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

Abstract：Hexaquonickel (II) bis-*p*-toluenesulfonate [$Ni(OTs)_2 \cdot 6H_2O$] was prepared from the reaction of *p*-toluenesulfonic acid (PTS) and nickel hydroxide [$Ni(OH)_2$]. Energy disperse spectroscopy, thermal-analysis instrument, infrared spectrometer, and X-ray diffractometer were used to characterize the product of $Ni(OTs)_2 \cdot 6H_2O$ 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 yield of the product is 90.86%.

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 [1-11]. In recent 20 years, researchers have shown great interest in synthetic process [12-18] and physiochemical information [19-26] of them. Kosumi *et al.*[15] proposed a process for producing zinc toluenesulfonate comprising 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.*[16] via an oxidation-reduction reaction using metal powders

and aqueous *p*-toluenesulfonic acid hydrate as the reducing and oxidizing reagents, respectively. Zhang *et al.*[19] 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, and investigated their physical and chemical properties. Ali *et al.*[3] studied the influence of the concentration of iron(III) *p*-toluenesulfonate hexahydrate 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.*[5] developed a solvent-free, one-pot synthesis technology of amidoalkyl naphthols using copper *p*-toluenesulfonate as 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 common tosylates, 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) $(CO)Fe(S_2C_3H_6)(\mu\text{-}H)Ni$-(dppe)]$BF_4$([2H]$BF_4$) to study [NiFe]-hydrogenase active site[27]. It is also of great importance in the synthesis and characterization of one- and two-dimensional octacyanometalate(V) networks[28] or one- and three-dimensional octacyanometalate (IV) networks[29], which are versatile building blocks for constructing clusters and extended arrays of metal centers linked via cyanides. Furthermore, $Ni(OTs)_2 \cdot 6H_2O$ is useful in preparation of 2,6-bis(hydroxymethyl) pyridine, which can act as chelating ligand in coordination compounds[1].

Generally, tosylates were prepared by the reaction of corresponding metal

hydroxides with *p*-toluenesulfonic acid (PTS)[30]. $Ni(OTs)_2 \cdot 6H_2O$ was prepared by Winter *et al.*[31] via the reaction between PTS and nickel hydroxide [$Ni(OH)_2$] obtained by nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) and sodium hydroxide (NaOH). However, the yield of $Ni(OTs)_2 \cdot 6H_2O$ was low(67%), and the effect of different reaction conditions on the yield of $Ni(OTs)_2 \cdot 6H_2O$ did not investigated, so an additional study is needed.

In this paper, $Ni(OTs)_2 \cdot 6H_2O$ 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, the influence 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

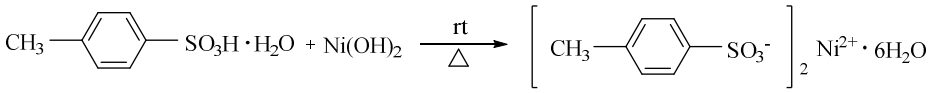
2.1 Materials

PTS was 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 and water (10 g/ 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 some time, 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 product could 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 by 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 deviation of each element are less than 0.64%, thus it can be determined that the measured sample is $Ni(OTs)_2 \cdot 6H_2O$.

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

elemental	Ni	C	O	S
theoretical percentages	11.53%	33.02%	37.71%	12.59%
actual percentages	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 the thermal stability, with a heating rate of 10 K min^{-1} from 298 to 1073 K. 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 accurate to ± 0.5 K. 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 appears at 398 K. The other two crystal water will be lost at 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 Schema 2. When the temperature reaches to about 700-850 K, $Ni(OTs)_2$ will decompose rapidly, and the weight loss peak appear at 824 K.

$$Ni(OTs)_2 \cdot 6H_2O \xrightarrow{320\text{-}415K} Ni(OTs)_2 \cdot 2H_2O \xrightarrow{415\text{-}480K} Ni(OTs)_2$$

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

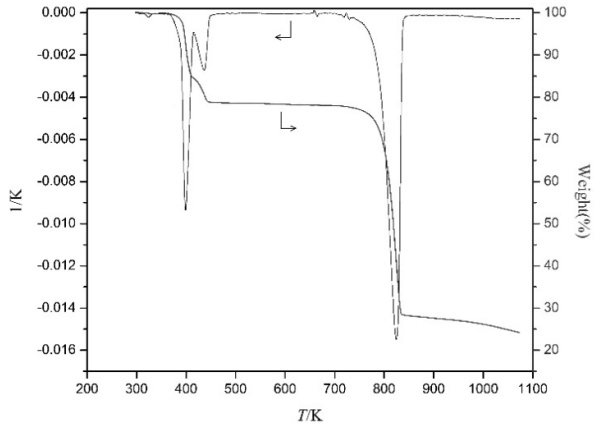


Figure 1. Thermogravimetric analysis of $Ni(OTs)_2 \cdot 6H_2O$

2.6 Infrared 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 692 cm^{-1} are assigned to a para-substituted compound on the benzene ring and the C-H out of plane bending in benzene derivative[32]. Therefore, the material can be considered as $Ni(OTs)_2 \cdot 6H_2O$.

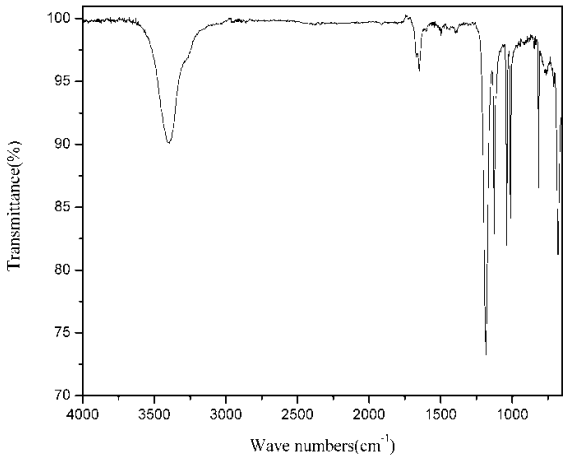


Figure 2. Infrared spectrum of $Ni(OTs)_2 \cdot 6H_2O$

2.7 X-ray powder diffraction (XRD).

The X-ray powder diffraction patterns (ESCALAB 250Xi, Thermo Fisher Corporation, USA) of $Ni(OTs)_2 \cdot 6H_2O$ is shown in Figure 3a, which is basically consistent with those reported in literature[33]. 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 3a, 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. From Figure 3a and Figure 3b, it can be seen that the XRD spectrum of anhydrous $Ni(OTs)_2$ is different from that of $Ni(OTs)_2 \cdot 6H_2O$ in peak position and intensity, which indicate that dehydration treatment will change the crystal structure of $Ni(OTs)_2 \cdot 6H_2O$. In addition, the diffraction peaks of $Ni(OTs)_2$ are broaden, indicating its crystal size (or crystallinity) is smaller than that of $Ni(OTs)_2 \cdot 6H_2O$.

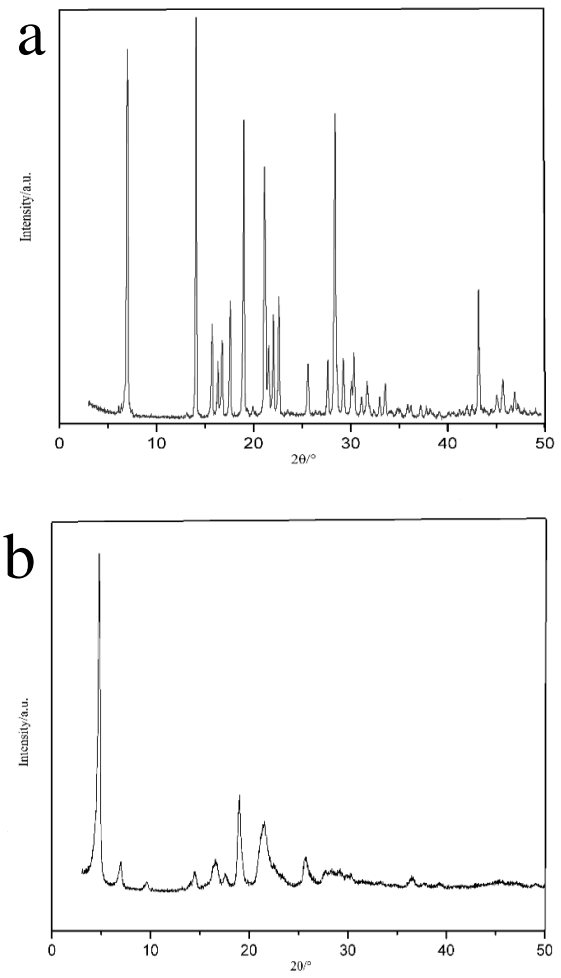


Figure 3. XRD of $Ni(OTs)_2 \cdot 6H_2O$ and $Ni(OTs)_2$

3. Results and discussion

The influence of reaction conditions on the yield of $Ni(OTs)_2.6H_2O$ 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 K and the reaction time is 3 h, the effect of equivalence ratio of reactants on the yield and purity of $Ni(OTs)_2.6H_2O$ 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 the yield of $Ni(OTs)_2.6H_2O$ 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 $Ni(OTs)_2.6H_2O$, 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 purity of the product has little change.

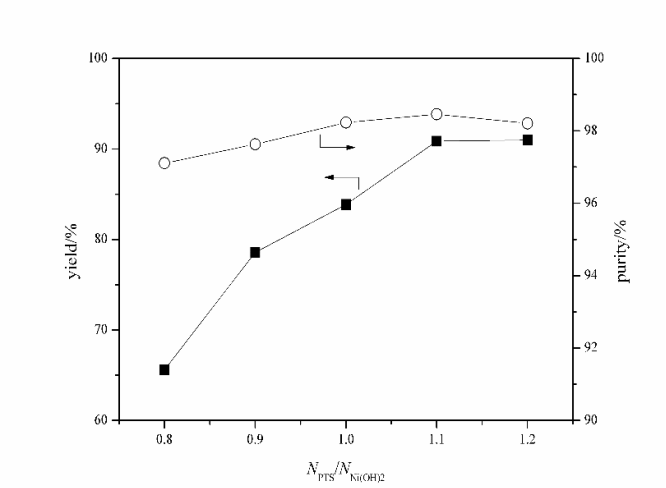


Figure 4. The effect of equivalence ratio for reactants on the yield and purity of $Ni(OTs)_2 \cdot 6H_2O$ (■,yield; ○, purity)

3.2 Effect of reaction temperature and reaction time

The chemical reaction rate is strongly affected by the reaction temperature [34]. Therefore, the effect of reaction temperature and reaction time on yield of $Ni(OTs)_2 \cdot 6H_2O$ was investigated when $N_{PTS}/N_{Ni(OH)2}$ is 1.1 and the reaction temperature varied between 323 K to 363 K in 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 achieves a relative stable value (Y*) when reaction time lager than a particular time (t*). Table 2 lists the values of Y* and

t* at different temperatures. From Table 2, it can be seen that when the temperature change 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.

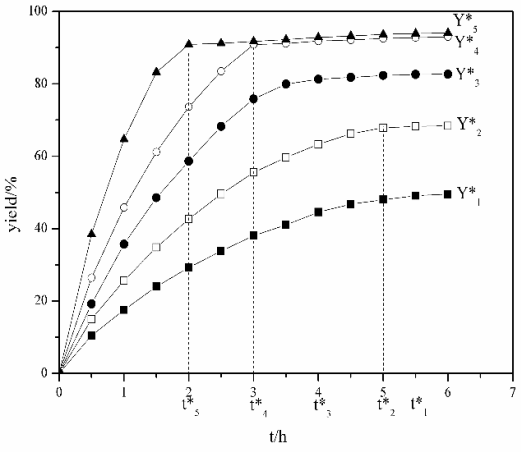


Figure 5. The effect of reaction temperature and reaction time on the yield of $Ni(OTs)_2 \cdot 6H_2O$ (■, 323 K;, □333 K; ●, 343 K; ○, 353 K; ▲, 363 K)

Table 2 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 and the faster the reaction rate. So the 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 equilibrium of $Ni(OH)_2$ 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 diffractometer prove 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 was investigated. The yield of $Ni(OTs)_2 \cdot 6H_2O$ increases with increasing of $N_{PTS}/N_{Ni(OH)2}$ 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 time. 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.

References

[1] Holmes SM, Mckinley SG, Girolami GS, Szalay PS, Dunbar KR. Transition metal *p*-toluenesulfonates. Inorg Synth, 2002, 33: 91-103.

[2] Purgato FLS, Ferreira MIC, Romero JR. Synthesis and structures of layered metal sulfonate salts. J Mol Catal A-Chem, 2000, 161: 99.

[3] Ali MA, Kim H, Lee C. Effects of iron(III) *p*-toluenesulfonate hexahydrate oxidant on the growth of conductive poly(3,4-ethylenedioxythiophene) (PEDOT) nanofilms by vapor phase polymerization. Synth Met, 2011, 161: 1347-1352.

[4] Deng B, Long SH. Catalytic synthesis of cyclohexyl acetate by copper *p*-toluenesulfonate. Advances in Fine Petrochemicals, 2007, 8: 23-25 (in Chinese).

[5] Wang Min, Liang Y. Solvent-free, one-pot synthesis of amidoalkyl naphthols by a copper *p*-toluenesulfonate catalyzed multicomponent reaction. Monatsh Chem, 2011, 142: 153-157.

[6] Wang M, Song ZG, Jiang H. Copper *p*-toluenesulfonate/acetic acid: a recyclable synergistic catalytic system for the tetrahydropyranylation of alcohols and phenols. Monatsh Chem, 2008, 139: 601–604.

[7] Wu CZ, Song XP. The catalytic synthesis of isoamyl butyrate with copper *p*-toluenesulfonate. Chemical Reagents, 2005, 27: 691-692 (in Chinese).

[8] Withers JR, Li D, Triplet J. A two-dimensional octacyanomolybdate(V)- based ferrimagnet: $\{[Mn(II)(DMF)_4]_3[Mo(V)(CN)_8]_2\}_n$. Inorg Chem, 2006, 45, 4307-4309.

[9] Baldwin NJ, Nord AN, O'Donnell BD. Iron(III) tosylate catalyzed acylation of alcohols, phenols, and aldehydes. Tetrahedron Lett, 2012, 53: 6946-6949.

[10] Qian B, Zhang GY, Ding YZ. Catalytic cross deoxygenative and dehydrogenative coupling of aldehydes and alkenes: a redox-neutral process to produce skipped dienes. Chem Comm, 2013, 49: 9839-9841.

[11] Spafford MJ, Anderson ED, Lacey JR. Iron(III) *p*-toluenesulfonate catalyzed synthesis of homoallyl ethers from acetals and aldehydes [J]. Tetrahedron Lett, 2007, 48: 8665-8667.

[12] Ferko PJ, Withers JR, Nguyen H. Synthesis and characterization of first row transition metal *p*-toluenesulfonate complexes and chains. Polyhedron, 2017, 123: 344-352.

[13] Gong H, Su TT, Wang R. Synthesis and thermo-gravimetric analysis of *p* -toluenesulfonates : Alkali Earth Metal and Transition Metal. Journal of Liaoning University of Petroleum &Chemical Technology, 2006, 26(1):8-11 (in Chinese).

[14] Holmes SM, Mckinley SG, Girolami GS. Facile syntheses of useful divalent and trivalent transition metal *p*-toluenesulfonate salts (M = Ti, V, Cr, Mn, Fe, Co, Ni). Acs National Meeting Book of Abstracts, 1998, 216.

[15] Kosumi K, Fukuda T, Sasaki M. Process for production of zinc toluenesulfonate, zinc toluenesulfonate, and process for production of carbamate: US patent, 2527297A1, 2014.

[16] Ferko PJ, Withers JR, Nguyen H. Simultaneous Introduction of Redox and Coordination Chemistry Concepts in a Single Laboratory Experiment. J Chem

Educ, 2017, 94: 95-100.

[17] Jung MS, Kim WS, Shin YH. Chemoselective activities of Fe(III) catalysts in the hydrofunctionalization of allenes. Org Lett, 2012, 14: 6262-6265.

[18] Masaaki S. Preparation of solutions of aromatic sulfonic acid iron(III) salts and heterocyclic conjugated conducting polymers manufactured using the solutions: Jpn. Kokai Tokkyo Koho, 2009155263. 2009-07-16.

[19] Zhang LH, Jiang H, Gong H. Characteristics of thermal decomposition products of rare earth, alkali earth metal and transition metal *p*-toluenesulfonates. J. Therm. Anal. Calorm, 2005, 79: 731-735.

[20] Junk PC, Steed JW. A structural study of late transition metal diethylenetriamine complexes. Inorg Chim Acta, 2007, 360: 1661-1668.

[21] Yu C, Wu ST, Huang ZJ. Water/ethanol complexation induced solubility variation of hexaquocobalt(II) bis (*p*-toluenesulfonate) and hexaquonickel(II) bis (p-toluenesulfonate). J Mol Liq, 2016, 224: 139-145.

[22] Yu C, Huang ZJ, Zeng ZX. Thermodynamic models for correlation of solubility of hexaquocobalt(II) bis(*p*-toluenesulfonate) in liquid mixtures of water and ethanol from 288.15 to 333.15 K. J. Solution. Chem, 2016, 45: 395-409.

[23] Huang ZJ, Yu C, Xue WL. Solubility and dissolution thermodynamics of hexaquoiron(III)tris(*p*-toluenesulfonate) in (ethanol + water) binary mixtures within 291.15-333.15 K. Korean. J Chem Eng, 2017, 34: 206-213.

[24] Bonner OD, Holland VF. Activity coefficients of *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate in mixed solutions. J Am Chem Soc, 1955, 77:

5828-5829.

[25] Bombín M, Guerrero A, Ma MZ, et al. Thermal decomposition of Co(II), Ni(II), Cu(II), Zn(II), Cd(I1) and Pb(I1) *p*-toluenesulphonates. Thermochimica Acta, 1989, 146: 341-352.

[26] Hargreaves A. Crystal structure of zinc *p*-toluenesulphonate. Nature, 1946, 158 :620-621.

[27] Barton BE, Whaley CM, Rauchfuss TB. Nickel-Iron dithiolato hydrides relevant to the [NiFe]-hydrogenase active site. J Am Chem Soc, 2009, 131: 6942-6943.

[28] Withers JR, Li DF, Triplet J, Ruschman C, Parkin S, Wang GB, Yee GT, Holmes SM. Synthesis and characterization of one- and two-dimensional octacyano-metalate(V) networks: $\{[trans\text{-}M^{II}(DMF)_4][cis\text{-}M^{II}(DMF)_4]_2[M^{V}(CN)_8]_2\}_n$ (M^{II}= Mn, Fe, Ni; M^{V}= Mo, W). Polyhedron, 2007, 26: 2353-2366.

[29] Withers JR, Ruschman C, Parkin S, Holmes SM. One- and three-dimensional octacyanometalate(IV) networks constructed via a building block approach: $\{[trans\text{-}Ni^{II}(tn)_2(OH_2)][trans\text{-}Ni^{II}(tn)_2][(\mu\text{-}NC)_3M^{IV}(CN)_5]\cdot 6H_2O\}$ (M^{IV}=Mo,W) and $Cs_4[Cu^{II}(OH_2)_4]_2[Cu^{II}(NH_3)]_4[Mo^{IV}(CN)_8]_4\cdot 2H_2O$. Polyhedron, 2005, 24: 1845-1854.

[30] Debevc KO, Pohar C, Vlachy V. Enthalpies of dilution of alkaline and alkaline earth *p*-toluenesulfonates. J Soln Chem, 1996, 25: 787-795.

[31] Winter S, Seichter W, Weber E. Syntheses and crystal structures of cobalt and nickel complexes of 2,6-bis(hydroxymethyl) pyridine. J Coord Chem, 2004, 57: 997-1014.

[32] David JH, Leslie Cr, Harold H. Organic Chemistry: A Brief Course. 13th Ed. Cengage Learning: Boston, 2011.

[33] Stober HP. PDF#, $Ni(OTs)_2 \cdot 6H_2O$: 48-2311, ICDD, Grant-in-Aid, 1996.

[34] Gholami Z, Abdullah AZ, Lee KT. Selective Etherification of Glycerol over Heterogeneous Mixed Oxide Catalyst: Optimization of Reaction Parameters. Chemical Engineering and Science, 2013, 1: 79-86.