



Reversible phase transformation gel-type ionic liquid compounds based on tungstovanadosilicates



Tianpei Huang^a, Zhirong Xie^a, Qingyin Wu^{a,*}, Wenfu Yan^b

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

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

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ABSTRACT

A series of new reversible phase transformation gel-type ionic liquid compounds, [PyPS]₅SiW₁₁VO₄₀, [PyPS]₇SiW₉V₃O₄₀, [TEAPS]₅SiW₁₁VO₄₀ and [TEAPS]₇SiW₉V₃O₄₀, have been synthesized from two organic ammoniums 1-(3-sulfonic group) propyl-pyridine (PyPS), 1-(3-sulfonic group) propyl-triethylammonium (TEAPS) and vanadium-substituted heteropoly acids H₅SiW₁₁VO₄₀ and H₇SiW₉V₃O₄₀. The products can undergo a phase transformation from viscous gel-state to liquid-state below 100 °C, and ionic conductivity up to 10⁻³ S cm⁻¹ was observed at 110 °C for these gel-type POM-ILs. The relationship between the component elements of the products and their physicochemical property has been studied. Their thermostability was measured using thermogravimetric and differential thermal analysis (TG-DTA), and the result indicates that the less vanadium atoms there are inside the heteropoly anion, the more stable the POM-IL is at high temperature. Cyclic voltammetry is carried out to study their electrochemical properties in organic solution. The potential values of redox waves confirm that the oxidability of these gel-type POM-ILs can be controlled upon changing the number of vanadium atoms in the heteropolyanions.

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1. Introduction

Heteropoly acids (HPAs) are a fascinating kind of inorganic metal-oxygen cluster compounds [1]. They play very important roles in catalysis, biology, electrochemistry and materials science as a consequence of their nanoscale size, simple composition, unique structures and tunable electronic and physical properties [2–5]. However, the demerits of HPAs, such as weak thermal stability, high sensitivity to atmospheric moisture and the difficulty in machining impeded their potential application [6]. For this reason, the design and synthesis of HPA derivatives have attracted researchers' attention. Recently, the massive range of applications has led to many deliberate assembly tactics for the design and synthesis of various HPA derivatives by exchanging the surface protons of the HPA core cluster by organic cations [7,8].

Ionic liquids (ILs) are fascinating molten salts that remain in the liquid state at low temperatures [9], and they are being increasingly studied owing to their various attractive properties [10–12]. It is interesting to note that some ILs can present in a gelled or semi-solid form, while still maintain the intrinsic properties of ILs,

such as ionic conductivity, drug activity and solvent ability [13,14]. Such IL gels are easily shaped, and they can broaden the array of applications of ILs.

In the past decade, the design and synthesis of novel polyoxometalate-based ionic liquids (POM-ILs), which consisted of heteropoly anions and organic cations, have drawn a great deal of attention. They have emerged as the most potential compounds for their applications in catalysis, electrochemistry and nanotechnology [15,16]. In fact, it was found that the nature of cations has a remarkable influence on the structure and the characteristics of the heteropoly compounds [17]. One of the most important findings is that the POMs can be modified by certain organic cations through weak intermolecular interactions, such as H-bonding, π - π stacking and van der Waals interactions to prepare interesting gel-type hybrid materials [18–20]. Such POM-based gel-type materials are much easier to machine, and with some significant physical characters such as temperature-responsive behavior. They can be applied in some particular fields, for instance electrochemical capacitors and fuel cells [21].

Herein, we chose two sulfo-group grafted ammoniums cations (1-(3-sulfonic group) propyl-pyridine and 1-(3-sulfonic group) propyl-triethylammonium, abbreviated as PyPS and TEAPS, respectively) and two Keggin-type vanadium-substituted

* Corresponding author.

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

heteropoly acids ($\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ and $\text{H}_7\text{SiW}_9\text{V}_3\text{O}_{40}$) to synthesize a series of gel-type POM-based ionic liquids, which exhibit reversible phase transformation from gel state to liquid state below 100°C . Specifically, an investigation has been done on the effects of the elementary composition on the thermal stability and electrochemical properties of these gel-type ionic liquids. These new gel-type materials may be good candidates for the phase transformation electrolyte because of their advantages for both liquid electrolyte and solid state electrolyte. They will facilitate the application of POMs as functional materials in the area of electrochemistry.

2. Experimental section

2.1. Synthesis of the gel-type POM-ILs

1-(3-sulfonic group) propyl-pyridine (abbreviated as PyPS) and 1-(3-sulfonic group) propyl-triethylammonium (abbreviated as TEAPS) were synthesized according to the literature [8]. Pyridine (0.055 mol) and 1,3-propanesultone (0.05 mol) were dissolved in acetone (25 ml) and stirred at 50°C for 4 h. A white precipitate (PyPS) was obtained and washed by acetone for three times, then dried under vacuum. Similarly, TEAPS can be prepared. $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ and $\text{H}_7\text{SiW}_9\text{V}_3\text{O}_{40}$ were synthesized by modification of the method according to the literature available [22,23].

The presynthesized PyPS and $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ ($\text{H}_7\text{SiW}_9\text{V}_3\text{O}_{40}$) were taken in 5:1 (7:1) mole ratio to give 1 mol of $[\text{PyPS}]_5\text{SiW}_{11}\text{VO}_{40}$ ($[\text{PyPS}]_7\text{SiW}_9\text{V}_3\text{O}_{40}$). Firstly, PyPS was added to an aqueous solution of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ ($\text{H}_7\text{SiW}_9\text{V}_3\text{O}_{40}$), and then the mixture was stirred for 12 h at room temperature. Water was evaporated in a water bath at first and then removed in vacuum to give the products which exhibit gel-state. $[\text{TEAPS}]_5\text{SiW}_{11}\text{VO}_{40}$ and $[\text{TEAPS}]_7\text{SiW}_9\text{V}_3\text{O}_{40}$ were prepared accordingly. Scheme 1 shows the idealized reaction used to prepare the four POM-ILs. The obtained compounds are highly insoluble in tetrahydrofuran, acetone and ethyl acetate, and soluble in N, N-dimethylformamide and dimethyl sulfoxide.

Carbon, nitrogen, sulfur, silicon, tungsten and vanadium were analyzed by elemental analysis. Calculated for $[\text{PyPS}]_5\text{SiW}_{11}\text{VO}_{40}$: C: 12.80%; N: 1.87%; S: 4.27%; Si: 0.75%; W: 53.89%; V: 1.36%. Found: C: 11.68%; N: 1.73%; S: 4.32%; Si: 0.82%; W: 54.94%; V: 1.53%.

Calculated for $[\text{PyPS}]_7\text{SiW}_9\text{V}_3\text{O}_{40}$: C: 17.29%; N: 2.52%; S: 5.77%; Si: 0.72%; W: 42.52%; V: 3.93%. Found: C: 15.85%; N: 2.36%; S: 5.02%; Si: 0.89%; W: 43.98%; V: 4.17%. Calculated for $[\text{TEAPS}]_5\text{SiW}_{11}\text{VO}_{40}$: C: 13.99%; N: 1.81%; S: 4.15%; Si: 0.73%; W: 52.35%; V: 1.32%. Found: C: 12.85%; N: 1.65%; S: 4.08%; Si: 0.86%; W: 53.78%; V: 1.44%. Calculated for $[\text{TEAPS}]_7\text{SiW}_9\text{V}_3\text{O}_{40}$: C: 18.70%; N: 2.42%; S: 5.55%; Si: 0.69%; W: 40.90%; V: 3.78%. Found: C: 17.68%; N: 2.66%; S: 5.42%; Si: 0.77%; W: 41.97%; V: 3.93%. The results indicate that the actual measurement values are consistent with the calculated values, which confirms the composition of four POM-ILs [24].

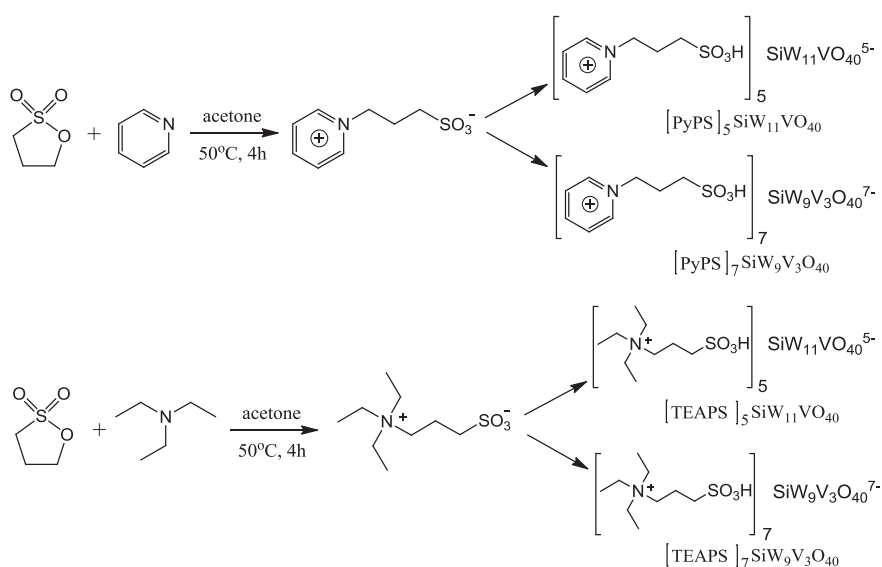
2.2. Chemicals and instrumentation

Inductively coupled plasma mass spectrometry (ICP-MS) analysis was determined on a Shimadzu V-1012 ICP-MS spectrometer. FTIR spectrum was recorded on a Nicolet Nexus 470 FT/IR spectrometer over the wave number range $400\text{--}4000\text{ cm}^{-1}$ using KBr pellets. X-ray powder diffraction pattern 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 $0.02^\circ \cdot \text{s}^{-1}$. The thermal stability of the sample was investigated using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) techniques from room temperature to 600°C . Measurement was performed using a Shimadzu thermal analyzer in a Nitrogen stream, with a scanning rate of $10^\circ\text{C min}^{-1}$. The conductivity measurement of the product was obtained using a DDS-11A conductivity meter. Cyclic voltammetry (CV) was performed with a CHI650C electrochemical workstation in N,N-dimethylformamide (DMF). All potentials were given with respect to a Ag/AgCl reference electrode. A glass electrode was used as the working electrode and platinum was used as the counter electrode in organic media. The concentration of substrate was 0.5 mM, and 0.1 M NaClO_4 was assigned as supporting electrolyte. All reagents were analysis grade.

3. Results and discussion

3.1. IR spectra

Fig. 1 shows IR spectra of the gel-type POM-ILs. Vibrations corresponding to heteropoly anions with Keggin structure appear at $700\text{--}1100\text{ cm}^{-1}$. The vibrational frequencies fall in the sequence of



Scheme 1. Synthesis of the four POM-ILs.

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