



Study on Synthesis and Characterization of Hexaquonickel(II) bis-*p*-toluenesulfonate

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Authors' contributions

This work was carried out in collaboration between all authors. Authors WS and ZZ designed the study. Authors WS and ZQ performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors X. Weilan, GW and TS managed the analyses of the study. Author X. Wanil managed the literature searches. Author ZZ revised the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Hexaquonickel (II) bis-*p*-toluenesulfonate [Ni(OTs)₂·6H₂O] 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)₂·6H₂O 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.

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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 physicochemical information [5-7] of them. Kosumi et al. [8] 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. [9] via an oxidation-reduction reaction using metal powders and aqueous *p*-toluenesulfonic acid hydrate as the reducing and oxidizing reagents, 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, and investigated their physical and chemical properties. Ali et al. [11] 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. [12] developed a solvent-free, one-pot synthesis technology of amidoalkyl naphthols using copper *p*-toluenesulfonate as catalyst.

Hexaquaonickel(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 $[(dppe)(CO)Fe(S_2C_3H_6)(\mu-H)Ni(dppe)]BF_4 \cdot [2H]BF_4$ 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, $Ni(OTs)_2 \cdot 6H_2O$ is useful in preparation of 2,6-bis(hydroxymethyl) pyridine, which can act as chelating ligand in coordination compounds [16].

Generally, tosylates were prepared by the reaction of corresponding metal hydroxides with

p-toluenesulfonic acid (PTS) [17]. Winter et al. [18] had prepared $Ni(OTs)_2 \cdot 6H_2O$ 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 $Ni(OTs)_2 \cdot 6H_2O$ was studied by changing the equivalence ratio of reactants $[N_{PTS}/N_{Ni(OH)_2}]$, reaction temperature, and the reaction time.

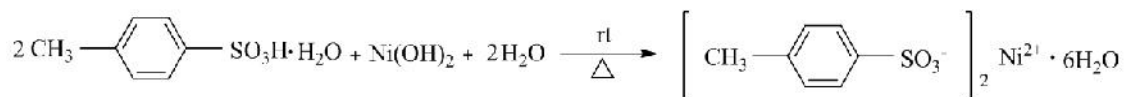
2. EXPERIMENTAL AND CHARACTERIZATION

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 un reacted 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)₂·6H₂O

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-C₁₈ 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 additive 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)₂·6H₂O 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)₂·6H₂O were given in Table 1. From Table 1 we know

that the deviation of each element is less than 0.64%, thus it can be determined that the measured sample is Ni(OTs)₂·6H₂O.

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)₂·6H₂O is shown in Fig. 1. From Fig. 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 appears at 824 K.



Schema 2. The process of dehydration for Ni(OTs)₂·6H₂O

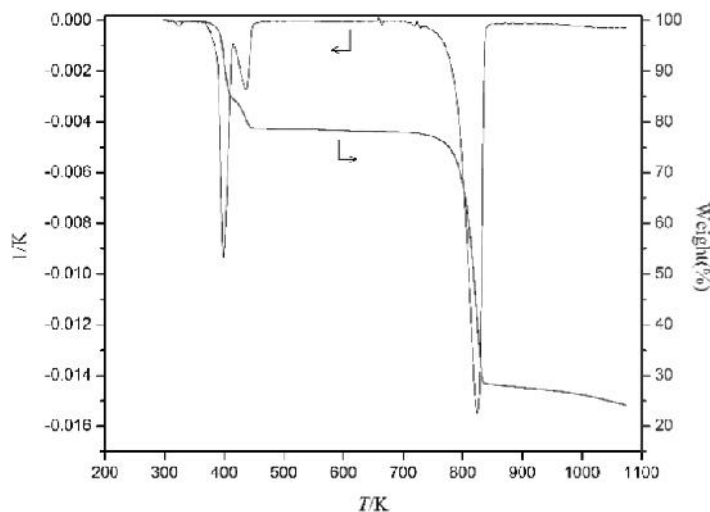


Fig. 1. Thermogravimetric analysis of Ni(OTs)₂·6H₂O

Table 1. The elemental analysis of Ni(OTs)₂·6H₂O

| 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% |

2.6 Infrared Spectra (IR)

The infrared spectra of Ni(OTs)₂·6H₂O 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)₂·6H₂O is shown in Fig. 2. It can be seen from Fig. 2 that the characteristic peaks of the infrared spectrum of Ni(OTs)₂·6H₂O 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 [19]. Therefore, the material can be considered as Ni(OTs)₂·6H₂O.

2.7 X-ray Powder Diffraction (XRD)

The X-ray powder diffraction patterns (ESCALAB 250Xi, Thermo Fisher Corporation, USA) of Ni(OTs)₂·6H₂O is shown in Fig. 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 Fig. 1, the samples of anhydrous Ni(OTs)₂ would be obtained when Ni(OTs)₂·6H₂O were dried at 498 K for 8 h, and the X-ray spectrums of the anhydrous Ni(OTs)₂ is shown in Fig. 3b. The interplanar spacings(d) and hkl values of Ni(OTs)₂·6H₂O and Ni(OTs)₂ are shown in Table 2 and Table 3. From Fig. 3a and Fig. 3b, it can be seen that the XRD spectrum of anhydrous Ni(OTs)₂ is different from that of

Ni(OTs)₂·6H₂O in peak position and intensity, which indicate that dehydration treatment will change the crystal structure of Ni(OTs)₂·6H₂O. In addition, the diffraction peaks of Ni(OTs)₂ are broaden, indicating its crystal size (or crystallinity) is smaller than that of Ni(OTs)₂·6H₂O.

Table 2. Interplanar crystal spacing and hkl values of Ni(OTs)₂·6H₂O

| 2θ/° | d/nm | (hkl) |
|-------|-------|--------|
| 7.01 | 12.80 | (200) |
| 14.11 | 6.19 | (400) |
| 15.74 | 5.63 | (210) |
| 16.41 | 5.49 | (-301) |
| 16.78 | 5.34 | (301) |
| 17.66 | 5.26 | (310) |
| 19.00 | 4.58 | (-111) |
| 21.11 | 4.25 | (600) |
| 21.59 | 4.10 | (-501) |
| 22.07 | 4.03 | (501) |
| 22.65 | 3.96 | (510) |
| 25.62 | 3.31 | (002) |
| 27.64 | 3.22 | (-701) |
| 28.41 | 3.15 | (701) |
| 29.27 | 3.08 | (220) |
| 30.04 | 2.97 | (-212) |
| 30.33 | 2.96 | (320) |
| 31.67 | 2.94 | (711) |
| 33.59 | 2.65 | (520) |
| 43.19 | 2.16 | (1200) |
| 45.11 | 2.01 | (1002) |
| 45.68 | 1.98 | (1210) |

Table 3. Interplanar crystal spacing and hkl values of Ni(OTs)₂

| 2θ/° | d/nm | (hkl) |
|-------|-------|--------|
| 4.80 | 18.39 | (010) |
| 6.98 | 12.66 | (200) |
| 13.96 | 6.34 | (400) |
| 16.58 | 5.34 | (-301) |
| 17.52 | 5.06 | (310) |
| 19.02 | 4.66 | (011) |
| 21.54 | 4.12 | (-501) |
| 25.76 | 3.46 | (002) |
| 27.67 | 3.22 | (-701) |
| 29.97 | 2.98 | (-212) |

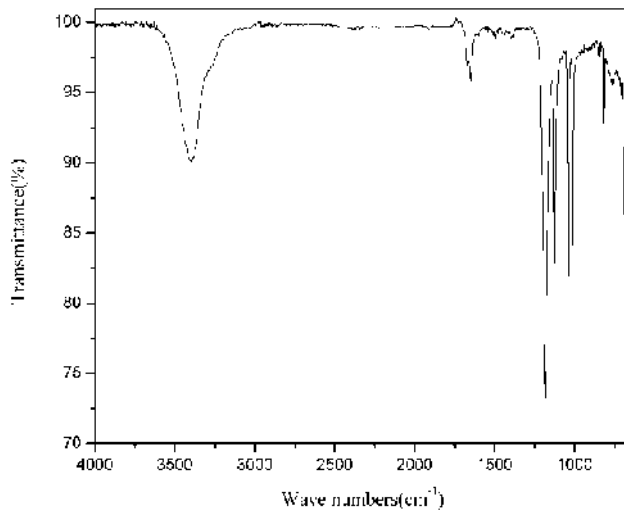


Fig. 2. Infrared spectrum of Ni(OTs)₂·6H₂O

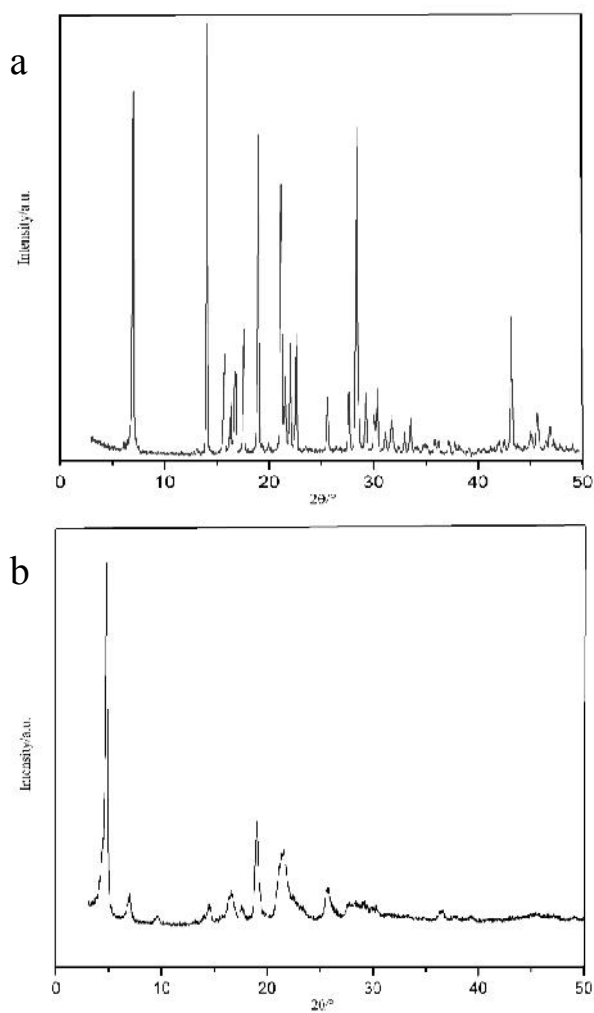


Fig. 3. XRD of Ni(OTs)₂·6H₂O (a) and Ni(OTs)₂ (b)

3. RESULTS AND DISCUSSION

The influence of reaction conditions on the yield of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ was investigated by varying $N_{\text{PTS}}/N_{\text{Ni}(\text{OH})_2}$ from 0.8 to 1.2, and the results are shown in Fig. 4. From Fig. 4, it can be seen that the yield of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ increases with increasing of equivalence ratio of PTS to $\text{Ni}(\text{OH})_2$ until $N_{\text{PTS}}/N_{\text{Ni}(\text{OH})_2} = 1.1$ (yield, 90.86%), and then tends to constant. This perhaps because the higher concentration of acid is beneficial to the formation of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$, and this rule becomes invalid when $N_{\text{PTS}}/N_{\text{Ni}(\text{OH})_2}$ is larger than 1.1. From Fig. 4, it can also be seen the purity of the product has little change with the increase of equivalence ratio of reactants.

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 $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ was investigated when $N_{\text{PTS}}/N_{\text{Ni}(\text{OH})_2}$ 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 Fig. 5. From

Fig. 5, at constant temperature the yield of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ tends to be stable. For example, the values of t^* at 323 K and 363 K are 5.5 h and 2 h, respectively.

On the bases of above results, the reaction may be controlled by the dissolve process of $\text{Ni}(\text{OH})_2$. The reasons can be described as follow: (1) Because $\text{Ni}(\text{OH})_2$ is insoluble in water, the reaction rate between PTS and $\text{Ni}(\text{OH})_2$ (belongs to acid-base neutralization) is related to the concentration of $\text{Ni}(\text{OH})_2$ in the liquid phase. (2) Because the concentration of $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ 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.

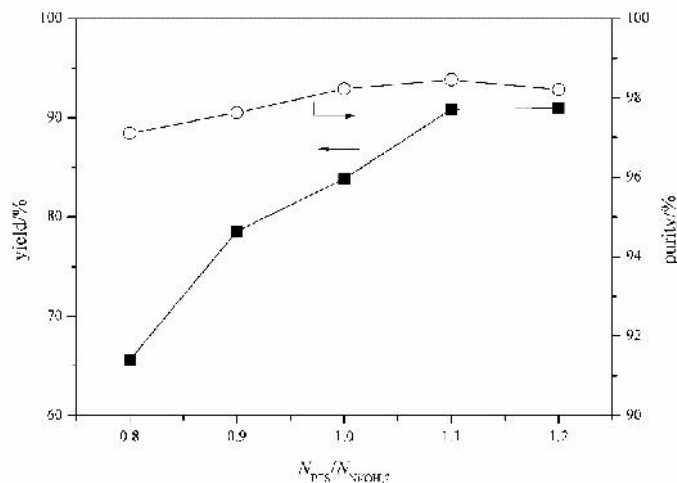


Fig. 4. The effect of equivalence ratio for reactants on the yield and purity of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ (■, yield; ○, purity)

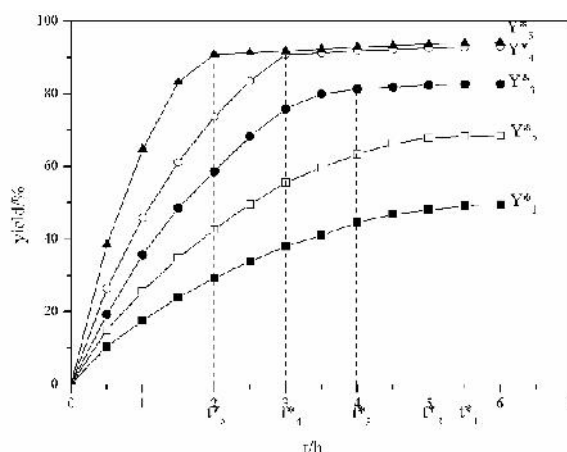


Fig. 5. The effect of reaction temperature and reaction time on the yield of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ (■, 323 K; ●, 333 K; ○, 343 K; □, 353 K; ▲, 363 K)

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 |

4. CONCLUSION

Hexaquonickel (II) bis-*p*-toluenesulfonate [$\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$] was prepared from the reaction of *p*-toluenesulfonic acid (PTS) and nickel hydroxide [$\text{Ni}(\text{OH})_2$]. The results of energy disperse spectroscopy, thermal-analysis instrument, infrared spectrometer, and X-ray diffractometer prove that the substance tested can be considered as $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$. The influence of mole ratio of reactants [PTS versus $\text{Ni}(\text{OH})_2$], reaction temperature and reaction time on the yield of products was investigated. The yield of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ increases with increasing of $N_{\text{PTS}}/N_{\text{Ni}(\text{OH})_2}$ until it is 1.1 (yield, 90.86%), and then tends to constant. When the temperature keep constant the yield of $\text{Ni}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ 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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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