



Economical and efficient recovery of Pd and Al₂O₃ from spent Pd/Al₂O₃ catalyst with integrated sodium roasting–reductive leaching process

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Abstract: An integrated sodium roasting–reductive leaching process was developed to recover Pd and Al₂O₃ from spent Pd/Al₂O₃ catalyst. The thermodynamic analysis of sodium roasting indicated that NaOH, Na₂CO₃ and Na₂C₂O₄ could completely react with Al₂O₃ to form NaAlO₂ at the optimal Na₂O/Al₂O₃ molar ratio and temperature. The Al₂O₃ leaching ratios were 99.6%, 61.0% and 55.3%, respectively, when the roasted residues from NaOH, Na₂CO₃ and Na₂C₂O₄ roasting were subjected to water leaching. Mechanical activation–dry NaOH roasting process avoided the consolidation of roasted residue, and high Al₂O₃ leaching ratio could be obtained. Reductive leaching with N₂H₄·H₂O averted Pd dissolution loss during water leaching, and 99.7% of Al₂O₃ in the catalyst was leached. NaAlO₂ leachate and Pd-enriched residue were finally obtained, and the valuable Al and Pd can be further recovered.

Key words: spent Pd/Al₂O₃ catalyst; Pd and Al₂O₃ recovery; sodium roasting; mechanical activation; reductive leaching

1 Introduction

Palladium (Pd) is a precious metal and has strong catalytic activity [1–3]. To improve the catalytic performance, Pd is generally loaded on Al₂O₃ carrier [4]. During service, the catalyst can be deactivated due to fouling, poisoning and thermal degradation/sintering, leading to the production of large amounts of spent Pd/Al₂O₃ catalysts that has become an important secondary source for recovering Pd [5].

The reported routines to recover Pd from spent Pd/Al₂O₃ catalyst can be categorized into pyro-metallurgical and hydrometallurgical processes [6]. The pyro-metallurgical processes mainly include the chlorination volatilization [7] and metal trapping [8,9]. High Pd recovery can be obtained, but pyro-metallurgical processes generally suffer from

high initial investment, high energy consumption and potential atmospheric pollution [10]. Furthermore, the valuable Al₂O₃ carrier goes into the slag and is difficult to be recovered [11]. Therefore, more attention has been paid to hydrometallurgical processes, which can be divided into two types: direct Pd leaching, and Al₂O₃ carrier pre-dissolution followed by Pd leaching.

Direct Pd leaching commonly requires acidic and highly oxidizing environment. The most widely reported method is the combination of HCl and oxidants (HNO₃, NaClO, NaClO₃, H₂O₂ and CuCl₂) [12–17]. However, during service, part of Pd is oxidized into PdO which is less amenable to lixiviant attack [18]. Also, Pd may penetrate into the inner layer of the Al₂O₃ carrier due to thermal diffusion during high-temperature catalytic reaction, resulting in its difficult contact with the lixiviant. In addition, the spent Pd/Al₂O₃ catalyst generally has a

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high carbon content, resulting in the adsorption of the leached Pd. The above reasons make it difficult to obtain a high Pd leaching percentage. Therefore, pretreatments such as grinding [19], oxidative roasting [10], reductive roasting [15], sulfation roasting [20], reduction leaching [21] and alkaline pressure leaching [18] are generally conducted to remove the encapsulation of Al_2O_3 carrier and reduce PdO into easily-leached metallic Pd, which complicates the direct leaching process. Moreover, the dissolution of a considerable part of Al_2O_3 is inevitable during Pd leaching, which significantly increases reagent consumption and makes subsequent Pd separation from the leachate difficult.

In comparison, Al_2O_3 carrier pre-dissolution followed by Pd leaching may be a more appropriate routine. Al_2O_3 is an amphoteric oxide that can be leached by common acids and bases [22–25]. However, high reagent consumption and long leaching time are required, and the Al_2O_3 leaching percentage is generally low because during service, part of initial $\gamma\text{-Al}_2\text{O}_3$ is transformed into $\alpha\text{-Al}_2\text{O}_3$ that is difficult to be dissolved [18].

Using the evident difference of roasting property of Pd and Al_2O_3 , sodium roasting is proposed to transform Al_2O_3 into NaAlO_2 that can be easily leached with water while Pd is remained in the roasted residue, and thus the efficient separation of Pd and Al_2O_3 in the spent catalyst is realized. The thermodynamics of sodium roasting, sodium agent selection, roasting behavior of spent catalyst and leaching behavior of roasted residue were systematically researched in this study. The obtained results are valuable for the comprehensive utilization of spent Pd/ Al_2O_3 catalyst.

2 Experimental

2.1 Material and reagents

The spent Pd/ Al_2O_3 catalyst used in this study was from petrochemical industry. The catalyst was mainly black spherical particle with the size from 1.5 to 2.5 mm, and it was milled in a rod mill to the size of 75% less than 74 μm for subsequent chemical analyses and experiments.

The chemical composition analysis for the spent catalyst in Table 1 showed that the contents of Al_2O_3 and Pd achieved 86.87% and 4389 g/t, respectively. Thus, the catalyst has high economic

value and it is our goal to recover the two valuable components. The XRD pattern in Fig. 1 indicated that the only phase in the catalyst is Al_2O_3 . The SEM-EDS analysis for the catalyst displayed in Figs. S1(a–c) in Supporting materials manifested that the O and Al contents varied greatly in different regions. The Al_2O_3 content and its purity on the large white particle (Point B) were high while those on the small white particle (Point A) were low, indicating that the Al_2O_3 distribution in the catalyst was not uniform. Reagents used in this work, such as NaOH, Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ were of analytical grade. Ultrapure water was used throughout all experiments.

Table 1 Chemical composition of spent catalyst (wt.%)

Al_2O_3	Pd*	C	SiO_2	Fe
86.87	4389	2.79	0.44	0.15
Zn	CaO	TiO_2	Cu	Ni
0.011	0.056	0.0072	0.001	0.0036

* Unit: g/t

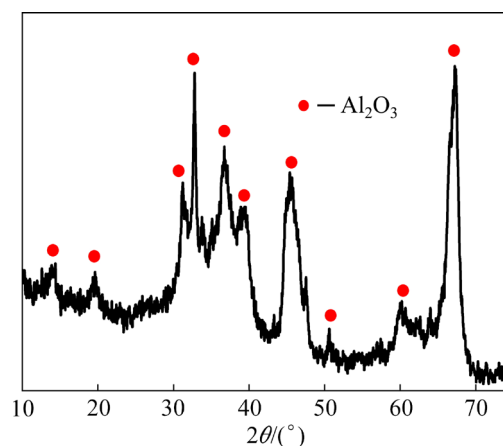


Fig. 1 XRD pattern of spent Pd/ Al_2O_3 catalyst

2.2 Experimental methods

The mechanical activation test was conducted in a planetary ball mill. The spent Pd/ Al_2O_3 catalyst and sodium agent were put into the mill and ground for 5 min. Then, the mixed material was transformed into the muffle furnace for sodium roasting. The roasted residue was leached in a beaker placed in an electric-heated water bath equipped with a mechanical stirrer. For each experiment, the predetermined quantities of water, reagents (if used) and roasted residue were consecutively added into the beaker, and the pulp was agitated. When the reaction was finished, the

pulp was filtrated. The leachate and residue were subjected to chemical composition analysis [26].

2.3 Analytical methods

The elemental concentration was determined by inductively coupled plasma–optical emission spectrometer (ICP–OES, Optima 8300 DV, Shelton). Mineralogical compositions of the solid samples were analyzed by an X-ray diffractometer (XRD, D/Max 2500, Rigaku) with a scanning angle from 5° to 70° . Scanning electron microscope coupled with energy dispersive spectrometer (SEM–EDS, MIA3, TESCAN) was adopted to research the surface morphology and composition of solid samples.

3 Results and discussion

3.1 Thermodynamic analysis of sodium roasting

As displayed in Fig. 1, aluminium in the spent catalyst existed as Al_2O_3 which can be transformed into water-soluble NaAlO_2 through the sodium roasting [27]. Here, NaOH , Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ were selected as the potential sodium agents, and the phase diagrams of $\text{NaOH–Al}_2\text{O}_3$, $\text{Na}_2\text{CO}_3\text{–Al}_2\text{O}_3$ and $\text{Na}_2\text{C}_2\text{O}_4\text{–Al}_2\text{O}_3$ systems under air atmosphere were drawn by Factsage 7.0 software, as shown in Figs. S2(a–c) and Tables S1–S3.

When the $\text{NaOH}/(\text{NaOH}+\text{Al}_2\text{O}_3)$ molar ratio is less than 0.18, no NaAlO_2 but intermediate product of $\text{NaAl}_9\text{O}_{14}$ is formed at the temperature below 200°C . No new phase appears as the temperature rises, and there is merely the evaporation of water vapor and transformations of Al_2O_3 and $\text{NaAl}_9\text{O}_{14}$ crystal phases. While the molar ratio is between 0.18 and 0.22, new intermediate product of $\text{Na}_2\text{Al}_{12}\text{O}_{19}$ occurs. With the increase of molar ratio to 0.22–0.5, NaAlO_2 phase begins to form, and when the temperature is higher than 200°C , Al_2O_3 completely participates in the reaction to form NaAlO_2 and $\text{NaAl}_9\text{O}_{14}$. As the molar ratio augments to 0.67–1, Al_2O_3 phase disappears and it can be transformed into NaAlO_2 in the temperature range of $25\text{--}1100^\circ\text{C}$.

The phase diagrams of $\text{Na}_2\text{CO}_3\text{–Al}_2\text{O}_3$ and $\text{Na}_2\text{C}_2\text{O}_4\text{–Al}_2\text{O}_3$ systems are similar to that of $\text{NaOH–Al}_2\text{O}_3$ system. When the temperatures are lower than 750°C and 700°C , NaAlO_2 cannot be generated. As the temperatures are over the two values, NaAlO_2 phase starts to appear, and

when the molar ratios of $\text{Na}_2\text{CO}_3/(\text{Na}_2\text{CO}_3+\text{Al}_2\text{O}_3)$ and $\text{Na}_2\text{C}_2\text{O}_4/(\text{Na}_2\text{C}_2\text{O}_4+\text{Al}_2\text{O}_3)$ are beyond 0.5 and 0.5, Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ can totally react with Al_2O_3 to form NaAlO_2 .

3.2 Selection of sodium agent

3.2.1 Roasting–leaching performance of three sodium agents

Based on the above theoretical calculation result, sodium roasting followed by water leaching of the spent catalyst was carried out to compare the performances of NaOH , Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ as the sodium agents. The water leaching experiment was conducted under the conditions of liquid to solid ratio 2, temperature 25°C and time 60 min. The effect of roasting temperature on the Al_2O_3 leaching ratio is shown in Fig. 2. Here, the roasting time was 2 h, the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio was 2, i.e., the molar ratios of $\text{NaOH}/(\text{NaOH}+\text{Al}_2\text{O}_3)$, $\text{Na}_2\text{CO}_3/(\text{Na}_2\text{CO}_3+\text{Al}_2\text{O}_3)$ and $\text{Na}_2\text{C}_2\text{O}_4/(\text{Na}_2\text{C}_2\text{O}_4+\text{Al}_2\text{O}_3)$ were 0.8, 0.67 and 0.67, respectively.

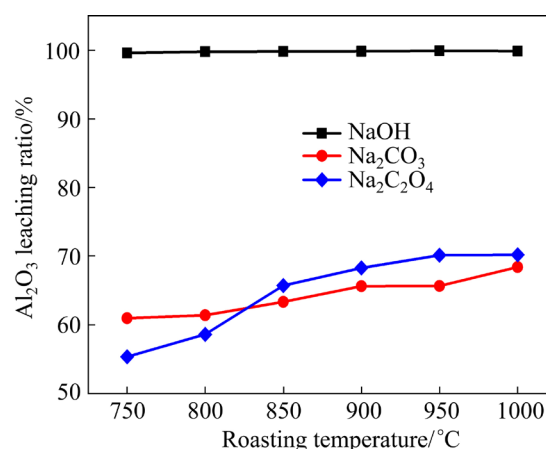


Fig. 2 Effect of roasting temperature on Al_2O_3 leaching ratio with three sodium agents

The Al_2O_3 leaching ratio achieved 99.6% at 750°C for NaOH roasting, and it basically remained stable with the increase of temperature to 1000°C . By comparison, the Al_2O_3 leaching ratios were only 61.0% and 55.3% at 750°C for Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ roasting, respectively, and they only slightly increased to 68.4% and 70.2% as the temperature increased to 1000°C , which may be ascribed to the insufficient Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ dosages. Therefore, the effects of Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ dosages on the Al_2O_3 leaching ratio at 900°C were studied.

As presented in Table 2, when the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio increased from 2 to 4, the Al_2O_3 leaching ratios only rose from 65.6% and 68.3% to 71.5% and 79.3% for Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ roasting, respectively. Therefore, compared with NaOH roasting, the Al_2O_3 leaching ratios were still unsatisfactory for Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ roasting even at higher roasting temperature and reagent dosage.

Table 2 Effect of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio on Al_2O_3 leaching ratio at 900 °C

Sodium agent	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio	Al_2O_3 leaching ratio/%
Na_2CO_3	2:1	65.6
Na_2CO_3	4:1	71.5
$\text{Na}_2\text{C}_2\text{O}_4$	2:1	68.3
$\text{Na}_2\text{C}_2\text{O}_4$	4:1	79.3

3.2.2 Mechanism of sodium roasting–leaching process

To explore the reason causing the different Al_2O_3 leaching ratios for NaOH , Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$, XRD analyses for the roasted residues and leached residues were performed. As shown in Fig. 3(a), the XRD patterns of three roasted residues were similar, and both NaAlO_2 and $x\text{NaAlO}_2 \cdot y\text{Al}_2\text{O}_3$ were detected. Thus, the difference of roasting–leaching performance of three sodium agents cannot be judged based on the XRD patterns of roasted residues. As displayed in Fig. 3(b), $\text{CaPd}_{(3-x)}(\text{Fe}, \text{Al})_{2x/3}\text{O}_4$, $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ were the phases in the leached residues from NaOH , Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ roasting.

The SEM–EDS results of three leached residues in Figs. S3(a–c), Figs. S4(a–c) and Figs. S5(a–c) in Supplementary materials were also different. For the leached residue from NaOH roasting, the Al contents were only 0.72% and 28.97%. Also, compared with Fig. S1(a), the amount of white large particles with high Al content was significantly decreased while that of black fine particles with high Pd content was considerably increased, showing that a large amount of Al in the catalyst was leached while Pd was enriched in the residue. For the leached residue from Na_2CO_3 roasting, the particle size was large, and the Al contents were as high as 48.51% and 39.25%. This indicated that a considerable amount of Al remained in the residue after water leaching, which was in

accordance with the low Al_2O_3 leaching ratio in Section 3.2.1. For the leached residue from $\text{Na}_2\text{C}_2\text{O}_4$ roasting, the particle size was also large, and the Al contents (36.95% and 34.13%) were lower than those in the leached residue from Na_2CO_3 roasting, showing that its Al_2O_3 leaching ratio was higher, which was consistent with the leaching results in Section 3.2.1.

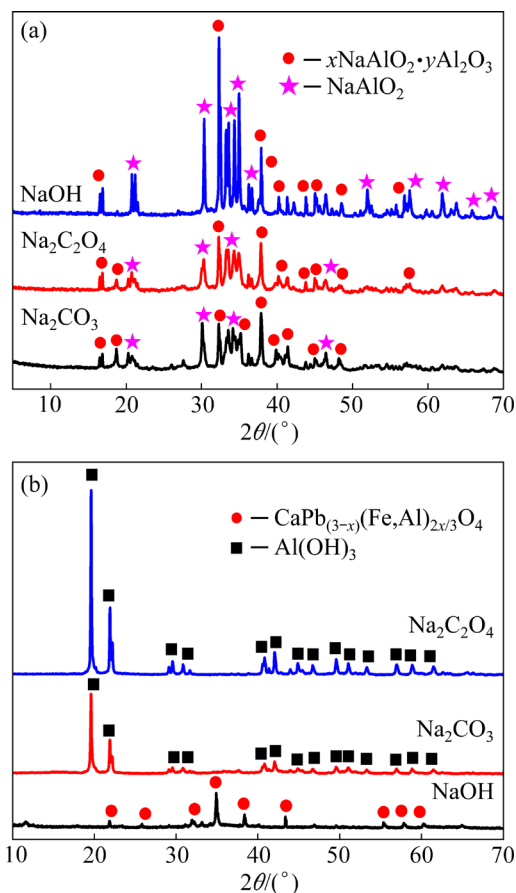


Fig. 3 XRD patterns of roasted residues (a) and leached residues (b) from NaOH , Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ roasting

Based on the above results, the potential reason for the low Al_2O_3 leaching ratios for Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ roasting was that the roasted product of NaAlO_2 and $x\text{NaAlO}_2 \cdot y\text{Al}_2\text{O}_3$ massively hydrolyzed during water leaching due to their low relatively pulp pH values. As a result, large amounts of $\text{Al}(\text{OH})_3$ precipitate was generated, leading to the low Al_2O_3 leaching percentages. To verify this hypothesis, the intensified leaching of the two roasted residues with 5% NaOH solution instead of ultrapure water was performed, and the results are displayed in Figs. 4(a, b). Clearly, compared with the results with water leaching, the Al_2O_3 leaching ratio was obviously higher at the same roasting

temperature. 99.8% and 99.6% of the Al_2O_3 in the spent catalyst were leached after it was roasted by Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ at 1000 °C. Therefore, the results supported the above hypothesis.

A detailed comparison among three sodium agents for treating 1 t spent catalyst is shown in Table 3. Obviously, to obtain close Al_2O_3 leaching ratio, the required agent dosage and temperature with NaOH roasting were lower than those with Na_2CO_3 and $\text{Na}_2\text{C}_2\text{O}_4$ roasting. Therefore, NaOH was selected as the most economical sodium reagent for treating the spent catalyst.

3.3 Sodium roasting behavior of spent catalyst

3.3.1 Effect of roasting temperature

The effect of roasting temperature on the Al_2O_3 leaching ratio was first researched under the conditions of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio 2:1 and time 2 h. As indicated in Fig. 5(a), the Al_2O_3 leaching percentage was only 50.2% at 400 °C and rose to 78.0% as the temperature increased to 800 °C when dry roasting (without adding water) was adopted. Figure 5(b) shows the pictures of the roasted residue. Clearly, the white NaOH particle was observed. Thus, the low leaching percentage can be ascribed to the incomplete solid–solid reaction between NaOH and Al_2O_3 . To improve the roasting

reaction, appropriate amount of water was added in the mixed material, i.e., the material was subjected to wet roasting. The Al_2O_3 leaching ratios were all higher than 99% at 400–800 °C (Fig. 5(a)). However, severe consolidation of roasted residue occurred and it was difficult to separate the roasted residue from the roasting container (Fig. 5(c)), which was unbeneficial to the industrial application of this process.

Mechanical activation is an effective way to strengthen the metallurgical process, and it was adopted to increase the mixing degree of NaOH and spent catalyst [28–32]. As shown in Fig. 5(d), the roasted residue was loose and easy to be separated from the container. Moreover, the Al_2O_3 leaching ratio achieved 99.7% when the roasting temperature was 700 °C (Fig. 5(a)). Thus, a high Al_2O_3 leaching percentage could be gotten and the consolidation of roasted residue was also avoided when mechanical activation–dry roasting process was adopted.

3.3.2 Effects of roasting time and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio

The effects of roasting time and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio on Al_2O_3 leaching ratio for mechanical activation–dry roasting was studied, and the roasting temperature was 700 °C. As presented in Fig. S6(a), the Al_2O_3 leaching ratio reached 99.2%

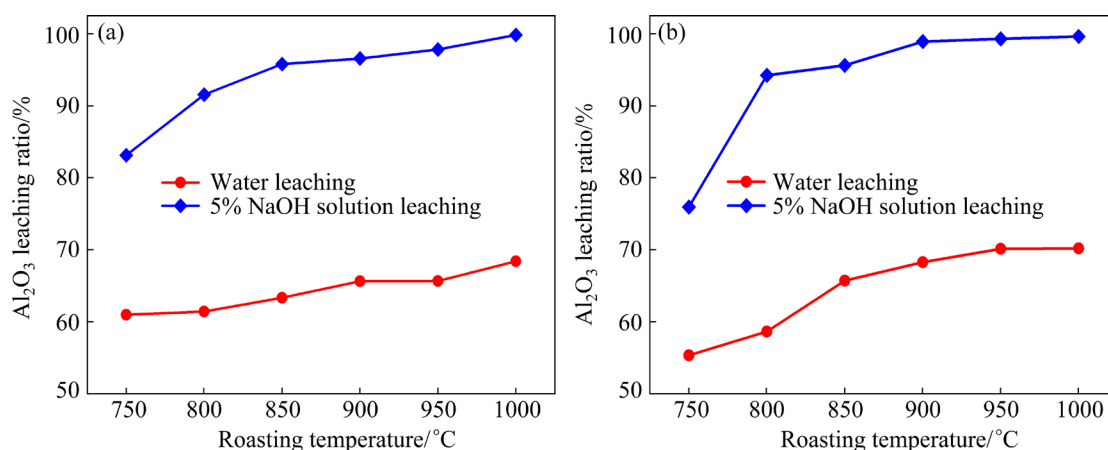


Fig. 4 Comparison between water and 5% NaOH solution leaching of roasted residue from Na_2CO_3 (a) and $\text{Na}_2\text{C}_2\text{O}_4$ (b) roasting

Table 3 Comparisons among three sodium agents in treating 1 t spent catalyst

Sodium agent	Dosage for roasting/t	Dosage for leaching/t	Price/ (CNY·t ⁻¹)	Reagent cost/ CNY	Temperature/ °C	Al_2O_3 leaching ratio/%
NaOH	1.36	0	2200	2992	750	99.6
Na_2CO_3	1.81	0.35	1450	3395	1000	99.8
$\text{Na}_2\text{C}_2\text{O}_4$	2.28	0.35	6800	16274	1000	99.6

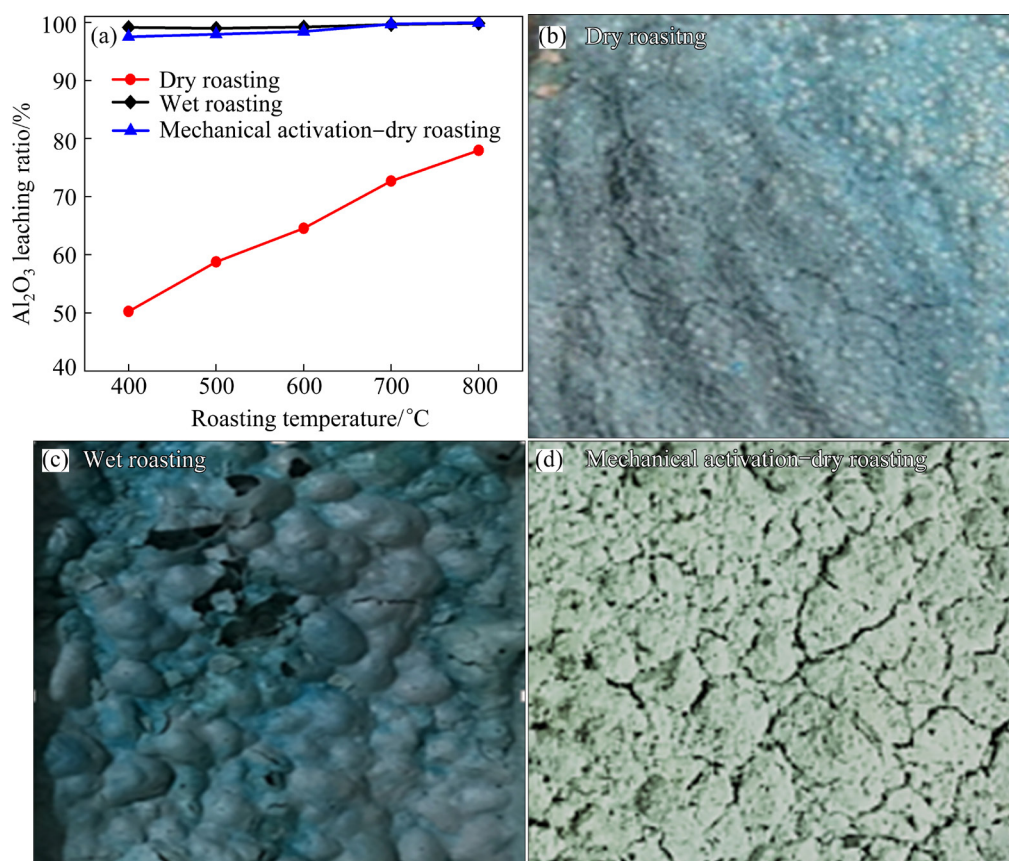


Fig. 5 Effect of roasting temperature on Al_2O_3 leaching ratio for dry roasting, wet roasting and mechanical activation-dry roasting (a), and pictures of their roasted residues (b–d)

after roasting for 1 h. When the time was increased to 1.5 h, the leaching ratio augmented to 99.8%. Further increase of roasting time did not contribute to the evident increase of Al_2O_3 leaching ratio. Thus, the optimal roasting time was 1.5 h.

As displayed in Fig. S6(b), the Al_2O_3 leaching percentage was only 45.4% at $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio of 1:1. However, according to the thermodynamic calculation results in Section 3.1, the Al_2O_3 in the spent catalyst can be completely transformed into NaAlO_2 at the theoretical value of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio of 1:1. Thus, the low Al_2O_3 leaching ratio can be ascribed to the inadequate solid phase reaction between NaOH and Al_2O_3 . With the increase of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio, the leaching percentage first increased considerably and then basically kept steady, and it achieved the maximum (i.e. 99.8%) at the ratio of 2:1. Therefore, the optimum $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio was 2:1.

3.4 Leaching behavior of roasted residue

3.4.1 Water leaching

The effect of liquid to solid ratio on the Al_2O_3 leaching ratio is indicated in Fig. S7(a). The Al_2O_3

leaching ratio was only 94.1% at liquid to solid ratio 1:1. To investigate the reason for the low leaching ratio, XRD analysis for the leached residue was performed. As shown in Fig. 6, apart from $\text{CaPd}_{(3-x)}(\text{Fe},\text{Al})_{2x/3}\text{O}_4$, NaAlO_2 and $\text{Al}(\text{OH})_3$ were also detected, which indicated that NaAlO_2 was not dissolved completely at the low liquid to solid ratio. Furthermore, in the experiment we found that the pulp had large viscosity and its filtration rate was slow. Because of this, NaAlO_2 reacted with CO_2 in the air to form $\text{Al}(\text{OH})_3$ precipitate, leading to the low Al_2O_3 leaching ratio. With the increase of liquid to solid ratio to 2:1, the leaching ratio increased to 99.8%. The XRD pattern of the leached residue (Fig. 6) indicated that $\text{CaPd}_{(3-x)}(\text{Fe},\text{Al})_{2x/3}\text{O}_4$ was the only phase, showing that the generated NaAlO_2 during roasting was fully dissolved into the water. As displayed in Figs. S7(b, c), both the leaching temperature and time exerted no evident effect on the Al_2O_3 leaching ratio which reached its maximum under the conditions of temperature 25 $^{\circ}\text{C}$ and time 10 min.

The result of chemical composition analysis for the leaching solution under the optimum

leaching conditions is given in Table S4. The Al and Na concentrations were high while those of other impurities were very low. However, the Pd concentration in the solution reached 39.09 mg/L, and the calculated Pd loss percentage achieved 3.92%. This may be because during high-temperature roasting at air atmosphere, part of Pd in the catalyst reacted with O₂ and NaOH to form water-soluble Na₂Pd(OH)₄ that went into the solution during leaching [33,34], and the reactions are given in Eqs. (1) and (2):

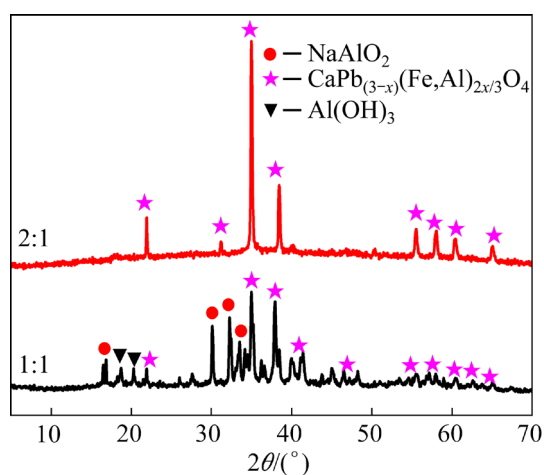
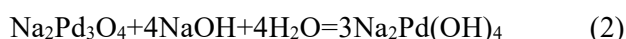
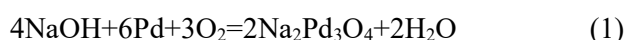
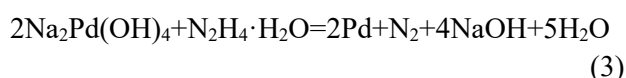


Fig. 6 XRD patterns of leaching residues with different liquid to solid ratios during water leaching

3.4.2 Reductive leaching

Hydrazine hydrate (N₂H₄·H₂O) was added during water leaching to restrain Pd dissolution, and the reaction can be described in Eq. (3). Under the optimum leaching conditions obtained in Section 3.3.2, the effect of N₂H₄·H₂O concentration on the Al₂O₃ leaching ratio and Pd loss ratio was investigated. As displayed in Fig. 7(a), with the increase of N₂H₄·H₂O concentration, the Al₂O₃ leaching ratio first kept unchanged and then declined evidently as N₂H₄·H₂O concentration was over 0.032 mol/L. Pd loss ratio gradually decreased with increasing the N₂H₄·H₂O concentration and declined to zero at 0.008 mol/L N₂H₄·H₂O, and the Al₂O₃ leaching ratio reached 99.7%.



The chemical composition of the reductive leaching solution in Table S5 showed that Pd was

not detected. The chemical composition of the reductive leaching residue presented in Table S6 indicated that the Pd content reached 203.20 kg/t (i.e. 20.32%). Thus, after NaOH roasting–reductive leaching, Pd was enriched by nearly 50 times. The XRD pattern of reductive leaching residue in Fig. 7(b) is similar to that of water leaching residue, i.e., only CaPd_(3-x)(Fe,Al)_{2x/3}O₄ phase was determined.

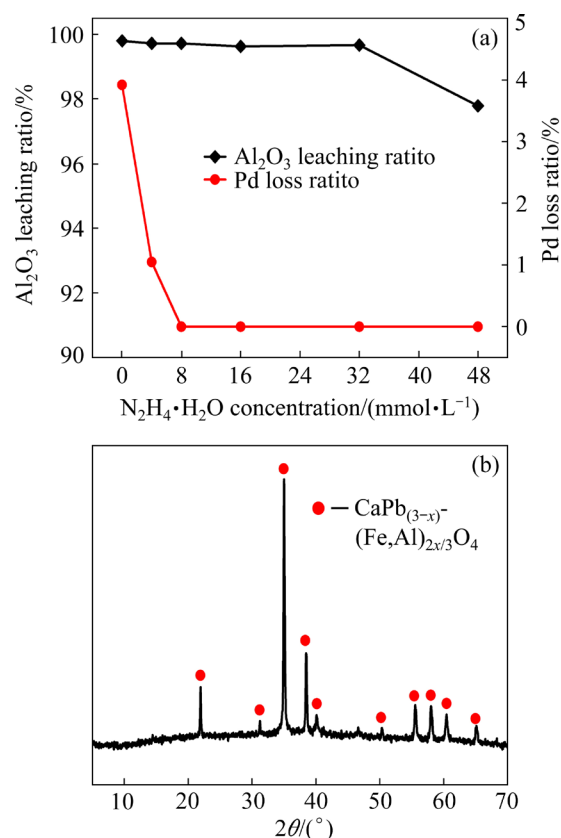


Fig. 7 Effect of N₂H₄·H₂O concentration on Al₂O₃ leaching ratio and Pd loss ratio (a) and XRD pattern of reductive leaching residue (b)

Based on the above studies, an economical and efficient sodium roasting–reductive leaching process was put forward to recover Pd and Al₂O₃ from the spent Pd/Al₂O₃ catalyst, and the flow sheet is displayed in Fig. 8. First, the spent catalyst and NaOH were mixed and milled in the rod mill to the size of 75% less than 0.074 mm. Afterwards, the finely ground material was roasted at 750 °C for 1.5 h, and the roasted residue was subjected to reductive leaching under the conditions of N₂H₄·H₂O concentration 0.008 mol/L, liquid to solid ratio 2:1, temperature 25 °C and time 10 min. After filtering the pulp, the NaAlO₂ solution and Pd-enriched residue were gotten. The NaAlO₂ solution can be used for remaking the Al₂O₃ catalyst

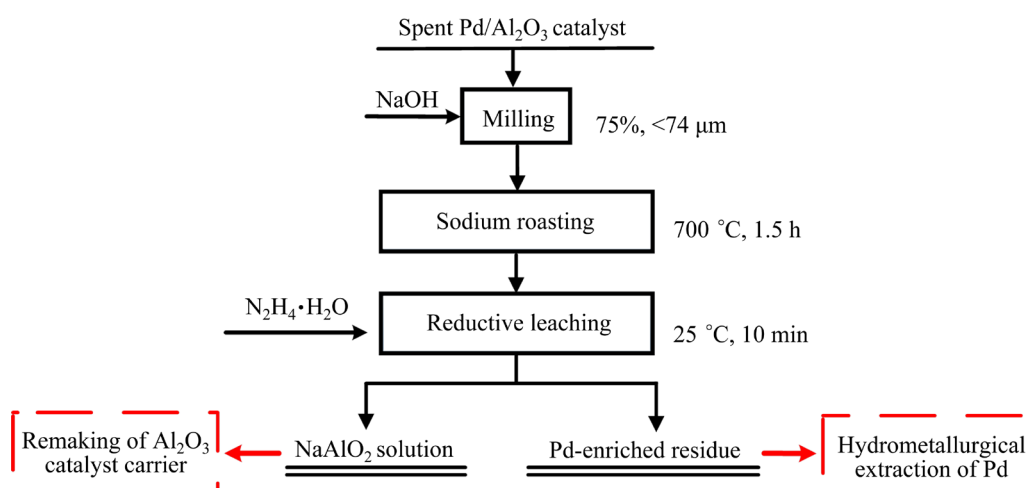


Fig. 8 Sodium roasting–reductive leaching process for recovering Pd and Al₂O₃ from spent Pd/Al₂O₃ catalyst

carrier while the Pd-enriched residue is subjected to hydrometallurgical chloride leaching–sulfide precipitation for Pd recovery.

4 Conclusions

(1) The thermodynamic analysis of sodium roasting indicated that NaOH, Na₂CO₃ and Na₂C₂O₄ could completely react with Al₂O₃ to form NaAlO₂ when the molar ratios of NaOH/(NaOH+Al₂O₃), Na₂CO₃/(Na₂CO₃+Al₂O₃) and Na₂C₂O₄/(Na₂C₂O₄+Al₂O₃) were beyond 0.67:1, 0.5:1 and 0.5:1, and the roasting temperatures were over 25, 750 and 700 °C, respectively.

(2) 99.6%, 61.0% and 55.3% of Al₂O₃ in the spent catalyst was leached by water after it was roasted by NaOH, Na₂CO₃ and Na₂C₂O₄. The Al₂O₃ leaching ratios increased to 99.8% and 99.6% when the roasted residue of Na₂CO₃ and Na₂C₂O₄ roasting was leached with 5% NaOH solution, but their roasting temperature and reagent cost were higher than those of NaOH roasting.

(3) The roasted residue was consolidated severely using wet roasting with NaOH as the sodium agent. Dry roasting solved the consolidation problem, but the Al₂O₃ leaching ratio was low. The consolidation of roasted residue was avoided and the Al₂O₃ leaching ratio achieved 99.7% when mechanical activation was performed before dry roasting.

(4) 3.92% of Pd was dissolved during water leaching. Reductive leaching with N₂H₄·H₂O completely averted Pd dissolution, and the Al₂O₃ leaching ratio achieved 99.7%. After NaOH

roasting–reductive leaching, NaAlO₂ leachate and Pd-enriched residue were obtained, and they could be further used for remaking Al₂O₃ catalyst carrier and recovering Pd, respectively.

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Supplementary Materials

Supplementary materials in this paper can be found at: http://tnmsc.csu.edu.cn/download/22-p2245-2022-0245Supplementary_Materials.pdf.

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采用钠化焙烧–还原浸出联合工艺从废 $\text{Pd}/\text{Al}_2\text{O}_3$ 催化剂中经济高效回收 Pd 和 Al_2O_3

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摘 要: 开发了钠焙烧–还原浸出联合工艺从废 $\text{Pd}/\text{Al}_2\text{O}_3$ 催化剂中回收 Pd 和 Al_2O_3 。钠化焙烧热力学分析表明, 在最佳的 $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ 摩尔比和温度下, NaOH 、 Na_2CO_3 和 $\text{Na}_2\text{C}_2\text{O}_4$ 均可以与 Al_2O_3 完全反应生成 NaAlO_2 。 NaOH 、 Na_2CO_3 和 $\text{Na}_2\text{C}_2\text{O}_4$ 的焙烧渣经水浸后, Al_2O_3 浸出率分别为 99.6%、61.0%和 55.3%。机械活化– NaOH 无水焙烧工艺避免了焙烧渣的固结且可获得较高的 Al_2O_3 浸出率。 $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ 还原浸出避免了水浸过程中 Pd 的溶解损失且催化剂中 99.7%的 Al_2O_3 被浸出。最终得到 NaAlO_2 浸出液和富钯渣, 其中有价的铝和钯可被进一步回收。

关键词: 废 $\text{Pd}/\text{Al}_2\text{O}_3$ 催化剂; Pd 和 Al_2O_3 的回收; 钠化焙烧; 机械活化; 还原浸出

(Edited by Bing YANG)