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SYNTHESIS OF *N*-METHYL-2-THIOIMIDAZOLE RESIN AND ITS COMPLEX BEHAVIOR FOR NOBLE METAL IONS

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ABSTRACT

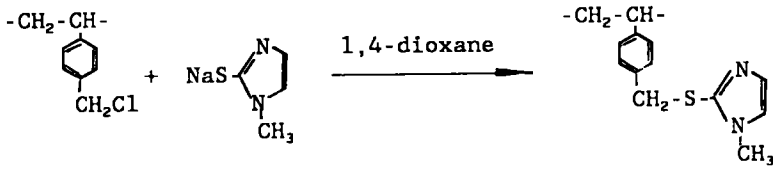
The functional group capacity and the percentage of functional group conversion of crosslinked polystyrene resin bearing *N*-methyl-2-thioimidazole (MTIR) synthesized under optimum conditions are as high as 4.08 mmol/g resin and 96.0%, respectively. The apparent activation energies of sorption of MTIR for Au(III) and Pt(IV) are 13.1 and 13.4 kJ/mol, respectively. The sorption behavior of MTIR for Au(III), Pt(IV), and Pd(II) obeys the Freundlich and Langmuir isotherms. The sorption capacities of MTIR for Au(III), Pt(IV), and Pd(II) are as high as 4.33, 2.12, and 2.33 mmol/g resin, respectively. Au(III), Pt(IV), and Pd(II) adsorbed on MTIR can be eluted quantitatively by the eluant. The resin can be regenerated easily and reused without an obvious decrease in the sorption capacity for Au(III) and Pd(II). The resin has high sorption selectivity for noble metal ions. Au(III) can be separated quantitatively in the presence of high concentrations of Cu^{2+}, Fe^{3+}, Ni^{2+}, and Mn^{2+}. The recovery of platinum from the spent industrial catalysts is 98.6% by MTIR. The preconcentration and separation of palladium and platinum from the anode deposits of electrolysis of crude copper have been investigated. The resin may have potential industrial uses.

INTRODUCTION

The functional resins are useful in the preconcentration, separation, recovery, purification, and hydrometallurgy of noble metals. Many kinds of functional resins have been synthesized, and the sorption properties of the resins were determined recently by the author and his coworkers [1–4].

We have developed a new functional resin system to recover platinum from waste firebrick in the glass fiber industry and from spent catalyst in the petroleum chemical industry with a high purity of platinum and a high percentage of recovery.

Crosslinked polystyrene resin bearing *N*-methyl-2-thioimidazole (MTIR) has been synthesized according to the following reaction:



MTIR has high sorption capacity and selectivity for noble metal ions. Au(III), Pt(IV), and Pd(II) adsorbed on MTIR can be eluted quantitatively by eluant. The resin is easily regenerated and reused without an obvious decrease of sorption capacity for Au(III) and Pd(II). Au(III) can be separated quantitatively by MTIR in the presence of large amounts of Cu^{2+}, Fe^{3+}, Ni^{2+}, and Mn^{2+}, and therefore MTIR may have many potential industrial uses.

EXPERIMENTAL

Materials

Macroporous chloromethylated polystyrene beads: Degree of crosslinking 6%, chlorine content 22.08%, specific surface area 43 m^2/g.

N-Methyl-2-thioimidazole (MTI): Extracted from the drug Thiamazolum; mp 142°C, literature value 144°C [5]; NMR δCH_3 3.56, δCH 6.73, δNH 11.84, literature values δCH_3 3.57, δCH 6.73, δNH 11.93 [6]; IR spectra found to be identical with the literature [6].

1,4-Dioxane A.R.: Treated with metallic sodium wire and distilled before use.

Synthesis of *N*-Methyl-2-thioimidazole Resin

After swelling in 10 mL of purified 1,4-dioxane, 1.0 g (6.23 mmol Cl) macroporous chloromethylated polystyrene beads were treated with NaMTI which was prepared from MTI and an equal molar amount of metallic sodium and heated with stirring. After reaction, the resin was washed thoroughly with 1,4-dioxane and 2% aqueous NaOH and deionized water to remove Cl^-, and then with acetone and ether successively. The resin was then dried at 50°C under vacuum.

Sorption Property

The concentration of metal ions was measured by a UV-VIS photometer and AAS (atomic absorption spectrometer).

RESULTS AND DISCUSSION

Functional Group Capacity, Functional Group Conversion, and Structure of MTIR

Because chloromethylated polystyrene beads can easily swell in 1,4-dioxane which is miscible with water, we selected 1,4-dioxane as solvent. The synthesis of MTIR was investigated under the following conditions: molar ratio of reagents (thio group SH/Cl = 1–4, SH/Na = 1), reaction temperature (40–100°C), reaction time (1–30 h), 1,4-dioxane as the solvent.

The N content of MTIR increases slightly with reaction temperature, but this influence is not obvious between 70 and 100°C. The influence of the molar ratio of reagents and the reaction time are shown in Fig. 1. The optimum ratio of reagents was SH : Na : Cl = 3 : 3 : 1, reaction temperature 100°C, reaction time 23 h.

MTIR synthesized under optimum conditions has nitrogen content 11.44%, sulfur content 13.07%, and residual chlorine 0.30%. The functional group capacity and the percentage of functional group conversion of MTIR were 4.08 mmol/g resin and 96.0%, respectively, which were calculated either from nitrogen or sulfur content.

IR spectra show that the two strong peaks (674.08, 1264.26 cm^{-1}) of the chloromethyl group of the chloromethylated polystyrene beads al-

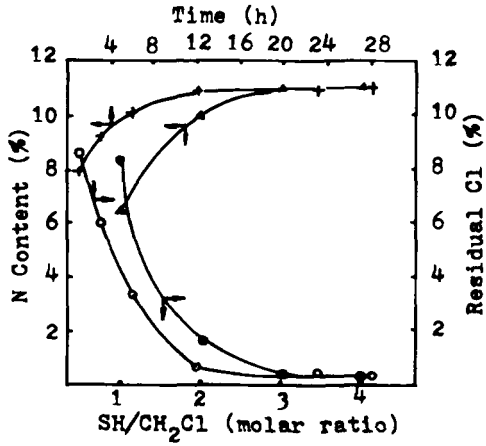


FIG. 1. Influence of molar ratio of reagent and reaction time on N and residual Cl content of resin. Thio group SH/Na = 1 (molar ratio), 100°C, 28 h; SH : Na : Cl = 3 : 3 : 1 (molar ratio), 100°C.

most disappear in MTIR, but the two peaks corresponding to the imidazole ring of MTI are present in MTIR at 1450.38 and 1278.73 cm^{-1}. The peak at 1150.47 cm^{-1} due to the C=S bonds of MTI disappears completely and a new peak corresponding to C—S appears in MTIR at 747.37 cm^{-1}.

The results show that MTI is anchored on the polymeric support via a reaction between the chloromethyl and mercaptol groups, and the degree of reaction is very high. The degree of substitution has also been confirmed by elemental analysis.

Optimum Sorption Acidity, Sorption Selectivity, Sorption Capacity, and Complex Ratio of MTIR for Au(III), Pt(IV), and Pd(II)

The influence of the pH and the amount of acid on the sorption percentage of MTIR for Au(III), Pt(IV), and Pd(II) was determined over a range of 1-6 *N* HCl and pH 1-6. The experimental results show that the optimum sorption acidity and pH of MTIR for Au(III), Pt(IV), and Pd(II) are pH 3 in 6 *N* HCl, pH 1, and pH 1 in 1 *N* HCl, respectively.

Figure 2 shows that in the presence of equimolar amounts of four

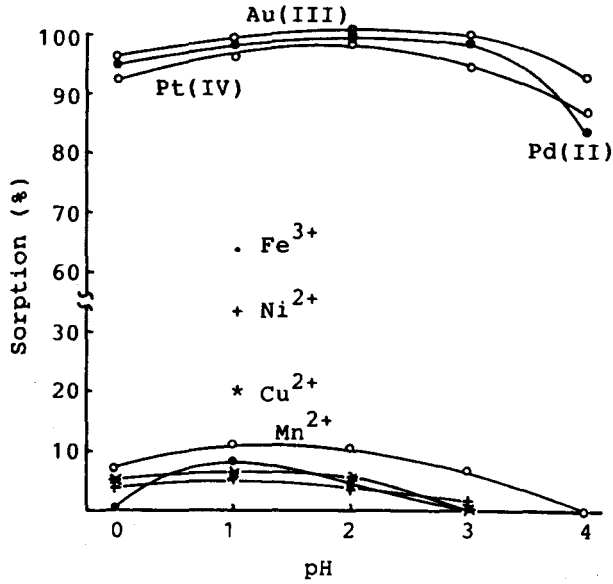


FIG. 2. Selective sorption of MTIR. MTIR 50 mg, total volume of solution 30 mL containing various metal ions each in 5 μmol quantities, 25°C, shaking for 1.5 h.

kinds of 3d divalent transition metal ions, Au(III), Pt(IV), and Pd(II) can be adsorbed by MTIR selectively over a range of pH 0–4. Especially at pH 2, these three noble metal ions can be adsorbed quantitatively, but the sorption percentage of 3d divalent metal ions is less than 10%. Thus, MTIR has excellent sorption selectivity for the three noble metal ions.

Under optimum conditions, the sorption parameters of MTIR for Au(III), Pt(IV), and Pd(II) are as listed in Table 1.

The results show that MTIR has a very high sorption capacity for Au(III), Pt(IV), and Pd(II). From the $T_{1/2}$ value, we know that the sorption rate for Au(III) is faster than that for Pt(IV). Thus, it is possible to separate Pt(IV) from Au(III). The K_d values are also very high. This is very important since it shows that Au(III) and Pt(IV) can be effectively adsorbed even in very dilute solutions. The complex ratio shows that one Au(III) is complexed by one MTI group, but Pt(IV) and Pd(II) require two MTI groups.

TABLE 1. Sorption Parameter of MTIR for Au(III), Pt(IV), and Pd(II)

Ion	Functional group capacity, mmol/g	Sorption capacity		$T_{1/2}$,[a] h	Distribution coefficient, K_d[b]	Complex ratio n[c]
		mmol/g	mg/g			
Au(III)	4.08	4.33	852.3	0.5	1516	1 : 1.07
Pt(IV)	4.08	2.12	414.7	2.5	1556	1 : 0.53
Pd(II)	4.08	2.33	247.9			1 : 0.57

[a] $T_{1/2}$ is the time required to reach half of the equilibrium sorption capacity.

[b] $$K_d = \frac{\text{amount of metal ion on the resin}}{\text{amount of metal ion in solution}} \times \frac{\text{volume of solution (mL)}}{\text{weight of resin (g)}}.$$

[c] $$n = \frac{\text{sorption capacity of resin for metal ion (mmol/g)}}{\text{functional group capacity of resin (mmol/g)}}.$$

Determination of Rate Constant and Activation Energy of Sorption

According to the Brykina method [7], the sorption rate constant k can be calculated from

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

where $F = Q_t/Q$, and Q_t and Q are the sorption amounts at sorption time t and at equilibrium, respectively. The slope of the straight line plot of ln $(1 - F)$ vs t yields the sorption rate constant k. The results are shown in Fig. 3 and Table 2; the sorption rate constant increases with temperature.

The apparent activation energy of sorption (E_a) can be calculated by means of the data in Table 2 (assuming E_a is independent of temperature) and the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

The results are given in Table 3.

Facile adsorption of these ions by MTIR is implied by these low activa-

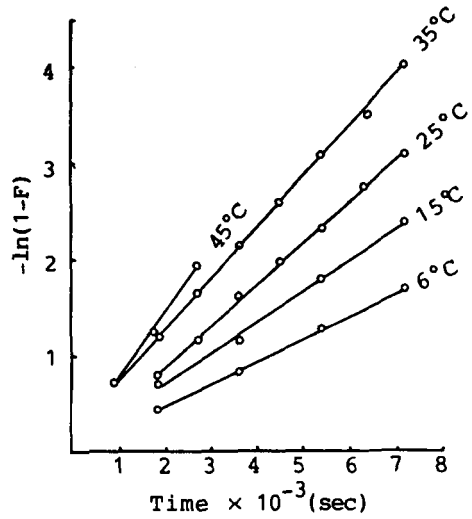


FIG. 3. Curves of sorption rate of MTIR for Au(III) at various temperatures. MTIR 30 mg, pH 2 buffer solution 50 mL. The Au(III) concentration of the solution is 1.444 mg Au(III)/mL while shaking at a defined constant temperature. Shaking speed 300 rpm.

tion energies as compared to those of typical chemical reactions of 65–250 kJ/mol.

Isotherm Sorption Curves

The isotherm sorption of MTIR for Au(III) and Pt(IV) has been investigated by using the Langmuir isotherm and Freundlich isotherm methods.

Langmuir Isotherm

The Langmuir isotherm is given by

TABLE 2. Sorption Rate Constant of MTIR for Au(III) under Various Temperatures

T, K	279	288	298	308	318
$k \times 10^4$, s	3.19	3.58	4.25	5.14	5.96

TABLE 3. Apparent Sorption Activation Energy of MTIR for Au(III), Pt(IV), and Pd(II)

	Ion		
	$AuCl_4^-$	$PtCl_6^{2-}$	$PdCl_4^{2-}$
Apparent activation energy of sorption, E_a, kJ/mol	13.1	13.4	13.3

$$\frac{C}{Q} = \frac{C}{Q_\infty} + \frac{1}{aQ_\infty}$$

where C = the concentration of metal ion in the solution at sorption equilibrium
Q = equilibrium sorption amount of the resin for metal ion when the equilibrium concentration is C
Q_∞ = saturated sorption amount
a = constant

From the Langmuir isotherm sorption curve (Fig. 4), one can obtain the values of a and Q_∞ from the slope and intercept of the straight line, respectively. The data are listed in Table 4.

Freundlich Isotherm

The Freundlich isotherm is expressed as

$$Q = PC^q$$

or

$$\ln Q = \ln P + q \ln C$$

where the meanings of Q and C are the same as for the Langmuir isotherm, P is a constant, and q is the Freundlich constant.

The Freundlich isotherm sorption curve of MTIR for Au(III) is also shown in Fig. 4. The values of P and q calculated from the slope and the intercept of the straight line are listed in Table 4. Table 4 also lists the

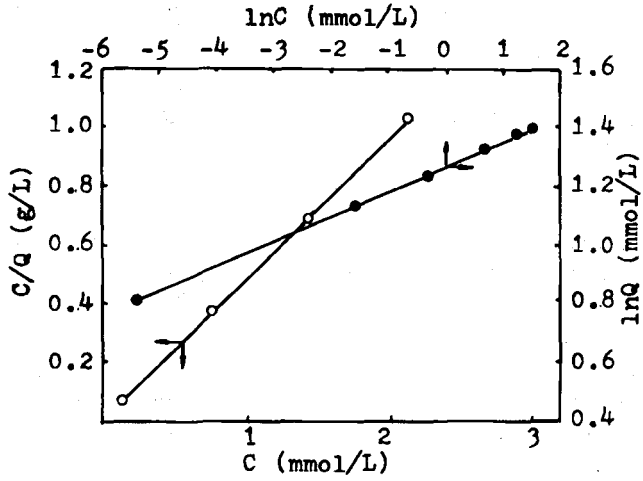


FIG. 4. Langmuir isotherm sorption for Pt(IV) and Freundlich isotherm sorption for Au(III). To each portion of MTIR (20.0 mg), add 4.096 mg Pt(IV)/mL solution (1, 2, 3, 4, 5, and 6 mL, respectively). Keep at 25°C while shaking for 24 h. To each portion of MTIR (20.0 mg), add 9.01 mg Au(III)/mL solution (0.5, 1.5, 2, 3, 4, and 5 mL, respectively) at 25°C and shake for 24 h.

parameters of the Langmuir isotherm sorption of MTIR for Au(III) and the Freundlich isotherm sorption of MTIR for Pt(IV). The values of the correlation coefficients show that the isothermal sorption of MTIR for Au(III) and Pt(IV) obeys the Langmuir isotherm and that Au(III) also shows excellent agreement with the Freundlich isotherm.

TABLE 4. Parameters of Isothermal Sorption of MTIR for Au(III) and Pt(IV)

	Langmuir isotherm			Freundlich isotherm		
Ion	*Q*, mmol/g	*a*, L/mol	Correlation coefficient	*P*	*q*	Correlation coefficient
Au(III)	4.08	8,710	0.9998	3.536	0.084	0.9991
Pt(IV)	2.05	98,900	1.0000	2.017	0.061	0.9620

Influence of Chloride on the Sorption Amount of MTIR for Au(III)

The influence of sodium chloride on the equilibrium sorption amount of MTIR for Au(III) is shown in Fig. 5.

The equilibrium sorption amount decreases slightly with an increasing concentration ratio of $C_{NaCl}/[AuCl_4^-]$ during the initial stage, and then it remains constant in the 40 to 80 concentration ratio range.

This phenomenon can be explained as follows: The equilibrium sorption amount comprises two parts: chemical sorption and physical adsorption. In the initial stage, Cl^- is present instead of $AuCl_4^-$, and thus physical adsorption plays a minor role. For high ratios of $C_{NaCl}/[AuCl_4^-]$, the amount of equilibrium sorption remains constant. In this case, chemical sorption plays a major role. The definite equilibrium sorption amount is 4.04 mmol Au(III)/g, and the functional group capacity of MTIR is 4.08 mmol/g, which means the complex ratio is 1.0. The result shows that the sorption of MTIR for Au(III) is predominantly chemical sorption. The polymeric ligand complex with Au(III) is via chemical bonding and is not due to a simple ion-exchange reaction. Excess Cl^- does not interfere with bonding of $AuCl_4^-$ to the resin.

Elution and Regeneration

The sorption and elution of MTIR for Au(III), Pd(II), and Pt(IV) and the regeneration of MTIR have been investigated statically and dynamically.

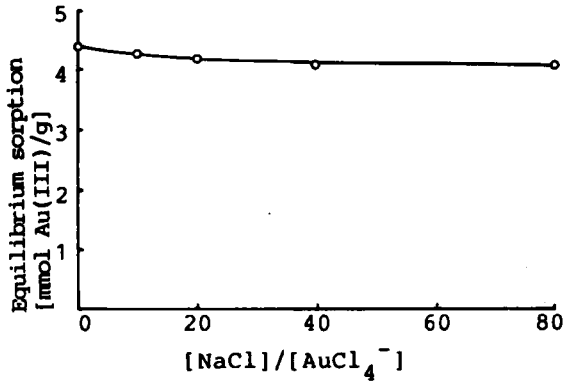


FIG. 5. Influence of NaCl on the sorption capacity of MTIR for Au(III). MTIR 30 mg, initial concentration of Au(III) 5.47 mol Au(III)/L, pH 2 buffer solution 55 mL, 35°C, 24 h.

The data listed in Table 5 show that Au(III) adsorbed on MTIR can be eluted quantitatively by 2% aqueous thiourea. After the resin is washed thoroughly with water, it can be reused. After three regenerations, the sorption capacity of the regenerated MTIR for Au(III) was found to be 4.28 mmol Au(III)/g, which is 99% of the original sorption capacity. The Au(III) adsorbed on the regenerated resin can also be eluted quantitatively.

The dynamic sorption and elution of MTIR for Pt(IV) have been investigated. The results show that Pt(IV) can be adsorbed quantitatively. The elution percentage of Pt(IV) is found to be 101% when using 2% aqueous thiourea as an eluant. Thus, the sorption and elution of MTIR for Pt(IV) are also quantitative.

In the case of Pd(II), MTIR can also be regenerated and reused. A solution comprised of thiourea : hydrochloric acid : acetone (1 : 1 : 1) is an excellent eluant for Pd(II), which quantitatively removes this ion from MTIR. The percentages of sorption and elution of the quadruply regenerated MTIR for Pd(II) are higher than 98%.

Separation of Au(III) from Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+}

The data listed in Table 6 show that Au(III) can be separated by MTIR quantitatively in the presence of Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+} when each of the four is 30 times more concentrated than Au(III).

In another case, a mixed solution containing 1.34 mg Au(III) and 1000 times that amount of Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+} was treated as described previously. A quantitative recovery of 1.36 mg Au(III) was observed.

These results show that Au(III) can be separated by MTIR in the

TABLE 5. Sorption, Elution, and Regeneration of MTIR[a]

	Regeneration times			
	0	1	2	3
Sorption capacity, mmol Au(III)/g	4.33	4.26	4.30	4.28
Elution, %	100.2	98	98	98

[a]Determination conditions: MTIR 30 mg, initial concentration 1.078 mg Au(III)/mL, pH 2 buffer solution, total volume 50 mL, 25°C, shaken for 24 h; eluted with 15 mL of 2% aqueous thiourea, shaken for 1 h at room temperature.

TABLE 6. Separation of Au(III) from Mixed Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+} [a]

Ion	Amount in mixed solution, μmol	Flow out,[b] μmol	Elute out, μmol
Au(III)	25	0	25.5
Cu^{2+}	750	755.0	0
Fe^{3+}	750	744.1	0
Mn^{2+}	750	750.3	0
Ni^{2+}	750	763.7	0

[a]Determination conditions: MTIR 1.09 g, resin bed 0.8 × 4.5 cm, a solution of 100 mL containing the above-mentioned metal ions, in 1 *N* HCl. After adsorbing, the resin bed is washed with 1 *N* HCl 100 mL and then eluted with 2% aqueous thiourea.

[b]The amount of ions including flowing out and washing out.

presence of large amounts of Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+}. Thus, MTIR may have potential industrial uses.

Application

Recovery of Platinum from the Waste Catalyst

Waste catalyst is obtained from the petroleum chemical industry. Platinum is dissolved from waste catalyst powder by using a mixed solution of HNO_3, HCl, and water under heat with stirring. This platinum solution contains a large amount of Al^{3+} and Fe^{3+}. Platinum is recovered by using MTIR. The percentage of recovery is 98.6%.

Recovery and Separation of Palladium from a Copper Anode Deposit

An anode deposit obtained from the electrolysis of crude copper containing gold, platinum, and palladium was used to demonstrate the characteristics of the resin.

The diluted waste solution in which gold was removed by a chemical method was found to contain 1.05 mg Pd(II)/L and 0.25 mg Pt(IV)/L. Three liters of the solution in 1 *N* HCl was passed through a MTIR bed. Pd(II) and Pt(IV) are adsorbed on MTIR completely. Then Pd(II) is eluted with 15 mL of a mixed eluant (thiourea : HCl : acetone (1 : 1 : 1). The eluant contained 3.07 mg Pd(II), which corresponds to a concentration of 205 mg/L. The result shows that the concentration of Pd(II) had increased about 200 times. Pt(IV) is also concentrated at the same time.

The following process can be used to separate Pd(II) and Pt(IV) from each other. Pd(II) is precipitated out by dimethylglyoxime in the form of $Pd(C_4H_7O_2N_2)_2$. Pt(IV) is precipitated out by NH_4Cl in the form of $(NH_4)_2PtCl_6$. Thus, both Pd(II) and Pt(IV) can be concentrated by MTIR and then separated from each other in the concentrated solution.

ACKNOWLEDGMENT

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