_2\text{O}\). The chemical shift (–11.9 ppm) for \([\text{PW}_{11}\text{O}_{39}(\text{Sn-OH})]^{4{+}}\) (Fig. 2A(d)) is the same as that for \([\text{PW}_{11}\text{O}_{39}(\text{Sn}-n\text{-C}_4\text{H}_9)]^{4{+}}\), indicating that \([\text{Sn-OH}]^{3{+}}\) could be introduced into the lacunal sites of \([\text{PW}_{11}\text{O}_{39}]^{7–}\) as \([\text{PW}_{11}\text{O}_{39}(\text{Sn}-n\text{-C}_4\text{H}_9)]^{5–}\). Since the chemical shift was changed from –12.4 ppm for \([\text{PW}_{11}\text{O}_{39}\text{Sn}]^{5–}\) into –11.9 ppm for \([\text{PW}_{11}\text{O}_{39}(\text{Sn-OH})]^{4{+}}\) by the treatment with bromine water, \(\text{Sn}^{3{+}}\) incorporated in \([\text{PW}_{11}\text{O}_{39}\text{Sn}]^{5–}\) was successfully oxidized.

Figure 2B shows solid-state \(31^\text{P}\) MAS NMR spectra of \(\text{Cs}_3\text{-PW}_{12}, \text{Cs}_4\text{-PW}_{11}(\text{Sn}-n\text{-Bu}), \text{and}\)
Cs$_4$-PW11(Sn-OH), which were obtained by reacting Cs$^+$ with [PW$_{12}$O$_{40}$]$^{3-}$, [PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)$_3$]$^{4+}$, and [PW$_{11}$O$_{39}$(Sn-OH)]$^{4+}$, respectively, in the corresponding aqueous solutions. The $^{31}$P NMR chemical shifts for the three Cs salts are basically the same as those in the corresponding solutions, as shown in Fig. 2A. In addition, each Cs salt gave only one peak, indicating that no decomposition and no reconstruction of the heteropoly anions occurred during the formation of the Cs salts.

IR spectra of Cs$_3$-PW12, K$_7$-PW11, Cs$_4$-PW11(Sn-$n$-Bu), Cs$_4$-PW11(Sn-OH), and Cs$_4$-SiW12 are shown in Fig. 3. In the IR spectra of Cs$_3$-PW12, there were four IR bands at 1080, 985, 890, and 804 cm$^{-1}$, which were assigned as $v_{as}$ (P-O), $v_{as}$ (W=O), $v_{as}$ (W-O-W), and $v_{as}$ (W-O-W) for Keggin-type [PW$_{12}$O$_{40}$]$^{3-}$ (Fig. 3a) [42]. In the IR spectrum for the mono-lacunal heteropoly anion K$_7$-PW11, $v_{as}$ (P-O) was split into two bands at 1086 and 1042 cm$^{-1}$, and the band due to $v_{as}$ (W-O-W) was split into several bands (Fig. 3b) because the symmetry of the heteropoly anion changed from $T_d$ to $C_3$ [42]. On the other hand, the IR spectrum of Cs$_4$-PW11(Sn-$n$-Bu) (Fig. 3c) is similar to that of Cs$_3$-PW12, clearly indicating that the heteropoly anion in Cs$_4$-PW11(Sn-$n$-Bu) has $T_d$ symmetry. In other words, [Sn-$n$-C$_4$H$_9$]$^{3+}$ was incorporated into the lacunal site of [PW$_{11}$O$_{39}$]$^{7-}$, forming a complete Keggin-POM. The IR bands for CH$_3$ and CH$_2$ stretching were only observed for Cs$_4$-PW11(Sn-$n$-Bu) in the range of 2800–3000 cm$^{-1}$. The IR spectrum for
Cs₄-PW11(Sn-OH) is similar to that for Cs₄-PW11(Sn-n-Bu), except that νas(P-O) was split into two bands. Since [Sn-OH]³⁺ was incorporated into the lacunal site of [PW₁₁O₃₉]⁷⁻ on the basis of the ³¹P MAS NMR spectrum (Fig. 2g), the splitting of the IR band was not due to the presence of impurities like [PW₁₁O₃₉]⁷⁻. In fact, the IR spectra for Cs₄-PW11(Sn-OH), except for the νas(P-O) bands, are different from those for K₇-PW11. Although the ionic radius of the Sn⁴⁺ ion (rSn⁴⁺ = 0.055 nm) is close to that of the W⁶⁺ ion (rW⁶⁺ = 0.060 nm), that of a Sn³⁺ ion coordinated by a OH group is probably much smaller than that of a bare Sn⁴⁺ ion due to the electron withdrawing character of the OH group. This would result in the deformation of the Keggin unit from pure T₄ symmetry, leading to the splitting of the νas(P-O) bands. For Cs₄-SiW₁₂, four bands due to the Keggin structure were observed at 980, 926, 878, and 779 cm⁻¹, which were assigned as νas(W=O), νas(Si-O), νas(W-O-W), and νas(W-O-W), respectively [42].

Fig. 4 shows TG-DTA profiles for Cs₃-PW₁₂, Cs₄-PW₁₁(Sn-n-Bu), Cs₄-PW₁₁(Sn-OH), and Cs₄-SiW₁₂ in air. Weight loss due to desorption of water was observed in the range of 300–380 K. An exothermic weight loss of 1.21 wt% in the temperature range of 550–780 K was only observed for Cs₄-PW₁₁(Sn-n-Bu), which was due to the combustion of the n-butyl group. This result indicates that Cs₄-PW₁₁(Sn-n-Bu) is stable in air up to 550 K.

Table 1 summarizes the elemental analysis data for Cs₃-PW₁₂, Cs₄-SiW₁₂,
Cs₄-PW11(Sn-n-Bu), and Cs₄-PW11(Sn-OH). The figures in parenthesis in Table 1 are the weight percent of each element calculated from the chemical formulae shown in the rightmost column of Table 1. The numbers of crystalline waters were estimated from the weight loss observed in the TG profiles below 403 K. For each Cs salt, the elemental analysis data were consistent with the values calculated from the formula. On the basis of the elemental analysis and 3¹P NMR and IR spectra, it was concluded that the Cs salts of the tetravalent Keggin-POM with n-butyl and hydroxyl groups could be synthesized.

Powder XRD patterns for Cs₃-PW12, Cs₄-SiW12, Cs₄-PW11(Sn-n-Bu), and Cs₄-PW11(Sn-OH) are shown in Fig. 5. The XRD pattern for Cs₃-PW12 (Fig. 5a) was assigned to a body-centered cubic (bcc) structure [26]. The XRD pattern for Cs₄-SiW12, which has a bcc structure [31] (Fig. 5b), is similar to that for Cs₄-PW12, although the diffraction lines were very sharp and intense in comparison to Cs₃-PW12, indicating that the crystallites of Cs₄-SiW12 are large. It should be noted that Cs₄-PW11(Sn-n-Bu) (Fig. 5c) and Cs₄-PW11(Sn-OH) (Fig. 5d) also show XRD patterns consistent with a bcc structure, and the diffraction angles for Cs₄-PW11(Sn-n-Bu) and Cs₄-PW11(Sn-OH) are almost the same as those for Cs₄-SiW12. The XRD patterns clearly showed that the crystalline structures of the four Cs salts were basically the same regardless of the charges of the anion (–3 or –4) and the presence or absence of functional
groups (n-butyl and hydroxyl groups).

From the diffraction lines, the lattice constants \((a)\) were calculated to be 1.182, 1.178, 1.179, and 1.180 nm for \(\text{Cs}_3\text{PW}_{12}\), \(\text{Cs}_4\text{SiW}_{12}\), \(\text{Cs}_4\text{PW}_{11}\text{Sn}-n\text{-Bu}\), and \(\text{Cs}_4\text{PW}_{11}\text{Sn-OH}\), respectively (Table 2). The crystallite sizes were estimated from the diffraction line at around \(2\theta = 26.1^\circ\) to be 11.7, 45.3, 50.9, and 34.0 nm for \(\text{Cs}_3\text{PW}_{12}\), \(\text{Cs}_4\text{SiW}_{12}\), \(\text{Cs}_4\text{PW}_{11}\text{Sn}-n\text{-Bu}\), and \(\text{Cs}_4\text{PW}_{11}\text{Sn-OH}\), respectively (Table 2). It should be noted that the crystallite sizes for the Cs salts of tetravalent Keggin-POMs are much larger than that for \(\text{Cs}_3\text{PW}_{12}\).

### 3.2 Surface areas, porosities, and pore structures of Cs salts

Fig. 6 shows adsorption-desorption isotherms of \(\text{N}_2\) at 77 K for \(\text{Cs}_3\text{PW}_{12}\), \(\text{Cs}_4\text{SiW}_{12}\), \(\text{Cs}_4\text{PW}_{11}\text{Sn}-n\text{-Bu}\), and \(\text{Cs}_4\text{PW}_{11}\text{Sn-OH}\). The insets in Fig. 6 are \(t\)-plots calculated from the corresponding adsorption isotherms. For each Cs salt, a steep increase in the adsorption amounts at low-pressure \((P/P_0 < 0.05)\) was observed, suggesting the presence of micropores. Only \(\text{Cs}_3\text{PW}_{12}\) gave a type IV isotherm (Fig. 6a), indicating that this material had mesopores. Okuhara et al. have reported that \(\text{Cs}_3\text{PW}_{12}\text{O}_{40}\), prepared by using a similar procedure to that used in the present study, is a porous material having both micropores and mesopores and that the mesopores are ca. 4 nm in size [29,30]. The results shown in Fig. 6a are consistent with previous
reports [29,30]. On the other hand, Cs₄-SiW₁₂, Cs₄-PW₁₁(Sn-n-Bu), and Cs₄-PW₁₁(Sn-OH) gave type I isotherms. In addition, N₂ uptakes in the range of \( 0.1 < P/P₀ < 0.8 \) were small, indicating that they have small external surface areas.

The total and external surface areas were estimated from the slopes of the \( t \)-plots and are summarized in Table 2. Although the total surface area of Cs₄-PW₁₂ was 138 m² g⁻¹, 73% of it is the external surface area (100 m² g⁻¹). This is consistent with the fact that Cs₄-PW₁₂ has pores with bimodal distributions. The total surface area of Cs₄-SiW₁₂ was large (168 m² g⁻¹), but its external surface area was small (8 m² g⁻¹), the value of which corresponds to less than 5% of the total surface area. The total surface areas of Cs₄-PW₁₁(Sn-n-Bu) and Cs₄-PW₁₁(Sn-OH) were 208 and 177 m² g⁻¹, respectively, which are comparable to that of Cs₄-SiW₁₂. In addition, the ratios of the external to the total surface areas were 2% and 6% for Cs₄-PW₁₁(Sn-n-Bu) and Cs₄-PW₁₁(Sn-OH), respectively, indicating that their micropores are highly-developed.

Fig. 7 shows pore-size distributions of the micropores and mesopores for Cs₄-PW₁₂, Cs₄-SiW₁₂, Cs₄-PW₁₁(Sn-n-Bu), and Cs₄-PW₁₁(Sn-OH). In the micropore-size distribution for Cs₄-PW₁₂, an intense peak at 0.56 nm and a broad shoulder in the range of 0.7–0.9 nm were observed. In addition, a large peak in the range of 3–5 nm was present in the mesopore region. The micropore-size distributions of the Cs salts of tetravalent Keggin-POMs, including Cs₄-SiW₁₂,
Cs$_4$-PW$_{11}$(Sn-$n$-Bu), and Cs$_4$-PW$_{11}$(Sn-OH), which showed sharp peaks at 0.59 nm and shoulders at 0.62 nm in the micropore region and only a little peak in the mesopore region, are very similar to each other.

For the microporous Cs salts (Cs$_4$-SiW$_{12}$, Cs$_4$-PW$_{11}$(Sn-$n$-Bu), and Cs$_4$-PW$_{11}$(Sn-OH)), the micropore volumes ($V_{\text{Micro}}$: cm$^3$ g$^{-1}$) were estimated by applying the following equation to the intercept ($I$: cm$^3$ g$^{-1}$) of line B in the $t$-plot shown in the inset of Fig. 6:

$$V_{\text{Micro}} = \frac{I}{C} \times \frac{M}{\rho}$$  \hspace{1cm} (1)

where, $M$, $C$, and $\rho$ are the molecular weight of N$_2$ (28.01 g mol$^{-1}$), the volume of an ideal gas per mole ($22.4 \times 10^3$ cm$^3$ mol$^{-1}$), and the density of liquid N$_2$ at 77 K (0.808 g cm$^{-3}$), respectively. The micropore volumes for Cs$_4$-SiW$_{12}$, Cs$_4$-PW$_{11}$(Sn-$n$-Bu), and Cs$_4$-PW$_{11}$(Sn-OH) were 0.056, 0.074, and 0.055 cm$^3$ g$^{-1}$, respectively (Table 2).

As shown in Fig. 5, the four Cs salts have the same bcc structure, and the lattice constants are similar to each other regardless of the charges of the anions (Table 2). However, the size distributions of the micropores in the Cs salts of the trivalent Keggin-POM Cs$_3$-PW$_{12}$ and those for tetravalent Keggin-POMs Cs$_4$-SiW$_{12}$, Cs$_4$-PW$_{11}$(Sn-$n$-Bu), and Cs$_4$-PW$_{11}$(Sn-OH) are different. This suggests that the formation mechanisms for the micropores in the former and latter Cs salts are different. Misono and Mizuno have reported that Cs$_3$PW$_{12}$O$_{40}$ has no intrinsic micropores in the
crystal lattice since the BET surface area of Cs$_3$PW$_{12}$O$_{40}$, estimated from the adsorption isotherm of N$_2$ is consistent with the surface area of the outer surface of the Cs$_3$PW$_{12}$O$_{40}$ particles, which was calculated from the real density of Cs$_3$PW$_{12}$O$_{40}$ and the particle size estimated from TEM images [42]. Okuhara and co-workers have proposed a model in which the micropores of the Cs salts of [PW$_{12}$O$_{40}$]$^{3-}$, like Cs$_3$PW$_{12}$O$_{40}$, are the intercrystallite spaces formed at crystallographic mismatches between the crystal faces of the microcrystallites [26,27,29]. As shown in Table 2, in the case of Cs$_3$-PW12, the total surface area (136 m$^2$ g$^{-1}$), which was estimated from N$_2$ adsorption isotherms, is actually close to the surface area of the outer surface ($S_{os}$: m$^2$ g$^{-1}$), calculated from the real density and crystallite size estimated from the XRD pattern by using:

$$S_{os} = \frac{6000}{\rho \times d} \quad (2)$$

where $\rho$ and $d$ are the real density of Cs$_3$PW$_{12}$O$_{40}$ (6.5 g cm$^{-3}$) and the crystallite size (nm) estimated from the XRD line at $\sim$26.1° by using Scherrer’s equation, respectively.

For Cs$_4$-SiW12, we calculated $S_{os}$ by using a method similar to that for Cs$_3$-PW12 (Table 2). $S_{os}$ of Cs$_4$-SiW12 was calculated to be 20 m$^2$ g$^{-1}$. However, this value is significantly smaller than the actual surface area (168 m$^2$ g$^{-1}$) estimated from the N$_2$ adsorption isotherm. This large difference can be explained if micropores are present inside the crystallites of Cs$_4$-SiW12, unlike Cs$_3$-PW12. For Cs$_4$-PW11(Sn-$n$-Bu) and Cs$_4$-PW11(Sn-OH), $S_{os}$ were 18 and 27 m$^2$ g$^{-1}$.
respectively, which are much smaller than the actual surface areas (Table 2), suggesting that both

\( \text{Cs}_4\text{PW}11(\text{Sn-n-Bu}) \) and \( \text{Cs}_4\text{PW}11(\text{Sn-OH}) \) have micropores inside the crystallites, like

\( \text{Cs}_4\text{SiW}12. \)

In the bcc structure, heteropoly anions can be located in the center and at each corner of the unit cell, and \( \text{Cs}^+ \) ions are located between two heteropoly anions (Fig. 8). To construct the bcc structure, the ratio of the cations (\( \text{Cs}^+ \)) to the heteropoly anions must be three. In the case of

\( \text{Cs}_3\text{PW}12 \), the ratio of \( \text{Cs}^+/\text{(heteropoly anion)} \) required to achieve charge balance was three due to the trivalent \textit{Keggin-POM} and is consistent with that required for a bcc structure. In other words, all of the cation and anion sites are occupied with \( \text{Cs}^+ \) and \( [\text{PW}_{12}\text{O}_{40}]^{3-} \) ions, respectively (Fig. 8A). However, for the Cs salts of the tetravalent \textit{Keggin-POMs}, the ratio of \( \text{Cs}^+/\text{(heteropoly anion)} \) was four, which is necessary in order to achieve charge balance. Thus, the ratio of \( \text{Cs}^+/\text{(heteropoly anion)} \) is not consistent with that required for a bcc structure, which is three. If a quarter of the heteropoly anions are defective in the Cs salts of the tetravalent \textit{Keggin-POMs}, i.e., anion vacancies are present in the crystallites (Fig. 8B), the \( \text{Cs}^+\)-heteropoly anion mismatch can be avoided. Therefore, we speculate that anion vacancies are the origins of the micropores. Schlögl and co-workers have proposed a similar model for the micropores in the crystallites of

\( \text{Cs}_4[\text{PMo}_{11}\text{VO}_{40}]\cdot5\text{H}_2\text{O} \) [19].
On the basis of the anion vacancy model, we calculated the number of anion vacancies per unit weight of the Cs salt by using:

\[ N_{\text{defect}} = \frac{N_A}{3 \times F_W} \]  \hspace{1cm} (3)

where \( N_{\text{defect}} \), \( F_W \), and \( N_A \) are the number of the anion vacancies per unit weight of the Cs salt (g\(^{-1}\)), the formula weight of the Cs salt, and Avogadro’s number, respectively. If the heteropoly anion is a sphere with a diameter of 1.1 nm [44], the total volume of the anion vacancies per unit weight of the Cs salt (\( V_{\text{defect}} \), cm\(^3\) g\(^{-1}\)) can be calculated by using:

\[ V_{\text{defect}} = N_{\text{defect}} \times (7.0 \times 10^{-22}) \]  \hspace{1cm} (4)

where the constant 7.0 \( \times \) 10\(^{-22}\) (cm\(^3\)) is the volume of one Keggin-POM. \( V_{\text{defect}} \) was calculated to be 0.041 cm\(^3\) g\(^{-1}\) for Cs\(_4\)-SiW\(_{12}\) (Table 2). This value is consistent with the micropore volume estimated from the N\(_2\) adsorption isotherms (0.056 cm\(^3\) g\(^{-1}\), Table 2). In addition, \( V_{\text{defect}} \) for Cs\(_4\)-PW\(_{11}\)(Sn-n-Bu) and Cs\(_4\)-PW\(_{11}\)(Sn-OH) are consistent with the micropore volumes. For all microporous Cs salts, the micropore volumes estimated from the N\(_2\) adsorption isotherms are slightly larger than the corresponding \( V_{\text{defect}} \). We think that the N\(_2\) adsorption method determines the spaces connecting the anion vacancies, into which N\(_2\) can approach from the outside of the crystallite. Thus, the micropore volumes estimated from N\(_2\) adsorption isotherms are larger than \( V_{\text{defect}} \).
3.2 Adsorption properties of the microporous Cs salts

As discussed in 3.1, $n$-butyl groups were introduced into Keggin-POM to afford Cs$_4$-PW$_{11}$(Sn-$n$-Bu). However, we believe that only a part of the $n$-butyl groups is exposed on the surface. In other words, some of them are directed away from the micropores. Thus, we estimated the number of $n$-butyl groups exposed on the surface as follows. The Sn-C$_4$H$_9$ bond in Cs$_4$-PW$_{11}$(Sn-$n$-Bu) was hydrolyzed by heating it in a He flow containing H$_2$O vapor (3.3 kPa) at 473 K for 6 h, and we compared the carbon contents of the samples before and after the treatment to estimate the number of -C$_4$H$_9$ groups exposed on the micropores. Before treatment, Cs$_4$-PW$_{11}$(Sn-$n$-Bu) had a carbon content of 1.56 wt%, which corresponds to 0.324 mmol g$^{-1}$ being $n$-butyl groups, and after treatment, the carbon content was 1.23 wt%, indicating that 21% of the $n$-butyl groups were eliminated by using the treatment. This result suggested that 21% of $n$-butyl groups were exposed on the surface. The crystalline structure was not changed during the treatment, and the micropore was also retained even after the treatment (see Fig. S3 in Supplementary information). In a separate experiment, it was confirmed that the carbon content did not decrease further with an increase in the treatment time under the present conditions. As discussed in section 3.1, a quarter of the heteropoly anions in Cs$_4$-PW$_{11}$(Sn-$n$-Bu) have defects,
which form the micropores. If it is assumed that the heteropoly anions are arranged in a parallel manner within the crystallite, the heteropoly anions in which n-butyl groups directed towards the micropores are a quarter of the total heteropoly anions, which roughly corresponds to the fraction of the n-butyl groups exposed on the surface.

In addition, for \textbf{Cs}_4\textit{PW}11(\textit{Sn-OH}), we estimated the fraction of hydroxyl groups exposed on the surface by using a method similar to that for estimating the amount of the n-butyl groups exposed on the surface, except that chlorotrimethylsilane (ClSiMe\textsubscript{3}) was used instead of H\textsubscript{2}O. \textbf{Cs}_4\textit{PW}11(\textit{Sn-OH}) was treated under a He flow containing an excess amount of ClSiMe\textsubscript{3} at 473 K for 6 h to convert only the Sn-OH groups exposed on the surface to Sn-O-SiMe\textsubscript{3}. After treatment, the carbon content was 0.24 wt\%, which corresponded to an SiMe\textsubscript{3} content of 0.067 mmol g\textsuperscript{-1}. Introduction of -SiMe\textsubscript{3} was also confirmed by \textsuperscript{29}Si MAS NMR (see Fig. S4 in Supplementary information). The crystalline structure was not changed by the treatment and the micropore volume was decreased due to the introduction of -SiMe\textsubscript{3} groups (see Fig. S5 in Supplementary information). Since the total number of Sn-OH groups in the untreated \textbf{Cs}_4\textit{PW}11(\textit{Sn-OH}) was 0.29 mmol g\textsuperscript{-1}, 23\% of the hydroxyl groups were exposed on the surface. This value is similar to that of the n-butyl groups exposed on the surface.

Fig. 9 shows a comparison of the adsorption isotherms of water, primary alcohols (C\textsubscript{1}-C\textsubscript{3}),
benzene and \( n \)-hexane at 298 K on microporous \( \text{Cs}_4\text{SiW12} \), \( \text{Cs}_4\text{PW11}(\text{Sn-}n\text{-Bu}) \), and \( \text{Cs}_4\text{PW11}(\text{Sn-OH}) \). The adsorption amounts per unit surface area are plotted in Fig. 9, making it possible to ignore the differences in the surface areas. The \( n \)-butyl groups had a big effect on the adsorption of the water. As shown in Fig. 9a, the amount of water adsorbed at \( P = 2 \) Torr on \( \text{Cs}_4\text{SiW12} \) was 0.14 cm\(^3\) m\(^{-2}\), whereas that on \( \text{Cs}_4\text{PW11}(\text{Sn-}n\text{-Bu}) \) was only one-third of that on \( \text{Cs}_4\text{SiW12} \). Since the adsorption amounts at nearly the saturated vapor pressure (\( P/P_0 = 0.95 \)) are similar to each other, it seems unlikely that the difference in the low-pressure region is due to the difference in the micropore volumes. Thus, the difference in the hydrophobicity is a plausible explanation for the different amounts of \( \text{H}_2\text{O} \) adsorbed. It has been reported that the surfaces of the Cs salts of Keggin-type heteropolyacids, like \( \text{Cs}_{2.5}\text{H}_{0.5}[\text{PW}_{12}\text{O}_{40}] \), are rather hydrophobic [45]. The \( \text{H}_2\text{O} \) adsorption isotherms clearly showed that the introduction of \( n \)-butyl groups into the \textit{Keggin-POM} increased the hydrophobicity.

The surface density of the \( n \)-butyl groups on \( \text{Cs}_4\text{PW11}(\text{Sn-}n\text{-Bu}) \) was estimated from the surface area and the number of \( n \)-butyl groups exposed on the surface to be only 0.20 nm\(^2\). In other words, only one \( n \)-butyl group was present per 5.0 nm\(^2\) of the surface. This surface area is extremely large in comparison with the cross-sectional area of adsorbed water (0.125 nm\(^2\)). In other words, the \( n \)-butyl groups greatly affect the hydrophobicity of the surface despite the low
surface density. Inumaru et al. have demonstrated by using $^{13}$C MAS NMR that $n$-alkyl groups (C8 and C5) grafted on the surface of mesoporous silica are highly mobile near room temperature [46]. Thus, we concluded that the $n$-butyl groups on the surface of Cs$_4$-PW11(Sn-$n$-Bu) were active like the $n$-alkyl groups on the mesoporous silica. Considering the length (~0.7 nm) and the active movement of the $n$-butyl groups, it is likely that they affect the hydrophobicity of the surface of Cs$_4$-PW11(Sn-$n$-Bu), although the surface density was low (Fig. 10A). On the other hand, the OH groups present on the surface of Cs$_4$-PW11(Sn-OH) have little impact on the adsorption properties, although the surface density was almost the same as that for the $n$-butyl groups in Cs$_4$-PW11(Sn-$n$-Bu). In fact, the adsorption isotherms of various adsorbates on Cs$_4$-PW11(Sn-OH), except for 1-propanol and benzene, which preferentially adsorbed on Cs$_4$-PW11(Sn-OH), are similar to those on Cs$_4$-SiW12 (Fig. 9). Since the hydroxyl groups are short, they have less impact on the adsorption properties (Fig. 10B).

Although there were no differences among the adsorption isotherms of $n$-hexane on the Cs salts, there were considerable differences in the adsorption isotherms of benzene on Cs$_4$-PW11(Sn-$n$-Bu), Cs$_4$-PW11(Sn-OH), and Cs$_4$-SiW12. Since the interactions between the C-H moieties of saturated hydrocarbons and aromatic compounds, i.e., -CH···π interactions, are extremely weak [47, 48], it is reasonable that the adsorbability of benzene onto the surface of
Cs$_4$-PW$_{11}$(Sn-$n$-Bu) is low, meaning that benzene is not included in the micropores of Cs$_4$-PW$_{11}$(Sn-$n$-Bu). In contrast, Cs$_4$-PW$_{11}$(Sn-OH) adsorbed benzene strongly, as indicated by the steep increase in the amount of benzene adsorbed at low pressure (Fig. 9). It has been reported that a weak -OH···π hydrogen bond can occur [47]. In general hydrogen bonds are not strong; however, they would explain preferential adsorption of benzene in the micropores of Cs$_4$-PW$_{11}$(Sn-OH). For the adsorption isotherms of C$_2$H$_5$OH, there was a large difference in the adsorption amount between Cs$_4$-SiW$_{12}$ and Cs$_4$-PW$_{11}$(Sn-$n$-Bu) at low pressure (P < 3 Torr). However, the difference in the adsorption amounts was a little for C$_3$H$_7$OH. This is probably due to lower polarity of C$_3$H$_7$OH than C$_2$H$_5$OH.

4. Conclusions

Neutral Cs salts of the tetravalent Keggin-POMs Cs$_4$[SiW$_{12}$O$_{40}$], Cs$_4$[PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)], and Cs$_4$[PW$_{11}$O$_{39}$(Sn-OH)] were synthesized, and their molecular, crystalline, and pore structures were investigated. All of the Cs salts formed ionic crystals with similar body-centered cubic structures to that of a Cs salt of a trivalent Keggin-POM, Cs$_3$[PW$_{12}$O$_{48}$]. The crystalline structures of the Cs salts were similar to each other regardless of the presence or absence of functional groups ($n$-butyl and hydroxyl) and the charges of the anions (−3 or −4). The Cs salts of the tetravalent
Keggin-POMs had only micropores, which appeared as a sharp peak at 0.59 nm and shoulder at 0.62 nm in the micropore region. The ratios of the external surface areas to the total surface areas of the Cs salts of the tetravalent Keggin-POMs were less than 6%. The surface of the Cs salt with $n$-butyl groups showed a hydrophobic nature in comparison with that of the unmodified Cs salt, although the surface density of the $n$-butyl groups was low. On the other hand, the hydroxyl groups present on the surface of the Cs salt barely affected the adsorption properties except for benzene and propanol.

5. Appendix A

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.micromeso.xxxxxxx.

Acknowledgement

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References


Table 1

Elemental analysis of the Cs salts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental analysis/wt%&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Formula&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
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<tr>
<td></td>
<td>P</td>
<td>Si</td>
</tr>
<tr>
<td>Cs&lt;sub&gt;3&lt;/sub&gt;-PW12</td>
<td>0.92</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>(0.92)</td>
<td>(65.2)</td>
</tr>
<tr>
<td>Cs&lt;sub&gt;4&lt;/sub&gt;-SiW12</td>
<td>---</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>(0.80)</td>
<td>(61.8)</td>
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<tr>
<td>Cs&lt;sub&gt;4&lt;/sub&gt;-PW11(Sn-&lt;i&gt;n&lt;/i&gt;-Bu)</td>
<td>0.79</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>(0.88)</td>
<td>(57.3)</td>
</tr>
<tr>
<td>Cs&lt;sub&gt;4&lt;/sub&gt;-PW11(Sn-OH)</td>
<td>0.91</td>
<td>---</td>
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<td>(0.90)</td>
<td>(58.6)</td>
</tr>
</tbody>
</table>

a) Figures in parenthesis are the values calculated from the formulae.
b) Number of crystalline water was estimated from the weight loss in TG profile.
### Table 2

Lattice constants, crystallite sizes, surface areas, and micropore volumes for the Cs salts.

<table>
<thead>
<tr>
<th>Negative charge of heteropoly anion</th>
<th>Sample</th>
<th>Lattice constant</th>
<th>Crystallite size</th>
<th>Surface area$^a$/m² g⁻¹</th>
<th>Micropore volume$^b$/m³ g⁻¹</th>
<th>$S_{os}^c$</th>
<th>$V_{defect}^d$/cm³ g⁻¹</th>
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<tr>
<td>−3</td>
<td>Cs₃-PW12</td>
<td>1.182</td>
<td>11.7</td>
<td>136</td>
<td>100</td>
<td>****</td>
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<td>Cs₄-SiW12</td>
<td>1.178</td>
<td>45.3</td>
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<td>8</td>
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<td>20</td>
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<tr>
<td>−4</td>
<td>Cs₄-PW11(Sn-η-Bu)</td>
<td>1.179</td>
<td>50.9</td>
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<td>3</td>
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<td>18</td>
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<td></td>
<td>Cs₄-PW11(Sn-OH)</td>
<td>1.180</td>
<td>34.0</td>
<td>177</td>
<td>10</td>
<td>0.055</td>
<td>27</td>
</tr>
</tbody>
</table>

a) Surface area was estimated from the slopes of the $t$-plots calculated from N₂ adsorption isotherms.

b) Micropore volume was estimated from the intercept of line B in the $t$-plot shown in Fig. 6.

c) Surface area of the outer surface of crystallite calculated from crystallite size (XRD) and real density by using eq. 3.

d) Total volume of the anion vacancies per unit weight of the Cs salt calculated by using eqs. 4 and 5.
Figure captions

Fig. 1  Polyhedral representations of tetravalent Keggin-type polyoxometalates.  (a) [SiW$_{12}$O$_{40}$]$^{4-}$, (b) [PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)]$^{7-}$, and (c) [PW$_{11}$O$_{39}$(Sn-OH)]$^{4+}$. ( ) Sn, ( ) O, ( ) C, and ( ) H.

Fig. 2.  (A) $^{31}$P NMR spectra of (a) [PW$_{12}$O$_{40}$]$^{3-}$, (b) [PW$_{11}$O$_{39}$]$^{7-}$, (c) [PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)]$^{1+}$, and (d) [PW$_{11}$O$_{39}$(Sn-OH)]$^{1+}$ in 5:1 H$_2$O/D$_2$O (v/v) and (B) solid-state $^{31}$P MAS NMR spectra of (e) Cs$_3$-PW12, (f) Cs$_4$-PW11(Sn-$n$-Bu), and (g) Cs$_4$-PW11(Sn-OH).

Fig. 3.  IR spectra of (a) Cs$_3$-PW12, (b) K$_7$-PW11, (c) Cs$_4$-PW11(Sn-$n$-Bu), (d) Cs$_4$-PW11(Sn-OH), and (e) Cs$_4$-SiW12.  All the samples were diluted with KBr to 0.5 wt%.

Fig. 4.  TG-DTA profiles in air for (a) Cs$_3$-PW12, (b) Cs$_4$-PW11(Sn-$n$-Bu), (c) Cs$_4$-PW11(Sn-OH), and (d) Cs$_4$-SiW12.

Fig. 5.  XRD patterns for (a) Cs$_3$-PW12, (b) Cs$_4$-SiW12, (c) Cs$_4$-PW11(Sn-$n$-Bu), and (d) Cs$_4$-PW11(Sn-OH).
Fig. 6. Adsorption-desorption isotherms of \( \text{N}_2 \) at 77 K for (a) \( \text{Cs}_3\text{-PW12} \), (b) \( \text{Cs}_4\text{-SiW12} \), (c) \( \text{Cs}_4\text{-PW11(Sn-n-Bu)} \), and (d) \( \text{Cs}_4\text{-PW11(Sn-OH)} \). Insets are \( t \)-plots calculated from corresponding \( \text{N}_2 \) adsorption isotherms.

Fig. 7. Micropore and mesopore size distributions for (a) \( \text{Cs}_3\text{-PW12} \), (b) \( \text{Cs}_4\text{-SiW12} \), (c) \( \text{Cs}_4\text{-PW11(Sn-n-Bu)} \), and (d) \( \text{Cs}_4\text{-PW11(Sn-OH)} \).

Fig. 8. Model of crystalline structure of (A) a Cs salt of a trivalent \textit{Keggin-POM}, like \( \text{Cs}_3\text{-PW12} \), and (B) a Cs salt of a tetravalent \textit{Keggin-POM}, like \( \text{Cs}_4\text{-SiW12} \), \( \text{Cs}_4\text{-PW11(Sn-n-Bu)} \), and \( \text{Cs}_4\text{-PW11(Sn-OH)} \). Only heteropoly anions are depicted in the illustrations, although there are cesium ions located between two heteropoly anions. The unit cells expand in the vertical direction. In structure B, a quarter of the heteropoly anions have defects to avoid the mismatch in the Cs\(^+/\text{(heteropoly anion)}\) ratios required for charge balance (\( = 4 \)) and for a bcc structure (\( = 3 \)), and these anion defects form micropores.

Fig. 9. Adsorption isotherms of water, methanol, ethanol, 1-propanol, benzene, and \( n \)-hexane on microporous Cs salts. (○) \( \text{Cs}_4\text{-SiW12} \), (▲) \( \text{Cs}_4\text{-PW11(Sn-n-Bu)} \), and (■) \( \text{Cs}_4\text{-PW11(Sn-OH)} \).
**Fig. 10.** Schematic images of (A) an $n$-butyl group on the surface of $\text{Cs}_4\text{PW11(Sn-}n\text{-Bu)}$ and (B) a hydroxyl group on the surface of $\text{Cs}_4\text{PW11(Sn-OH)}$. 
Fig. 1 Polyhedral representations of tetravalent Keggin-type polyoxometalates. (a) $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, (b) $[\text{PW}_{11}\text{O}_{39}(\text{Sn-}n\text{-C}_4\text{H}_9)]^{4+}$, and (c) $[\text{PW}_{11}\text{O}_{39}(\text{Sn-OH})]^{4+}$. ( ) Sn, ( ) O, ( ) C, and ( ) H.
Fig. 2. (A) $^{31}$P NMR spectra of (a) [PW$_{12}$O$_{40}$]$^{3-}$, (b) [PW$_{11}$O$_{39}$]$^{7-}$, (c) [PW$_{11}$O$_{39}$(Sn-$n$-C$_4$H$_9$)]$^4^-$, and (d) [PW$_{11}$O$_{39}$(Sn-OH)]$^5^-$ in 5:1 H$_2$O/D$_2$O (v/v) and (B) solid-state $^{31}$P MAS NMR spectra of (e) Cs$_3$-PW12, (f) Cs$_4$-PW11(Sn-$n$-Bu), and (g) Cs$_r$-PW11(Sn-OH).
Fig. 3. IR spectra of (a) Cs$_3$-PW12, (b) K$_7$-PW11, (c) Cs$_7$-PW11(Sn-$n$-Bu), (d) Cs$_7$-PW11(Sn-OH), and (e) Cs$_4$-SiW12. All the samples were diluted with KBr to 0.5 wt%.
Fig. 4. TG-DTA profiles in air for (a) Cs$_3$-PW12, (b) Cs$_4$-PW11(Sn-$n$-Bu), (c) Cs$_4$-PW11(Sn-OH), and (d) Cs$_4$-SiW12.
Fig. 5. XRD patterns for (a) Cs$_3$-PW12, (b) Cs$_4$-SiW12, (c) Cs$_4$-PW11(Sn-n-Bu), and (d) Cs$_4$-PW11(Sn-OH).
Fig. 6. Adsorption-desorption isotherms of N\textsubscript{2} at 77 K for (a) Cs\textsubscript{3}-PW12, (b) Cs\textsubscript{4}-SiW12, (c) Cs\textsubscript{4}-PW11(Sn-\textit{n}-Bu), and (d) Cs\textsubscript{4}-PW11(Sn-OH). Insets are \textit{t}-plots calculated from corresponding N\textsubscript{2} adsorption isotherms.
Fig. 7. Micropore and mesopore size distributions for (a) Cs$_3$-PW12, (b) Cs$_4$-SiW12, (c) Cs$_4$-PW11(Sn-$n$-Bu), and (d) Cs$_4$-PW11(Sn-OH).
Fig. 8. Model of crystalline structure of (A) a Cs salt of a trivalent Keggin-POM, like Cs$_3$-PW12, and (B) a Cs salt of a tervalent Keggin-POM, like Cs$_4$-SiW12, Cs$_4$-PW11(Sn-$n$-Bu), and Cs$_4$-PW11(Sn-OH). Only heteropoly anions are depicted in the illustrations, although there are cesium ions located between two heteropoly anions. The unit cells expand in the vertical direction. In structure B, a quarter of the heteropoly anions have defects to avoid the mismatch in the Cs$^+$/heteropoly anion) ratios required for charge balance (= 4) and for a bcc structure (= 3), and these anion defects form micropores.
Fig. 9. Adsorption isotherms of water, methanol, ethanol, 1-propanol, benzene, and $n$-hexane on microporous Cs salts. (○) $\text{Cs}_4\text{-SiW}_{12}$, (▲) $\text{Cs}_4\text{-PW}_{11}(\text{Sn-}n\text{-Bu})$, and (■) $\text{Cs}_4\text{-PW}_{11}(\text{Sn-OH})$. 
Fig. 10. Schematic images of (A) an \( n \)-butyl group on the surface of \( \text{Cs}_4\text{PW11}(\text{Sn}-n\text{-Bu}) \) and (B) a hydroxyl group on the surface of \( \text{Cs}_4\text{PW11}(\text{Sn-OH}) \).