Kinetic Study on the Leaching of Pt, Pd and Rh from Automotive Catalyst Residue by Using Chloride Solutions

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Recycling platinum group metals (PGMs) from waste and/or secondary resources is becoming quite important due to the limitation of the natural resource deposits of PGMs. Among the processes of PGMs' recycling from secondary resources, the hydrometallurgical method draws extensive concerns, particularly for the selection of leaching solution. The present work evaluated the ability of chloride leaching solutions, *i.e.* HCl–H₂O₂ and NaClO–HCl–H₂O₂ to extract Pt, Pd and Rh from a kinetic point of view. The effect of temperature in the range of 277–307 K and time were also examined under the conditions of –500 µm of particle size and 100 g L^{–1} of pulp density.

$$\text{The kinetic model (I): } ((1 - \alpha)^{-1/3} - 1) + \frac{1}{3} \ln(1 - \alpha) = k_1 t$$

was found to be the most suitable to describe the leaching process of Pt, Pd and Rh in the NaClO contained solution. In this model the interface transfer and diffusion across the leached support layer both affect the rate of leaching reaction.

$$\text{Model (II): } (1 - (1 - \alpha)^{1/3})^2 = k_2 \ln(t)$$

fits the kinetic data very well for the dissolution of Pd in the HCl–H₂O₂ solution, showing that the diffusion across the leached support layer mainly affect the kinetic behaviors and the diffusion coefficient is inversely proportional to leaching time *t*.

The NaClO contained solution and HCl–H₂O₂ solution leaching of Pt, Pd and Rh are strongly dependent on the leaching temperature. In the case of the NaClO contained solution, the activation energy based on model (I) for Pd, Pt and Rh was 63.5, 59.1 and 77.9 kJ mol^{–1}, respectively. It is probably because of that the diffusion of NaClO contained solution across the leached support layer was very slow due to the micro-porous structure of the catalyst; and a high activation energy was needed in effect. Regarding to the leaching in the HCl–H₂O₂ solution, the activation energy for Pd was 13.4 kJ mol^{–1} on the basis of model (II). [doi:10.2320/matertrans.47.2015]

(Received September 12, 2005; Accepted May 15, 2006; Published August 15, 2006)

Keywords: PGMs, sodium hypochlorite, recycling, kinetics, support layer, diffusion-controlled, one-step leaching

1. Introduction

Recently, the limited natural resource of precious metals arouses people to make efforts to recycle them from the waste as a secondary resource. Spent automotive catalyst and/or catalyst residue containing PGMs (Platinum Group Metals) are potential secondary resources of platinum (Pt), palladium (Pd) and rhodium (Rh). Therefore, many studies were conducted to maximize the recovery of PGMs from the spent automotive catalyst and catalyst residue.

There are several processes to recycle PGMs from the spent automotive catalyst. Generally, hydrometallurgical process is one of the most employed, including a leaching step. In this process, aqua regia and mineral acids, such as hydrochloric acid, nitric acid and sulfuric acid were usually utilized to dissolve PGMs. Many works have been carried out to obtain a maximum recovery of PGMs with various conditions of leaching.^{1–5)}

In the previous report,⁶⁾ the leaching of Pt, Pd and Rh was undertaken in NaClO–HCl–H₂O₂ and HCl–H₂O₂ solutions.

The recovery of PGMs has an order from the highest of Pd, Pt and Rh. However, the results are still not enough to provide a satisfied explanation for the reaction mechanism in terms of the leaching of PGMs from the automotive catalyst residue. Based on the thermodynamic data, the formation potential of chloro-complex follows the order below:

The leaching of Rh was found to be somewhat difficult among the three metals.⁶⁾ It is necessary to confirm whether there are any difference in the leaching kinetics of PGMs, because the kinetics is also one of the most important aspects for a leaching reaction.

A kinetic study on the leaching of gold (Au), one of the precious metals, using reagents such as aqua regia and mineral acids, was conducted.⁷⁾ Another kinetic study on the cyanidation of gold ore was also carried out.⁸⁾ However, the kinetic data and model analysis were not available for the other precious metals. Those works will not be reviewed further in this part because of the difference of the leaching system. The kinetic study on the leaching of PGMs from the automotive catalyst residue is very limited. In fact, the

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Fig. 1 Schematic representation of solid-liquid reaction model for the leaching of catalyst residues (PGMs contained catalyst A, Leaching active components B and leached support layer AB).

automotive catalyst was composed of supported PGMs as active components and support material being of micro-porous structure and high surface area. Whether or not the structure of the catalyst residue will affect the leaching behavior of PGMs is still left as a question. Accordingly, the leaching kinetics of PGMs from the automotive catalyst residue is fairly important and necessary to be elucidated. The present study aims to study the kinetic of the reaction by comparing the kinetic parameters, leaching rate and activation energy to understand the possible mechanism occurred during the leaching of PGMs from automobile catalyst residue. The leaching solution containing chloride based leaching reagents *i.e.* NaClO–HCl–H₂O₂ and HCl–H₂O₂ was employed.

2. Kinetic Model

In the present work, we assume the automotive catalyst residue is of uniform radii being spherical with homogenous structure and dispersion of PGMs, and is surrounded by the leaching active components as illustrated schematically in Fig. 1. In the diffusion controlled process the active components (noted as B in Fig. 1) *e.g.* HCl and NaClO must penetrate through the layer of the micro-porous support material being leached (noted as AB) before reacting with the PGMs (noted as A) supported on the internal surface of the un-reacted core of catalyst. In the case of traditional derivation of kinetic model, a product layer was formed. However, in this case the products will dissolved in the solution instead of forming product layer. Using different assumptions for the leaching processes it is possible to derive kinetic equations that could be tested against the experimental data for a better fit. The assumptions and the derivation for the equations are set out below, starting from the first principles.

Referring to Fig. 1, let the original radius of the catalyst be r_0 . At time t the interface has spread inwards a distance x , leaving sphere of un-reacted catalyst A of radius r :

$$r = r_0 - x \quad (1)$$

$$\text{Volume of the original sphere: } \frac{4}{3}\pi(r_0)^3$$

$$\text{Volume of sphere at time } t: \frac{4}{3}\pi(r_0 - x)^3$$

$$\text{Value of fraction un-reacted is: } (1 - \alpha) = \frac{(r_0 - x)^3}{(r_0)^3}$$

$$\therefore (1 - \alpha)^{1/3} = \frac{(r_0 - x)}{(r_0)} = 1 - \frac{x}{r_0}$$

$$\therefore x = r_0(1 - (1 - \alpha)^{1/3}) \quad (2)$$

$$\frac{dx}{d\alpha} = \frac{1}{3}r_0(1 - \alpha)^{-2/3} \quad (3)$$

If the model is a diffusion-controlled mechanism, a number of possible assumptions can be made to derive rate equations. The time dependence of the gradual upbuild of the leached layer of the porous support material can be described by the parabolic law. Rate varies inversely with x .

$$x^2 = 2D_e V_m C_0 t$$

$$\therefore \frac{dx}{dt} = \frac{D_e V_m C_0}{x} \quad (4)$$

where x is the thickness of the leached layer, D_e is the diffusion coefficient (slowest transport), V_m is the volume of the leached layer formed from 1 mol of the slowest penetrating component, and C_0 is the concentration of the penetrating species at the surface of the catalyst.

If the interface transfer and diffusion across the leached support layer both affect the rate, Equation (4) can evolved further:

$$\frac{dx}{dt} = \frac{D_e V_m C_0}{x} \cdot 4\pi r^2 = \frac{k_1 r^2}{x} \quad (5)$$

where $k_1 = 4\pi D_e V_m C_0$.

Substitute for x , dx and r^2 using eqs. (1), (2) and (3):

$$(1 - (1 - \alpha)^{1/3})(1 - \alpha)^{-4/3} d\alpha = 3k_1 dt$$

Integrate and use boundary condition, $t = 0$ and $\alpha = 0$:

$$((1 - \alpha)^{-1/3} - 1) + \frac{1}{3} \ln(1 - \alpha) = k_1 t \quad (6)$$

If the diffusion equation is

$$\frac{dx}{dt} = \frac{V_m C_0}{x} \cdot \frac{a}{t} \quad (7)$$

where D_e was replaced by a/t , and a is a constant. It means that the diffusion constant is inversely proportional to the reaction time. Integrate back:

$$x^2 = 2D_e V_m C_0 a \ln t$$

$$\therefore r_0^2(1 - (1 - \alpha)^{1/3})^2 = 2D_e V_m C_0 a \ln t$$

$$\text{or } (1 - (1 - \alpha)^{1/3})^2 = k_2 \ln t \quad (8)$$

where $k_2 = 2D_e V_m C_0 a$.

With different assumptions other equations can also be derived based on eq. (4). A literature search for the kinetic equations and new equation derivation by Dickinson *et al.*⁽⁹⁾ have identified 29 equations in total and 12 of these are based on the diffusion-controlled mechanism. In addition, three

Table 1 The kinetic equations based on diffusion controlled mechanism.⁹⁾

Equation	Type	Notation
$kt = \alpha^2$	One-dimensional	D1
$kt = (1 - \alpha) \ln(1 - \alpha) + \alpha$	Two-dimensional	D2
$kt = (1 - (1 - \alpha)^{1/3})^2$	Jander (three-dimensional)	D3
$kt = 1 - 2\alpha/3 - (1 - \alpha)^{2/3}$	Ginstling-Brounshtein	D4
$kt = (1/(1 - \alpha)^{1/3} - 1)^2$	Zhuravlev, Lesokhin and Templeman	D5
$kt = ((1 + \alpha)^{1/3} - 1)^2$	Anti-Jander (three-dimensional)	D6
$k \ln t = (1 - (1 - \alpha)^{1/3})^2$	Kröger and Ziegler	D7
$kt = (1 - (1 - \alpha)^{1/2})^2$	Jander (cylindrical diffusion)	D8
$kt = (1 - (1 + \alpha)^{1/3})^2$	Anti-Jander (cylindrical diffusion)	D9
$kt = 1/(1 - \alpha)^{1/3} - 1$	New equation by Dickinson <i>et al.</i> ⁹⁾	D10
$kt = 1/(1 - \alpha)^{1/3} + 1/3 \ln(1 - \alpha) - 1$	New equation by Dickinson <i>et al.</i> ⁹⁾	D11
$kt = 1/5(1 - \alpha)^{-5/3} - 1/4(1 - \alpha)^{-4/3} + 1/20$	New equation by Dickinson <i>et al.</i> ⁹⁾	D12

Table 2 The kinetic equations for liquid-solid reaction.⁹⁾

Equation	Type	Notation
$kt = [-\ln(1 - \alpha)]^{1/4}$	Avrami-Erofeev	A1
$kt = [-\ln(1 - \alpha)]^{1/2}$	Avrami-Erofeev	A2
$kt = [-\ln(1 - \alpha)]^{1/3}$	Avrami-Erofeev	A3
$kt = [-\ln(1 - \alpha)]^{3/4}$	Avrami-Erofeev	A4
$kt = [-\ln(1 - \alpha)]^{2/5}$	Avrami-Erofeev	A5
$kt = \alpha$	Zero order	F0
$kt = -\ln(1 - \alpha)$	First order	F1
$kt = (1 - \alpha)^{-1}$	Second order	F2
$kt = 1 - (1 - \alpha)^{1/2}$	Interface (contracting area)	R2
$kt = 1 - (1 - \alpha)^{1/3}$	Interface (contracting volume)	R3
$kt = 1 - (1 - \alpha)^{2/3}$	Interface	R4
$kt = \alpha^{1/2}$	Power law (half)	Pl ($n = 2$)
$kt = \alpha^{1/3}$	Power law (third)	Pl ($n = 3$)
$kt = \alpha^{1/4}$	Power law (quarter)	Pl ($n = 4$)
$kt = \ln \alpha$	Exponential	E1
$kt = \exp(-(1 - \alpha)) - \exp(-1)$	Exponential	E2
$kt = \ln(\alpha/(1 - \alpha))$	Prout-Tompkinsa	B1

Table 3 Composition of PGM analyzed by ICP (wet-analysis) after alkali leaching.

Elements	[PR] (mass%)
Pt	0.379
Pd	0.582
Rh	0.239

new equations were deduced on the basis of diffusion-controlled mechanism. Table 1 lists the diffusion-controlled equations and Table 2 lists the other 17 equations. The notation used in the tables was listed according to literature.

Rate constant (k , s^{-1}), considered as a function of reaction temperature, can be formulated by the following equation, known as Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (9)$$

where E_a is the apparent activation energy (kJ mol^{-1}); R is the ideal gas constant, $8.314 \times 10^{-3} \text{ (J mol}^{-1} \text{ K}^{-1})$; T is the reaction temperature (K); and A is the pre-exponential factor (s^{-1}).

3. Experimental Method

The automotive catalyst residue containing PGMs *i.e.* the residue of the automotive catalyst rejected from the manufacturing process was supplied by Cataler Co. Additional processes such as pelletizing and reduction by using hydro-

gen gas were also conducted to the sample in the company. In the present experiments the received sample was ground and sieved to powder with a size of less than $500 \mu\text{m}$ ($-500 \mu\text{m}$). The powder sample was kept in a desiccator to avoid contamination. The PGMs' compositions of the powder are listed in Table 3. The sample also contained more than 90 mass% of support materials such as Al_2O_3 and silicate and doped components *e.g.* CeO_2 , ZrO_2 , BaO and other oxides. The reagents used in the experiments were NaClO solution (8.5–13.5% active chlorine, Nacalai tesque), HCl (35–37% = 12 M, Nacalai tesque) and H_2O_2 (30%, Nacalai tesque). Bi-distilled water was used for rinsing, washing and diluting the solution in all the experiments. Two kinds of leaching solution were prepared, *i.e.*, NaClO (3 vol%)– HCl (5 M)– H_2O_2 (1 vol%) noted as NaClO contained solution and HCl (11.6 M)– H_2O_2 (1 vol%) noted as HCl – H_2O_2 solution.

A glass beaker filled with a leaching solution was put into the water bath and being controlled to the working temperature within a limited error level. For the effective controlling of temperature and convenience of sampling, the temperatures of the kinetic experiment was lower than that for the application of leaching process to obtain observable data of the reaction. The leaching temperature was isothermally set at 277, 297 and 307 K. For low temperature (277 K), ice water was utilized to cool the glass beaker. To eliminate the increasing of temperature due to the heat released from the reaction and to keep the experiment under the isothermal condition, cooling water in the bath was flowed continuously during the leaching at temperature 297 and 307 K. The pulp density for the leaching was set at 100 g L^{-1} (20 g sample in 200 mL solution). Twenty grams of the sample powder was added at once into the agitated leaching solution in the 500 mL glass beaker at the required temperature. The magnetic stirrer rotation was kept constant at 600 rpm. At a certain time interval, 1-mL leaching solution sample was taken by using a

Fig. 2 Effect of leaching time and temperature on the dissolution of Pd, Pt and Rh in NaClO based leaching solution: (a) 277 K; (b) 297 K and (c) 307 K.

syringe filter of 0.45 μm pore size. Rinsing of syringe was undertaken with 3 mL bi-distilled water. Since the solid and liquid mixture was in the homogenous suspension form, the solid-liquid ratio (pulp density) was maintained constant (100 g L^{-1}). The total volume of sampling solution removed from the glass beaker was about 6% of the original, and did not show apparent effect on the kinetic measurement.

The solution samples were diluted with bi-distilled water and then analyzed by using induction coupling plasma spectrophotometer (ICP, Seiko Instrument, Inc.). In order to decrease the deviation of the kinetic analysis, for each case of leaching the utmost of the leaching rate was extrapolated according to the time-on-stream behavior, and then was used as the base to calculate dissolution fraction α .

Fig. 3 Effect of leaching time and temperature on the dissolution of Pd, Pt and Rh in HCl-H₂O₂ based leaching solution: (a) 277 K; (b) 297 K and (c) 307 K.

4. Results and Discussion

4.1 Results

The effect of leaching time and temperature on the dissolution of Pt, Pd and Rh in the NaClO contained leaching solution was shown in Fig. 2 (a) 277 K; (b) 297 K and (c) 307 K, and the leaching behaviors in the HCl-H₂O₂ solution were shown in Fig. 3 (a) 277 K; (b) 297 K and (c) 307 K. The results in Figs. 2 and 3 showed that the dissolution of each PGMs increases with increasing leaching temperature and time on stream for both solutions. The dissolution of Pt, Pd and Rh in the HCl-H₂O₂ solution was relatively faster as compared with that of the NaClO contained solution. For instance, it takes more than 100 minutes to maximize the dissolution of Pd (>95%) at 307 K for the NaClO contained solution, whilst for the HCl-H₂O₂ solution it only takes about

Fig. 4 Plot of kinetic equation parameter (D12, D4 and D3, see Table 1) versus leaching time for the leaching of Pd in NaClO contained leaching solution at 277 K (a) and 307 K (b).

several minutes to get a maximum dissolution of Pd (>95%) at the same temperature, meaning that the HCl-H₂O₂ solution is more active than the NaClO contained solution to dissolve PGMs. In fact, the HCl concentration of the HCl-H₂O₂ solution is remarkably higher than that of the NaClO contained solution (11.6 mol L⁻¹ vs 5.0 mol L⁻¹). If we employ solutions with the same HCl concentration of 5 mol L⁻¹ to dissolve PGMs, the leaching rate of PGMs will be lower in the solution without the addition of NaClO, manifesting a significant promoting effect of NaClO.⁶⁾ For both solutions, the dissolution of PGMs follows the order of Pd, Pt and Rh from the highest.

4.2 Data analysis

The authors attempted to use the equations listed in Tables 1 and 2 to analyze the kinetic data. The initial kinetic analysis did not give a perfect fit to the equations in Table 2. This suggests that the leaching of PGMs from automotive catalyst residue under the present experimental conditions was not a reaction-controlled process. On the contrary, the diffusion-controlled mechanism seems to be dominant in this case. It was decided, therefore, to analyze the isothermal data again by using the equations in Table 1 based on diffusion-controlled reaction model.

Figure 4 showed the kinetic plot between the equation

Fig. 5 Plot of kinetic equation parameter (D11, D10 and D5, see Table 1) versus leaching time for the leaching of Pd in NaClO contained leaching solution at 307 K.

Fig. 6 Plot of kinetic equation parameter (D7, see Table 1) versus $\ln t$ for the leaching of Pd in NaClO contained leaching solution: Effect of temperature.

parameter (D12, D4 and D3) and time on stream for the leaching of Pd in the NaClO contained solution at 277 K (a) and 307 (b), respectively. A good linear relationship cannot be found. The data analysis with regard to the kinetic behavior of the Pd leaching in the same solution at 307 K was shown in Fig. 5 by using kinetic eq. D5, D10 and D11 (Table 1). eq. D11 can well fit the kinetic data and with an intercept near to zero, although for D5 and D10 such kind of behavior cannot be found. In addition, the diffusion-controlled equation D7 cannot well fit the kinetic data for the leaching of Pd in the NaClO contained solution (Fig. 6).

Regarding to the leaching of Pd in the HCl-H₂O₂ solution system, similar behavior can be found (Fig. 7). Among these equations, model D11 showed a good linear relation and an intercept near to zero. Whether or not the kinetic equation D11 can describe the leaching behavior of Pt and Rh also, we will analyze the kinetic data further using equation D11.

For the leaching of Pd (a), Pt (b) and Rh (c) in the NaClO contained leaching solution, Figure 8 plotted the parameter $(1/(1-\alpha)^{1/3} - 1) + 1/3 \ln(1-\alpha)$ (see D11 in Table 1)

Fig. 7 Plot of kinetic equation parameter versus leaching time for the leaching of Pd in HCl-H₂O₂ leaching solution at 277 K: (a) D12, D4 and D3; (b) D11, D10 and D5 (see Table 1).

versus the leaching time with different temperature. Indeed, eq. D11 fits the kinetic data well, showing a good linear relationship for the total leaching period studied. The correlations for each line were calculated with values from 0.983 to 0.998.

Figure 9 shows the plot of parameter $(1/(1-\alpha)^{1/3} - 1) + 1/3 \ln(1-\alpha)$ versus leaching time in terms of the leaching of Pd (a), Pt (b) and Rh (c) in HCl-H₂O₂ based leaching solution. During the temperature range of 277 K–307 K, eq. D11 can describe the leaching process of Pd (Fig. 9(a)), particularly for the beginning of the dissolution (0–10 min), showing correlations >0.97 . Figure 10 plots $(1 - (1 - \alpha)^{1/3})^2$ versus $\ln t$ for the leaching of Pd (a), Pt (b) and Rh (c) in the HCl-H₂O₂ solution. Good linear correlation can be found for the leaching of Pd with $R > 0.99$. However, in the case of Pt (Figs. 9(b) and 9(c)), Rh (Figs. 10(b) and 10(c)), the plot severely deviated from linear correlation, meaning that in the HCl-H₂O₂ solution the leaching kinetics of Pt and Rh was far different from that as in the case of Pd. All the 29 equations were questionable for the leaching of Pt and Rh by using HCl-H₂O₂ solution with high concentration of HCl, because of the big discrepancies, and it is believed that they are not suitable models, although D11 was proven to be perfect to fit the kinetic data in the case of NaClO contained solution. A more suitable kinetic equation is absolutely

Fig. 8 Plot of kinetic equation parameter (D11, see Table 1) versus leaching time for the leaching of Pd (a), Pt (b) and Rh (c) in NaClO contained leaching solution: Effect of temperature.

necessary to fit the leaching kinetic data for the HCl-H₂O₂ solution system. Further works are continuing to derivate new models by modifying assumptions according to the characteristics of the present system.

Figure 11 showed the Arrhenius plot for the leaching of Pt, Pd and Rh, the data for the leaching of Pt and Rh in the HCl-H₂O₂ solution are not available. Indeed, good linear relations were exhibited as well. The activation energies were calculated as listed in Table 4. In the case of the NaClO contained solution (Fig. 11(a)), the activation energy for Pd,

Fig. 9 Plot of kinetic equation parameter (D11, see Table 1) versus leaching time for the leaching of Pd (a), Pt (b) and Rh (c) in HCl-H₂O₂ leaching solution: Effect of temperature.

Pt and Rh was 63.5, 59.1 and 77.9 kJ mol⁻¹, respectively. It is interesting that activation energy is positively related to the formation potential of the chloro-complexes of the corresponding metals (see R1, R2 and R3 in the section of introduction). A correlation of 0.978 can be found, although one is the thermodynamic and the other is based on the reaction kinetics. Regarding to the leaching in the HCl-H₂O₂ solution (Fig. 11(b)), the activation energy for Pd was 49.5 kJ mol⁻¹ based on eq. D11, being lower than the corresponding value from the NaClO contained solution

Fig. 10 Plot of $(1 - (1 - \alpha)^{1/3})^2$ versus $\ln t$ for the leaching of Pd (a), Pt (b) and Rh (c) in HCl-H₂O₂ leaching solution: Effect of temperature.

with 14 kJ mol⁻¹. However, the activation energy for Pd was only 13.4 kJ mol⁻¹ on the basis of eq. D7.

4.3 Discussion

The kinetic aspect in terms of the leaching of Pt, Pd and Rh in the NaClO contained and HCl-H₂O₂ leaching solutions has been analyzed and discussed based on the degree of correlations and best fitting to the zero intercept of each proposed models. The model D11 was found to be the most suitable to describe the leaching process of PGMs in the NaClO contained solution. According to the model deriva-

Fig. 11 Arrhenius plot for the leaching of PGMs: (a) NaClO-HCl-H₂O₂; (b) HCl-H₂O₂.

tion of D11, it was shown that the interface transfer and diffusion across the leached support layer would both affect the rate of leaching reaction. In other words, a diffusion-controlled mechanism will be dominant, although for the Pt and Rh leaching in the case of the HCl-H₂O₂ solution, big deviations were found when using model D11 to fit the kinetic data. In this case, the support material will act as a product layer or ash layer (as called in some textbooks),¹⁰⁻¹² and was supposed to be stable during the reaction, and can remain constant particle size. In fact, in our experiment, more than 95 mass% of the starting samples can be recovered as residues for the NaClO contained solution, although some other metals in the leaching solution can be detected by ICP, which might come from the doping layer of the support, showing that the reaction between the leaching solution and

the support material was limited, and the support material is stable enough to form a leached support layer for the diffusion of leaching active components, and diffusion coefficient, D_e , would basically be a constant if the structure of the catalyst was homogenous, which was a basic assumption during the model derivation of D11.

The interface transfer and diffusion-controlled mechanism seems can also be determined for those deviation situations particularly for Pd, since the present HCl-H₂O₂ solution is more active than the NaClO contained solution. That means the reaction rate of PGMs' dissolution in the HCl-H₂O₂ solution will far faster than that in the NaClO contained solution intrinsically if the diffusion-controlled process did not exist in both cases, and since the diffusion-controlled mechanism is dominant in the case of NaClO contained solution, the same conclusion seems can be drawn for the HCl-H₂O₂ solution. However, two additional aspects have to be considered. The first is that the diffusion of the main reactants *e.g.* HCl in the HCl-H₂O₂ solution will be faster than that in the case of NaClO contained solution, because of the higher concentration of chloride ions. The fast diffusion of the reactant will promote the leaching of PGMs. The most important is that the increase of diffusion rate of the reactants will cause the kinetic mechanism of leaching prefer to the reaction control or a combination of both diffusion and reaction control. So, in this case the kinetic mechanism will depend on the intensity of the diffusion rate and intrinsic reaction rate. The second is that the HCl solution might react with the support materials more severely and might destroy the pore structure of the support materials to some extent, and make it easy to diffuse across the support layer for the leaching solution, corresponding to D_e of large value in effect. In fact, the leaching residue from the NaClO contained solution is slightly heavier than that from the HCl-H₂O₂ solution, according to our experiment results (not shown here). The possibility of this kind of effect exists, although the leaching of Pd seems subject to the interface transfer and diffusion-controlled mechanism as suggested in the case of NaClO (Fig. 9(a)).

Further, the activation energy was also taken into account to analyze the reaction mechanism during the leaching of Pt, Pd and Rh. In general, the activation energy for a diffusion-controlled process is characterized as being less than 21 kJ mol⁻¹ (= 5 kcal mol⁻¹).¹² On the contrary, the activation energy of a reaction-controlled process is usually greater than 42 kJ mol⁻¹ or more specifically in the range of 42–84 kJ mol⁻¹.^{12,13} However, recent findings showed that the activation energies of some diffusion controlled reactions in the leaching processes of some metals can be more than 21 kJ mol⁻¹, as listed in Table 5.¹⁴⁻¹⁹ Although, there is no

Table 4 Activation energy of Pt, Pd and Rh leaching in chloride solutions.

Leaching solution	Rate equations	Activation energy (kJ mol ⁻¹)		
		Pd	Pt	Rh
NaClO-HCl-H ₂ O ₂	$kt = 1/(1-\alpha)^{1/3} + 1/3 \ln(1-\alpha) - 1$	63.5	59.1	77.9
HCl-H ₂ O ₂	$kt = 1/(1-\alpha)^{1/3} + 1/3 \ln(1-\alpha) - 1$	49.5	n.a.	n.a.
HCl-H ₂ O ₂	$k \ln t = (1 - (1-\alpha)^{1/3})^2$	13.4	n.a.	n.a.

n.a.: not available

Table 5 Activation energy of some diffusion controlled reaction in the leaching processes.

Authors	Metal extracted	Leaching solution	Activation energy (kJ mol ⁻¹)	Ref.
P. K. Gbor, I. B. Ahmed and C. Q. Jia	Ni, Co and Fe from nickel smelter slag	SO ₂ (aq)	E_a (Co, Fe) = 70 kJ mol ⁻¹ ; Ni = 50 kJ mol ⁻¹	14)
H. Tsuchida, E. Narita, H. Takeuchi, M. Adachi and T. Okabe	Ti and Fe from ilmenite ore	HCl (aq)	E_a (Ti) = 48.9 kJ mol ⁻¹ ; E_a (Fe) = 53.7 kJ mol ⁻¹ .	15)
Y. Paspaliaris and Y. Tsolakis	Fe from diasporic bauxite	HCl (aq)	E_a (Fe) = 62–79 kJ mol ⁻¹ .	16)
D. Georgiou	Ni from limonitic laterite	Pressurized H ₂ SO ₄	E_a (Ni) = 49–79 kJ mol ⁻¹ .	17)
P. K. Jena, O. Barbosa-Filho and I. C. Vasconcelos	Zn from sphalerite slurry	Cl ₂ (g)	E_a (Zn) = 49.6 kJ mol ⁻¹ .	18)
E. Olanipekun	Ti and Fe from Nigerian ilmenite ore	HCl (aq)	E_a (Ti) = 67.1 kJ mol ⁻¹ ; E_a (Fe) = 62.4 kJ mol ⁻¹ .	19)

satisfied explanation about those phenomena, they might be occur due to some special kinds of diffusion behaviors in the product layer, and higher activation energies were necessary.

As listed in Table 4, the activation energies for Pt, Pd and Rh leaching in the NaClO solution disagree with the category above, exhibiting a contradicting behavior. The possible reason is that the micro-porous structure of the catalyst in this case is quite different from the structure of product layer formed during the reaction, and the diffusion of NaClO contained leaching solution across the leached support layer of the catalyst residue might be very slow because of the micro-porous structure of the catalyst, higher activation energy was needed for the leaching reaction.

On the other hand, for the leaching in the HCl–H₂O₂ solution, the activation energy for Pd was 49.5 kJ mol⁻¹ based on eq. D11, being lower than the corresponding value from the NaClO contained solution with 14 kJ mol⁻¹. At least, this can manifest to some extent that the diffusion of the HCl–H₂O₂ solution is easier due to lower activation energy as compared with the corresponding value for the NaClO contained solution in spite of kinetic models. In fact, the activation energy was only 13.4 kJ mol⁻¹ on the basis of model D7. According to the category, the kinetic model D7 works well for the leaching of Pd in the HCl–H₂O₂ solution.

There is a question left to answer that why does the activation energy for the HCl–H₂O₂ system quite differ from that for the NaClO system. We ascribe this to the reason that the HCl–H₂O₂ solution was more active than the NaClO contained solution to wash the doping layer in the inner surface of the catalyst to expend micro-pores. This hypothesis is consistent with the kinetic data, which shows a rapid increase in the leaching rate for the HCl–H₂O₂ solution.

Anyway, in the case of Pd leaching in the HCl–H₂O₂ solution system, instead of interface transfer and diffusion-controlled mechanism, the pure diffusion-controlled mechanism can be determined on the basis of model D7 according to the criterion of activation energy. In this model the diffusion constant was inversely proportional to the reaction time t . The reason for this phenomenon is still unclear, and for the leaching of Pt and Rh, there must be some other unknown factors affecting the reactions, further works are in progress.

5. Conclusion

The kinetics on the leaching of Pt, Pd and Rh from automotive catalyst residue in NaClO (3 vol%)–HCl (5 M)–H₂O₂ (1 vol%) and HCl (11.6 M)–H₂O₂ (1 vol%) solutions has been investigated. The results obtained in the present study are summarized as follows:

It is observed from the experiments and kinetic analysis that the kinetic model:

$$((1 - \alpha)^{-1/3} - 1) + \frac{1}{3} \ln(1 - \alpha) = k_1 t$$

was found to be the most suitable to describe the leaching process of PGMs in the NaClO contained solution. The interface transfer and diffusion across the leached support layer both affect the rate of leaching reaction.

$$\text{Model (II): } (1 - (1 - \alpha)^{1/3})^2 = k_2 \ln(t)$$

fits the kinetic data very well for the dissolution of Pd in the HCl–H₂O₂ solution, showing that the diffusion across the leached support layer mainly affect the kinetic behaviors and the diffusion coefficient is inversely proportional to leaching time t .

For Pt and Rh leaching in the HCl–H₂O₂ solution, apparent deviation was found when use this model to fit the kinetic data, thus, there must be some other unknown factors affecting the reaction.

The NaClO contained solution and HCl–H₂O₂ solution leaching of Pt, Pd and Rh are strongly dependent on the leaching temperature. In the case of the NaClO contained solution, the activation energy for Pd, Pt and Rh was 63.5, 59.1 and 77.9 kJ mol⁻¹, respectively. Due to the micro-porous structure of the catalyst, the diffusion of NaClO contained leaching solution across the leached support layer of the catalyst residue might be very slow, higher activation energy was needed for the leaching reaction. Regarding to the leaching in the HCl–H₂O₂ solution, the activation energy for Pd was 13.4 kJ mol⁻¹.

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