



Synthesis, crystal structure and conductive mechanism of solid high-proton conductor tungstovanadosilic heteropoly acid



Tianpei Huang^a, Naiqin Tian^a, Qingyin Wu^{a,*}, Yan Yan^b, Wenfu Yan^b

^a Department of Chemistry, Zhejiang University, Hangzhou 310027, China

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, China

HIGHLIGHTS

- The single crystal of H₅SiW₁₁VO₄₀·15H₂O was firstly determined.
- It has excellent conductivity, which is $7.93 \times 10^{-3} \text{ S cm}^{-1}$ at 15 °C and 50% RH.
- The mechanism of proton conduction of H₅SiW₁₁VO₄₀·15H₂O is Vehicle mechanism.

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ABSTRACT

Tungstovanadosilic heteropoly acid H₅SiW₁₁VO₄₀·15H₂O has been successfully synthesized and characterized. The single crystal of this solid proton conductor was firstly obtained and the crystal structure was determined from single crystal X-ray diffraction. The complex crystallizes in the monoclinic system, space group C2/c, with $a = 12.716(3) \text{ \AA}$, $b = 19.881(5) \text{ \AA}$, $c = 19.099(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90.796^\circ$, $\gamma = 90^\circ$, $V = 4828(2) \text{ \AA}^3$, $Z = 4$. Its proton conductivity was measured using electrochemical impedance spectroscopy (EIS) in the temperature range 15–55 °C, and the activation energy of the conductivity was determined. The results show that it has appreciable proton conductivity ($7.93 \times 10^{-3} \text{ S cm}^{-1}$) at 15 °C and 50% relative humidity, with an activation energy of 21.59 kJ mol⁻¹ for proton conduction. The conductive mechanism is Vehicle mechanism.

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1. Introduction

Heteropolyacids (HPAs) and their salts, a class of nanosized metal-oxygen anionic clusters, have a wide range of interesting physical and chemical properties [1]. During the past few decades, they have attracted considerable attention because of their significant applications in many fields such as catalysis, medicine and materials science [2–5]. HPAs are considered to be a kind of solid state super acids, two types of protons have been found in them: (1) non-localized hydrated protons bound to one heteropolyanion as a whole and rapidly exchanging with the protons of the water molecules in the hydration shell of the acid; (2) non-hydrated protons localized at the peripheral oxygen atoms of the polyanion [6]. Because the non-localized hydrated protons have good mobility, the HPAs exhibit the characteristic named “pseudo-liquid phase”. For this reason, most of the HPAs show high conductivities at

ambient temperature. They are excellent proton conductors, and their potential applications in fuel cells, electrochromic devices, sensors etc. became possible [7–9].

The conductive performance varies widely depending on the type of the HPAs' structure. The basic structural unit investigated in HPAs is the Keggin anion, which is a thermally stable metal-oxygen anionic cluster. HPAs based on this structure were reported to show highest solid-state conductivity, and proton transport in these materials has been studied [10]. Our recent studies show that changing the constitutional elements of polyanion may lead to the difference in the degree of hydration and proton mobility [11]. On the other hand, there are many reports about synthesis and single-crystal structures of Keggin-type HPAs and their salts. However, few complete single crystal X-ray investigation about monosubstituted HPA seems to have been carried out. In order to obtain the arrangements of heteroatoms within the monosubstituted heteropoly acid, and to further investigate the effect of elemental composition on the conductive performance of heteropoly acids, we synthesized a Keggin-type mono-vanadium-substituted

* Corresponding author.

E-mail address: qywu@zju.edu.cn (Q. Wu).

tungstosilicic acid $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$, its preparation procedure, single-crystal structure and conductive performance are presented in this paper.

2. Experimental

2.1. Synthesis of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$

Vanadium substituted tungstosilicic acid $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$ was prepared by the stepwise acidification and the stepwise addition of element solutions. Firstly, the lacunary $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ (SiW_{11}) was synthesized by the literature method [12]. Secondly, vanadium ion is added to the solution of lacunary precursor under the appropriate condition. A detailed description of each step is given as follows. Sodium metavanadate (1.58 g, 10 mmol) was added to 100 mL of aqueous solution containing 32.21 g SiW_{11} and stirred vigorously until completely dissolved. The solution was adjusted pH to 5.5 with 6 M HCl and kept boiling for 1 min. After cooled to room temperature, it was filtered and the pH of filtrate was readjusted to between 2 and 2.5 by addition of sulfuric acid (1:1) solution. Subsequently, it is boiled for 1.5 h and allowed to stand at ambient temperature for half an hour. The cooled solution was extracted with ether in a sulfuric acid medium. The orange powder was obtained after the ether was removed in vacuum dryer. Silicon, tungsten and vanadium were analyzed by inductively coupled plasma mass spectrometry (ICP-MS); the water content was determined by thermogravimetry. Found: Si, 0.91%; W, 66.11%; V, 1.71%; H_2O , 8.87%. Calculated for $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$: Si, 0.93%; W, 67.06%; V, 1.69%; H_2O , 8.95%.

2.2. Characterization techniques

Elemental analysis was performed on an 8410 inductively coupled plasma spectrometer (Australia Labtam Company). Infrared (IR) spectrum was recorded on an NICOLET NEXUS 470 FT/IR spectrometer using KBr pellet in the 4000–400 cm^{-1} ranges. The UV spectrum was carried out using an SHIMADZU U-2550 UV-Vis spectrophotometer. Suitable single crystal of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$ was selected for single-crystal X-ray diffraction analysis. The determinations of the unit cell and data collections for the crystal of this compound were carried out on a BRUKER SMART APEX II diffractometer. The diffraction measurements were performed using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ nm) at ambient temperature. The structures were solved by direct methods and refined by full-matrix least-squares techniques with the SHELXTL program. X-ray powder diffraction analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer using a Cu tube operated at 40 kV and 40 mA in the range of $2\theta = 4\text{--}40^\circ$ at a rate of 0.02°s^{-1} . The thermogravimetric-differential thermal analysis (TG-DTA) was performed using an SHIMADZU thermal analyzer. Measurements were made heating from 35 to 800 $^\circ\text{C}$, at a heating rate of $10^\circ\text{C min}^{-1}$ in a Nitrogen stream. Complex impedance measurements were carried out on a VMP2 Multi-channel potentiostat electrochemical impedance analyzer over a frequency range from 9.99×10^4 to 0.01 Hz.

2.3. Measurement of conductivity

At room temperature, the powder sample was pressed at 20 MPa into a compacted pellet with 10.00 mm in diameter, 2.56 mm in thickness. Two copper sheets were attached to two sides of the pellet. Copper slices and copper wires were used as electrodes and lines, respectively. The proton conductivity was measured using a cell: copper | sample | copper. The complex impedance spectra of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$ (in frequency range

from 9.99×10^4 to 0.01 Hz) were recorded at temperature range of 15–55 $^\circ\text{C}$ and 50% relative humidity.

3. Results and discussion

3.1. Crystal structure

The crystallographic data and structural refinement results of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$ are listed in Table 1. Fig. 1 shows the crystal structure of the $\text{SiW}_{11}\text{VO}_{40}^{5-}$ anion. The central atom Si tetrahedrally coordinated to four oxygen atoms. The central SiO_4 tetrahedron is surrounded by four M_3O_{13} groups, which can be subdivided into three edge-sharing MO_6 octahedra. Furthermore, each M_3O_{13} group is linked to its neighbor by sharing corner. The marked M atom shows a statistically disordered state and each position was shared by W and V at the atomic stoichiometric ratio of $n(\text{W}):n(\text{V}) = 11:1$. This structure has a ball-like shape and is often named the Keggin molecule. The relevant bond lengths (\AA) and angles ($^\circ$) of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$ are listed in Table 2. All metal atoms have a distorted MO_6 octahedral environment with M–O distances 1.705(11)–2.402(10) \AA and bond angles $72.9(4)$ – $171.7(5)^\circ$. The disordered SiO_4 tetrahedron was located in the center of the host cage with Si(1)–O distances and O–Si(1)–O angles in the range 1.561(11)–1.619(11) \AA , $107.7(5)$ – $111.6(8)^\circ$ separately. The most likely explanation is that the atomic radius and electronegativity of vanadium atom are different from that of the tungsten atom, so the substitution of vanadium atom will cause the change of bond lengths and bond angles, leading to a distortion of the MO_6 octahedral and SiO_4 tetrahedron.

3.2. IR and UV spectra

The IR spectroscopy is conveniently and widely used for the characterization of heteropoly compounds [13]. There are four kinds of oxygen atoms in $\text{SiW}_{11}\text{VO}_{40}^{5-}$, four Si-O_a in which oxygen atom connects with heteroatom, twelve $\text{M-O}_b\text{-M}$ oxygen-bridges (corner-sharing oxygen-bridge between different M_3O_{13} sets), twelve $\text{M-O}_c\text{-M}$ oxygen-bridges (edge-sharing oxygen-bridge within M_3O_{13} sets) and twelve M-O_d terminal oxygen atoms. Fig. 2 presents the IR spectrum of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$. In the range of 700–1100 cm^{-1} , five absorption bands at 1016, 980, 923, 876 and

Table 1
Summary of crystal structure determination for $\text{H}_5\text{SiW}_{11}\text{VO}_{40}\cdot 15\text{H}_2\text{O}$.

Empirical formula	$\text{H}_5\text{SiW}_{11}\text{VO}_{40}(\text{H}_2\text{O})_{15}$
Formula weight	3016.38
Temperature/K	293(2)
$a/\text{\AA}$	12.716(3)
$b/\text{\AA}$	19.881(5)
$c/\text{\AA}$	19.099(5)
$\alpha/^\circ$	90
$\beta/^\circ$	90.796
$\gamma/^\circ$	90
Crystal symmetry	Monoclinic
Space group	C2/c
Volume/ \AA^3	4828(2)
Calculated density/ Mg m^{-3}	3.816
Z	4
Crystal size/ mm^3	$0.21 \times 0.19 \times 0.18$
Absorption coefficient/ mm^{-1}	26.386
F(000)	4748
Theta range for data collection	$1.90\text{--}26.19^\circ$
Completeness to theta = 26.19	99.9%
Max. and min. transmission	0.7457, 0.2847
$R_1(F_0)$	0.0948
$wR_2(F_0^2)$	0.2346
Goodness-of-fit on F^2	0.910

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