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Factors affecting platinum extraction from used reforming catalysts in iodine solutions at temperatures up to 95 °C

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ABSTRACT

Platinum extraction from the spent reforming catalysts in iodine–iodide solutions at temperatures from 25 to 95 °C was investigated. The reforming catalyst mostly consists of a porous gamma alumina support with metallic platinum finely dispersed on the walls of the nano-pores of the catalyst support. The effect of a variety of factors, including catalyst particle size, impeller agitation speed, reactant concentrations, liquid to solid mass ratio, temperature and the solution pH on the Pt extraction rate and recovery were investigated. It was found that the catalyst particle sizes less than 106 μm and impeller agitation speed higher than 700 rpm eliminated the effects of catalyst size and agitation level, respectively, on platinum leaching. The initial iodine–iodide concentrations and the liquid to solid ratio were mostly affecting the solution pH and the concentration of "active" iodine species, which in turn, affected the rate of Pt extraction. Higher acidities, generated by adding concentrated HCl, resulted in faster Pt extractions. Increasing the reaction temperature also produced faster platinum extraction kinetics. The "active" iodine species (HIO, I_2(aq), and I_3^-) concentration decreased mostly due to conversion to "inactive" iodine–oxygen species and evaporation from the solution.

1. Introduction

The platinum group metals are employed as the active species of many catalysts, such as the one used in the catalytic reforming process. This process is implemented to upgrade the low octane naphtha to higher octane aromatic hydrocarbons. A significant step in the development of these catalysts was made by commercialization of bimetallic catalysts. The platinum/rhenium bimetallic catalyst is widely used throughout the world due to its activity, stability and selectivity (Kluksdahl, 1971; McCoy and Munk, 1971). The deactivated catalysts are replaced periodically by fresh catalysts. The cycle time of replacement is usually short because of rapid permanent deactivation of the catalysts by such mechanisms as structural changes and metallic poisoning. Platinum and rhenium remain imbedded in the matrix of the porous alumina support of the spent catalysts. There is a high platinum value in the spent catalysts. Hence, platinum must be recovered before proper disposal of the spent catalyst.

A variety of authors have investigated the recovery of platinum group metals from spent catalysts through pyro- or hydrometallurgical processes. Pyrometallurgical processes are highly energy consuming. Hydrometallurgical processes are based on the selective dissolution of the noble metal. A variety of complexing agents such as neutral ammonium solution and bromide ions and oxidizing agents such as oxygen, iodine, and bromine have been employed for this purpose (Duyvesteyn et al., 1994; Meng and Han, 1995; Han and Meng, 1996). The oxidant concentration must be sufficient to oxidize the noble metal to an ionic form that can be complexed by the complexing agent.

Platinum recovery from spent reforming and isomerization catalysts has been studied by selective dissolution of base metals in 50% H_2SO_4 and treating the insoluble residue with aqua regia from which platinum was recovered (Jeliyaskova et al., 1982). Platinum was also recovered from a spent Pt-aluminosilicate catalyst by slurring in sulfuric acid to give an aluminum sulfate solution and platinum solid residue. The later was leached with concentrated hydrochloric acid and treated with chlorine gas at 95 °C to dissolve the platinum (Eugenia et al., 1983). The leachate was an aqua regia type solution in which, part of the hydrochloric acid content was replaced by aluminum chloride to lower the acid consumption.

Chen and Huang (2006) examined PGM extraction from spent catalysts by cyanidation. However, at room temperature and pressure, contrary to gold leaching, platinum extraction with cyanide exhibits very poor kinetics. The consumption of cyanide in the Pt leach process from catalysts is also high. This is due to cyanide side reaction with the other parts of the catalyst. To achieve faster platinum leaching kinetics in cyanide solutions, high pressures and temperatures are required (Shams et. al., 2004).

Many major precious metal producers and research groups are actively developing alternate processes. For instance, the merits of

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using hypochlorite/NaCl alternate lixiviate system for gold extraction from ores was examined in our group (Baghalha, 2007). De sa Pinheiro et al. (2004) considered the solubility of Pt in HF, NaF, HCl, HNO_3, H_2O_2 and binary mixture of them. However, the platinum solubility and hence, the extraction efficiency in such mixtures is low.

Platinum extraction from used catalysts by aqua regia solution has been investigated by three groups: 1. Barakat and Mahmoud (2004) examined the effects of some limited factors on Pt extraction; 2. Jafarifar et al. (2005) tested microwave assisted leaching followed by chemical precipitation to recover platinum; 3. Kinetics of platinum leaching in aqua regia solutions from mild to severe conditions was also investigated in our group (Baghalha et al., 2009). Although platinum extraction is very high and fast in aqua regia solutions, the economy of the process is challenging. This is due to the fact that the alumina matrix of the catalyst support dissolves considerably; hence, platinum separation and purification from the leached solution is expensive.

Iodide/iodine solution is also suggested for extraction of precious metals under pressure in an autoclave (Mahmoud, 2007). Platinum extraction using iodine/iodide solutions seems more promising than the other halogen systems. The standard redox potentials of Pt^{4+}, $PtCl_6^{2-}$, $PtBr_6^{2-}$, and PtI_6^{2-} at 25 °C are 1.15, 0.744, 0.657, and 0.40 V, respectively (Bard et. al., 1985). As a result, platinum–iodide complex forms more easily (i.e., at lower potentials) and it is more stable in solution than the other platinum–halogen complexes. It should be noted the iodine/iodide solution chemistry is rather complicated. In such a system, the aqueous ions I^-, I_2, I_3^-, HIO, and IO^- readily form. HIO and IO^- species, then slowly disproportionate to IO_3^- and other highly oxidized iodine–oxygen species (Bard et. al., 1985).

Although promising, very little work has been done so far on platinum/iodine leaching system. In this work, we experimentally studied the effect of various parameters on platinum extraction from the spent reforming catalysts using iodine–iodide solutions. The conditions that produce maximum platinum recovery in iodine/iodide solutions are also discussed.

2. Experimental

The batch platinum leaching tests were performed in a sealed 1.5 L Pyrex reactor, equipped with a coated stainless steel turbine-type impeller. A reflux condenser was used to recover the water vapor and send it back to the reactor. Any non-condensable gases at the exit of the condenser were scrubbed into an alkaline solution. A hot-plate heater and temperature sensor-controller were used to control the reactor temperature at the desired level within ±1 °C.

The spent naphtha reforming catalysts was obtained from a petroleum refinery. The catalysts were dried in an oven at 110 °C overnight and then pulverized into particle sizes less than 106 µm to minimize the internal mass transfer resistances. The crystalline phase of the catalyst was identified by powder XRD. The major components of the catalyst were identified by XRF elemental analysis. The concentration of platinum in the catalyst was measured by dissolving 5 g of the catalyst in hot aqua-regia solution for up to one week. When the solution was finally clear and the catalyst was totally dissolved, the aqua-regia solution was made to 100 mL volume with de-ionized water and then analyzed for platinum by a UV/Visible spectrophotometer (as explained below).

For each experiment, a total of 600 g de-ionized water was used to prepare the lixiviant solution. 500 g of the water and the desired amount of the powdered catalyst was placed in the reactor. The slurry was agitated at 700 rpm and then heated to a temperature slightly higher than the desired temperature. In a separate beaker, the desired amounts of iodide, iodine, and concentrated HCl were dissolved in 100 g de-ionized water. This solution was then quickly added to the reactor and the time was set to zero. At specified times, the solution pH was measured using a pH electrode and a 10 mL slurry sample was taken using a pipette. The sample was then quickly centrifuged and the supernatant solution was decanted to stop further Pt extraction for that sample. The supernatant solution was then analyzed for platinum concentration.

A UV/Visible spectrophotometer (M501 single beam scanning, Camspec) was used to measure platinum concentration in solution, based on the absorbance at the wavelength of 403 nm. The instrument was calibrated with 10, 20 and 30 ppm standard platinum solutions. For each Pt measurement, 1.00 mL of the leached solution sample was placed in a 25 mL measuring flask. 8.75 mL of 37% hydrochloric acid and 10 mL of 1 M stannous chloride solution was added. The solution was then brought to the 25 mL mark volume by adding de-ionized water. The Pt concentration of the obtained solution was then measured by the spectrophotometer (ASTM D4642-04, 1998). Based on the UV/Vis measurement of known Pt concentrations in a few synthetic solutions with matching matrix of the dissolved catalyst, the accuracy of the measured Pt values was determined to be within ±1%.

The “active” iodine species (HIO, $I_2(aq)$, and I_3^-) concentrations in the leached solutions were measured based on the redox titration with standard thiosulfate solution (Clesceri et. al., 1999). Acetic acid was used to buffer the solution pH between 3 and 4. 1 mL of starch solution was used as indicator. The titration endpoint was the disappearance of the starch–iodine blue color. The iodine concentration in the leached solution was then calculated according to Eq. (1).

$$I_2(\mathrm{g/L}) = 0.2575 * V_{\mathrm{thiosulfate}}(\mathrm{mL}) / V_{\mathrm{sample}}(\mathrm{mL}) * 4.93. \tag{1}$$

3. Results

The elemental analyses of the main components of the spent catalysts are shown in Table 1. The concentration of platinum in the catalyst was measured by aqua-regia dissolution and UV/Visible measurement. The platinum wt.% measured by this method was virtually the same platinum percentage reported by the catalyst manufacturer. XRD of the used catalyst is shown in Fig. 1. As shown in this figure, the major crystalline phase in these catalysts is γ-alumina. In the present work, 13 iodine–iodide leaching tests were performed. The experimental conditions of these tests are reported in Table 2. The tests were designed to study the effects of various factors, including catalysts size, agitation speed, solution pH, temperature and liquid to solid ratio on the Pt extraction rate and its maximum recovery. Decoking of the catalyst is another factor which may impact Pt extraction rate and recovery (Baghalha et al., 2009). However, according to the XRF result presented in Table 1, the coke content of the spent catalysts was only 0.28%. Since, the spent catalysts had been decoked in-situ before removal from the industrial reactor, these catalysts were, in fact, considered as “decoked”.

It is noticeable that aqueous iodine solutions slowly disproportionate into highly oxidized iodine–oxygen species, such as IO_3^- (Bard

Table 1
Chemical composition of spent catalysts by XRF.

Component	wt.%
Al_2O_3	91.93
SiO_2	0.19
S	0.30
Cl	0.59
CaO	0.04
TiO_2	0.13
Fe_2O_3	0.05
Re	0.24
Pt	0.24
C	0.28
LOI	5.98

The concentration of platinum in the catalyst was measured by aqua-regia dissolution and UV/Visible measurement.