

Reusability Investigation of a Ruthenium Catalyst during Ruthenium Ion-Catalyzed Oxidative Depolymerization of Lignite for the Production of Valuable Organic Acids

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Cite This: *ACS Omega* 2021, 6, 26613–26622



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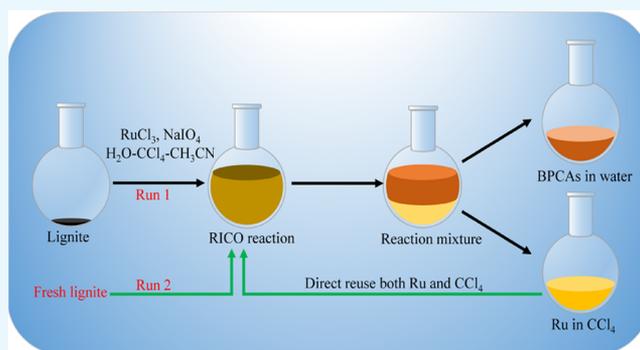


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ABSTRACT: A clean and efficient conversion process is essential for the utilization of low-rank coals. Lignite, a typical representative of the low-rank coal family, has huge potential for the production of valuable chemicals via the oxidative depolymerization reaction. Ruthenium ion-catalyzed oxidation (RICO) is an effective route for lignite depolymerization under mild conditions, but the high cost of precious Ru limits the potential large-scale application of RICO. How to recycle and reuse Ru is critical to promote the application of RICO. In this work, a novel and efficient approach for reusing Ru through recycling the solvent mixture containing Ru was established for RICO. First, the influence of different reaction parameters on the depolymerization degree of lignite and benzene polycarboxylic acid (BPCA) yields was investigated. Second, the distribution of Ru in the organic phase (OP), aqueous phase (AP), and residual solid phase (RSP) was analyzed after the RICO reaction. Finally, based on the distribution of Ru in different phases, a novel route of recycling Ru by reusing the Ru-containing solvents was proposed. The results showed that the dosage of RuCl_3 and NaIO_4 had a significant influence on both the depolymerization degree of lignite and BPCA yields. The distribution of Ru had a close relationship with the depolymerization degree of lignite and the dosage of NaIO_4 . After the depolymerization reaction, the CCl_4 phase containing Ru was reused directly as the solvent for the next run, which could fulfill the reuse of both CCl_4 and Ru. The results proved that the Ru-containing CCl_4 phase could maintain catalytic performance for 5 runs. This work provides an efficient route to reuse Ru for the RICO depolymerization of lignite into valuable organic acids. As far as we know, this is the first report concerning the recycling and reuse of Ru during the RICO of lignite. This work is important for the application of RICO in lignite depolymerization.



1. INTRODUCTION

Coal, as abundant fossil energy and resource, plays an important role in promoting the development of industry and social progress all over the world.^{1,2} Lignite, a kind of low-rank coal, is commonly regarded as an inferior fuel because of its high ash yield, high moisture content, low calorific value, etc.^{3,4} However, because of the high oxygen content and abundance of organic structural units such as an aromatic nucleus it is potentially useful to convert lignite into polycarboxylic acids through oxidation processes, especially valuable benzene polycarboxylic acids (BPCAs) used intensively in the pharmaceuticals industry and the polymer industry.^{5–11} Oxidative depolymerization of lignite is an important non-energy-intensive route to produce valuable organic acids (VOAs). Many oxidants and oxidation systems have been explored, such as the H_2O_2 system,^{12,13} NaClO aqueous system,^{14–16} alkali-oxygen oxidation,^{17–19} catalytic oxidation, etc.^{20,21} Miura et al.²² studied the oxidation of Morwell coal with H_2O_2 aqueous solution at 60 °C and

obtained a lot of water-soluble small-molecule compounds. With H_2O_2 , oxidation of lignite was carried out under mild reaction conditions, the conversion of lignite was low and the main products obtained were low-molecular-weight fatty acids. Sodium hypochlorite was also considered an effective oxidant for the low-temperature oxidation of lignite. Gong et al.²³ oxidized Huolinguole lignite with aqueous NaClO solution for 24 h at 30 °C, and the results showed that this oxidation method was effective for the depolymerization of coal. However, there were amounts of chlorinated compounds in the products, which was not conducive to product separation.

Received: July 25, 2021

Accepted: September 13, 2021

Published: September 28, 2021



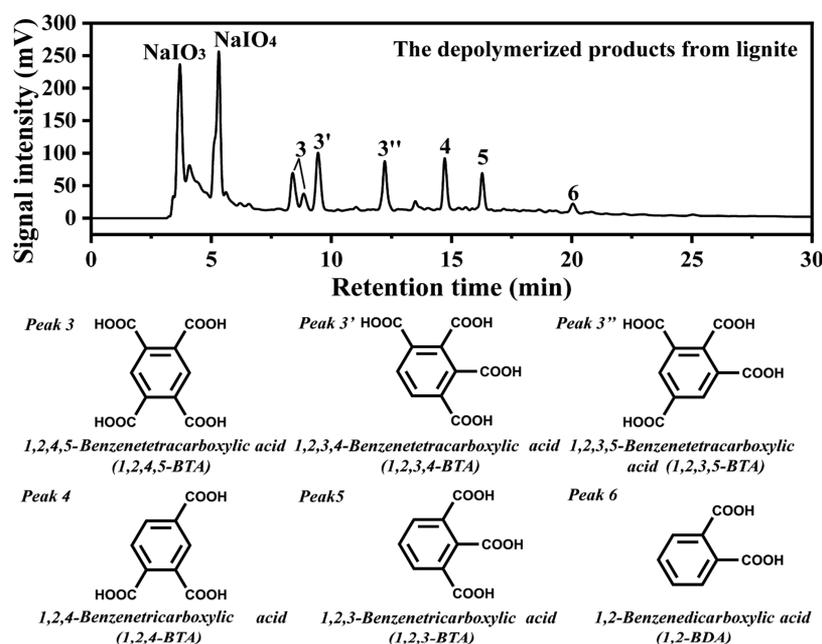


Figure 1. HPLC profile of the depolymerized products from lignite and the structures of the main and known components in the depolymerized products.

The alkali-oxygen oxidation system has often been used for the depolymerization of lignite,^{24,25} and lignite could be depolymerized effectively into large amounts of small-molecule organic acids, especially oxalic acid and BPCAs. Due to the harsh reaction conditions, nearly total depolymerization of lignite could be fulfilled via this method. However, large amounts of thermal energy, inorganic acids, and bases were consumed during the oxidation process, which were the drawbacks of this method. Yang et al.^{26,27} investigated the oxidation of lignite in aqueous NaVO₃-O₂ and FeCl₃-O₂, respectively, and high yields of BPCAs were obtained. But these two oxidation systems were conducted typically at 170 and 200 °C, respectively, which also required consumption of a lot of energy.

In view of the reaction conditions, the depolymerization degree of lignite and the depolymerized products, ruthenium ion-catalyzed oxidation (RICO) is considered as an effective method to meet the above requirements, i.e., fulfilling the nearly complete depolymerization of lignite under mild conditions with high yields of BPCAs.²⁸ To date, as a highly effective route of lignite depolymerization, RICO was often used for obtaining information about the spatial macromolecular structure of coal by analyzing the structures of the depolymerized products.^{29–33} RICO can not only open the weak bridge links in coal but also more effectively oxidize the aromatic rings in the large molecular structure of coals. Murata et al.³² carried out RICO on sub-bituminous coal and bituminous coal at 40 °C, and demonstrated that the content of shorter alkyl side chains (<C5) in two coals was similar, while long-chain alkyl side chains (>C30) were richer in sub-bituminous coal. RICO was also used by Stock et al.³⁴ on several different coals at room temperature, and the results showed that higher rank coal contained more benzene tricarboxylic acids and benzene tetracarboxylic acids, which meant that the high-rank coal had more condensed carbocyclic structures. Wei et al. conducted in-depth systematic research on the oxidative degradation of different coals through RICO at mild temperatures and confirmed that $-\text{CH}_2\text{CH}_2-$ and

$-\text{CH}_2\text{CH}_2\text{CH}_2-$ were the main bridge bond structures connecting aromatic rings in low-rank lignite.³⁵ It was further revealed that lignite contained abundant condensed aromatic species and hydroxyl-, methoxy-, and methyl-substituted benzene rings.³⁶ Meanwhile, the types of products (mainly aromatic organic acids) and their approximate distribution after oxidative degradation were also further analyzed deeply.^{35,37–39}

Due to the efficiency of RICO, it is potentially useful in the depolymerization of lignite for the production of valuable organic acids. However, several critical issues are still not very clear, which limit further applications of RICO. One issue is that the distribution of Ru in the complex RICO reaction system after depolymerization reaction is not well known. Another issue is that Ru is a typical precious metal, which results in the high cost of RICO especially considering the potential large-scale use. One of the solutions for decreasing the cost of RICO is to recycle and reuse Ru, but as far as we know, there has been no report concerning the recycling and reusing Ru during RICO of lignite to date. In this work, RICO was used to depolymerize lignite for producing BPCAs, and special attention was paid to the distribution of Ru in different phases and the possible approaches of recycling Ru. First, the influence of different depolymerization reaction parameters on the depolymerization efficiency was investigated to obtain the optimal depolymerization conditions. Second, the distribution of Ru after the depolymerization reaction was analyzed under the optimized conditions. Finally, the approach of recycling the Ru-containing solvent system without complex separation of Ru out of the reaction system was established, and the feasibility of the proposed approach was analyzed. The recycling performance of two different routes was compared, one is to recycle the whole liquid phase (CCl₄ phase and water phase) and the other is to recycle the single CCl₄ phase. This work provides a potential approach of reusing Ru for the RICO depolymerization of lignite.

2. RESULTS AND DISCUSSION

2.1. Comparison of Raw and Demineralized Lignite.

Figure 1 shows the typical HPLC profile of depolymerized products after the RICO reaction and the structures of the main and known components in the depolymerized products from lignite. Several typical organic acids with relatively higher concentrations in the depolymerized mixture were quantitatively analyzed to evaluate the efficiency of the depolymerization reaction. To further identify the structures of the depolymerized products, the obtained products were esterified by CH_3I and the esterified products were analyzed by GC-MS. The results are given in Figures S1–S7, which shows that the structures of the depolymerized products were consistent with those shown in Figure 1.

To study the effects of the inherent minerals on depolymerization, both raw lignite and demineralized lignite were used for depolymerization and the depolymerization degree and the yields of BPCAs were compared. The results are shown in Figure 2. It can be seen that the depolymerization

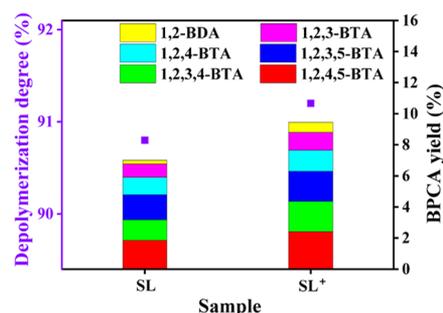


Figure 2. RICO of raw and demineralized lignite. Reaction conditions: lignite sample (0.4 g), lignite/ RuCl_3 mass ratio of 10.0/1, NaIO_4 /lignite mass ratio of 20.0/1, CCl_4 (20 mL), CH_3CN (20 mL), H_2O (30 mL), 35 °C, 6 h.

degree was similar for raw and demineralized lignite, but the yields of BPCAs were different. The yields of BPCAs for demineralized lignite were higher than those of raw lignite. Proximate and ultimate analysis showed that much less ash and higher contents of O and C existed in demineralized lignite compared to raw lignite (Table 1). In addition, it was reported that the content of aliphatic structures decreased while the content of the oxygenated species increased after the demineralization of coal.⁴⁰ Less content of ash and higher content of O- and C-containing species may result in high yields of BPCAs for the demineralized lignite. Thus, demineralized lignite was used in this work.

2.2. Effects of Reaction Conditions on the RICO Reaction. During the RICO reaction, the dosage of RuCl_3 and NaIO_4 can not only determine the efficiency of the depolymerization process but also influence the cost of the process and the amount of the by-product inorganic salt (NaIO_3). Therefore, the dosage of RuCl_3 and NaIO_4 was

optimized. Figure 3a shows the effect of RuCl_3 /lignite and NaIO_4 /lignite mass ratios on the depolymerization degree of lignite and BPCA yields. It could be seen that both the depolymerization degree of lignite and the BPCA yields were extremely low in the absence of RuCl_3 , indicating the critical role of RuCl_3 for the oxidative depolymerization of lignite. In the presence of RuCl_3 , the lignite conversion increased to nearly 80% at the RuCl_3 /lignite mass ratio of 0.025, and upon further increasing the ratio of RuCl_3 /lignite no obvious promotion was observed on the depolymerization degree and BPCA yields. This result indicated that SL^+ could be easily depolymerized even at a low RuCl_3 /lignite mass ratio. The maximum yield of BPCAs was obtained at a mass ratio of RuCl_3 /lignite of 0.1, which was adopted in the following studies.

The NaIO_4 /substrate ratios play a key role in RICO as the oxidant.⁴¹ Large dosages of NaIO_4 would result in the formation of a large amount of NaIO_3 , which is not conducive to the separation of BPCAs. Therefore, the effect of NaIO_4 /lignite mass ratios on the depolymerization degree of lignite and BPCA yields was also investigated (Figure 3b). Both the depolymerization degree of lignite and BPCA yields increased notably with increasing NaIO_4 /lignite mass ratios from 0.0 to 20.0. However, the yields of BPCA decreased when the NaIO_4 /lignite mass ratio was 25.0/1, which due to the excessive salt might decrease the oxidation rate by restraining the diffusion of intermediates generated on the coal surface into the water phase.¹⁸ From the above results, it can be seen that both RuCl_3 and NaIO_4 were essential during the RICO reaction.

The effect of reaction temperature on the depolymerization degree of lignite and BPCA yields could be seen in Figure 4a. In the studied temperature range (5–50 °C), the reaction temperature had little influence on the depolymerization degree of lignite, and the depolymerization degree reached 82.7% at 25 °C, showing that RICO was an effective method for depolymerizing lignite even at room temperature. The yield of BPCAs was increased by enhancing the temperature and the maximum yield was achieved when the temperature was increased to 35 °C. Upon further increasing the reaction temperature to 45 °C, the yield of BPCAs showed a slight decrease. Therefore, 35 °C was chosen as the optimal temperature in the following studies. As shown in Figure 4b, the depolymerization degree of lignite reached nearly 90% in 3 h and there was little growth further prolonging the reaction time. BPCA yields increased obviously when the reaction time was increased to 6 h. Upon further prolonging the reaction time to 9 h, the BPCA yields showed a slight decrease. Under the present reaction conditions, 6 h was long enough for the complete depolymerization of lignite. The slight decrease in BPCA yields at high temperatures and long reaction time might be caused by the deep oxidation of the produced BPCAs.

Table 1. Proximate and Ultimate Analysis of Coal Samples^a

samples	proximate analysis (wt %)				ultimate analysis (d, wt %)				
	M_{ad}	A_d	V_d	FC_d	C	H	N	S	O*
SL	1.52	13.92	33.37	52.71	57.59	3.58	0.89	1.81	22.21
SL*	2.18	1.14	41.97	56.89	64.90	4.88	0.91	1.69	26.48

^aM: moisture; A: ash; V: volatile matter; FC: fixed carbon; ad: air dried; d: dry basis; *By difference.

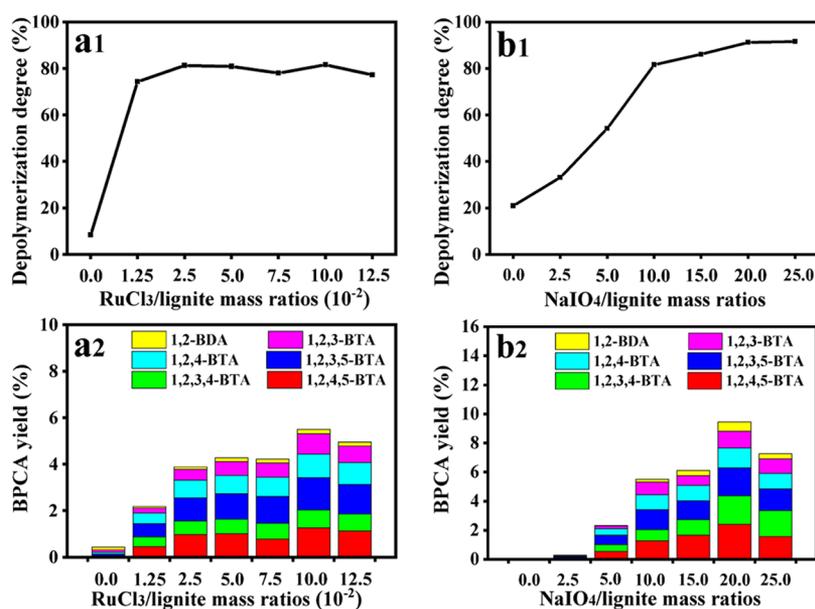


Figure 3. Effect of RuCl₃/lignite mass ratios (a1, a2) and NaIO₄/lignite mass ratios (b1, b2) on the depolymerization degree of lignite and BPCA yields. Reaction conditions: SL⁺ (0.4 g), CCl₄ (20 mL), CH₃CN (20 mL), H₂O (30 mL), 35 °C, 6 h, (a1, a2) NaIO₄/lignite mass ratio of 10.0/1, (b1, b2) lignite/RuCl₃ mass ratio of 10.0/1.

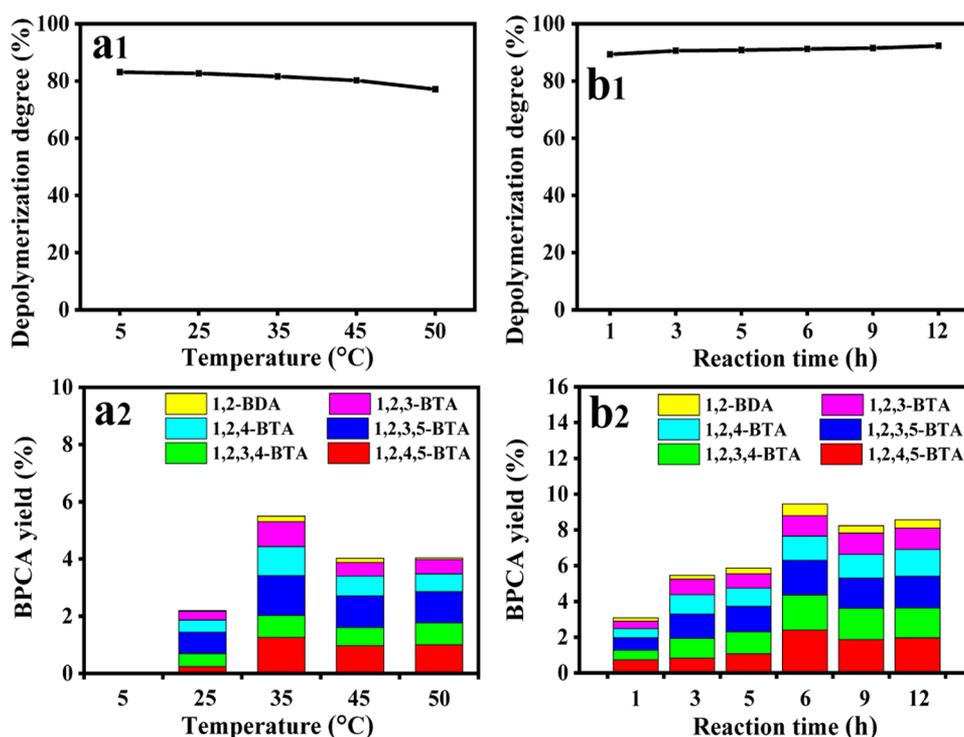


Figure 4. Effect of the reaction temperature (a1, a2) and the reaction time (b1, b2) on the depolymerization degree of lignite and BPCA yields. Reaction conditions: SL⁺ (0.4 g), lignite/RuCl₃ mass ratio of 10.0/1, CCl₄ (20 mL), CH₃CN (20 mL), H₂O (30 mL), (a1, a2) NaIO₄/lignite mass ratio of 10.0/1, 6 h, (b1, b2) NaIO₄/lignite mass ratio of 20.0/1, 35 °C.

2.3. Distribution of Ru after the Depolymerization Reaction. Understanding the distribution of Ru in different phases is crucial for the recycling of the precious Ru catalyst after the RICO reaction. Therefore, the distributions of Ru after the RICO reaction in the organic phase, aqueous phase, and lignite residual solid phase under different depolymerization degrees of lignite were analyzed. As shown in Table 2, when the depolymerization degree of lignite was around 50.8%, Ru existed in all three phases, and the proportions of

Ru in the organic phase, aqueous phase, and lignite solid residue phase among the total amount of Ru were 8.2, 76.1, and 15.7%, respectively. When the nearly complete depolymerization of lignite (e.g., 90.3%) was achieved, the mass of the lignite residual solid could be neglected and almost all Ru (up to 97.0%) existed in the organic phase and around 2.9% of Ru existed in the aqueous phase. The results showed that the distribution of the Ru species was closely correlated with the degree of lignite depolymerization. As shown in the above

Table 2. Distribution of the Ru Element after the Depolymerization Reaction^a

depolymerization degree (%)	proportions of Ru element in different phases (wt %)		
	organic phase	aqueous phase	residual solid phase
50.8 ^a	8.2	76.1	15.7
90.3 ^b	97.0	2.9	<0.1

^aReaction conditions: SL⁺ (2.0 g), RuCl₃ (50 mg), NaIO₄/lignite mass ratios of 5/1, CCl₄ (50 mL), CH₃CN (50 mL), H₂O (75 mL), 35 °C, 48 h. ^bSL⁺ (0.4 g), RuCl₃ (50 mg), NaIO₄/lignite mass ratios of 20/1, CCl₄ (20 mL), CH₃CN (20 mL), H₂O (30 mL), 35 °C, 6 h.

results, when the dosage of RuCl₃ was fixed, the dosage of NaIO₄ has significant effects on the depolymerization degree of lignite. Therefore, it could be speculated that the distribution of Ru also has a relationship with the dosage of NaIO₄. Under a low dosage of NaIO₄ (NaIO₄/lignite mass ratio of 5.0/1), the depolymerization degree of lignite was medium (50.8%), most of Ru existing in the form of Ru-containing salts with lower chemical valence (Ru^{III/II}),⁴² which were water soluble and tended to present in the aqueous phase. On further increasing the ratio of NaIO₄/lignite to 20.0, nearly complete depolymerization of lignite was achieved, and the Ru^{III/II} could be oxidized by excess NaIO₄ into Ru^{VIII} (RuO₄),⁴² which had high solubility in the CCl₄ phase.

To confirm the role of NaIO₄ in the RICO reaction, the Ru chemical valence after the RICO reaction was investigated by characterizing the organic phase containing Ru by FTIR and Raman spectroscopy. The results are shown in Figure 5. After the addition of NaIO₄, the characteristic peak assigned to RuO₄ appeared in both FTIR (916 cm⁻¹) and Raman (881 cm⁻¹) spectra.⁴³ The results indicated that NaIO₄ could oxidize RuCl₃ into RuO₄, which could further oxidize lignite into BPCAs.

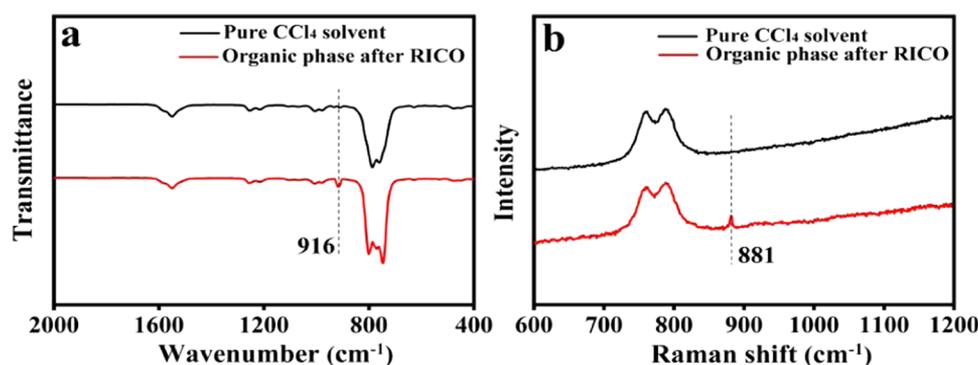
Besides the change in the chemical valence of Ru during RICO, the content of Ru in the aqueous phase or the organic phase was also investigated (Table 3). It was found that the contents of Ru in the aqueous phase or the organic phase depended on the mole ratio of NaIO₄/RuCl₃. When the mole ratio of NaIO₄/RuCl₃ was extremely low (<1:1), Ru existed mainly in the form of RuCl₃ and existed in the aqueous phase. When the mole ratio of NaIO₄/RuCl₃ (>3:1) improved, RuCl₃ was oxidized into RuO₄ by excess NaIO₄ and RuO₄, mainly present in the organic CCl₄ phase.

2.4. Reuse of the Ru Catalyst System. To cut the cost of Ru for the RICO reaction, besides decreasing the usage of

Table 3. Distribution of the Ru Element in Different Phases

mole ratio (NaIO ₄ /RuCl ₃)	proportions of Ru in different phases (wt %)	
	aqueous phase	organic phase
0/1	>99.9	<0.1
1/1	99.8	0.2
3/1	0.5	99.5
20/1	<0.1	>99.9

RuCl₃, another effective approach is to recycle and reuse Ru. The recycling of Ru is still challenging due to the low concentration of Ru and the complexity of the reaction system after the RICO reaction. Through the above distribution analysis of Ru, around 97.0% Ru could be transferred into the organic phase, and the Ru contents in the residual solid phase could be ignored at a high depolymerization degree. It is hard and tedious to extract Ru with a high separation yield from such a complex system, so we attempted to recycle the whole liquid phase containing Ru without separating the BPCA products and Ru from the system. The recycling of the solvent system containing Ru could fulfill the reuse of both Ru and the solvents. After one cycle of the RICO reaction, solid lignite and additional NaIO₄ were added into the reaction system for the subsequent cycle. This process was repeated 5 times to see the efficiency of each cycle. Two recycling routes were adopted and compared, (1) recycling the whole liquid phase (CCl₄ phase and water phase) and (2) recycling the single CCl₄ phase. The results for route 1 are shown in Figure 6a–c. Figure 6a shows the depolymerization degree of lignite during the 5 cycles. It could be seen that the depolymerization degree of lignite reached ca. 92% and maintained well during the 5 cycles. The accumulative yields of BPCAs increased linearly in the initial three cycles, and the increase rate became slow in the last two cycles (Figure 6b). As shown in another way (Figure 6c), the BPCA yields for each cycle showed no obvious change in the initial 3 cycles, but decreased sharply during the last two cycles. These results showed that the recycled whole liquid system could effectively convert solid lignite into the soluble fractions for at least 5 cycles, but the performance of converting the soluble fractions into BPCAs decreased after the third cycle. Based on the distribution of Ru, ca. 97.0% Ru existed in the CCl₄ phase, and the Ru in the aqueous phase was much less (ca. 2.9%). Besides, the depolymerized products (BPCAs) existed in the aqueous phase, and no obvious BPCAs were detected in the CCl₄ phase. Therefore, the recycling of the single CCl₄ phase was further studied (route 2, Figure

**Figure 5.** FTIR (a) and Raman (b) spectra of the Ru-containing CCl₄ phase after RICO.

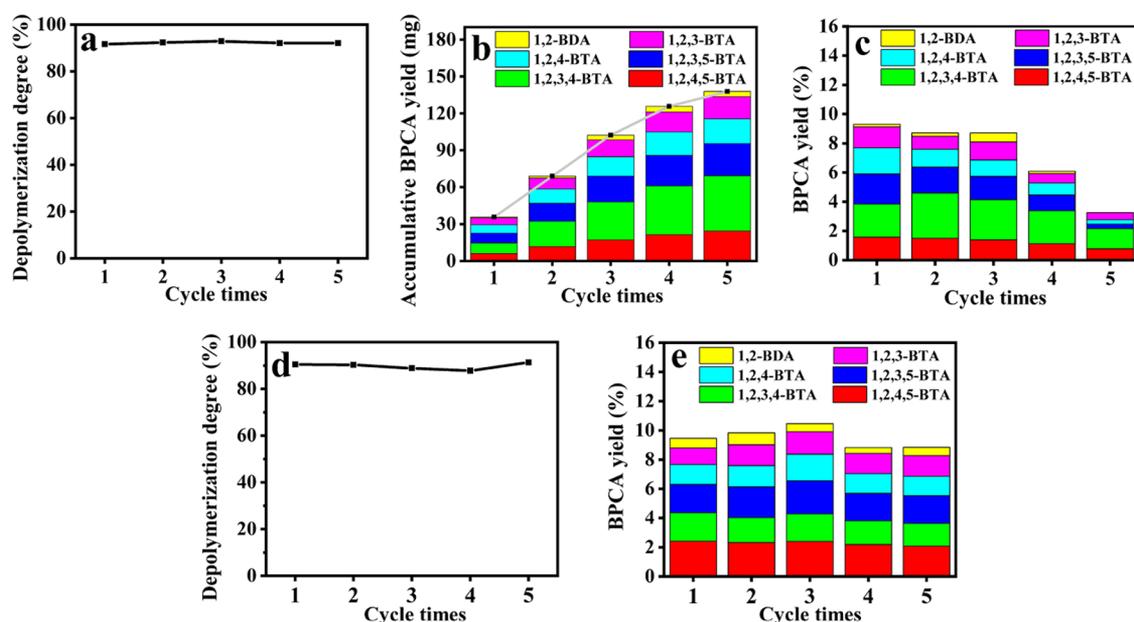


Figure 6. Reuse of the whole liquid phase (a–c) and the single CCl_4 phase without reusing the water phase containing BPCAs (d, e). Reaction conditions: lignite (0.4 g), RuCl_3 (40 mg), CCl_4 (20 mL), CH_3CN (20 mL), H_2O (30 mL), NaIO_4 (8 g), 35 °C, (a–c) 24 h, (d,e) 6 h.

6d,e). The results showed that the CCl_4 phase containing Ru could be reused for 5 cycles without an obvious decrease in both depolymerization degree of lignite and BPCA yields.

It was reported that the salting-out effect caused by the excessive inorganic salt occurred in high-temperature alkali-oxygen oxidation of lignite.¹⁸ The excessive inorganic salt could not only decrease the oxidation rate through restraining the diffusion of intermediates generated on the coal surface into the water phase but could also decrease the yield of BPCAs because of excessive oxidation. To explore the reason for the unsatisfactory performance of the whole liquid phase circulation after the initial three cycles, the effect of the inorganic salt (NaIO_3) during the recycling processes and the excessive oxidation of BPCAs were investigated. The results are shown in Table 4. The concentration of the Na salt

conditions are shown in Figure 7. Clearly, an increase in the amount of NaIO_3 in the system led to the decrease of BPCAs

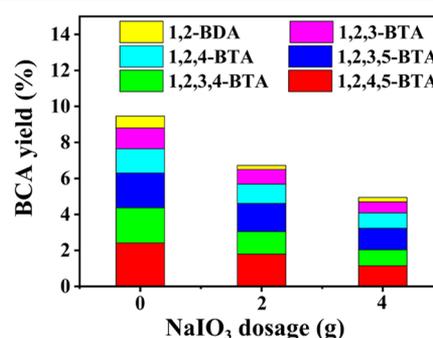


Figure 7. Effect of different amounts of NaIO_3 on yield of BPCAs. Reaction conditions: lignite (0.4 g), RuCl_3 (40 mg), CCl_4 (20 mL), CH_3CN (20 mL), H_2O (30 mL), NaIO_4 (8 g), 35 °C, 6 h.

Table 4. Salt Distribution in Different Phases during Circulation

cycle	Na^+ distribution in the two phases (mg/mL)				
	whole liquid circulation			organic phase circulation	
	aqueous phase	organic phase	solid phase ^a	aqueous phase	organic phase
1	9.3	0.016	4.2	8.8	0.017
2	14.1	0.173	4.9	9.2	0.028
3	15.8	0.201	5.3	9.1	0.101
4	16.6	0.488	6.2	8.8	0.054
5	17.7	0.976	7.3	8.7	0.098

^a Na salt distribution in the solid phase (g); solid phase obtained by the phase separation after RICO of lignite.

constantly increased during the recycling processes in the catalytic system. Meanwhile, the solid inorganic salt obtained after phase separation of the RICO reaction also increased sharply from 4.2 g (first cycle) to 6.2 g (fourth cycle). To further prove the negative role of the salting-out effect, different amounts of NaIO_3 were added into the reaction system during RICO, and the yields of BPCAs under different

yield, indicating that the salting-out effect could indeed decrease the yields of BPCAs. Then, four kinds BPCAs were used to check whether the excessive oxidation would happen in RICO. In Figure 8, it was found that to a certain extent excessive oxidation of BPCA indeed occurred when the dosage of NaIO_4 and reaction temperature were increased, and the reaction time was prolonged. Based on the above results, we speculated that the decrease of BPCAs during the whole liquid phase circulation might be caused by the combined effect of salting out and excessive oxidation.

Reusing the CCl_4 phase containing Ru could avoid the probable excessive oxidation of the produced BPCAs and the accumulation of salt. Thus, the recycling and reuse of the CCl_4 phase was more efficient than those of the whole liquid phase (CCl_4 and water phase). As shown in Table 5, after repeatedly reusing the CCl_4 phase containing Ru 5 times, still 93.1% Ru could be recycled. Above all, the proposed approach of recycling and reusing the solvent system containing Ru to fulfill the reuse of Ru during RICO was identified to be feasible and

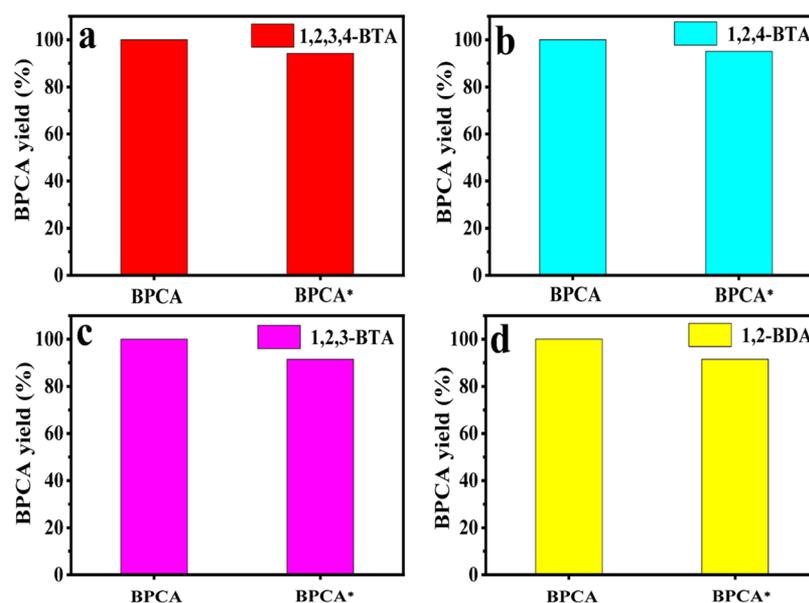


Figure 8. Excessive oxidation of (a) 1,2,3,4-BTA, (b) 1,2,4-BTA, (c) 1,2,3-BTA, and (d) 1,2-BDA. Reaction conditions: BPCA (1 mmol), RuCl_3 (50 mg), NaIO_4 10 g, CCl_4 (20 mL), CH_3CN (20 mL), H_2O (30 mL), 45 °C, 12 h. BPCA: The BPCA before excessive oxidation reaction. BPCA*: The residual BPCA after excessive oxidation reaction.

Table 5. Recycling Efficiency of Ru in RICO Organic Phase Circulation

cycle times	Ru recycled content (mg)	Ru recycle rate (%)
1	18.3	97.3
5	17.5	93.1

highly efficient, which was conducive to the potential application of RICO in the utilization of lignite.

2.5. Extraction of BPCAs from the Aqueous Phase of RICO. The separation of BPCAs is an important issue for the RICO process. After the RICO reaction, both depolymerized products BPCAs and a large amount NaIO_3 were present in the aqueous phase, which is not conducive to the separation of BPCA from the oxidation system. Therefore, the extraction of BPCAs from the aqueous phase was investigated. Butanone was considered as a solvent with good solubility, which could efficiently extract BPCAs from lignite depolymerization system.²⁷ As shown in Table 6, most of the BPCAs (>90%) could be efficiently extracted from the depolymerization system by butanone, and only the extraction yields of 1,2-BDA were relatively lower than other BPCAs, which might be attributed to its low solubility in butanone.

Table 6. Extraction of BPCAs by Butanone from Depolymerized Products^a

entry	BPCA	BPCA yield (mg)	extraction yield (%)
1	1,2,4,5-BTA	9.3	99.3
2	1,2,3,4-BTA	7.5	97.0
3	1,2,3,5-BTA	7.4	99.2
4	1,2,4-BTA	5.2	96.8
5	1,2,3-BTA	4.4	92.3
6	1,2-BDA	2.5	77.0

^aExtraction conditions: RICO depolymerization water phase (30 mL), butanone (30 mL), extraction 3 times (1 h each time).

3. CONCLUSIONS

In summary, RICO was used to depolymerize Shengli lignite for the production of BPCAs, and the influence of different reaction parameters on the depolymerization efficiency was studied. Special attention was paid to the distribution of Ru in different phases after the RICO reaction and to the reuse of the precious Ru catalyst. The results showed that the dosage of RuCl_3 and NaIO_4 had significant effects on the depolymerization degree of lignite and BPCA yields. The distribution of Ru after the RICO reaction showed a close relationship with the depolymerization degree of lignite and the dosage of NaIO_4 . Under moderate depolymerization degree of lignite (50.8%) with a low dosage of NaIO_4 , ca. 76.1% of Ru distributed in the water phase. Under the high depolymerization degree of lignite (>90%) with a high dosage of NaIO_4 , ca. 97.0% of Ru distributed in the CCl_4 phase. Based on the result of the distribution of Ru, a new route for reusing Ru via recycling the CCl_4 phase containing Ru was proposed, and it was proved that Ru together with CCl_4 solvent could be reused for 5 cycles without an obvious decrease in both the depolymerization degree of lignite and BPCA yields. As far as we know, this is the first work concerning the recycling and reuse of the Ru catalyst during RICO depolymerization of lignite. With the advantage of recycling both Ru and the organic solvent in one single process, the proposed approach was beneficial for the potential application of RICO in the oxidative depolymerization of lignite into valuable organic acids.

4. EXPERIMENTAL SECTION

4.1. Materials. Shengli lignite (SL), from Inner Mongolia Shengli Coalfield in China, was used in this work. Ruthenium(III) chloride (RuCl_3 , AR, 99.5%), sodium periodate (NaIO_4 , AR, 99.5%), sodium iodate (NaIO_3 , AR, 99.5%), acetonitrile (CH_3CN , AR, 99.5%), carbon tetrachloride (CCl_4 , AR, 99.5%), iodomethane (CH_3I , AR, 99%), dry *N,N*-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, AR, 99.9%), and potassium carbonate (K_2CO_3 , AR, 99%) were purchased from Beijing Innochem Technology Co., Ltd. All organic solvents used in the

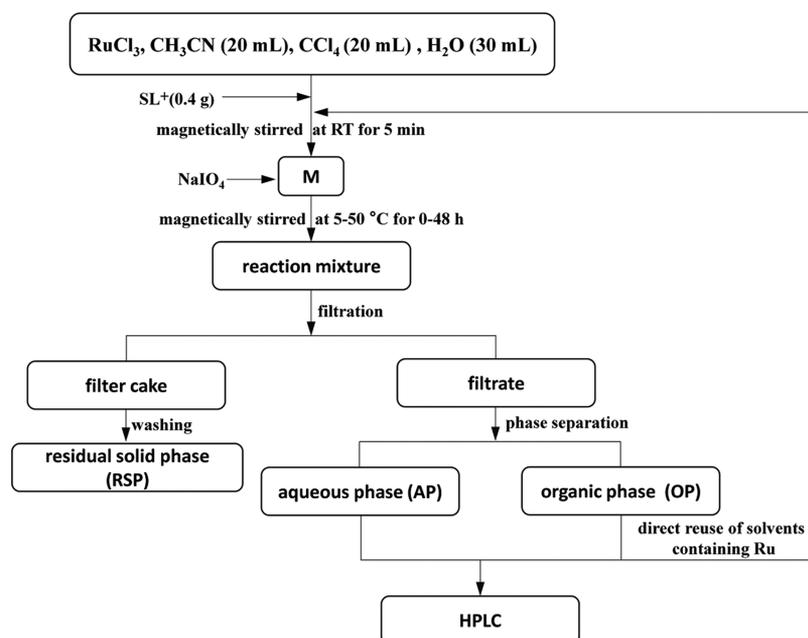


Figure 9. Procedure of the RICO reaction, subsequent sample treatment, and the recycling of the Ru-containing solvent.

experiments were analytical grade reagents and directly used as received without further treatment.

4.2. Lignite Demineralization. To avoid the influence of the inherent minerals on the RICO reaction, lignite was pulverized to the average sizes ca. 38–75 μm and demineralized by HCl wash. HCl aqueous solution with a concentration of 18 wt % and HCl/lignite ratio of 10 mL/g were mixed and stirred at room temperature for 48 h. Demineralized lignite was rinsed with distilled water until the pH of the supernatant was neutral. The obtained solid was dried, ground into powders with the average sizes of ca. 38–75 μm , and labeled as SL^+ .

4.3. RICO Depolymerization Reaction. The RICO depolymerization reaction of lignite was conducted based on the reported procedures.^{36,37} As shown in Figure 9, SL^+ (0.4 g), RuCl_3 (typically 40 mg), and $\text{CCl}_4/\text{CH}_3\text{CN}/\text{H}_2\text{O}$ with a volume ratio of 2:2:3 (total volume, 70 mL) were added into a 250 mL spherical flask and the mixture was magnetically stirred for 5 min at room temperature. Then, NaIO_4 was slowly added to a spherical flask using a funnel to obtain the mixture (M). Slurry M was allowed to react under the desired temperature (5–50 $^\circ\text{C}$) and reaction time (0–48 h). After the reaction, the reaction mixture was filtered to afford the filter cake and the filtrate was subjected to phase separation to obtain organic phase (OP) and aqueous phase (AP). The filter cake was washed with hot distilled water for 1 h to remove NaIO_4 and NaIO_3 and the obtained residual solid was dried at 105 $^\circ\text{C}$ for about 12 h and then weighed. The depolymerization degree of lignite and the yields of BPCAs were calculated using the following formulas.

depolymerization degree of lignite

$$= \left(1 - \frac{\text{the mass of the residual solid}}{\text{the initial mass of the lignite}} \right) \times 100\%$$

$$\text{yield (BPCAs)} = \frac{\text{mass of BPCAs}}{\text{mass of organic matter in lignite}} \times 100\%$$

where the mass of organic matter in lignite = mass of lignite – mass of ash – mass of moisture.

To select the optimal RICO reaction for SL^+ sample and decrease the usage of RuCl_3 and NaIO_4 , the parameters during the RICO reaction were investigated, including the mass ratio of $\text{RuCl}_3/\text{SL}^+$, $\text{NaIO}_4/\text{SL}^+$, depolymerization temperature, and depolymerization time.

4.4. Detection of Ru in Different Phases and Recycling of the Ru-Containing Solvent System. Under the low depolymerization degree of lignite, there were typical three phases after the RICO reaction, including the organic phase (OP), the aqueous phase (AP), and the lignite residual solid phase (RSP). When the depolymerization degree of lignite was high (>90%), the residual lignite was less. The distribution of Ru in different phases under different depolymerization conditions was detected using an inductively coupled plasma atomic emission spectrometer (ICP-AES). For the recycling of Ru, two routes were adopted. (1) The whole Ru-containing the solvent system (CCl_4 , CH_3CN , and water) was recycled and directly reused in the next RICO reaction run only by replenishing CCl_4 , CH_3CN , H_2O , and 8 g of NaIO_4 considering the solvent loss during operation and consumption of NaIO_4 , without adding additional RuCl_3 . An amount of 0.4 g of fresh SL^+ was added for each run. Due to the low concentration of Ru and the depolymerized products, both Ru and the depolymerized products were not separated from the solvent system, i.e., the whole liquid system was repeatedly used 5 times to check the feasibility of this route for Ru recycling. (2) Only the CCl_4 phase containing Ru was recycled and reused and other processes were similar to the above route.

4.5. Analysis of the Depolymerized Products. The structures of the depolymerized products BPCAs were identified by HPLC (SHIMADZU LC-20AT, Japan) and GC-MS (Agilent 7890 series GC with a 5977 MS detector).⁴⁴ The depolymerized products have been esterized before GC-MS analysis. Before esterification, the depolymerization product BPCAs and the salt in RICO, the aqueous phase

were separated. The depolymerization BPCA products were obtained by butanone extraction (butanone/aqueous phase volume ratio 1:1) of the RICO aqueous phase three times and butanone was removed via rotary evaporation under reduced pressure and 40 °C. The esterification of depolymerized products was carried out based on the reported procedures with some minor changes.⁴⁵ Typically, depolymerized products and K₂CO₃ were added to a three-necked flask and the flask was flushed with nitrogen until the reaction finished. Then, dry N,N-dimethylformamide and iodomethane were added dropwise in the flask over a period of 15 min. The mixture was stirred at room temperature for 10 h, poured into water, and the esterification products were extracted with hexane/ethyl acetate (20:1, v/v). Then, the extracted products were analyzed by GC-MS after being condensed.

The quantification of BPCAs using HPLC. The procedure for the HPLC analysis of BPCAs was binary gradient elution. Acetonitrile (organic phase) and 0.1% (volume fraction) phosphoric acid aqueous solution (aqueous phase) were used as the mobile phase, and the stationary phase was C18 bonded to silica gel (Shim-pack GIST C18, 5 μm). The BPCAs were quantified using a UV detector at 235 nm. The column temperature was 45 °C, and the flow rate of the mobile phase was 0.8 mL/min. The gradient elution procedure was as follows: in the beginning, the volume ratio of organic phase to the aqueous phase was 5:95; the ratio was linearly increased to 15:85 during 10 min and then maintained for 20 min, and finally, the ratio was decreased to 5:95 over 2 min.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c03970>.

Procedure of GC-MS analysis and GC-MS profiles of esterized RICO products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21968021 and 21676149), the Natural Science Foundation of Inner Mongolia (2019MS02025), the Innovative and Entrepreneurial Talents Grassland Talents Engineering of Inner Mongolia (Q2017011), the Grassland Talents Engineering of Inner Mongolia, CAS “Light of West China” Program, and the Local Science and Technology Development Fund Projects Guided by the Central Government (2020ZY0010).

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