Selective Extraction of Precious Metal from Automotive Catalyst Residue by Thiacalix[6]arene Derivatives

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Two new thiacaIix[6]arene (TC6A) derivatives modified at the lower rims, which are TC6A-COOCH3 (1) and TC6A-COOC2H5 (2), respectively, were synthesized. The metal extraction properties of TC4A, TC6A, 1 and 2 from automotive catalyst residue solution containing platinum-group metal cations have been investigated. TC6A shows the highest extraction capability for Pd cation with higher selectivity. On the other hand, 1 shows the remarkable higher extraction ability for Zr cation between metal cations examined.

Key Words : calix[n]arenes, thiacalix[n]arenes, liquid-liquid extraction, precious metals

1. Introduction

Precious metals are important materials in many industrial fields such as fuel cell, solar cell, photocatalyst, and automotive catalyst, etc. Platinum-group metals (PGM) belonged in precious metals are important because they are used as catalyst materials, especially as an automotive catalyst. It is well known that three-way catalyst (TWC), which was composed of PGM such as platinum (Pt), palladium (Pd) and rhodium (Rh), can reduce more than 99% of emission of autoexhaust. It can respond to catalyze the reaction simultaneously, such as CO oxidation, hydrocarbon oxidation and NO reduction. Unfortunately, these three metals containing PGM are strictly limited in natural resource deposits. That's why a recycle of PGM from wastes and/or secondary resource such as spent automotive catalyst or residue is very important. For example, the recovery of PGM by the leaching from automotive catalyst residue has been reported [1]. So far, separation of precious metals is done by the solvent extraction because industrial process is very easy. It is usual way that dihexylsulfide (DHS), trioctylamine (TOA), tributylphosphate (TBP) are used as industrial extracting reagents. It is well known that these extracting reagents can extract precious metal from base metals selectivity. Unfortunately, these reagents can hardly separate particular precious metals from various precious metals. Therefore, novel reagents, which can separate precious metals effectively, are required.

On the other hand, calix[n]arenes (CnAs) and thiacalix[n]arenes (TCnAs) as a counterpart of CnAs are versatile materials that have been attracting much attention as a host molecule in molecular recognition chemistry and supramolecular chemistry [2]. Considerable attention has been recently focused on TCnAs because there are many features that are not presented in chemistry of CnAs [3]. TCnAs are composed benzene rings, linked via sulfur bridges instead of methylene units, which itself can make host-guest complexation with metal cations because sulfide functional groups has affinity for metal cations [4]. In a previous paper, we first reported a metal sensor system based on water soluble di-, tri-dansyl modified thiacalix[4]arene [5]. These compounds show the highest sensitivity for Cd2+ [6]. Iki et al reported the introduction of (ethoxycarbonyl) methoxy groups into TC4A on the lower rim [6]. The conformational isomers of 5,11,17,23-tetra-tert-butyl-37,38,39,40-tetrakis[(ethoxycarbonyl)methoxy]-2,8,14,20-tetrahexathiacalix[4]arene which were found to be able to extract particular alkali metal ions selectively. However, to our best knowledge, there is few reports on molecular extraction system including organic and inorganic compounds by modified TC6A and TC6A itself [7, 8]. It is because that the synthesis of TC6A is still difficult [9].

In this article, we would like to report the synthesis method of new TC6A derivatives, 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexakis[(methoxycarbonyl) methoxy]-2,8,14,20,26,32-hexathiacalix[6]arene (TC6A-COOCH3, 1), and 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexakis[(ethoxycarbonyl)methoxy]-2,8,14,20,26,32-hexathiacalix[6]arene (TC6A-COOC2H5, 2). The structures of these compounds are abbreviated in Scheme 1. Also, we would like to report the extraction capability of TC6A, 1 and 2.
with high selectivity from automotive catalyst residues, which is named as PGM solution [1].

2. Experimental


A suspension of TC6A (1.08 g, 1 mmol), K2CO3 (1.25 g, 9 mmol), and methyl bromoacetate (1.25 mL, 12 mmol) in acetone (100 mL) was stirred and refluxed for 24 h under nitrogen atmosphere. After cooling down to room temperature, the solvent was removed under reduced pressure. The unreacted methyl bromoacetate was removed in vacuo at 60°C for several hours. The resultant material added CHCl3, and then insoluble material was filtered. The solvent was removed under reduced pressure. The crude yellow powder was obtained, which was recrystallized from EtOH to give pure 1: yield: 1.2 g (82%), '1H NMR (300 MHz, CDCl3) δ 7.60-6.80 (br s, 12H, Ar), 4.66 (s, 12H, OCH,CO), 3.72 (s, 18H, COOCH3), 1.15-0.8 (br s, 54H, C(CH3)3). IR (KBr): 2961 (CH), 1769 and 1741 (C=O), 1206 (C-O) cm⁻¹. Anal. Calcld for C96H1200S6: C, 61.88; H, 6.39. Found: C, 61.85; H, 6.41.


A suspension of TC6A (1.08 g, 1 mmol), Cs2CO3 (2.94 g, 9 mmol), and ethyl bromoacetate (1.34 mL, 12 mmol) in acetone (100 mL) was stirred and refluxed for 3 h under nitrogen atmosphere. After cooling down to room temperature, the solvent was removed under reduced pressure. The unreacted ethyl bromoacetate was removed in vacuo at 60°C for several hours. The resultant material added CHCl3, and then insoluble material was filtered. The solvent was removed under reduced pressure. The crude yellow powder was obtained, which was recrystallized from EtOH to give pure 2: yield: 1.10 g (89%), '1H NMR (300 MHz, CDCl3) δ 8.15-6.55 (br s, 12H, Ar), 4.70 (s, 12H, OCH,CO), 4.22 (q, 12H, COOCH3), 1.28 (t, 18H, CH3), 1.23-0.65 (br s, 54H, C(CH3)3). IR (KBr): 2961 (CH), 1769 and 1737 (C=O), 1197 (C-O) cm⁻¹. Anal. Calcld for C96H1200S6: C, 61.88; H, 6.39. Found: C, 61.85; H, 6.41.

3. Results and Discussion

3.1 Synthesis of 1 and 2

The compounds of 1 and 2 were synthesized in reference to reported previous methods, which showed esterification of C4A and TC4A [6,10]. The modification of TC6A with methyl bromoacetate gave 1 in 82% yields. The '1H NMR spectrum shows no definite conformations in solution because those signals of tert-butyl and phenyl group were observed as broad singlet.

Also, TC6A was converted to 2 with ethyl bromoacetate in 69% yields. It is shown that '1H NMR spectrum indicates no definite conformations in solution because those signals of tert-butyl and phenyl groups were observed as broad singlet.

3.2 Liquid-liquid extraction

We studied a selective liquid-liquid extraction of metal cations in PGM solution by TC6A, 1 and 2. Additionally, to compare the extraction ability of TC4A also examined in liquid-liquid extraction with same condition. The composition and concentration of metal cations in PGM solution are shown in Table 1. The extractability, E%, was calculated by Eq. 1 and 2,

\[
E\% = \frac{[\text{metal}]_{\text{aq, final}}}{[\text{metal}]_{\text{aq, init}}} \times 100\%
\]

\[
[\text{metal}]_{\text{aq, init}} = [\text{metal}]_{\text{aq, init}} - [\text{metal}]_{\text{aq, final}}
\]

where [metal]_{aq, init} and [metal]_{aq, final} are initial and final concentration of metal cation in aqueous phase. The correct valences of metal cations are not known that automotive catalyst residue was leached by HCl and H2O.

Figure 1 shows extractability of TC4A and TC6A for PGM solution containing several metal cations. TC4A shows a small extractability for all metal cations and the selectivity for particular metal cation is not found. On the other hand, TC6A behaves quite differently from that of TC4A. TC6A shows the highest extractability for Zr and second highest one for Pd, which is ca. 50% and 60%, respectively. It is shown that the other metals were

<table>
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<tr>
<th>Metal cation</th>
<th>[metal]_{aq, init} (ppm)</th>
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<tr>
<td>Rh</td>
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</tr>
<tr>
<td>Pd</td>
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<tr>
<td>Pt</td>
<td>8.407</td>
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<td>Ce</td>
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<td>La</td>
<td>13.504</td>
</tr>
<tr>
<td>Y</td>
<td>0.731</td>
</tr>
</tbody>
</table>

Table 1 The composition and concentration of metal cations in PGM solution.
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Extracted with under ca. 10%. The high selectivity for metal cations by TC6A was recognized. Why the reason of the high selectivity for Pd and Zr by TC6A is not clear. It is undergoing to study of the mechanism. It might be explained that cavity size of TC6A would contribute extractability, because TC4A, which has smaller cavity size, does not show any extractability for metal cations examined.

Figure 2 shows extractability of TC6A, 1 and 2 for PGM solution. It is interesting that 1 shows high affinity for Zr with ca. 90% extractability, which is 30% increase than that of TC6A. However, 1 showed a little extractability for other metal cations examined. It is suggested that the remarkable high Zr selectivity by 1 should be resulted from corporative effect between carbonyl ester and sulfide groups of TC6A. However, 2, which differs only alkyl chain of ester group from that of 1, shows not so high extractability for metal cations examined. It might be a reason that the mobility of the ester groups goes down than that of 1 when host-guest complexation happens, which causes the weaker interaction between 2 and metal cation. The host 2 shows from 20 to 40% extraction ability for most metal cations except Ce and Ba. It is suggested that 2 can take middle rate favorable configuration for most metal cations except Ce and Ba.

4. Conclusion

In this study, we have demonstrated the liquid-liquid extraction of automotive catalyst residue solution (PGM solution) using TC4A, TC6A and TC6A derivatives. TC6A shows the remarkable high affinity for Pd and Zr with high selectivity. The ability of 1 for Zr extraction is higher than TC4A, TC6A and 2. These compounds such as TC6A and 1 are expected to be new extracting reagents to separate particular precious metals from various precious metals, with high selectivity. Now, we are undergoing to make different types of TC6A derivatives as metal ligands.

References


