SYNTHESIS OF 1H-1, 2, 4-TRIAZOLE-3-THIOL RESIN AND ITS SORPTION BEHAVIOR FOR PLATINUM AND GOLD IONS[①]

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ABSTRACT The optimum conditions for synthesis of 1H-1, 2, 4-triazole-3-thiol resin (TATR) are as follows: molar ratio of SH: Cl= 2.5: 1 in DMF, reaction temperature 80 ℃, reaction time 8 h. The functional group of TATR is 3.77 mmol FG/ g resin. The structure of the resin has been confirmed by elementary analysis, FT-IR and XPS. The sorption capacities of TATR for Au(III), Pt(IV) are as high as 3.71, 0.76mmol ion/ g resin, respectively. The apparent activation energy of sorption of TATR for Au (III) is 14.6kJ/ mol.

Key words 1H-1, 2, 4-triazole-3-thiol resin   sorption   gold   platinum

1 INTRODUCTION

A series of new functional resins were recently reported by Chen Yiyong and his coworkers; their sorption properties for a variety of precious[1-5], heavy[6], rare[7] and rare earth[8] metals were determined. These resins are useful in separation, preconcentration, determination, recovery and purification of precious metals, etc. In this paper, the synthesis and characterization of a new functional resin bearing 1H-1, 2, 4-triazole-3-thiol group is described according to the reaction shown in Fig. 1.
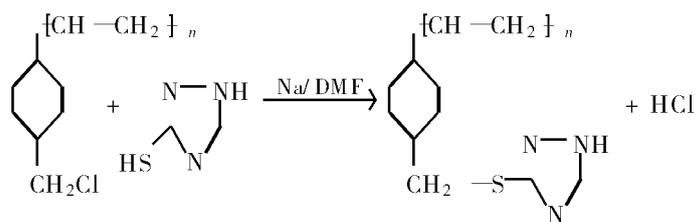

Fig. 1   **Synthesis of 1H-1, 2, 4-triazole-3-thiole resin (TATR)**

2 EXPERIMENTAL

2.1 Materials

Macroporous chloromethylated polystyrene beads (chloro-beads): degree of cross-linking 6% DVB, chlorine content 22.08%, specific surface area 43 m^2/g.

1H-1, 2, 4-triazole-3-thiol (TAT): Fluka AG, purity> 97%, m.p. ~ 220 ℃.

Dimethyl formamide (DMF): analytical reagent (AR), treated with metallic sodium wire and distilled before use.

Aurichlorohydric acid, AR; chloroplatinic acid, AR.

2.2 Instruments

Elemental analyzer, Mod. 1106 Carlo Erba strumentazione.

Alpha centauri FT-IR, Mattson Instruments Inc.

UV-265 UV/VIS spectrophotometer, Shimadzu.

ICP plasma-spec, Leeman Labs Inc.

Escalab MK- II X-ray photoelectron spec-troscope, VG Scientific Instruments Co.

2.3 Synthesis of TATR

After swelled in 10 mL purified DMF, the 0. 200 g macroporous chloromethylated polystyrene beads were treated with TAT and Na whose mole concentration is equal to that of TAT, and then heated with stirring. After reac-tion, the resin was washed thoroughly with DMF, 2% aqueous NaOH and deionized water to remove Cl^-, then with acetone and ether suc-cessively, and finally dried at 50 ℃ in vacuum.

2.4 Analysis and confirmation of resin

The dried resin was ground into powder and dried at 50 ℃ in vacuum. The nitrogen content of the resin was determined using elemental ana-lyzer. The residual chlorine content was deter-mined using the oxygen-flask burning method.

2.5 Sorption property

The concentrations of mixed residual metal ions were measured by ICP and the concentra-tion of single ion was measured individually by a UV-VIS spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 Synthesis of TATR

DMF was selected as a solvent, because chloromethylated polystyrene beads can easily be swelled in DMF which is miscible with water and TAT is soluable in DMF. The synthesis of TATR was investigated under the following con-ditions: molar ratio of reagents [TAT]: [Cl] = 1 ~ 4, reaction temperature 30~ 100 ℃, reaction time 1 ~ 12 h. The experimental results are shown in Figs. 2~ 4.

The optimum conditions for synthesis of TATR are [TAT]: [Cl] = 2. 5, reaction temper-ature 80 ℃, reaction time 8h. The nitrogen and residual chlorine content, the percentage of func-tional group conversion, and the functional group capacity of TATR synthesized under opti-mum conditions are 15. 84%, 0. 31%, 64. 34% and 3. 77 mmol/ g resin, respectively.

Fig. 2　Influence of molar ratio of [TAT]: [Cl] on N, residual Cl contents ($C(N)$, $C(Cl)$) and the conversion of functional group of TATR(R)
(80 ℃, 8 h)
$1 - C(N); 2 - R; 3 - C(Cl)$

Fig. 3　Influence of reaction temperature on N, residual Cl contents and the conversion of functional group of TATR
([TAT]: [Cl] = 2. 5, 8 h)
$1 - C(N); 2 - R; 3 - C(Cl)$

3.2 Determination of resin structure

The IR spectra in Fig. 5 shows that chloromethylated polystyrene has a strong peak at 670 cm^{-1} which is characteristic peak of C—Cl and a strong peak at 1 260 cm^{-1} can be assigned to the nonplanar wagging of CH_2, but these peaks almost disappear in TATR. The contraction vibration peaks of —C—N at 1 567 and 1 040 cm^{-1} in TAT still exist in TATR. The vibration peak at 2 515 cm^{-1} which

is the characteristic peak of —S—H in TAT becomes weak in TATR. The contraction vibration peak of CH₂—S—C at 695 cm⁻¹ appears in TATR.

The binding energy data of TAT and TATR is listed in Table 1. It shows that both nitrogen and surfur atoms take part in the reaction.
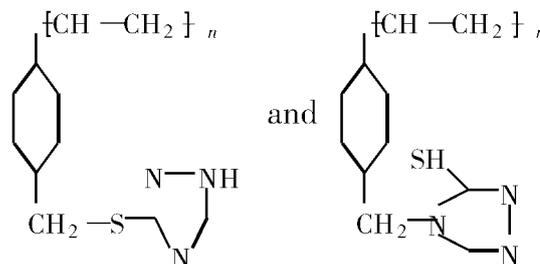
The structure of TATR is shown as following:

Table 1　The binding energy of TAT and TATR

Atoms	Binding energy / eV			
	TAT		TATR	
C_{1s}	285. 00	287. 00	285. 00	287. 00
N_{1s}	400. 70		400. 25	401. 30
S_{2p}	164. 30		164. 45	

3. 3　Sorption acidity and selectivity of TATR for precious metals

The influence of acidity on the sorption of TATR for precious metals was determined over a wide range of acidity (HCl, 0. 1~ 6 mol/ L). The optimum sorption acidities (HCl) of TATR for various precious metals are listed in Table 2.

Table 2　Optimum sorption acidities (HCl) of TATR for various precious metals

Metals	Au(III)	Pt(IV)	Pd(II)	Ir(IV)
Optimum sorption acidities/ mol·L⁻¹	1	2	2	1

The factors which affect the selective sorptions are very complex, such as the characters of resin, metal ions, the affinity of resin for metal ions, the acidity of medium and the stability constants of complexes, etc.

The selectivities of TATR for various ions over a range of acidity (HCl) 0. 1~ 6 mol/ L are shown in Fig. 6.

Fig. 4　Influence of reaction time on N, residual Cl contents and the conversions of functional group of TATR

(molar ratio of [TAT]: [Cl] = 2. 5,　80 ℃)

1 —C(N); 2 —R; 3 —C(Cl)

Fig. 5　FT- IR spectra

one Au(III) ion or about 1/4 Pt (IV) ion can be adsorbed by one TATR functional group.

3.5 Determination of rate constant and apparent activation energy of sorption

According to the following method, the sorption rate constant K can be calculated from

$$- \ln(1- F) = K_t$$

where $F = Q_t / Q_\infty$, Q_t and Q_∞ are the sorption amounts at sorption time t and at equilibrium, respectively. The slope of the straight line,

Fig. 6 Influence of acidity on the selective sorption of TATR for various precious ions in the presence of common ions

(TATR 30. 0mg; ion contents (mmol):
Au (III) 4.06×10^{-3}, Pt(IV) 4.10×10^{-3},
Pd (II) 4.60×10^{-3}, Ir(VI) 4.53×10^{-3},
Ni (II) 1.35×10^{-2}, Cu(II) 1.27×10^{-2},
Fe (III) 1.43×10^{-2}, Zn(II) 1.21×10^{-2};
total volume 30 mL; 25 ℃, shaking for 2 h)
1 —Au; 2 —Pt; 3 —Ni; 4 —Fe;
5 —Pd; 6 —Ir; 7 —Zn; 8 —Cu

The results show that the sorption capacity of TATR for precious metals is high, but it is remarkably low for base metals over a wide range of acidity. Thus, TATR has excellent sorption selectivity for precious metal ions.

3.4 Sorption rate curves of TATR for Au and Pt ions

Under optimum conditions, the sorption curves and parameters of TATR for Au and Pt ions are shown in Fig. 7 and listed in Table 3.

The results show that TATR has higher sorption capacity for the precious metals , especially for Au(III) . The $t_{1/2}$ values show that the sorption rates of TATR for the precious metal ions are different. The M/FG values show that

Fig. 7 Sorption (mg ion/ g resin) rate curves of TATR for Au (III) and Pt (IV)

(TATR in 2 parts, 30. 9 mg each; ratios of the amount of metal ion added (mg) to the volume of solution (mL) are 54∶ 25 for Au(III) and 20∶ 25 for Pt (IV); under optimum acidity, 25 ℃ and shaking for a period of time, an aliquot of 0. 100 mL was taken for analysis)
1 —Au(III); 2 —Pt(IV)

Table 3 Sorption parameters of TATR for precious metals

Ions	Sorption capacity		$t_{1/2}^{1)}$ /h	M/FG[2)]
	/ mg·g^{-1}	/ mol·g^{-1}		
Au(III)	731	3. 71	2	0. 99
Pt(IV)	148	0. 76	0. 5	0. 20

1) $t_{1/2}$ is the time required to reach half of the equilibrium sorption amount;

2) M/FG: sorption capacity of resin for metal ion (mmol/ g)/ functional group capacity of resin (mmol/ g)

by plotting $- \ln (1- F)$ versus t, yields the

sorption rate constant K. The results are shown in Fig. 8 and listed in Table 4.

The sorption rate constant increases with temperature as listed in Table 4. The apparent activation energy of sorption (E_a) can be calculated from the data in Table 4 (assuming independent of temperature) and the Arrhenius equation:

$$\ln K = - E_a / RT + \ln A$$

Plotting $\ln K$ against $1/T$, the apparent activation energy of sorption is obtained ($E_a = 14.6$ kJ/ mol).

lated by linear regression for Au(III) data.

Table 4 Sorption parameters of TATR for Au(III)

T / K	308	313	323
K / 10^5s	4.6	8.8	12.6

Facile sorption of Au(III) by TATR is implied by its lower activation energies as compared to those of typical chemical reactions.

As mentioned above, TATR shows remarkable sorption affinity for noble metallic ions and has widespread prospects for application.

Fig. 8 The sorption rate of TATR for Au (III) under different temperatures

(TATR 30. 0mg, Au(III) 12. 5 mg, acidity (HCl) 1 mol/ L, total volume 25 mL. Under a definite temperature, after shaking for a period of time, an aliquot of 0. 100 mL was taken for analysis)

1 —50 ℃; 2 —40 ℃; 3 —25 ℃

The correlation coefficient— 0. 948 is calcu-

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