Platinum Extraction Modeling from Used Catalyst by Iodine Solutions

Rashidi Moghaddam, Hamed; Baghalha, Morteza**

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. IRAN

ABSTRACT: Platinum extraction from spent reforming catalysts in iodine solutions under atmospheric pressure at different temperatures, acid concentration, and iodine spices concentration, catalyst particle size, and impeller agitation speed have been studied in our group. In this system, platinum is oxidized from spent catalyst with \( I_2 \) that is formed from the reaction of \( I_2 \) and \( I^- \) to produce \( PtI_6^{2-} \) as its main product. It is obvious that some of the platinum ions in aqueous solution are precipitated as \( PtI_4^- \), especially at high temperatures. Power-law rate equation was used in extraction and precipitation reactions for kinetic modeling. The effect of temperature was studied using the Arrhenius equation. The activation energy for the platinum surface dissolution reaction was calculated as 53 kJ/mol in extraction reaction which indicated that the rate determining step is surface chemical reaction step. The reaction order was 3.01 for platinum concentration in solid and 0.45 for the hydrogen ion concentration, 0.1 for the iodine spices concentration in extraction reaction and 0.54 for platinum ions concentration in precipitation reaction. This model shows good agreement with experimental data.

KEYWORDS: Kinetics; Pt extraction; Iodine solution; Platinum-iodine ions precipitation; Power-law equation.

INTRODUCTION

Pt/Al\(_2\)O\(_3\) is one of the most frequently used catalysts in refining as well as in petrochemical industries due to its activity, stability, and selectivity. The deactivated catalysts are replaced by fresh catalysts after being regenerated many times. Platinum remains in the matrix of the porous alumina support. A variety of agents such as neutral ammonium solution and bromide ions, aqua regia, as well as oxidizing agents such as oxygen, iodine, and bromine have been used for the hydrometallurgical extraction of platinum [1].

Cyanidation at different temperatures and pressures is the major method to extract precious metals, especially platinum [2, 3]. But this method has many environmental problems. Aqua regia solution properly extracts the platinum, but the alumina is dissolved from the matrix of the catalyst support; therefore, it is obvious that this method is not economic [4]. In another investigation, precious metals are recovered by carbon active [5]. Oxidizing agents are good alternatives to substitute that harmful and non-economic method. The most stable oxidizing agent for this system is iodine. Iodine shows a good selectivity in extracting platinum [6]. In our group, the effect

*To whom correspondence should be addressed.
+E-mail: baghalha@sharif.edu
1021-9986/2018/4/175-182 8/$5.08
of various parameters on platinum extraction from the spent reforming catalysts using iodine–iodide solutions were investigated recently [7].

A few kinetic modeling works have been performed on precious metal leaching in iodine solutions. P.H. Qi et al. [8] modeled gold extraction from ore in the Iodine/Iodide solution using a power law rate equation. The aforementioned models considered the effect of three parameters including iodine concentration, iodide concentration, and the reaction temperature on reaction kinetics. The order of reaction for iodine concentration and \( I^- \) concentration were 1 and 0.5 respectively. Dawson and Kelsall [9] studied the kinetics of palladium dissolution in iodine/iodide solution. \( \text{PdI}_2^- \) was precipitated as \( \text{PdI}_2(s) \) simultaneously. Dawson and Kelsall [10] showed that platinum ions precipitate at high temperature. The deposited platinum dissolved in a high concentration of iodine in constant pH.

The aim of the present study was to model the kinetics of platinum extraction in iodine-iodide solutions. Furthermore, the chemistry of the extraction and the precipitation reactions were studied.

**EXPERIMENTAL AND THEORETICAL SECTION**

The batch platinum leaching tests were performed in a sealed 1.5 L reactor, equipped with an impeller and condenser to reflux vapor to the reactor, a hot-plate heater and temperature sensor. The spent catalysts were dried in an oven at 110 °C and then pulverized into particle sizes smaller than 106 μm. The platinum concentration in the catalyst was measured by dissolving 5g of the catalyst in hot aqua-regia, which then was analyzed for platinum by a UV/Visible spectrophotometer [7].

For each experiment, 500g of the water and the desired amount of the powdered catalyst was agitated at 700 rpm and heated to the desired temperature in the reactor. The solution of iodide, iodine, and concentrated HCl were then quickly added to the reactor and the time was set to zero. The solution pH was measured using a pH electrode. A UV/Visible spectrophotometer was used to measure platinum concentration in solution. The “active” iodine spices concentrations in the leached solutions were measured based on the redox titration with standard thiosulfate solution. The results of each experiment summarized in Table 1. [7]

The effect of particle size and agitation speed were investigated in tests 1 to 3 for particle size below 106 μm and agitation speed over 700 rpm. It was concluded that the diffusions of reactants in the fluid film and inside the particles were not the limiting steps. Hence, it is assumed that the observed Pt extraction kinetics is solely governed by surface chemical reactions.

In a higher amount of liquid to solid mass ratio, the acid and iodine consumption are lower and platinum extraction rate is higher [7]. When temperature increases in this system, platinum extraction increases significantly, while the acid and iodine consumption decrease. This must be due to the very large activation energy of extraction reaction.

According to standard redox potential, Platinum-iodine ions are more stable than other platinum-halogen ions. In such a system, the aqueous ions \( \Gamma^- \), \( I_2^- \), \( I^- \) and \( IO^- \) are readily formed. Then, \( IO^- \) slowly disproportionate to \( IO_3^- \) in alkaline conditions [11]. At pH <7, the predominant spices present in the solution are \( I^- \) and \( IO^- \). In high acidic solution, \( I^- \) is converted to \( \Gamma^- \) more frequently [12].

[1] \( I_2(aq) + \Gamma^- \leftrightarrow I^-_3 \)  

The equilibrium constant of the Reaction (1) is reported as 723 L/mol at 25 °C [12]. Its temperature dependence is discussed in [14]. The conversion of Reaction (1) is near 1 under the experimental condition of this system. Hence, it is considered that the Reaction (1) is irreversible. On the other hand, Khosravian and Baghalha [7] performed titration to measure the \( I^-_3 \) concentration. Furthermore, the order of reaction for \( I^-_3 \) and \( I_2 \) is the same in gold extraction [8]. All of \( I_2(aq) \) is converted to \( I^-_3 \) that is the oxidizing agent. It can be said that the reported \( I_2 \) concentration is the concentration of \( I^-_3 \).

For pHs below 4, the major platinum specie is \( \text{PtI}_6^{2-} \). The oxidation, reduction, and overall reactions in this system are presented in Reactions (2) to (4), respectively [10, 11]:

\[
\text{Pt} + 6\Gamma^- \leftrightarrow \text{PtI}_6^{2-} + 4e^- \quad (2)
\]

\[
I^-_3 + 2e^- \leftrightarrow 3\Gamma^- \quad (3)
\]

\[
\text{Pt} + 2I^-_3 \leftrightarrow \text{PtI}_6^{2-} \quad (4)
\]
It is obvious that at high temperatures, a significant amount of platinum is precipitated, that must be considered in kinetics study. V. Balzani and F. Marfrin [15] studied the thermal decomposition of platinum-iodine ions. They verified that, aqueous and acid solutions of PtI₆⁻² rapidly gave rise to a black precipitate after some time. Elemental analysis and chemical properties showed that the black precipitate was PtI₄. During the reaction, the pH slowly decreased. They mentioned that the precipitation reaction in the presence of iodide ions is reversible. S.A. Cotton [16] mentioned that PtI₆⁻² is precipitated as PtI₄ that has a crystalline structure and black color with temperature increasing. Dawson and Kellsal [9, 10] showed that both platinum and palladium iodine are precipitated at high temperature as a solid. They said precipitation reaction is reversible in a high concentration of iodine in constant and high pH.

As mentioned above, the main precipitation reaction is according to Reaction (6). No thermodynamic data are available for the reaction.

\[
\text{PtI}_6{}^{2-} \leftrightarrow \text{PtI}_4 + 2I^- \tag{5}
\]

In all tests, the solutions are highly acidic. In this acidic solution, aluminum in Al₂O₃ is extracted according to Reaction (7). But the rate of this reaction is very lower than platinum extraction [17].

\[
\text{Al}_2\text{O}_3(s) + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O} \tag{6}
\]

The extraction of aluminum from the alumina matrix remains between 5 and 18% during all tests. Hence, it was assumed that the total solid weight remains constant.

The classical fluid–solid reaction models, Homogeneous Diffusion Model (HDM) [18, 19], Shrinking Core Model (SCM) [18, 19], Elovich equation [20], and Jander equation [21] did not produce meaningful results.

The empirical power–law equation has been successfully implemented to model gold extraction kinetics in aqueous iodine solution [8] and platinum extraction kinetics from the spent catalyst in aqua–regia solution [6].

The power–law rate Eq. (1) describes the Platinum extraction rate in terms of the concentrations of the reactants of Reaction (4).

\[
-r_{Pt} = k [\text{H}^+]^{n_1} [I_2]^{n_2} (W_P) ^{n_3} \tag{1}
\]

Where \(-r_{Pt}\) is the rate of platinum extraction in moles per minutes per unit mass of solids in the reactor, \(W_P\) is the weight fraction of platinum in the solid spent catalyst, \([\text{H}^+]\) is the molarity of the hydrogen ion in solution, \([I_2]\) is the molarity of active iodine spices, and \(n_1, n_2\) and \(n_3\) are the reaction orders. The parameter \(k\) is the overall reaction rate constant which is temperature dependent.

For temperature dependence of \(k\), the Arrhenius equation is employed. Arrhenius equation is:

\[
k = Ae^{\frac{-E}{RT}} \tag{2}
\]

Where \(A\) is the frequency factor, \(E\) is the surface-reaction activation energy in J/mol, \(R\) is the universal gas constant (8.3145 J/mol), and \(T\) is the reaction temperature in K.
The power-law rate Eq. (3) describes the platinum ions precipitation rate in terms of the concentrations of the reactants of Reaction (6).

\[ -r_{Pt} = k\left[PtI_6^{-2}\right]^n_{Pt\cdot I} \]  \tag{3}  

Where \(-r_{Pt}\) is the rate of platinum ions precipitation in moles per minutes per unit mass of liquid in the reactor, \([PtI_6^{-2}]\) is the molality of platinum ions in the solution in mol/g, and \(n_t\) is the reaction order. The parameter \(k\) is the precipitation reaction rate constant which is temperature dependent.

For temperature dependence of \(k\), the Arrhenius equation is employed. Arrhenius equation is:

\[ k' = A'e^{-\frac{E'}{RT}} \]  \tag{4}  

Where \(A'\) is the frequency factor, \(E'\) is the precipitation reaction activation energy in J/mol, \(R\) is the universal gas constant (8.3145 J/mol), and \(T\) is the reaction temperature in K.

For batch operation, a mass balance for platinum yields:

\[ -r_{Pt}M_{Pt}\text{W}_{\text{solids}} = -d\left(W_{Pt}\text{W}_{\text{solids}}\right)/dt \]  \tag{5}  

Where, \(W_{\text{solids}}\) is the total weight of the solids inside the reactor, and \(M_{Pt}\) is the molecular weight of Platinum. The total solid weight is constant and \(W_{\text{solids}}\) was canceled from both sides of Eq.(5). Then, replacing Eq.(1) into Eq.(5) results in:

\[ -dW_{Pt}/dt = kM_{Pt}\left[H^+\right]^{n_1}\left[I^-\right]^{n_2}\left(W_{Pt}\right)^{n_3} \]  \tag{6}  

In this system, we define two different conversions. \(X_T\) is the total conversion which shows the total amount of platinum that is extracted from spent catalyst. \(x_A\) is the apparent conversion which shows the amount of platinum that is present in aqueous solution and \(x_{PtA}\) is the conversion of platinum precipitated as PtI. Also, we can write this equation as:

\[ W_{Pt} = W_{Pt}^0(1 - x_T) \]  \tag{7}  

\[ [PtI_6^{-2}] = \frac{1}{M_{Pt}}\frac{1}{L}\frac{W_{Pt}^0}{S}x_A \]  \tag{8}  

\[ x_{PtA} = (x_T - x_A) \]  \tag{9}  

Where \(W_{Pt}^0\) is the initial platinum weight fraction in the catalyst which is fed, and \(\frac{L}{S}\) is the liquid to solid ratio in g/g. Eq.(6) is reduced to:

\[ dx_T / dt = kM_{Pt}(W_{Pt}^0)^{n_1-1}[H^+]^{n_1}[I^-]^{n_2}(1 - x_T)^{n_3} \]  \tag{10}  

The PtI_6^{2-} ions are produced in moles per minutes per solution per unit mass of liquid:

\[ r_{PtI_6^{-2}} = \frac{1}{L} - r_{Pt} \]  \tag{11}  

\[ r_{PtI_6^{-2}} = d[PtI_6^{-2}] / dt = \frac{1}{M_{Pt}}\frac{1}{L}\frac{W_{Pt}^0}{S}\left(x_A / dt\right) \]  \tag{12}  

With substitution of Eq. (1) to Eq. (4) in Eq. (11), and then substitution of Eq. (12) in Eq. (11), Eq. (12) is written as:

For all the tests, it was observed that Pt extraction increases sharply during the first 8 minutes of the test. No attempt was made to identify what happens in these times.

RESULTS AND DISCUSSION

Now, we have two differential equations: Eq.(10) and Eq.(13) that must be solved simultaneously. In \(t=t_1\) (=8 minutes), the rate of precipitation reaction can be assumed zero. The initial condition for the two differential equations is (at \(t=t_1\), then \(x=x_{i1}\)) for each test.

In these two differential equations, 8 parameters (\(A', A, E, E', n_1, n_2, n_3, n_4\)) must be fitted to the model all the kinetics. In order to find the best values for these parameters, two differential equations must be solved simultaneously for the data of 11 tests (test no.3 to 13) and then optimized.

These differential equations do not have an analytical solution. Therefore, they must be solved by a numerical method like Runge-Kutta. To optimize these parameters, the optimization toolbox of MATLAB software was used. Genetic algorithm and Nelder-Mead algorithm were used as an optimization algorithm.

The objective function for this optimization is Root Mean Square (RMS), as defined below:
**Table 2: The optimized value of kinetics equations parameters.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimized value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A ) (( \text{lit}^{0.55} \text{mol}^{0.45}/\text{min}) )</td>
<td>2041002619</td>
</tr>
<tr>
<td>( E ) (( \text{J/mol}) )</td>
<td>53586</td>
</tr>
<tr>
<td>( n_1 )</td>
<td>3.01</td>
</tr>
<tr>
<td>( n_2 )</td>
<td>0.10</td>
</tr>
<tr>
<td>( n_3 )</td>
<td>0.45</td>
</tr>
<tr>
<td>( A' ) (( \text{gr}^{0.54} \text{mol}^{0.46}/\text{min}) )</td>
<td>9660407</td>
</tr>
<tr>
<td>( E' ) (( \text{J/mol}) )</td>
<td>89204</td>
</tr>
<tr>
<td>( n_4 )</td>
<td>0.54</td>
</tr>
</tbody>
</table>

\[
\frac{\text{d}x}{\text{d}t} = Ae^{-\frac{E}{RT}}M_{Pt}(W_{Pt}^{0})^{n_1-1}[H^{+}]^{n_2}[I_{2}]^{n_3}(1-x_T)^{n_4} - \frac{A'e^{-\frac{E'}{RT}}(W_{I_{2}}^{0})^{n_4}x_{cal}^{n_4}}{S}
\]

Where \( x_{cal} \) is the calculated conversion, \( x_{exp} \) is experimental conversion, and \( n \) is the number of data being used in optimization.

After the optimization of all the 11 tests, it was observed that test no.7 and test no.9 have large error and total RMS was 0.104. Then, we eliminated these tests and repeated the optimization with 9 tests. The result from this optimization is very good and RMS is 0.049.

The value of parameters is reported in Table 1. The total, precipitation and apparent conversions in this system for 9 tests are shown in Fig. 1 to Fig. 9. The calculated data from Power-Law model and experimental data in different conditions are shown in Fig.10 to Fig.12.

In this system, the activation energy of extraction reaction is about 53 kJ/mol which confirms that the surface reaction is the rate determining step - as mentioned previously. For instance, the platinum dissolution in aqua-regia and gold dissolution in iodine/iodide solution have been reported as 72.1 kJ/mol and 34 kJ/mol, respectively [6, 8]. As a result, the calculated value of activation energy suggests that the overall extraction rate must be controlled by the surface chemical reaction [19].

Order of reaction for iodine spices is near 0.1. This shows that the effect of iodine concentration on platinum extraction is negligible. But we must consider that iodine concentration in this system is over the stoichiometric concentration.
Fig. 3: Conversion data according to Power-Law modeling for test No.05, T=25 °C, Liquid/Solid=10, initial HCL=0.66 mol/L, initial I₂=30 g/L; Precipitation Conversion, Apparent Conversion, Total Conversion.

Fig. 4: Conversion data according to Power-Law modeling for test No.06, T=25 °C, Liquid/Solid=10, initial HCL=0.66 mol/L, initial I₂=60 g/L; Precipitation Conversion, Apparent Conversion, Total Conversion.

Fig. 5: Conversion data according to Power-Law modeling for test No.08, T=50 °C, Liquid/Solid=10, initial HCL=0.66 mol/L, initial I₂=30 g/L; Precipitation Conversion, Apparent Conversion, Total Conversion.

Fig. 6: Conversion data according to Power-Law modeling for test No.10, T=75 °C, Liquid/Solid=10, initial HCL=0.66 mol/L, initial I₂=30 g/L; Precipitation Conversion, Apparent Conversion, Total Conversion.

Fig. 7: Conversion data according to Power-Law modeling for test No.11, T=75 °C, Liquid/Solid=10, initial HCL=0.66 mol/L, initial I₂=30 g/L; Precipitation Conversion, Apparent Conversion, Total Conversion.

Fig. 8: Conversion data according to Power-Law modeling for test No.12, T=95 °C, Liquid/Solid=10, initial HCL=0.00 mol/L, initial I₂=30 g/L; Precipitation Conversion, Apparent Conversion, Total Conversion.
and the usage of iodine is very low [8]. On the other hand, previous publication emphasized that in a high concentration of iodine solution, the platinum and palladium ions are more stable and the precipitation reactions of these ions are reversible [9, 10, 15].

CONCLUSIONS

External mass transfer resistance was eliminated in a reactor with agitation speed higher speed higher than 700 rpm and catalyst particle sizes below 100 µm. Platinum is extracted significantly in iodine solutions with order of reaction about 3.0. The order of extraction reaction for hydrogen ions, concentration and iodine spices concentration is about 0.45 and 0.1, respectively. If the temperature increases, the extraction rate is higher. However, platinum iodide solid precipitates at higher temperatures with an order of reaction of 0.54 for platinum iodide concentration in solution. The activation energy for the extraction reaction is 48 kJ/mol. This shows that the overall extraction reaction is controlled by the surface reaction.

The rate of reaction in the start of reaction is very high. This rate decreases as the reaction proceeds and Pt concentration in solid phase decreases. Low order of reaction for [H+] and iodine concentration that are presented by n2 and n3 show that these spices do not have a great effect on the reaction rate.
REFERENCES


