

Noble Metals Dissolution Catalyzed by  $[\text{AlCl}_4]^-$ -Based Ionic Liquids

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Cite This: *ACS Omega* 2023, 8, 8341–8345

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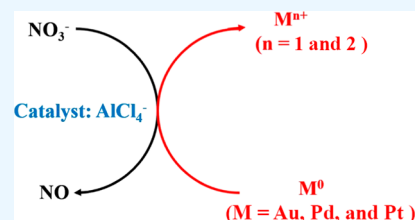
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**ABSTRACT:** Imidazolium-based ionic liquid mixtures with  $[\text{NO}_3]^-$  and  $[\text{AlCl}_4]^-$  anions were used as oxidizing agents for the dissolution of Au, Pd, and Pt metals under mild conditions. The thermodynamic reduction of  $[\text{NO}_3]^-$  to  $[\text{NO}]$  is catalyzed by  $[\text{AlCl}_4]^-$  anions and coupled with the oxidation process of noble metals. The developed ionic liquid system for dissolving Au can reactivate the  $\text{Au}^0$  formed in the deactivation process of the catalyst in vinyl chloride production. This demonstrates the relevance of the here-presented work for technical noble metal recycling.



## INTRODUCTION

The concept of green and recyclable development is currently the main focus of modern academic society. Clearly, the recycling of noble metals such as gold (Au), palladium (Pd), and platinum (Pt), important metals for jewelry, coins, and other industrial applications, is an important part of such development.<sup>1–4</sup> These metals are essential for sustainable applications as active sites of numerous catalysts used in various industrial areas, but their limited reserves and production monopolies in certain countries have restrained their large-scale use in practical industries.<sup>5</sup> The dissolution of noble metals from secondary resources—catalysts in this case—is necessary for the recyclable use of noble metals. Strong oxidizing conditions are required to dissolve noble metals. Aqua regia is a mixture of concentrated nitric acid ( $\text{HNO}_3$ ) and hydrochloric acid ( $\text{HCl}$ ) with a 1:3 volume ratio and is well-known as a leaching solvent for Au, Pd, and Pt. However, aqua regia is highly corrosive and hazardous<sup>6</sup> and may cause severe environmental impact and threatens the well-being of wildlife and humankind. Ionic liquids (ILs) are solvents composed entirely of ions, which have been identified as possible alternatives to traditional solvents, and are widely used in stabilizing metal nanoparticles and extracting metal ions,<sup>7</sup> but rarely used in dissolving noble metals.<sup>8–10</sup> Recently, ILs with trichloride anions ( $[\text{Cl}_3]^-$ ) combined with different cations have been reported as oxidizing agents for the dissolution of various metals and alloys under mild conditions,<sup>5,11</sup> which sparked a wave of research on the specific functionalized ILS for dissolving metals.<sup>12</sup>

Besides, IL composites always have a different but remarkable dissolving effect than when applied solely using any individual component of the IL composites. Considering the oxidation and the subsequent coordination ability of ILs in dissolving metals, such as the synergistic effect of  $\text{NO}_3^-$  and  $\text{Cl}^-$  in boiling aqua regia,<sup>13</sup> imidazole-based binary composite ILs system using  $[\text{NO}_3]^-$  and  $\text{Cl}^-$  as anions was studied on the dissolution of Au, Pd, and Pt metals in this work. Unfortunately, we found that this binary ILs system was

unable to trigger the oxidation process for dissolving metals, which is significantly different from the aqua regia system. Our subsequent studies have found that this problem can be solved when  $\text{Cl}^-$  was replaced by  $[\text{AlCl}_4]^-$ . A milder and greener noble metals recovery process was achieved under this strategy. Moreover, by applying the developed binary-IL dissolving system on the used Au-based catalysts for gas–liquid acetylene hydrochlorination, a very important industrial process to produce vinyl chloride monomer (VCM),  $\text{Au}^0$ , the inactive component formed from cationic  $\text{Au}^{3+}$  during the catalytic process, was successfully reactivated, which enabled the recycling of the noble metal catalyst.<sup>14–16</sup>

## RESULTS AND DISCUSSION

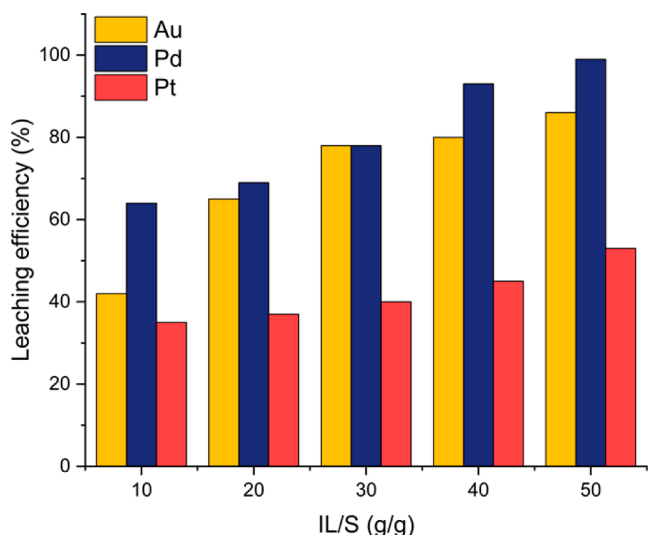
The leaching tests were performed by contacting the  $\text{Au}^0$ ,  $\text{Pd}^0$ , and  $\text{Pt}^0$  in glass vials with continuous stirring at 80 °C. Equal amounts of binary-ILs: 1-hexyl-3-methylimidazolium nitrate [ $\text{Hmim}^+ - \text{NO}_3^-$ ] and 1-hexyl-3-methylimidazolium aluminium tetrachloride [ $\text{Hmim}^+ - \text{AlCl}_4^-$ ] were used in the leaching test. As shown in Figure 1, the leaching efficiencies for  $\text{Au}^0$ ,  $\text{Pd}^0$ , and  $\text{Pt}^0$  samples were 42, 64, and 35%, respectively, when the mass ratio of ILs to metal sample (IL/S) was 10. Obviously,  $\text{Au}^0$ ,  $\text{Pd}^0$ , and  $\text{Pt}^0$  were dissolved successfully in the developed binary-ILs system. When the proportion of IL/S continued to increase, the leaching efficiencies of the three noble metals gradually increased and reached their maximum at the proportion of 40, achieving leaching efficiencies of 86% for  $\text{Au}^0$ , 99% for  $\text{Pd}^0$ , and 53% for  $\text{Pt}^0$ . For comparison, the reference-binary-IL system ( $[\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{Cl}^-]$ ) was used to try to dissolve the  $\text{Au}^0$ ,  $\text{Pd}^0$ , and  $\text{Pt}^0$ ;

Received: November 2, 2022

Accepted: January 19, 2023

Published: February 21, 2023

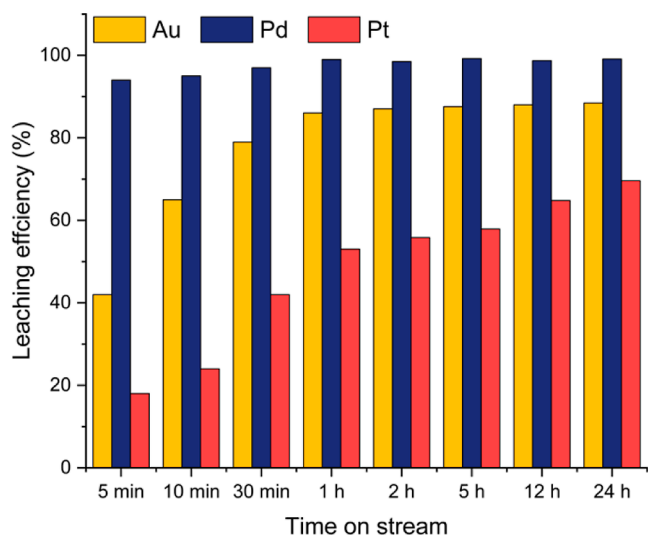




**Figure 1.** Leaching as a function of the binary-ILs ( $[\text{Hmim}^+-\text{AlCl}_4^-]$  vs  $[\text{Hmim}^+-\text{Cl}^-]$ ) metal samples (IL/S). Leaching conditions: 1 h, 60 °C, 600 rpm.

however, the leaching efficiency of the above metals was almost little (not shown), indicating the key role of  $[\text{AlCl}_4^-]$  in the dissolution process. Herein, the high IL/S ratio is necessary for promoting the thermodynamic equilibrium transformation of metal oxidation and coordination processes.

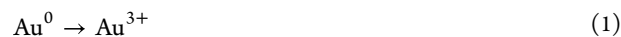
Based on this, the next series of leaching experiments as a function of dissolution time was conducted and recorded in Figure 2. We can clearly observe that the leaching efficiency of



**Figure 2.** Leaching as a function of the binary-ILs ( $[\text{Hmim}^+-\text{AlCl}_4^-]$  vs  $[\text{Hmim}^+-\text{Cl}^-]$ ) to dissolution time. Leaching conditions: 60 °C, 600 rpm, IL/S = 50.

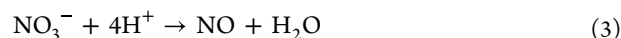
$\text{Au}^0$  and  $\text{Pt}^0$  systems increased significantly within 1 h at the initial stage of the dissolution process while increasing slightly in the following 1–24 h.  $\text{Pd}^0$  represents the most effective of the three leaching systems, reaching 99% leaching efficiency within 1 h, indicating that the developed binary-ILs system is more favorable for the dissolution of  $\text{Pd}^0$ . The electronic characteristics of Pd atoms determine their dissolution behavior, which is in agreement with many dissolution-related studies.<sup>11–13</sup>

As demonstrated in the aforementioned results, the selection of Cl-based IL ( $[\text{Hmim}^+-\text{AlCl}_4^-]$  vs  $[\text{Hmim}^+-\text{Cl}^-]$ ) in the binary-ILs system controls whether the reaction is triggered or not. In this dissolution system,  $\text{Cl}^-$  generally acts as a ligand donor to stabilize the oxidized noble metal cations,<sup>4</sup> such as  $\text{Au}^{3+}$ , following the following reaction



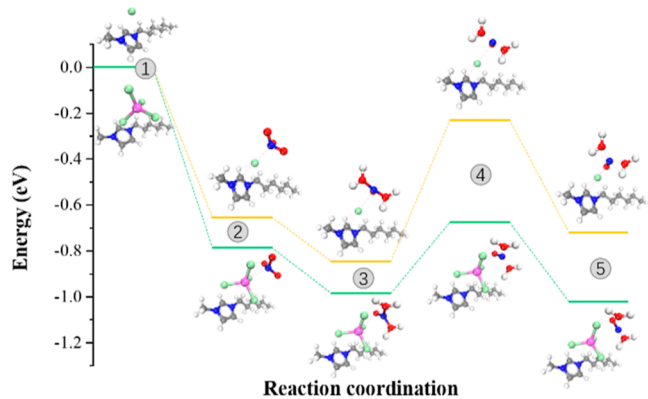
This process is necessary. On the one hand, the Cl ligand stabilizes the newly oxidized  $\text{Au}^{3+}$  in the form of  $[\text{AuCl}_4]^-$  complex. On the other hand, this process can reduce the electrode potential of Au from 1.498 V for  $[\text{Au}^{3+}/\text{Au}^0]$  to 1.002 V for  $[\text{AuCl}_4^-/\text{Au}^0]$ ,<sup>17</sup> enhancing the reduction ability of Au and promoting a rapid shift of the chemical equilibrium to the right. This mechanism can also be applied to the Pd and Pt systems. However, the curiosity lies in why this theory, which has been tested in the aqua regia system, does not fit here in the binary-ILs system, given that only  $[\text{AlCl}_4^-]$  can trigger the dissolution process rather than  $[\text{Cl}^-]$ . We speculate that an important reason for this is that the first process of noble metals dissolution, oxidation in eq 1, is not initiated in ( $[\text{Hmim}^+-\text{NO}_3^-] + [\text{Hmim}^+-\text{Cl}^-]$ ) system, which prevents taking advantage of the strong complexation ability of Cl-containing ligands.

The original intention of  $[\text{Hmim}^+-\text{NO}_3^-]$  selection was borrowed from the strong oxidizing property of  $\text{NO}_3^-$  in the aqua regia system. As shown in eq 3, this process releases NO as well as small amounts of other nitrogen oxides.



We conducted the following experiments to verify the above speculation. The released gases were collected and characterized during the in-situ dissolution of the  $\text{Au}^0$ , based on the results of mass spectrometry. As shown in Figure S1, the released NO(30) signal was successfully detected for the dissolution process of Au in ( $[\text{Hmim}^+-\text{NO}_3^-] + [\text{Hmim}^+-\text{AlCl}_4^-]$ ) system. No NO signal had been detected for the reference ( $[\text{Hmim}^+-\text{NO}_3^-] + [\text{Hmim}^+-\text{Cl}^-]$ ) system under the same conditions. In both systems, the cations of ILs are identical, so the differences in the above phenomena may originate from the functions of anions  $[\text{AlCl}_4^-]$  and  $[\text{Cl}^-]$ . The standard electrode potential of  $[\text{Al}^{3+}/\text{Al}^0]$  is  $-1.662$  V,<sup>18</sup> so the oxidation ability of Al to Au can be excluded first. Therefore, we speculate that the presence of  $[\text{AlCl}_4^-]$  may act as a catalyst to make the thermodynamic conversion of  $\text{NO}_3^-$  to NO more easily triggered in kinetics.

In addition, to the experimental approaches mentioned above, density functional theory (DFT) calculations were used to further understand the details of the  $[\text{NO}_3^-]$  conversion promoted by  $[\text{AlCl}_4^-]$  to generate NO (eq 3). Considering that binary-ILs system 1 differs from system 2 only by the  $[\text{AlCl}_4^-]$  vs  $[\text{Cl}^-]$  nature of the anions, this result points to an essential role for this parameter. Hence, we have attempted to probe the reaction mechanism using simplified models established by the Vienna Ab initio Simulation Package (VASP) based on first-principles DFT theory, as shown in Figure 3. Before conducting the catalytic reaction barrier simulation, a series of adsorption tests were performed to compare the adsorption properties of  $[\text{NO}_3^-]$  and  $[\text{H}^+]$  over both models. The results of the adsorption energy analysis indicated a more negative adsorption energy value for  $[\text{NO}_3^-]$ ,

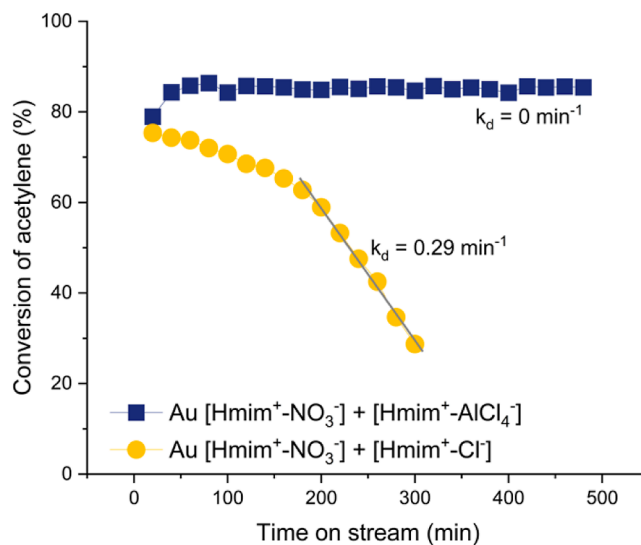


**Figure 3.** Reaction energy profiles for the conversion of  $\text{NO}_3^-$ . The blue, gray, white, pink, green, and red balls representing N, C, H, Al, Cl, and O atoms, respectively.

which represents the trapping mechanism of  $[\text{NO}_3^-]$  in the  $[\text{AlCl}_4]^-$  and  $[\text{Cl}^-]$ -based ILs. Since the high absolute value of the adsorption energy reflects a strong adsorption behavior. We, therefore, sought to study the transformation mechanism of the reaction that first takes place with the  $[\text{NO}_3^-]$  adsorption between  $[\text{NO}_3^-]$ - and  $[\text{AlCl}_4]^-$  or  $[\text{Cl}^-]$ -based ILs, shown in Figure 3 step 2. Compared to  $[\text{Cl}^-]$ -based ILs, the more negative adsorption free energy indicates the  $[\text{AlCl}_4]^-$ -based ILs exhibited stronger and spontaneous adsorption properties to  $[\text{NO}_3^-]$ . Directly following, negative binding values  $\sim 0.2$  eV represent that the adsorption of the  $[\text{H}^+]$  on anions is spontaneous in the two systems, leading to the formation of ion clusters. The adsorption energies for the most stable configurations are listed in Figure 3 step 3. In line with previous speculation, the decomposition of  $[\text{NO}_3^-]$  and the formation of water molecules will be a key to identifying the reaction over two systems which could occur easier. The calculated structures of transition states are illustrated in Figure 3 step 4. The reaction pathway over system 1 is likely to occur more easily than reaction system 2 since it demands a lower reaction energy barrier (0.35 eV). Therefore, the reaction could occur easier by  $[\text{AlCl}_4]^-$  catalysis. The calculation result describes the experimental data nicely and also confirms our previous conjecture. We have elaborated on the possible mechanism of the aforementioned mixed-ILs in the dissolution of noble metals through DFT theory. Given the important role  $[\text{AlCl}_4]^-$  and  $[\text{Cl}^-]$ -based anions in dissolving noble metals, the cation substitution in ILs can be expected, which provides a huge data source for the selection of the ILs accompanied by unique anionic characteristics.

To the best of our knowledge,  $\text{Au}^{3+}$  is reduced to  $\text{Au}^0$  by  $\text{C}_2\text{H}_2$ , resulting in the deactivation of the Au-based catalyst,<sup>19–21</sup> which seriously restricts the development of Au-based catalysts and the subsequent industrialization process. In addition to aqua regia, a green and safe solvent which should have the ability to oxidize  $\text{Au}^0$  and stabilize  $\text{Au}^{3+}$ , is urgently needed, especially for gas–liquid acetylene hydrochlorination.<sup>22–24</sup> Therefore, the developed binary-ILs system was applied in this reaction. Due to the requirement for gas–liquid acetylene hydrochlorination, excess ILs were employed in the catalytic performance evaluation process. As shown in Figure S2, the leaching efficiency of  $\text{Au}^0$  was almost completely dissolved in just 5 min at an 800 IL/S ratio. Apparently, concentration effects dominate the leaching process. This strategy provides a facile way to rapidly increase

the leaching efficiency of noble metals. The catalytic performance of gas–liquid acetylene hydrochlorination was shown in Figure 4. In the  $([\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{Cl}^-])$



**Figure 4.** Catalytic activity of gas–liquid acetylene hydrochlorination for the  $([\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{AlCl}_4^-])$  and  $([\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{Cl}^-])$  systems. Reaction conditions: IL/S(Au) = 800, 150 °C,  $V(\text{HCl})/V(\text{C}_2\text{H}_2) = 1$ , GHSV = 90  $\text{h}^{-1}$ .

system, the acetylene conversion decreased from an initial 75 to 28%, while 84% of the acetylene conversion was gained and stabilized within 480 min. The selectivity for VCM was higher than 99% for both tests. The deactivation rate was  $0.29 \text{ min}^{-1}$  for the first system and  $0 \text{ min}^{-1}$  for the second system, suggesting the superior catalytic stability in the  $([\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{AlCl}_4^-])$  system. The literature has demonstrated that the cationic  $\text{Au}^{3+}$  governs the activity and stability of Au catalytic systems. Obviously, the reduction deactivation of cationic  $\text{Au}^{3+}$  can be ignored in the  $([\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{AlCl}_4^-])$  system because  $\text{Au}^0$  can be oxidized quickly and timely in this system, which has been proved in the aforementioned studies. For the catalysts with cations Pd and Pt and other non-noble metal cations catalyzed acetylene hydrochlorination, the catalytic performance advantages of  $([\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{AlCl}_4^-])$  system can be expected. It should be noted that the presence of HCl has a significant impact on ILs, especially under the conditions of a long-term reaction process.<sup>25</sup> The imidazolium-based ILs with chloride anion can substantially absorb the HCl gas through the formation of chemical bonds between Cl- and HCl.<sup>26</sup> The instability of the developed ILs under a long-term reaction process may be the focus of future studies.

## CONCLUSIONS

In summary, an easy and rapid protocol for dissolving noble metals is developed.  $[\text{AlCl}_4]^-$  acts as a catalyst to make the thermodynamic conversion of  $[\text{NO}_3^-]$  to NO easier in kinetics. The developed binary-ILs system was applied in gas–liquid acetylene hydrochlorination, which is a very important industrial process to produce VCM. The reduction deactivation of cationic  $\text{Au}^{3+}$  can be solved in the presence of the binary-ILs of  $([\text{Hmim}^+ - \text{NO}_3^-] + [\text{Hmim}^+ - \text{AlCl}_4^-])$  system, expanding the practical applications of ILs dissolution systems on recycling noble metal catalysts.



## EXPERIMENTAL SECTION

**Materials and Methods.** *Materials.* Gold (Au), palladium (Pd), and platinum (Pt) powder were provided by Aladdin (Shanghai Aladdin Biochemical Technology Co., Ltd, Shanghai, China). 1-Hexyl-3-methylimidazolium nitrate [Hmim<sup>+</sup>-NO<sub>3</sub><sup>-</sup>], 1-hexyl-3-methylimidazolium aluminum tetrachloride [Hmim<sup>+</sup>-AlCl<sub>4</sub><sup>-</sup>] and 1-hexyl-3-methylimidazolium chloride [Hmim<sup>+</sup>-Cl<sup>-</sup>] were obtained from the Lanzhou Institute of Physical Chemistry, Chinese Academy of Sciences. High purity reactants C<sub>2</sub>H<sub>2</sub> (>99.9%) and HCl (>99.9%) were purchased from Hangzhou Jingong Special Gases, Ltd. and Shanghai Chengkung Gas Industry, Ltd. All chemicals were used as received without any further purification.

*Tests and Analytical Techniques.* Typically, the metal sources were mixed with imidazolium-based IL mixtures and stirred at a constant speed of 600 rpm for a target reaction time of 60 °C. The reactant solution was filtered by a 0.22 μm membrane, and the concentration of gold or other metals in the solution was determined by atomic absorption spectrometry (AAS) (Beijing Puxi General Instruments Co., Ltd., Beijing, China). Finally, the leaching yield for each metal was calculated according to eq 4.

$$\text{Leaching yield} = \frac{\text{Metal mass in solution}}{\text{Initial metal mass}} \times 100\% \text{ wt } \% \quad (4)$$

The gas–liquid acetylene hydrochlorination was performed in a self-designed glass reactor, similar to the bubbling reactor widely employed in gas–liquid reactions, under an atmospheric pressure, 150 °C, GHSV (C<sub>2</sub>H<sub>2</sub>) = 90 h<sup>-1</sup>, V(HCl)/V(C<sub>2</sub>H<sub>2</sub>) = 1. The gas phase products were passed through an absorption bottle containing NaOH solution to remove excess HCl first and then analyzed online by GC equipped with a flame ionization detector (FID). Chromatographic separation and identification of the products were carried out using a Porapak N packed column (6 ft × 1/800 stainless steel).

*DFT Calculations.* All the calculations were implemented using the plane wave basis of the Vienna Ab-initio Simulation Package (VASP). The Perdew–Becke–Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) as the exchange–correlation functional was implemented. The kinetic energy cutoff for the plane wave basis sets was 500 eV to approximate the valence electron densities and the projector augmented wave (PAW) method to account for the core–valence interaction. The Brillouin-zone sampling was restricted to the Gamma point as we used a large computational cell. All investigated structures are presented in Figure 3. During the geometry relaxation, the shape and volume of the unit cell as well as the atomic positions in the unit cell of each configuration are fully optimized. The convergence threshold for self-consistent-field iteration is set to 10<sup>-5</sup> eV, and the geometry optimization was iterated until all atomic forces became smaller than 0.02 eV/Å.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c07064>.

Detected desorption gas signals during the leaching process for the Au<sup>0</sup> powder and visual leaching process of the Au<sup>0</sup> powder in the [Hmim<sup>+</sup>-NO<sub>3</sub><sup>-</sup>] + [Hmim<sup>+</sup>-AlCl<sub>4</sub><sup>-</sup>] system (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (52070035 and 22078302) and the Jilin Province Scientific and Technological Planning Project of China (no. 20200403001SF) are gratefully acknowledged.

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