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New compound N-methyl-N-isopropyl octanthioamide for palladium selective extraction and separation from HCl media

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Abstract: To seek more efficient extractant for Pd recovery from leaching solution of spent automotive catalysts, a new compound N-methyl-N-isopropyl octanthioamide (TA-813) was synthesized and characterized through FT-IR, ^{1}H NMR, ESI-MS and elemental analysis. Its extraction and stripping behaviors for Pd were studied. To evaluate its reusability performance, extraction−stripping cycles were carried out. Finally, TA-813 was applied to separating Pd from simulated leaching solution of spent automotive catalysts. TA-813 shows fast extraction kinetics, high extraction efficiency and specific selectivity for Pd. During extraction two TA-813 molecules coordinate with one Pd. The loaded Pd in the organic phase is efficiently stripped by neutral and acidic thiourea solutions. TA-813 shows no loss in activity after eight extraction−stripping cycles. Even from simulated leaching solution of spent automotive catalysts, in which the concentrations of some purities (La, Ce, Mg, Al) are much higher than that of Pd, Pd is still selectively extracted.
Key words: palladium; recovery; separation; spent automotive catalyst; thioamide

1 Introduction

Platinum group metals (PGMs), of which total proved reserves are only 70000 t in the world, are very rare and concentrated in a few countries (89.9% in South Africa, and 5.6% in Russia) [1]. The recovery of PGMs from spent automotive catalysts is an urgent and effective way to relieve the contradiction between their supply and demand.

To recover PGMs from spent automotive catalysts, two main steps are necessary: transferring PGMs from spent automotive catalyst into solutions, and PGMs individual separation to obtain pure Pd, Pt and Rh products. For the second step, precipitation [2,3], solvent extraction [4−6], solid phase extraction [7,8] and membrane separation [9] are commonly used. Among these methods, solvent extraction is widely adopted due to its simplicity, continuity and high selectivity. Pd selective extraction has always been challenging. Though commercialized di-*n*-octylsulfide (DOS), di-*n*-hexylsulfide (DHS), LIX 64N and LIX 84I have excellent selectivity for Pd, they are gradually oxidized during contact with high acidic PGM solutions, which greatly reduces the Pd separation efficiency. Besides, they have very slow extraction kinetics for Pd [10−12]. For example, DHS needs 1−3 h to reach equilibrium, while DOS needs several hours [13]. Other commercialized extractants TBP [14,15], Alamine 336 [16], Alamine 308 [14] and dibutyl sulfoxide [17] have

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no specific selectivity for Pd. They are not as efficient as sulfides and oximes on Pd recovery from leaching solution of spent automotive catalysts.

In recent years, many novel extractants have been synthesized and applied in Pd recovery from real/simulated leaching solution of spent automotive catalysts, such as alkylated dioxa-dithiacrown ether derivatives[18], thiophosphate compound 1,3-bis(diethoxythiophosphinoyloxy) benzene [19], SCS type pincer extractants [11,20], ionic liquid trioctyldodecyl phosphonium chloride ($P_{8,8,8,12}Cl$) [21], calix [4] arene-based di-*n*-alkylamino extractants [22−24], thiocarbamoyl substituted azothiacalix [4] arene derivatives [25], thiodiphenol-based *n*-dialkylamino extractants [26], heterocyclic dithioether [27] and asymmetric branched alkyl sulfoxides [28]. Most of these extractants have complex structures and the drawbacks of high price, slow extraction kinetics, poor selectivity, emulsification in commercialized diluents, or just suitable for Pd selective extraction from low acidic solutions (< 1 mol/L HCl).

To explore more efficient extractant to recover Pd economically and environment-friendly from leaching solution of spent automotive catalysts, we synthesized a new extractant of thioamide, namely N-methyl-N-isopropyl octanthioamide (marked as TA-813). Its structure is shown in Fig. 1. We confirmed its structure through FT-IR, ^{1}H NMR, ESI-MS and elemental analysis, and investigated the effect of various parameters such as oscillation time, TA-813 concentration and hydrochloric acid concentration on its extraction and separation performance for Pd. We evaluated the number of countercurrent extraction and stripping stages through McCabe-Thiele diagrams, and discussed the composition of the extracted complex based on the maximum Pd loading capacity and slope analysis method. We also did extraction−stripping cycles to evaluate its reusability performance. Finally, we selectively extracted Pd with TA-813 from the simulated leaching solution of spent automotive catalysts.

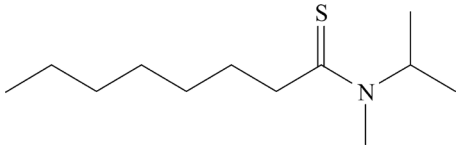


Fig. 1 Chemical structure of N-methyl-N-isopropyl octanthioamide (TA-813, structural formula: $C_{12}H_{25}SN$, MW=215.40)

2 Experimental

2.1 Reagents

n-octanoic acid (chemical purity, 98%) was purchased from Aladdin Reagent Company. Thionyl chloride ($SOCl_2$) with purity of 99% was bought from Shanghai Macklin Biochemical Co., Ltd. *N*-methylisopropylamine (98%) was provided by Beijing OuHe Technology Co., Ltd. Lawessons reagent (>98%) was produced by Adamas Reagent Ltd. Organic solvents absolute ethyl ether, toluene, petroleum ether (60−90 ℃) and ethyl acetate were all analytical reagents (A.R.) and bought from Sinopharm Chemical Reagent Co., Ltd. Column chromatography silica gel (180−250 μm) (Qingdao Haiyang Chemical Co., Ltd.) was used to purify the final product.

Platinum group metals (PGMs) $PdCl_2$ (A.R.), $PtCl_4$ (Pt ≥57%) and $RhCl_3·3H_2O$ (99%) were respectively bought from Sinopharm Chemical Reagent Co., Ltd, Shanghai Macklin Biochemical Co., Ltd and Energy Chemical. Non-PGMs $FeCl_3·6H_2O$, $MgCl_2·6H_2O$, $CuCl_2·2H_2O$, $CoCl_2·6H_2O$ and $NiCl_2·6H_2O$ were all A.R., while $ZrCl_4$ and $CeCl_3·7H_2O$ were both with purity of 99.9%. Hydrochloric acid (guarantee reagent, G.R.) and thiourea (A.R.) were both provided by Sinopharm Chemical Reagent Co., Ltd. Diluents kerosene (Aladdin Reagent Company) and 2-ethyl-1-hexanol (Macklin Biochemical Co., Ltd) were reagent grade and A.R., respectively.

2.2 Instrument

The synthesis of TA-813 was carried out on a DF−101S thermostatic magnetic stirrer with oil bath (Shanghai Lichen Bangxi Instrument Co., Ltd.). A R−1001−V Rotary Evaporator (Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd.) was adopted to remove organic solvent in vacuum. The FT-IR, ^{1}H NMR and ESI-MS spectra of TA-813 were recorded on a PerkinElmer Frontier FT-IR Spectrometer, a JOEL JNM-ECA600 spectrometer and a Bruker ESQUIRE-LC mass spectrometer, respectively. The elemental composition of TA-813 was analyzed by an Elemantar: Vario EL cube.

During extraction, a UMV−2 Multi-tube Vortexer (Beijing Usun Technologies Co., Ltd.) was used to mix aqueous and organic phases. A

Guanghe TD4C Low Speed Tabletop Centrifuge was used for assisting phase separation. The metal ion concentrations in the feed solutions and raffinates were determined on an iCAP 7400 ICP-OES (Thermo Fisher Scientific).

2.3 Extractant synthesis

TA-813 was synthesized through the following three steps (see Scheme 1).

Firstly, a mixture of 7.2 g *n*-caprylic acid and 8.0 g $SOCl_2$ was refluxed for 1 h. And then, the excess $SOCl_2$ was removed by evaporation in vacuum. After that, 30 mL absolute ethyl ether was added. Thus, the octanoyl chloride-ethyl ether solution was obtained.

Secondly, the octanoyl chloride-ethyl ether solution was slowly added to a mixture of 4.0 g N-methylisopropylamine and 8.4 g $NaHCO_3$ saturated aqueous solution under stirring at room temperature and reacted for 1 h. And then 50 mL ethyl ether was added and continued to react for 0.5 h. After that, the aqueous phase was separated out. The organic phase was sequentially washed with diluted HCl and saturated NaCl solutions, and then dried with anhydrous Na_2SO_4. After filtration, the ethyl ether was removed by evaporation in vacuum and 7.4 g N-methyl-N-isopropyl octanamide (yield: 74.4%) was obtained.

Thirdly, 9.45 g Lawessons reagent and 100 mL dried toluene were added to the N-methyl-N-isopropyl octanamide. This mixture was refluxed for 4 h. And then, 50 mL deionized water was added and maintained at 90 ℃ for 0.5 h. After cooling to room temperature, the aqueous phase was separated out, while the organic phase was washed with 10% $NaHCO_3$ solution three times and dried with anhydrous Na_2SO_4. After filtration, the toluene was removed by evaporation in vacuum and a yellow waxy solid was obtained. This crude product was purified by silica gel column chromatography with petroleum ether: ethyl acetate of 2:1 as eluent. Finally, a clear yellowish viscous liquid was obtained (6.9 g, yield: 86.3%).

2.4 General extraction procedure

Certain volumes of organic and aqueous solutions were sealed in a 10, 20 or 50 mL centrifugal tube, and oscillated on a Multi-tube Vortexer at 2500 r/min for 20 min. And then, the mixture was centrifugated at 2500 r/min for 5 min to accelerate phase separation. After that, the aqueous phase was separated for metal ion determination by ICP-OES. The corresponding metal ion concentration in the organic phase was calculated by mass balance.

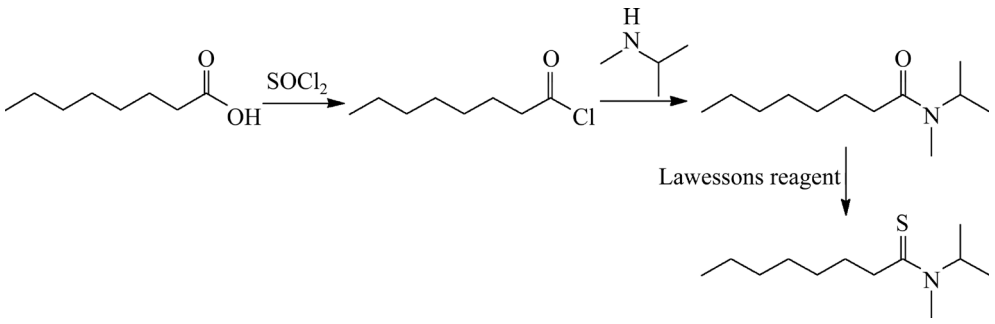
The diluent was a mixture of kerosene and 2-ethylhexanol with volume ratio of 1:1, namely 50% kerosene and 50% 2-ethylhexanol (*V*/*V*). All the extraction experiments were carried out at room temperature.

3 Results and discussion

3.1 TA-813 characterization

The purified TA-813 was first characterized by FT-IR to give the functional group information. The results are shown in Fig. 2. The peaks at 2856.08, 2927.36 and 2956.45 cm^{-1} are C—H stretching vibrations, while those at 1128.93, 1352.88 and 1486.72 cm^{-1} are three typical mixed vibrations of aliphatic tertiary thioamide group [29,30]. There are no peaks in the range of 1675−1645 cm^{-1}, indicating that all the C═O groups are transformed into C═S [31].

^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm: 0.882 (t, *J*=9.6 Hz, 3H, —CH_2—$C\underline{H}_3$), 1.187 and 1.275 (d, *J*=9.6 Hz, 6H, —N—$CH(C\underline{H}_3)_2$), 1.24−1.44 (m, 8H, CH_3—$(C\underline{H}_2)_4$—), 1.66−1.76 (m, 2H, —$C\underline{H}_2$—



Scheme 1 Synthesis route of N-methyl-N-isopropyl octanthioamide (TA-813)

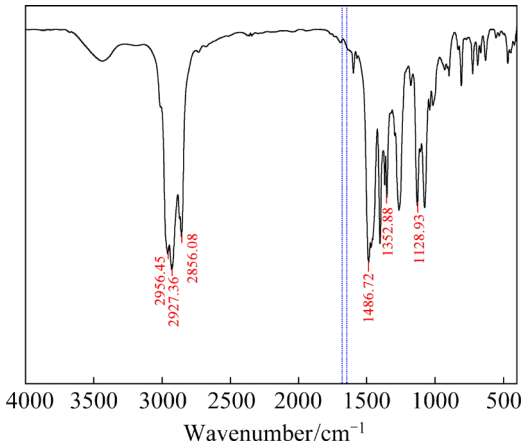


Fig. 2 FT-IR spectrum of TA-813

CH_2—C═S), 2.904 and 2.782 (t, *J*=12.0 Hz, 2H, —CH_2—C═S), 3.267 and 3.063 (s, 3H, N—CH_3), and 4.479 and 5.934 (sep, *J*=10.2 Hz, 1H, —N—C<u>H</u>(CH_3)$_2$). ESI-MS, *m*/*z*: 216.5 $(M+1)^+$. Elemental analysis/%: C 66.39 (Calcd. 66.91), H 11.31 (Calcd. 11.70), N 6.87 (Calcd. 6.50), and S 14.35 (Calcd. 14.89).

3.2 Effect of equilibrium time on Pd extraction

The effect of oscillation time on Pd extraction was first studied at a speed of 2500 r/min. The results are shown in Fig. 3. The Pd extraction rate (*E*) basically remains unchanged when the oscillation time exceeds 10 min. This indicates that TA-813 has relatively fast extraction kinetics for Pd. To ensure all the extractions reaching equilibrium, an oscillation time of 20 min is adopted in the following experiments.

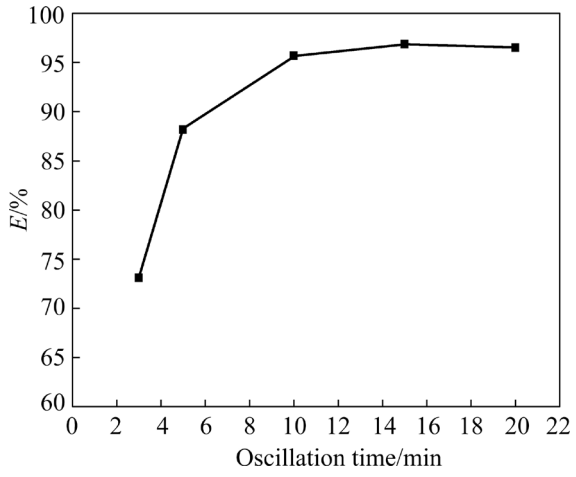


Fig. 3 Effect of oscillation time on Pd extraction (organic phase: [TA-813]=0.5 g/L; aqueous phase: [Pd]=58 mg/L, [HCl]=3 mol/L; A/O=2:1)

3.3 Effect of TA-813 concentration on Pd extraction

The effect of TA-813 concentration on Pd extraction was studied. The TA-813 concentration was in the range of 0.1−2.0 g/L. The relationship between Pd extraction rate and TA-813 concentration is shown in Fig. 4(a). The Pd extraction rate increases rapidly as the TA-813 concentration is increased from 0.1 to 0.5 g/L. When the TA-813 concentration exceeds 1.0 g/L, Pd in the aqueous phase is quantitatively extracted.

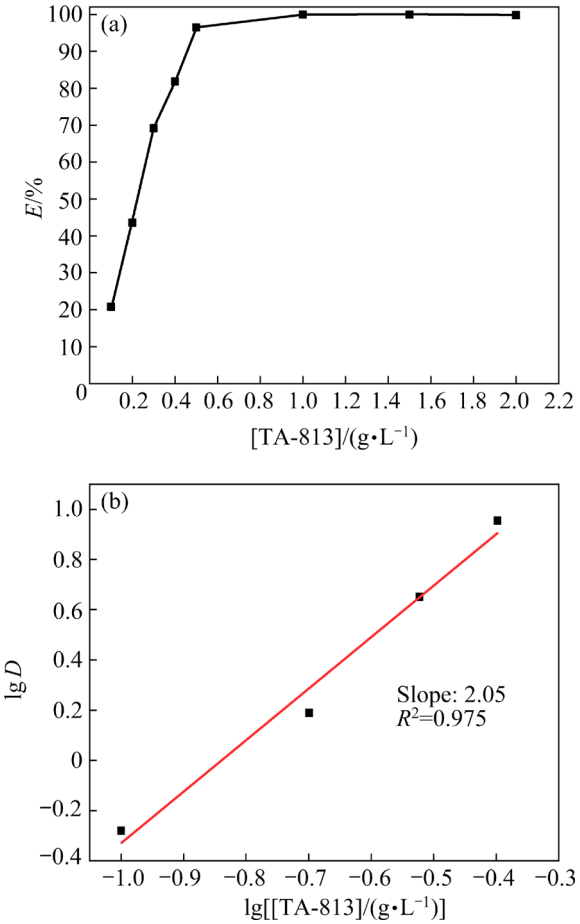


Fig. 4 Effect of TA-813 concentration on Pd extraction (a) and relationship between lg *D* and lg[TA-813] (b) (aqueous phase: [Pd]=58 mg/L, [HCl]=3 mol/L; A/O=2:1)

The molar ratios of TA-813 to Pd that extracted into the organic phase at the TA-813 concentration ≤0.5 g/L were calculated. The results are shown in Table 1. The Pd concentration in the organic phase after equilibrium, which is denoted as $[Pd]_{(o)}$, was calculated according to Eq. (1). The molar ratio of TA-813/Pd at different TA-813 concentrations are all about 2:1, indicating that two

TA-813 molecules coordinate with one Pd during extraction. This is proved by the relationship between lg D and lg [TA-813] (Fig. 4(b)), where D is the distribution ratio, and it equals to $[Pb]_{(o)}/[Pd]_{(a)}$ at equilibrium. The slope of the fitted line is 2.05 with correlation coefficient (R^2) of 0.975.

$$[Pd]_{(o)}=\frac{58\times 2E}{106.4}\times 10^{-5} \quad (1)$$

where 58 is Pd concentration in the aqueous phase before extraction (mg/L), 2 is the phase ratio (A/O), and 106.4 is molar mass of Pd (g/mol).

Table 1 Molar ratio of TA-813/Pd in organic phase

[TA-813]/ (g·L^{-1})	[TA-813]/ (mmol·L^{-1})	$[Pd]_{(O)}$/ (mmol·L^{-1})	TA-813/Pd molar ratio
0.1	0.46	0.23	2:1
0.2	0.93	0.48	1.9:1
0.3	1.39	0.75	1.9:1
0.4	1.86	0.89	2.1:1
0.5	2.32	1.05	2.2:1

According to the Pourbaix diagram [32,33], Pd exists in the form of $[PdCl_4]^{2-}$ in chloride leaching solutions. $[PdCl_4]^{2-}$ is a square-planar configuration, in which the four chloride ions occupy the four coordination sites [13]. According to the principle of electric neutrality, there should be two chloride ions in the TA-813-Pd complex. Thus, the TA-813-Pd complex probably is $PdCl_2L_2$, where L stands for one molecular of TA-813. The reaction formula can be written as

$$[PdCl_4]^{2-}+2L=PdCl_2L_2+2Cl^- \quad (2)$$

3.4 Selectivity of extractant TA-813

The most commonly used three-way automotive catalysts simultaneously contain Pd, Pt and Rh. Therefore, the Pd, Pt and Rh extraction behaviors by TA-813 at different acidities (1−8 mol/L HCl) were investigated. The aqueous feed solutions were ternary mixed solutions of Pd, Pt and Rh, whose concentrations were 55±2, 61±2 and (57±2) mg/L, respectively. The phase ratio A/O was 2:1. The results are shown in Fig. 5.

At any acidities of 1−8 mol/L HCl, Pd is all quantitatively extracted at both 1.0 and 2.0 g/L TA-813, while all Rh is hardly extracted. As to Pt, it is basically unextracted at lower acidities (1−4 mol/L HCl). By further increasing the acidity from 5 to 8 mol/L HCl, the Pt extraction steadily increases. The Pt extraction at 2.0 g/L TA-813 is apparently larger than that at 1.0 g/L TA-813.

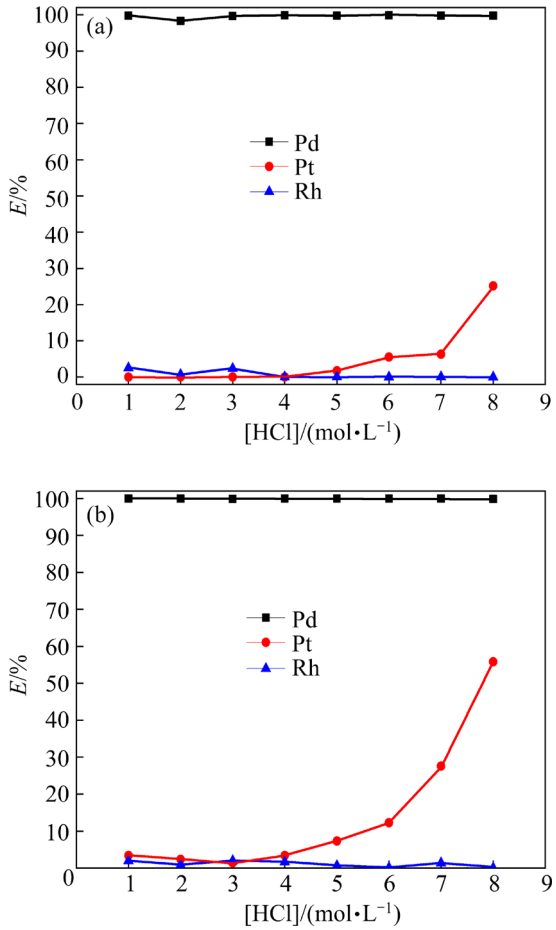


Fig. 5 Selectivity for Pd from Pd−Pt−Rh mixed solutions under different acidities and different extractant concentrations: (a) [TA-813]=1.0 g/L; (b) [TA-813]=2.0 g/L (aqueous phase: [Pd]=(55±2) mg/L, [Pt]=(61±2) mg/L, [Rh]=(57±2) mg/L; A/O=2:1)

In chloride leaching solutions, Pd, Pt and Rh exist in form of coordination anions, namely $[PdCl_4]^{2-}$, $[PtCl_6]^{2-}$ and $[RhCl_6]^{3-}$, respectively [32,33]. $[PdCl_4]^{2-}$ is labile and its Cl^- has a rapid exchange rate. TA-813 has a soft ligand — S atom, which has strong interaction with soft metal Pd. Therefore, Pd is quantitatively extracted. Both $[PtCl_6]^{2-}$ and $[RhCl_6]^{3-}$ are much more stable than $[PdCl_4]^{2-}$, and their Cl^- is hardly to be exchanged. Thus, $[PtCl_6]^{2-}$ and $[RhCl_6]^{3-}$ are hardly extracted in low acidic solutions (<4 mol/L HCl). With a further increase in acidity (>4 mol/L HCl), the S atom of TA-813 is protonated. The protonated TA-813 interacts with $[PtCl_6]^{2-}$ through electrostatic attraction. The more concentrated HCl media, the easier protonation of

TA-813, which results in an increase of Pt extraction.

Base metals also always coexist with Pd in leaching solution of automotive catalysts, such as Fe, Mg, Ce, La, Ni, Cu, Co and Zr. Thus, it is necessary to investigate these base metal extraction behaviors by TA-813. The aqueous feed solution was a mixture of Pd, Fe, Mg, Ce, Ni, Cu, Co and Zr with acidities of 1−8 mol/L HCl. As La and Ce are adjacent rare earth metals and they have similar chemical properties, La was not contained in the aqueous feed solution. The organic phase was 1.0 g/L or 2.0 g/L TA-813. The results are shown in Fig. 6.

At any investigated acidities, Pd is all quantitatively extracted, while Mg, Ce, Ni, Cu, Co and Zr are hardly extracted. At lower acidities (1−3 mol/L HCl), Fe is all hardly extracted. With a further increase in HCl concentration from 4 to 8 mol/L HCl, the Fe extraction efficiency increases rapidly. Pt has very similar extraction behavior to Fe. At the same conditions, Fe has much higher extraction than Pt (Figs. 5 and 6), indicating that Fe is more easily extracted than Pt by TA-813. Base metals Fe, Mg, Ce, Ni, Cu, Co and Zr are all hard metals. TA-813 cannot interact with them through coordination. Similar to $[PtCl_6]^{2-}$, Fe, which exists in the form of $[FeCl_4]^-$ in high acidic chloride media, can interact with protonated TA-813 through electrostatic attraction. Therefore, all base metals are not extracted when the acidity is ≤ 3 mol/L HCl, and the Fe extraction increases as the acidity is further increased from 4 to 8 mol/L HCl.

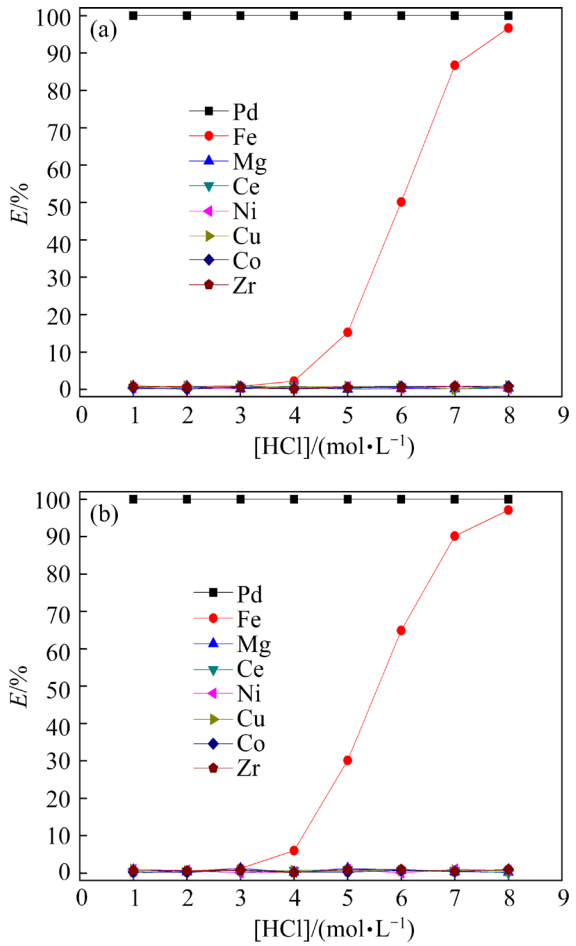


Fig. 6 Selectivity for Pd from Pd-base metal mixed solutions under different acidities and different extractant concentrations: (a) [TA-813]=1.0 g/L; (b) [TA-813]=2.0 g/L (aqueous phase: [Pd]=(52±2) mg/L, [Fe]=(60±2) mg/L, [Mg]=(61±2) mg/L, [Ce]=(59±20 mg/L, [Ni]=(55±2) mg/L, [Cu]=(58±2) mg/L, [Co]= (52±2) mg/L and [Zr]=(55±2) mg/L mixed solutions; A/O=2:1)

Based on the above results and discussion, TA-813 has excellent selectivity for Pd from low acidic chloride solutions (≤3 mol/L HCl). As TA-813 hardly extracts Fe and Pt at acidity of ≤3 mol/L HCl, the loaded Pt and Fe in the organic phase will be easily scrubbed by diluted HCl.

3.5 Pd extraction isotherm by 1.0 g/L TA-813

To evaluate the number of Pd countercurrent extraction stages by TA-813, the McCabeThiele diagram was drawn by varying the phase ratio A/O from 1:7 to 15:1. The aqueous feed solution contained 58 mg/L Pd with acidity of 3 mol/L HCl. The organic phase contained 1.0 g/L TA-813. The results are shown in Fig. 7. The McCabeThiele diagram indicates that nearly all Pd in the aqueous phase will be extracted into the organic phase after

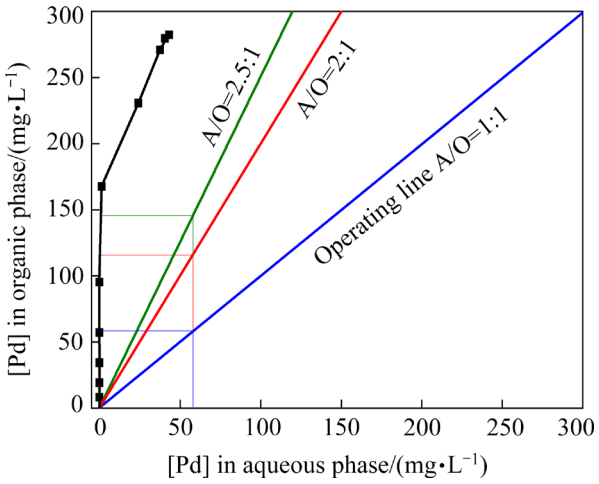


Fig. 7 McCabe-Thiele diagram for Pd extraction with TA-813 (organic phase: [TA-813]=1.0 g/L; aqueous phase: [Pd]=58 mg/L, [HCl]=3 mol/L)

only one extraction stage when the A/O is ≤2.5:1. TA-813 has high extraction efficiency and specific selectivity for Pd, which can avoid the dispersion of PGMs in the process of Pd separation.

The corresponding Pd concentration in the organic phase at different phase ratios are shown in Fig. 8. The Pd concentration in the organic phase basically levels off when the A/O is ≥13:1, which indicates that the maximum loading capacity of 1.0 g/L TA-813 for Pd is 280 mg/L. Under this condition, the molar ratio of TA-813 to Pd is also about 2:1. This is consistent with the results obtained in Section 3.3.

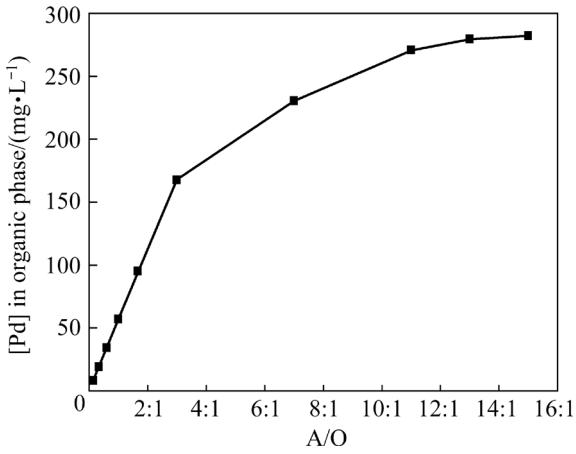


Fig. 8 Effect of phase ratio on Pd loading in organic phase

3.6 Pd stripping behaviors by neutral/acidic thiourea

Stripping behaviors of the loaded Pd in the organic phase were investigated by neutral ([HCl]= 0 mol/L) and acidic ([HCl]=0.1 and 0.5 mol/L) thiourea solutions. The thiourea concentration was set in the range of 0.1−1.0 mol/L. The results are shown in Fig. 9. The loaded Pd is easily stripped by either neutral or acidic thiourea solutions. Acidic thiourea solutions (0.1 and 0.5 mol/L HCl) are more efficient for Pd stripping than neutral thiourea solutions(0 mol/L HCl).

3.7 Pd stripping isotherm by acidic thiourea

Stripping phase ratio (O/A) and the number of countercurrent stripping stages are very important. Large O/A can obtain high concentrated metal solutions, which is beneficial to Pd recovery. Small number of countercurrent stripping stages can avoid Pd dispersion. The McCabe-Thiele diagram was drawn by varying O/A from 1:5 to 10:1 to find out the appropriate O/A and evaluate the corresponding number of stripping stages for Pd complete stripping. The organic phase was 1.0 g/L TA-813 loaded with 62 mg/L Pd, while the stripping solution was 0.2 mol/L thiourea + 0.5 mol/L HCl. The results are shown in Fig. 10.

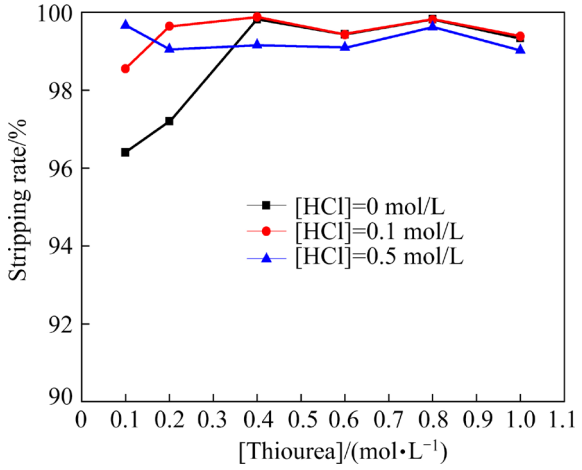


Fig. 9 Stripping behaviors of loaded Pd by neutral and acidic thiourea solutions (organic phase: [TA-813]= 1.0 g/L loaded with 58 mg/L Pd; O/A=1:1)

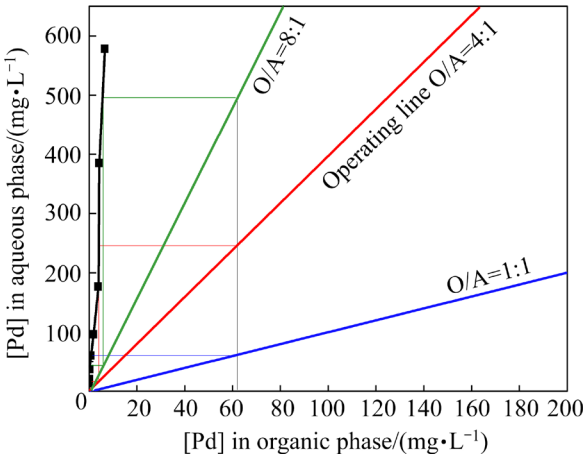


Fig. 10 McCabe-Thiele diagram for Pd stripping with 0.2 mol/L thiourea + 0.5 mol/L HCl mixed solution (organic phase: [TA-813]=1.0 g/L loaded with 62 mg/L Pd)

According to the McCabe-Thiele diagram, when the stripping phase ratio O/A is ≤1:1, only one stage is needed to almost completely strip the loaded Pd. By increasing O/A from 1:1 to 8:1, one more stage is needed. Even though, more concentrated Pd solution will be obtained when the O/A is >2:1. For the given stripping system, two stripping stages with O/A of 8:1 is the optimal condition.

3.8 Reusability performance of TA-813

To investigate the extractant stability in high acidic chloride media during extraction, TA-813 reutilization experiments were carried out. The TA-813 concentration in the organic phase is 1.0 g/L. The aqueous feed solution was 56 mg/L Pd with acidity of 3 mol/L HCl. The stripping solution was 0.2 mol/L thiourea + 0.5 mol/L HCl. After each stripping, the organic phase was scrubbed with 3 mol/L HCl to remove any residual thiourea. The phase ratios (A/O) of extraction, stripping and scrubbing are 2:1, 1:1 and 1:1, respectively. Eight extraction−stripping−scrubbing cycles were completed. The results are shown in Fig. 11. The Pd extraction rates are all more than 96% and basically remain unchanged during the eight extraction−stripping−scrubbing cycles. This indicates that TA-813 is stable in 3 mol/L HCl, of which acidity is optimal for Pd separation in the presence of Pt, Rh and base metals.

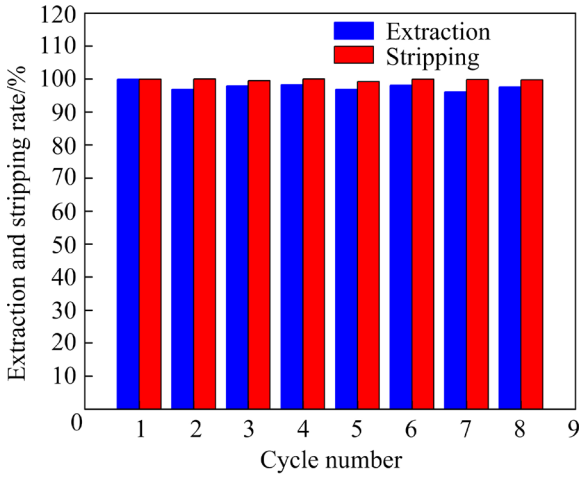


Fig. 11 Extraction and stripping rate of Pd in sequential extraction−stripping cycles

3.9 Pd extraction from simulated leaching solution of spent automotive catalysts

In leaching solution of spent automotive catalysts, some base metals usually have much thicker concentration than PGMs. The PGM concentrations are always different from each other. Hence, we prepared the simulated leaching solution according to Ref. [34], and separated Pd with TA-813. The metal concentrations are listed in Table 2. The organic phase was 1.0 g/L TA-813 dissolved in 50% kerosene−50% 2-ethylhexanol (*V*/*V*). Rh, Mg, Al and Zn are totally unextracted. Pd is completely extracted into the organic phase. The extraction rates of Pt, Fe, Cu, Ce and La are all ≤ 3.0% (see Fig. 12).

Table 2 Metal concentration in simulated leaching solution of spent automotive catalysts (mg/L)

Pd	Pt	Rh	Fe	Cu
133.4	60.6	15.0	40.6	7.3
Ce	La	Mg	Al	Zn
419.4	521.7	1106.0	3712.5	16.6

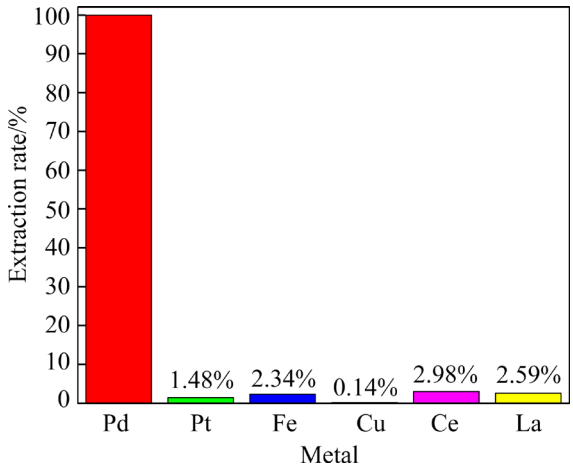


Fig. 12 Pd extraction from simulated leaching solution of spent automotive catalysts (organic phase: [TA-813]= 1.0 g/L; aqueous acidity: 3 mol/L HCl; A/O=1:1)

4 Conclusions

(1) A new extractant N-methyl-N-isopropyl octanthioamide (TA-813) was successfully synthesized. It has a simple structure and fast Pd extraction kinetics, less than 10 min to reach equilibrium at an oscillating speed of 2500 r/min.

(2) It has high efficiency to extract Pd, and it quantitatively extracts Pd with TA-813/Pd molar ratio of 2:1. At appropriate TA-813 concentration and phase ratio A/O, only one stage is needed to completely extract Pd.

(3) TA-813 has excellent selectivity for Pd. It quantitatively extracts Pd, while hardly extracts Pt, Rh, Fe, Mg, Ce, Ni, Cu, Co and Zr at acidities of [HCl] ≤3 mol/L.

(4) The loaded Pd in the organic phase is easily stripped by neutral and acidic thiourea solutions.

(5) TA-813 also shows good stability. The Pd extraction and stripping rates are unchanged in eight extraction−stripping cycles.

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新型化合物 N-甲基-N-异丙基硫代辛酰胺从盐酸介质中选择性萃取分离钯

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摘 要：为实现从废汽车尾气净化催化剂的浸出液中高效分离钯，合成一种新化合物 N-甲基-N-异丙基硫代辛酰胺(TA-813)。通过 FT-IR、^{1}H NMR、ESI-MS 和元素分析进行表征，研究 TA-813 对钯的萃取和反萃行为。通过萃取−反萃循环试验评估 TA-813 的循环使用性能，并用 TA-813 从废汽车尾气净化催化剂的模拟浸出液中选择性萃取分离钯。结果表明：TA-813 对钯萃取速度快、效率高、选择性好；2 个 TA-813 分子萃取 1 个 Pd；有机相中负载的钯可被中性和酸性硫脲高效反萃；TA-813 循环使用性能好，经过 8 次萃取−反萃循环，钯的萃取率没有降低。在废汽车尾气净化催化剂的模拟浸出液中，Pd 的浓度远低于杂质离子 La、Ce、Mg 和 Al 等，即便如此，TA-813 仍能实现钯的选择性高效分离。

关键词：钯；回收；分离；废汽车尾气净化催化剂；硫代酰胺

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