Study on synthesis and characterization of hexaquonickel(II) bis-*p*-toluenesulfonate

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Abstract: Hexaquonickel (II) bis-*p*-toluenesulfonate [$Ni(OTs)_2·6H_2O$] was prepared from the reaction of *p*-toluenesulfonic acid (PTS) and nickel hydroxide [$Ni(OH)_2$]. Energy disperse spectroscopy, thermal-analysis instrument, infrared spectrometer, and X-ray diffractometerwere used to characterize the product of $Ni(OTs)_2·6H_2O$purified by recrystallization. The influence of equivalence ratio of reactants [$N_{PTS}/N_{Ni(OH)2}$] , reaction temperature and reaction time on the yield of products was investigated. The results show that when the value of $N_{PTS}/N_{Ni(OH)2}$is 1.1, reaction temperature is 353 K, and reaction time is 3 h, the yieldof the productis90.86%.

Keywords: Hexaquonickel (II) bis-*p*-toluenesulfonate; Synthesis; Characterization; Yield

1. Introduction

Transition-metal *p*-toluenesulfonates (tosylates) have been known since the 1870s. They can be applied as catalysts and reactants in various reactions[1,2].In recent 20 years, researchers have shown great interest in synthetic process[3,4] and physiochemical information[5-7] of them.Kosumi *et al.*[8]proposed a process for producing zinc toluenesulfonatecomprising reacting a zinc compound comprising $Zn(OH)_2$ with toluenesulfonic acid and/or a salt thereof in the presence of an alcohol having 1 to 20 carbon atoms.Cobalt(II)and nickel (II) *p*-toluenesulfonate were prepared by Ferko*et al.*[9]via an oxidation-reduction reaction using metal powders and aqueous *p*-toluenesulfonicacid hydrate as the reducing and oxidizingreagents, respectively. Zhang *et al*.[10]synthesized a series of alkali earth *p*-toluenesulfonate (Ca, Ba), lanthanide (La, Ce, Pr, Nd,) and transition metal (Fe, Mn, Co, Ni, Cu, Zn, Cd)*p*-toluenesulfonates, andinvestigated their physical and chemical properties.Ali *et al*.[11]studied the influence of the concentration of iron(III) *p*-toluenesulfonatehexahydrate oxidant solution on the polymerization rate and final thickness of poly(3,4-ethylenedioxythiophene) (PEDOT) films,and found that the final film thickness was linearly dependent on oxidant concentration.Wang *et al.*[12]developeda solvent-free, one-pot synthesis technology of amidoalkylnaphtholsusing copper *p*-toluenesulfonateas catalyst.

Hexaquonickel(II)bis-*p*-toluenesulfonate ($Ni(OTs)_2{\cdot}6H_2O$, $C_{14}H_{14}NiO_6S_2{\cdot}6H_2O$, CAS No.124390-00-7) is one of the most commontosylates, and it is a type of light green, powdery crystal with the molecular weight of 509.18 Da.$Ni(OTs)_2{\cdot}6H_2O$ can be used as the raw material in the synthesis of $[(dppe)(CO)Fe(S_2C_3H_6)(\mu\text{-}H)Ni\text{-}(dppe)]BF_4$($[2H]BF_4$) to study[NiFe]-hydrogenase active site[13]. It is also of great importance in the synthesis and characterization of one- and two-dimensional octacyanometalate(V) networks[14] or one- and three-dimensional octacyanometalate(IV) networks[15], which are versatile building blocks for constructing clusters and extended arrays of metal centers linked via cyanides. Furthermore, $Ni(OTs)_2·6H_2O$ is useful in preparation of 2,6-bis(hydroxymethyl) pyridine, which can act as chelating ligand in coordination compounds[16].

Generally, tosylates wereprepared by the reaction of corresponding metal hydroxides with*p*-toluenesulfonic acid (PTS)[17]. Winter *et al.*[18] had prepared $Ni(OTs)_2·6H_2O$via the reaction between PTS and nickel hydroxide [$Ni(OH)_2$] obtained by nickel chloride hexahydrate ($NiCl_2·6H_2O$) and sodium hydroxide (NaOH).However, the yield of $Ni(OTs)_2·6H_2O$ was low(67%), and the effect of different reaction conditions on the yield of $Ni(OTs)_2·6H_2O$ did not investigated, so an additional study is needed.

In this paper, $Ni(OTs)_2·6H_2O$ was prepared by the reaction of $Ni(OH)_2$ with PTS. The resulting products were characterized by elemental analysis (EDS), thermogravimetric analysis (TGA), infrared spectroscopy (IR), and X-ray diffraction (XRD). Moreover, theinfluence of reaction conditions on the yield of$Ni(OTs)_2·6H_2O$ was studied by changing the equivalence ratio of reactants [$N_{PTS}/N_{Ni(OH)2}$], reaction temperature,and the reaction time.

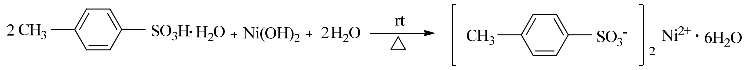
2. Experimental and Characterization

2.1 Materials

PTSwas supplied by Shanghai Lingfeng Chemical reagent Co.Ltd and$Ni(OH)_2$was supplied by Shanghai Macklin Biochemical Co. Ltd. All of them were analytical reagent grade and used without purification. Deionized water was made in our laboratory and purified by double distillation.

2.2 Preparation of $Ni(OTs)_2 \cdot 6H_2O$

A short description of the synthesis of $Ni(OTs)_2 \cdot 6H_2O$ is given as follows: A certain amount of PTS andwater(10g/g$Ni(OH)_2$) were added into a four-neck flask equipped with a stirrer, a mercury thermometer, and a reflux condenser and heated to the desired temperature. Then a known amount of $Ni(OH)_2$ was added to the flask. The reaction was carried out at the temperature for sometime, and the reaction mixture was filtered while hot to remove the by-product and unreacted raw material. The filtrate was cooled to 273 K and the precipitation came out. The productcould be obtained by filtration, and its purity was analyzed by high performance liquid chromatography (HPLC). The weight and purity of the product were recorded to calculate yield of $Ni(OTs)_2 \cdot 6H_2O$. The chemical equation for preparation of $Ni(OTs)_2 \cdot 6H_2O$ is shown in Schema 1:



Schema 1.Chemical equation for preparation of $Ni(OTs)_2 \cdot 6H_2O$

The above product was purified by recrystallization with deionized water at least three times, and used for the qualitative characterization testing.

2.3 The condition of HPLC

HPLC (Agilent 1200) equipped with XDB-C_{18} column (5 μm, 4.6 mm i.d.× 150 mm)was used to measure the purity of the product,acetonitrile: water = 5: 95(v/v) was used as the mobile phase at a flowrate of 1.0 mL/min. Methanesulfonic acid was used as mobile phase addictive to adjust pH to 2.5. The column temperature was 298

K, and a sample of 2 μm was applied to the column. The detector was refractive index detector (RID).

2.4 Energy Disperse Spectroscopy (EDS).

The elemental analysis of $Ni(OTs)_2 \cdot 6H_2O$ was carried out using a special microscope (TM3030) and a portable spectrometer (Swifted 3000, Hitachi Co., Ltd.). The mass percentages of the obtained elements and the theoretical percentages of each element in $Ni(OTs)_2 \cdot 6H_2O$ were given in Table 1. From Table 1 we know that the deviationof each element is less than 0.64%, thusit can be determined that the measured sample is $Ni(OTs)_2 \cdot 6H_2O$.

Table 1The Elemental Analysis of $Ni(OTs)_2 \cdot 6H_2O$

elemental	Ni	C	O	S
theoretical percentages	11.53%	33.02%	37.71%	12.59%
actualpercentages	11.50%	33.05%	37.72%	12.51%
relative error	-0.26 %	0.09 %	0.03 %	-0.64 %

2.5 Thermogravimetric Analysis (TGA).

TGA (TGA/SDTA851, Mettler Instrument Inc.) was used to measure thethermal stability, with a heating rate of 10K $min^{-1}$from 298to 1073K. The flow rate of nitrogen gas was 50 mL min^{-1},and the TGA sample had a mass of about 10.000 mg.Determination of the temperature was estimated to be accurateto ± 0.5K. The thermal analysis result of $Ni(OTs)_2 \cdot 6H_2O$ is shown in Figure 1.From Figure 1, it can be seen that the first four crystal water in sample will be lost in the temperature range of 375-415 K, and the weight loss peak appearsat398 K.The other two crystal waterwill be lostat the temperature between 415-480 K, corresponding to the weight loss peak of 437 K in the DTG curve.The process of dehydration is expressed as Schema2. When the temperature reaches to about700-850 K, $Ni(OTs)_2$ will decompose rapidly, and the weight loss peak appear at 824 K.

$$Ni(OTs)_2 \cdot 6H_2O \xrightarrow{375\text{-}415K} Ni(OTs)_2 \cdot 2H_2O \xrightarrow{415\text{-}480K} Ni(OTs)_2$$

Schema2. The process of dehydration for $Ni(OTs)_2 \cdot 6H_2O$

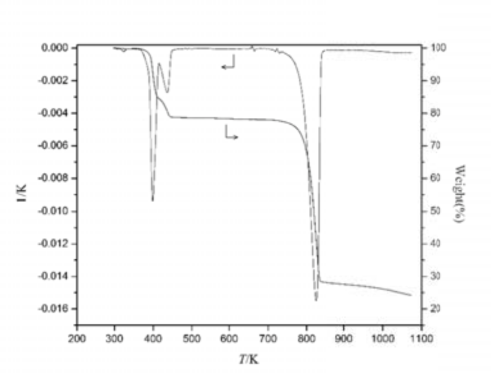


Figure 1.Thermogravimetric analysis of $Ni(OTs)_2 \cdot 6H_2O$

2.6Infrared Spectra(IR).

The infrared spectra of $Ni(OTs)_2 \cdot 6H_2O$ was determined by Nexus 670 infrared spectrometer (Thermo Nicolet Co. Ltd.). The sample and KBr were uniformly mixed into a transparent sheet by KBr compression method, and the infrared spectrum information of the sample was collected in the scanning range of 400-4000 cm^{-1}. The infrared spectra of $Ni(OTs)_2 \cdot 6H_2O$ is shown in Figure 2. It can be seen from Figure 2 that the characteristic peaks of the infrared spectrum of $Ni(OTs)_2 \cdot 6H_2O$ are 692 cm^{-1}, 817 cm^{-1}, 1183 cm^{-1}, 1658 cm^{-1} and 3392 cm^{-1}. The band at round 3392 cm^{-1} is associated with the O-H stretching vibration of -OH in the crystal water,the band at around 1658 cm^{-1} is due to the C=C vibrations of aromatic skeleton, while -S=O vibrations of sulfonic acid appear at 1183 cm^{-1},the bands at 817 and 692cm^{-1} are assigned to a para-substituted compound on the benzene ringand the C-H out of plane bending in benzene derivative[19]. Therefore, the material can be considered as $Ni(OTs)_2 \cdot 6H_2O$.

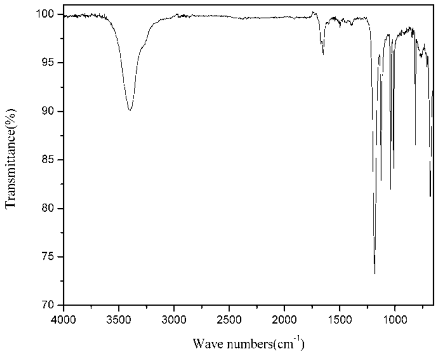


Figure 2. Infrared spectrum of $Ni(OTs)_2 \cdot 6H_2O$

2.7X-ray powder diffraction(XRD).

The X-ray powder diffraction patterns (ESCALAB 250Xi, ThermoFisher Corporation, USA) of $Ni(OTs)_2 \cdot 6H_2O$ is shown in Figure 3a, which is basically consistent with that reported in literature[20]. The Cu-Kα radiation is 1.54, the test process was performed on 2θ=3-50° with a step size of 0.02°, and the scanning rate was set at 1 step/s. According to thermogravimetric analysis shown in Figure 1, the samples of anhydrous $Ni(OTs)_2$ would be obtained when $Ni(OTs)_2 \cdot 6H_2O$ were dried at 498 K for 8 h, and the X-ray spectrums of the anhydrous $Ni(OTs)_2$ is shown in Figure 3b.Theinterplanarspacings(d) and hkl values of$Ni(OTs)_2 \cdot 6H_2O$and $Ni(OTs)_2$are shown in Table 2 and Table 3.From Figure 3a and Figure 3b, it can be seen that the XRD spectrum of anhydrous Ni(OTs)$_2$is different from that of Ni(OTs)$_2$·6H$_2$O in peak position and intensity, which indicate that dehydration treatment will change the crystal structure of Ni(OTs)$_2$·6H$_2$O.In addition, the diffraction peaks of Ni(OTs)$_2$ are broaden, indicatingits crystal size (or crystallinity) is smaller than that of Ni(OTs)$_2$·6H$_2$O.

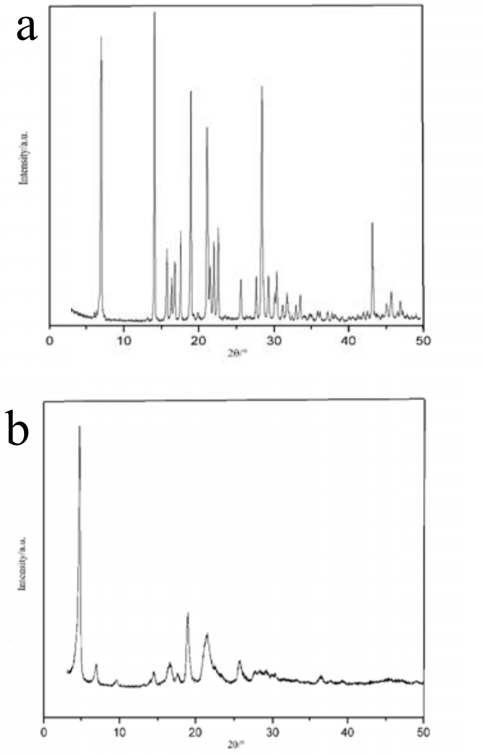


Figure3. XRD of Ni(OTs)$_2$·6H$_2$O and Ni(OTs)$_2$

Table 2 Interplanar crystal spacing and hkl values of $Ni(OTs)_2 \cdot 6H_2O$

2θ/°	d/nm	（h k l）
7.01	12.80	（2 0 0）
14.11	6.19	（4 0 0）
15.74	5.63	（2 1 0）
16.41	5.49	（-3 0 1）
16.78	5.34	（3 0 1）
17.66	5.26	（3 1 0）
19.00	4.58	（-1 1 1）
21.11	4.25	（6 0 0）
21.59	4.10	（-5 0 1）
22.07	4.03	（5 0 1）
22.65	3.96	（5 1 0）
25.62	3.31	（0 0 2）
27.64	3.22	（-7 0 1）
28.41	3.15	（7 0 1）
29.27	3.08	（2 2 0）
30.04	2.97	（-2 1 2）
30.33	2.96	（3 2 0）
31.67	2.94	（7 1 1）
33.59	2.65	（5 2 0）
43.19	2.16	（12 0 0）
45.11	2.01	（10 0 2）
45.68	1.98	（12 1 0）

Table 3 Interplanar crystal spacing and hkl values of $Ni(OTs)_2$

2θ/°	d/nm	（h k l）
4.80	18.39	（0 1 0）
6.98	12.66	（2 0 0）
13.96	6.34	（4 0 0）
16.58	5.34	（-3 0 1）
17.52	5.06	（3 1 0）
19.02	4.66	（0 1 1）
21.54	4.12	（-5 0 1）
25.76	3.46	（0 0 2）
27.67	3.22	（-7 0 1）
29.97	2.98	（-2 1 2）

3. Results and discussion

Theinfluence of reaction conditions on the yield of$Ni(OTs)_2{\cdot}6H_2O$ was studied by changing equivalence ratio of reactants, reaction temperature, and the reaction time.

3.1 Effect of equivalence ratio of reactants

When reaction temperature is 353 Kand the reaction time is 3 h, the effect of equivalence ratio of reactants on the yield and purityof $Ni(OTs)_2{\cdot}6H_2O$ was investigated by varying $N_{PTS}/N_{Ni(OH)2}$ from 0.8 to 1.2, and the results are shown in Figure 4. From Figure 4, it can be seen that theyieldof $Ni(OTs)_2{\cdot}6H_2O$ increases with increasing of equivalence ratio of PTS to $Ni(OH)_2$until $N_{PTS}/N_{Ni(OH)2}$ =1.1 (yield, 90.86%), and then tends to constant. This perhaps because the higher concentration of acid is beneficial to the formation of $Ni(OTs)_2{\cdot}6H_2O$, and this rule becomes invalid when$N_{PTS}/N_{Ni(OH)2}$ is larger than 1.1. From Figure 4, it can also be seen the purityof the producthas little changewith the increase of equivalence ratio of reactants.

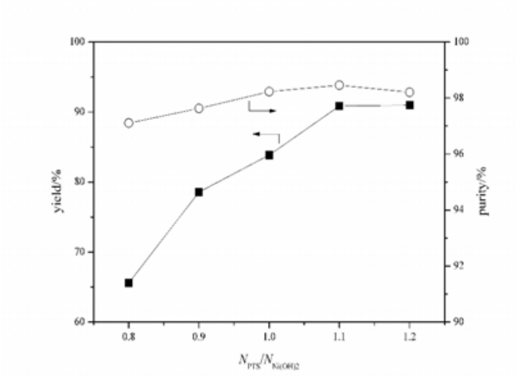


Figure4. The effect of equivalence ratio for reactants on the yield and purity of $Ni(OTs)_2{\cdot}6H_2O$ (■,yield;○, purity)

3.2 Effect of reaction temperature and reaction time

The chemical reaction rate is strongly affected by the reaction temperature[21]. Therefore, the effect of reaction temperature and reaction time on yield of $Ni(OTs)_2·6H_2O$ was investigated when $N_{PTS}/N_{Ni(OH)2}$ is 1.1 and the reaction temperature varied between 323 K to 363 Kin the range of 0 to 6 h. The results were shown in Figure 5. From Figure 5, at constant temperature the yield of $Ni(OTs)_2·6H_2O$increases with the increase of reaction time, and keeps a relative stable value (Y*) when reaction time larger than a particular value (t*). Table 4 lists the values of Y* and t* at different temperatures. From Table 4, it can be seen that when the temperature changes from 323 K to 353 K,the value of Y* increases from 49.01% to 90.86%. However, when the temperature is larger than 353 K, the value of Y* increases slightly. The higher the temperature, the shorter the particular time at which the yield of $Ni(OTs)_2·6H_2O$ tends to be stable. For example, the values of t* at 323 K and 363 K are 5.5 h and 2 h, respectively.

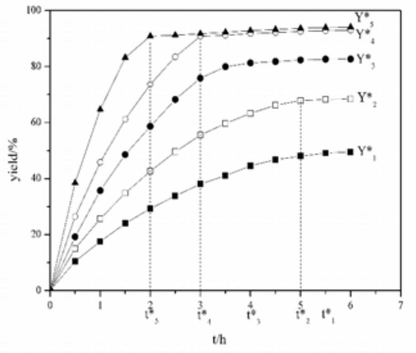


Figure 5. The effect of reaction temperature and reaction time on the yield of $Ni(OTs)_2·6H_2O$ (■, 323 K;, □333 K; ●, 343 K; ○, 353 K; ▲, 363 K)

Table 4 Particular time (t*) and relative stable value (Y*) at different temperatures

Reaction temperature / K	323	333	343	353	363
t*/ h	5.5	5.0	4.0	3.0	2.0
Y*/ %	49.01	67.88	81.28	90.86	90.89

On the bases of above results, the reaction may be controlled by the dissolve process of $Ni(OH)_2$. The reasons can be described as follow: (1) Because $Ni(OH)_2$ is insoluble in water, the reaction rate between PTS and $Ni(OH)_2$(belongs to acid-base neutralization)is related to the concentration of $Ni(OH)_2$ in the liquid phase. (2) Because the concentration of $Ni(OH)_2$ is related to its solubility which is determined by temperature, the higher the reaction temperature, the larger the solubility andthe faster the reaction rate. Sothe particular time to reach a constant yield (or the value of the constant yield) at a higher temperature is shorter(or higher) than that at a lower temperature.(3) Because the dissolution equilibriumof $Ni(OH)_2$is not established instantaneously, the higher the temperature, the shorter the time to establish the dissolution equilibrium. So the particular time to reach a constant yield at a higher temperature is shorter than that at a lower temperature.

4. Conclusion

Hexaquonickel (II) bis-*p*-toluenesulfonate [$Ni(OTs)_2\cdot 6H_2O$] was prepared from the reaction of *p*-toluenesulfonic acid (PTS) and nickel hydroxide [$Ni(OH)_2$]. The results of energy disperse spectroscopy, thermal-analysis instrument, infrared spectrometer, and X-ray diffractometerprove that the substance tested can be considered as $Ni(OTs)_2\cdot 6H_2O$. The influence of mole ratio of reactants [PTS versus $Ni(OH)_2$] , reaction temperature and reaction time on the yield of products wasinvestigated. The yield of $Ni(OTs)_2{\cdot}6H_2O$ increases with increasing of $N_{\mathrm{PTS}}/N_{\mathrm{Ni(OH)2}}$until it is 1.1 (yield, 90.86%), and then tends to constant. When the temperature keep constant the yield of $Ni(OTs)_2{\cdot}6H_2O$increases with the increase of reaction time, and achieves a relative stable value when reaction time lager than a particular value. In addition, the particular time (or the value of the constant yield) at a higher temperature is shorter(or higher) than that at a lower temperature.

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