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Recovery of the Rhodium(Ⅱ) Octanoate Dimer by Aminopyridine-modified Resin

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Abstract. Macroporous chloromethyl polystyrene resin (MCPR) was modified by (2, 3, 4-) amino pyridine. Then Rhodium (Ⅱ) octanoate dimer (ROD) was recovered by the amino pyridine-modified resin. The adsorption and elution of ROD on the modified resin were investigated. The results showed 2-amino pyridine modified resin was the best one.

Introduction

Rhodium (Ⅱ) Octanoate Dimer (ROD) (See Fig 1) is irreplaceable as a homogeneous catalyst**,** especial for the cyclopropanation [1], but Rhodium is very rare. Recycling of rhodium is a very important because of its very high value.

The recovery ROD from ethyl acetate solution which was used as catalyst for synthetic imipenem drugs in this article and the concentration of ROD in solution was about 1-3 ppm. It took long time in traditional recycling methods and needed heavy energy consumes. At First the ethyl acetate solution dissolved ROD was evaporated to get solid and the solid was dissolved by hydrochloric acid to got rhodium chloride. Finally rhodium chloride reacted with octanoic acid to obtain ROD. This recovery rate was very low and this method was uneconomic.

There were many reports about the synthesis of modified resins [2]: the modified resins which contain N, S, O, P elements which could complex with Rhodium or other metal ions, and there were some reported about synthesized amino pyridine modified resin which could complex with Pt(IV) [3] [4].

Ye Qing-song [5] found ROD could form stable complex with pyridine (See Fig 2). 3 kinds of amino pyridines were bonded with Macroporous chloromethyl polystyrene resin (MCRP) to get modified resin. Nitrogen atoms on the pyridines could coordinate with Rh on ROD, so ROD could be bonded from the solution through the chemical coordination.

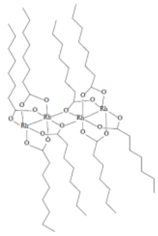


Fig.1 The structure of ROD

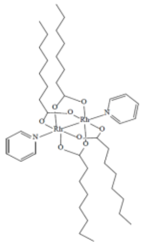


Fig.2 The structure of complex A(name)

In coordination experiments, 2-amino pyridine (2-AP) could form stable complex with ROD, but the complex formed by 3-minopyridine (3-AP) with ROD was not stable and 4-minopyridine (4-AP) could not form stable complex with ROD. So this article developed a new method for retrieve ROD in ethyl acetate by amino pyridine modified resin: MCPR reacted with amino pyridine to get modified resin, and ROD could be bonded on modified resin through the formation of complex between amino pyridine in MCPR, then the ROD could be recovered by elution.

Experimental

Complex from ROD with Amino Pyridines

Complex B of 2-AP and ROD. 2-AP (0.019g, 0.2mmol)/absolute alcohol (5mL) was added slowly ROD (0.077g, 0.1mmol) dissolved in 10 ml absolute alcohol and the mixture was kept stirring. The color of solution was changed from green to purple red. The mixture was still kept stirring for 2 h at room temperature and filtered. The purple red solid was got, yield 53%.

The purple red complex C was got from 3-AP and by similar method, yield 39%. But 4-AP could not form complex with ROD.

Modified MCPR and Examination

Modification of MCPR. Amino pyridine compounds (including 2-AP, 3-AP, 4-AP) were reacted with MCPR respectively to get three different modified resins (2-APR, 3-APR, 4-APR).

3.00 g of MCPR was added to 150 ml 1,4-dioxane and the mixture was kept overnight. 4.30 g of 3-AP was added and the mixture was stirred at 60℃ for 13h. After the resin was filtered and washed by water, it was soaked in 2% NaOH solution for 24h, then washed to pH=7 by deionized water and absolute alcohol in turn. The obtained modified resin was dried in vacuum. The similar methods were used for 3-APR, 4-APR.

Pretreatment: APR resin was washed by warm water, before it was soaked in 1mol/L NaOH for 24h and washed to pH=7 by deionized water. The obtained APR resin was mixed with 1mol/L HCl for 24h and then washed to pH=7 by deionized water. APR resin was soaked in l/L NaOH for 24h and washed to pH =7 by deionized water. At last APR resin was soaked in absolute alcohol for 12 h, filtered and dried.

Adsorption Experiment. After 100 mL of ROD in ethyl acetate solution was transferred into a dry Erlenmeyer flask, 3g of APR was added. 3ml of the solution was taken out at different time points for analysis. The samples were examined by Uv-vis spectrophotometry.

Elution. (your column, how much resin) 150 mL 2% thioura in ethanol as eluent, the flow rate was about 1 mL/min.

Result and Discussion

Constitution

The constitution was determined by PerkinElmer PE 2400II, the content of Rh determined by thermo ICAP6300.

Tab.1 Elemental Analysis of Complex B and C

Compound	(%)	C	H	O	N	Rh
B	Calc.	51.96	7.89	13.18	5.77	21.20
	Found.	51.90	7.90	13.17	5.74	21.29
C	Calc.	51.96	7.89	13.18	5.77	21.20
	Found.	51.92	7.71	13.16	5.75	21.46

Structures and Examinations

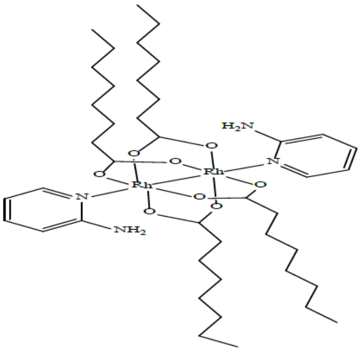
Tab.2 Selected bond lengths [Å] and angles [°] for complex B

Rh1-O1	2.020(4)	Rh1-O2	2.032(4)
Rh1-O4	2.039(4)	Rh1-O3	2.044(4)
Rh1 –N2	2.282(5)	Rh1-Rh1A	2.4047(8)
O1-Rh1-O2	91.03(19)	O1-Rh1-O4	175.42(16)
O2-Rh1-O4	89.91(19)	O1-Rh1-O3	88.49(18)
O2-Rh1-O3	175.45(16)	O4-Rh1-O3	90.22(18)
O1-Rh1-N2	89.29(17)	O2-Rh1-N2	88.02(17)
O4-Rh1-N2	95.22(17)	O3 Rh1 N2	96.50(17)
O1-Rh1-Rh1A	88.22(12)	O2-Rh1-Rh1A	87.72(13)
O4-Rh1-Rh1A	87.33(13)	O3-Rh1-Rh1A	87.75(12)
N2-Rh1-Rh1A	175.02(12)		

One crystal (0.27 x 0.28 x 0.26 mm) of complex B was taken to RXD By Bruker APEX-Ⅱ CCD, The diffraction light source was Graphite monochromated Mo Kα(λ=0.710730,the structure got by the SHELX 97 was shown in Fig 2, Fig3.

Tab.3 Crystal data and structure refinement summary for complex B

Formula	C21 H36 RhN2 O4	Crystal size (mm)	0.28 x 0.27 x 0.26
Mr	469.40	F(000)	980
Crystal system	Monoclinic	Reflections	4357/3383
Space group	P2(1)/c	collected/unique	
a(Å)	18.6226(16)	Data/restraints/Parameters	4357/260/246
b(Å)	15.5251(14)	Final R indice	R1= 0.0491
c(Å)	8.6869(7)	(I>2σ(I))	wR2=0.1421
β(°)	99.6850(10)	R indices(all data)	R1=0.0695
V	2475.7(4)		wR2=0.1714
Z	4	Goodness-of-fit on F2	1.175
Dcala(g cm-3)	1.259	Max. res peak nad hole (eÅ-3)	0.966 and -0.679



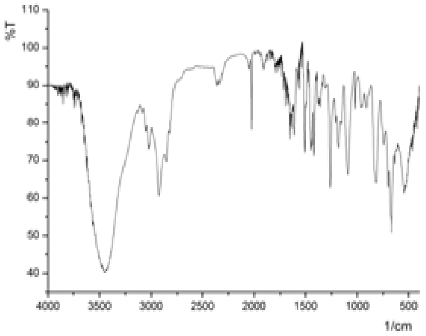
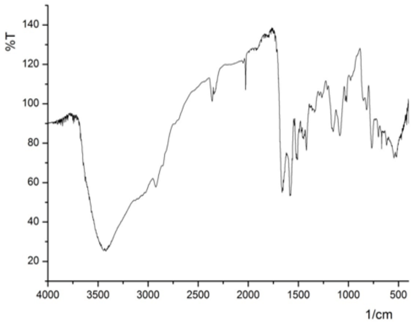


Fig.3 The structure of complex B

Fig.4 IR of MCPR



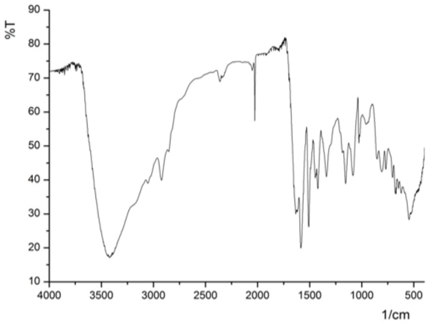
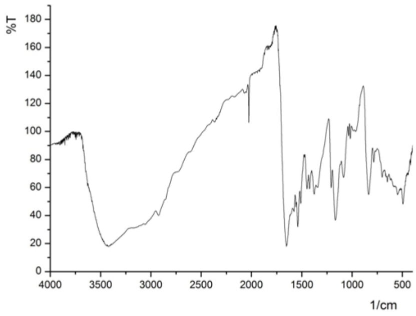


Fig.5 IR of 2-APR

Fig.6 IR of 3-APR



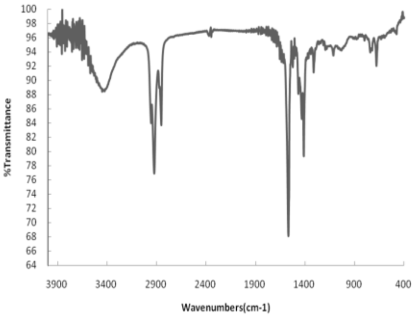


Fig.7 IR of 4-APR

Fig.8 IR of ROD

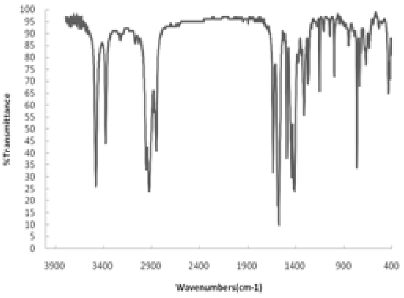


Fig.9 IR for complex B

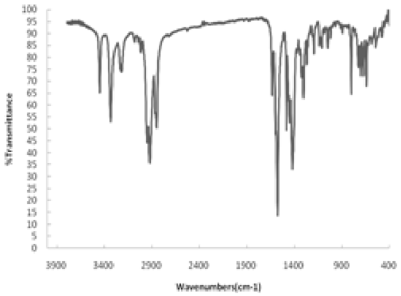


Fig.10 IR for complex C

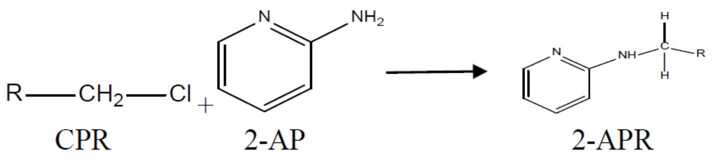


Fig.11 CPR +2-AP ——▶ 2-APR

Tab.5 The IR Data of 2-(3,4)- APR resin and MCPR

Compounds	N-H(cm^{-1})	C-N(cm^{-1})	C-Cl(cm^{-1})
MCPR	-	-	668.36
2-APR	1626.3,1578.2,1531.3	1171.8,1140.6,1078.1	-
3-APR	164036,1625.0,1593.2	1218.8,1127.5,1109.4	-
4-APR	1656.2,1593.8,1531.3	1203.1,1156.3,1062.5	-

There was one characteristic absorption peak for Cl-C at 668.36cm^{-1} in MCPR (Fig 1), but there were no absorption between 600-800 cm^{-1} in 2-APR(Fig 2)and 3-APR (Fig 4), which means that -Cl have been replaced by amino pyridine completely. In 3-APR (Fig 3), the absorption peak for Cl-C was disappeared, which means -Cl has been substituted by amino pyridine. In Fig 2-4 due to the bending vibration absorption of N-H, new absorption peaks were appeared at 1656.3~1531.3 cm^{-1}. New absorption peaks of stretching vibration of C-N were appeared at 1218.8~1062.5cm^{-1}. All these proved that (2, 3, 4-) amino pyridine have been grafted with MCPR. After modification the N contents of modified resins have been increased (see Table 3) (the data got by Kjeldahl determination).

Tab.6 Nitrogen content of 2-(3,4)- APR resin and MCPR

	MCPR	2-APR	3-APR	4-APR
N%	0.09	2.34	8.07	8.97
Amino pyridine, mmol/g	-	0.80	0.85	317
Cl-N replacement,%	-	16.7	59.4	66.0

The IR of complex B and C were list in Table 7, the difference between υas (COO^-) and υs (COO^-) means the carboxyls were bidentate-bridging ligands.

Tab.7 IR for complexes

Complex	N-H	C-H	C=N	pyridine	υas (COO-)	υs (COO-)	$C\text{-}N^-$
ORD		2954,2922,2851			1433	1412	
Complex B	3479,3376,3227	2956,2925,2854	1637	1579,1493	1446	1411	1315
Complex C	3449,3334,3221	2950,2924,2850	1634	1578,1484	1450	1421	1305

New peaks of C=N appeared at 1637 cm^{-1} and 1634 cm^{-1} respectively in IR spectrums of complex B and complex C, which proved that the amino pyridine have formed complex with ROD.

Adsorption Results

4-APR. The adsroption could be divided into two stages:(1)the adsorption amount reached to the Max. After 1.5 min, (2) the adsorption was dissociated almost ROD after 1.5 min. The equilibrium adsorption capacity was 0.32mg/g.

Tab.8 The adsorption data of 4-APR

t/min	0	0.5	1	1.5	2.0	2.5	3.0	3.5	4.5	5.5	10.5	15.5	20.5
adsorption mg/g	0.00	1.90	4.42	5.66	5.49	0.43	0.59	0.33	0.17	0.11	0.33	0.54	0.48

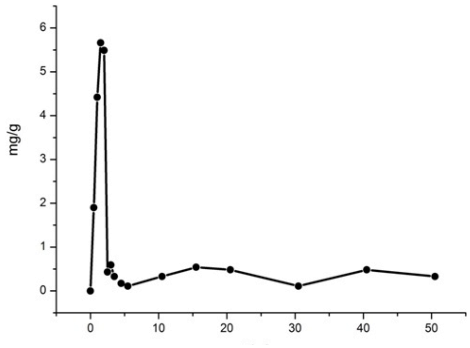


Fig.12 Adsorption curve of 4-APR

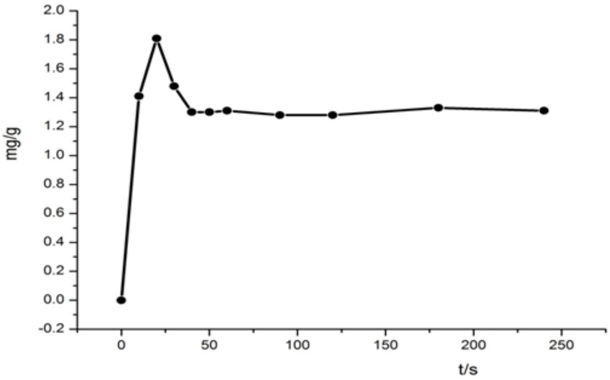


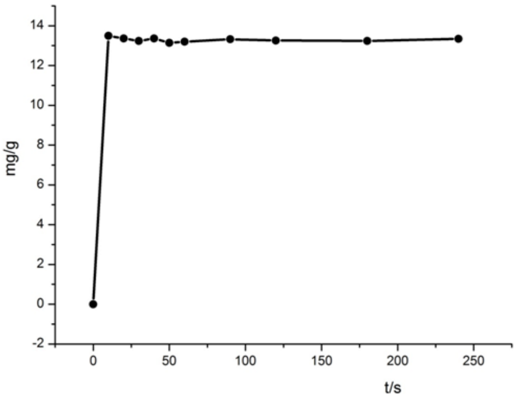
Fig.13 Adsorption curve of 3-APR

3-APR. The adsroption curve could be divided into two stages:(1)the adsorption amount reached the Max. after first 20 seconds. (2) the adsorption was kept stablely after 40 seconds. The equilibrium adsorption capacity was 1.44 mg/g.

Tab.9 The adsorption data of 3-APR

t/s	0	10	20	30	40	50	60	90	120	180	240
Adsorption mg/g	0.00	1.41	1.81	1.48	1.30	1.30	1.31	1.28	1.28	1.33	1.31

2-APR. The adsroption curve could also be divided into two stages at 25℃:(1)the adsorption was got the Max. value after first 10 seconds, (2) the adsorption was kept stablely after 10 seconds, the equilibrium adsorption capacity was 13.3 mg/g. When the temperature decreased to 0℃, the adsorption amount lowered to 2.40 mg/g.



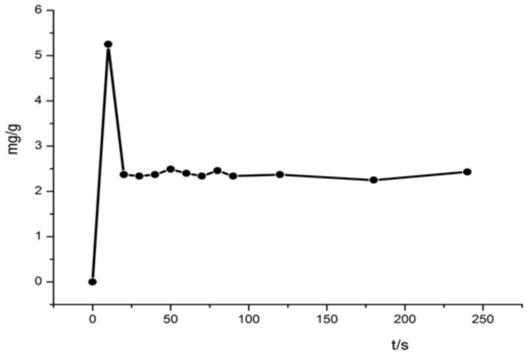


Fig.14 Adsorption curve of 2-APR at 25℃ Fig.15 Adsorption curve of 2-APR at 0℃

Tab.10 The adsorption data of 2- APR at 25℃

t/s	0	10	20	30	40	50	60	90	120	180	240
Adsorption mg/g	0.00	13.49	13.36	13.24	13.36	13.14	13.20	13.32	13.26	13.24	13.34

Tab.11 The adsorption data of 2- APR at 0℃

t/s	0	10	20	30	40	50	60	70	80	90	120	180	240
Adsorption mg/g	0.00	5.25	2.37	2.34	2.37	2.49	2.40	2.34	2.46	2.34	2.37	2.45	2.43

Elution Results

The adsorbed ROD was added into a solution of 2% thiourea in ethanol solution; the ROD concentration was tested by atomic absorption spectroscopy. The elution recovery was nearly 99.5%.After elution, IR spectrum of modified resin matched with the IR of modified resin before adsorption.

Conclusions

Amino pyridines (2-APR, 3-APR) could form complexes with ROD. The amino pyridine (2-APR, 3-APR, 4-APR)modified resin were prepared by MCPR reacted with amino pyridine compounds (2-AP, 3-AP, 4-AP), respectively. The adsorptive ability of amino pyridine compounds to ROD was tested. The complex formed by 4-APR and ROD was very unstable, and this was consistent with the fact that it could not form stable complex by ROD reacted with 4-amino pyridine. 3-APR could form stable complex with ROD. The 2-APR also could form stable complex with ROD, and its adsorption value was high to 2.43 mg/g. The adsorbed ROD could be eluted by 2% thiourea ethanol solution. The modified resin could be reused for fours times.

The rate for adsorption were very quick, different from other resin adsorption, the reason will be studied in the future.

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