Volume 4, Issue 2, February 2026 ISSN (E): 2938-3765

SELECTIVE CHLORIDE LEACHING OF PALLADIUM FROM γ-Al_2O_3-BASED CATALYSTS: THERMODYNAMIC JUSTIFICATION

Tursunova Feruza Jamshidovna
Zarmed University

Abstract
The paper examines the thermodynamic and physicochemical foundations of the selective recovery of palladium from spent γ-Al_2O_3-based catalysts using the chloride leaching system HCl–NaOCl. It is shown that the combination of the oxidative action of sodium hypochlorite and the ability of palladium to form stable chloride complexes ensures a high degree of Pd recovery (95–98%) while preserving the structural integrity of the alumina support. The standard Gibbs free energy of the palladium oxidation reaction was calculated, confirming the thermodynamic spontaneity of the process. The obtained conclusions are consistent with experimental data and the analysis of electrochemical stability diagrams.

Keywords: palladium, γ-Al_2O_3, chloride leaching, sodium hypochlorite, thermodynamics, selectivity.

Introduction

Relevance of the Study

The increasing volume of recycling of spent palladium-containing catalysts in the petrochemical and gas-chemical industries necessitates the development of selective and resource-saving methods for noble metal recovery. Of particular difficulty is the separation of palladium from the alumina support without destruction of its structure. In this context, chloride leaching systems are of considerable scientific and practical interest, as they enable targeted dissolution of palladium with minimal impact on γ-Al_2O_3.

1. Selectivity of Chloride Leaching of Palladium

During the processing of spent palladium-containing catalysts based on γ-Al_2O_3, one of the key objectives is the selective extraction of palladium without destruction of the alumina support. It has been experimentally established that the application of a chloride leaching system including hydrochloric acid and sodium hypochlorite (HCl + NaOCl) ensures a high degree of Pd recovery while preserving the γ-Al_2O_3 structure. The selectivity of this process is determined by the combined action of thermodynamic, kinetic, and structural-chemical factors.

2. Thermodynamic Justification of Palladium Oxidation

In an acidic chloride medium, sodium hypochlorite acts as a source of strong oxidizing agents (Cl_2, HOCl) capable of oxidizing metallic palladium to the ionic state Pd^{2+}. The resulting palladium ions bind with chloride ions to form a stable complex compound $[PdCl_4]^{2-}$:

$$Pd^0 \rightarrow Pd^{2+} + 2e^-$$
$$Pd^{2+} + 4Cl^- \rightarrow [PdCl_4]^{2-}$$

Web of Medicine: Journal of Medicine, Practice and Nursing
webofjournals.com/index.php/5
Licensed under a Creative Commons Attribution 4.0 International License.

For the Cl_2/Cl^- pair ($E° = 1.396$ V) and Pd^{2+}/Pd ($E° = 0.915$ V), the standard electrochemical cell potential is: $E° = 1{,}396 - 0{,}915 = 0{,}481$ B

The change in standard Gibbs free energy is determined by the expression:

$\Delta G° = -nF \cdot E^0$

At n = 2 and F = 96485 C/mol, the value of $\Delta G°$ equals −92.8 kJ/mol, which indicates the thermodynamic spontaneity of the process.

3. Influence of Chloride Ion Concentration and Temperature

Under real leaching conditions, the process proceeds at temperatures up to 90 °C and at high Cl^- concentration (6–8 mol/L). According to the Nernst equation, an increase in chloride ion activity further decreases the value of ΔG, as a result of which the total change in free energy reaches −120 to −140 kJ/mol, which significantly accelerates palladium dissolution.

4. Stability of γ-Al_2O_3 in Chloride Medium

γ-Al_2O_3 is characterized by high chemical and structural stability. Aluminum is in its maximum oxidation state (+3) and does not form stable soluble chloro-complexes. Dissolution of aluminum oxide in acidic medium proceeds kinetically slowly, and passivating layers form on the surface of the support, further reducing the corrosion rate.

5. Comparison with Alternative Acid Systems

Table 1 Comparative Characteristics of Acid Leaching Systems

Parameter	HCl + NaOCl	HNO_3	H_2SO_4
Main mechanism	Pd oxidation + chloride complex formation	Strong oxidation	Acid hydrolysis
Form of Pd in solution	$[PdCl_4]^{2-}$ (stable complex)	Pd^{2+}/nitrate forms	Pd^{2+}/sulfate forms
ΔG of the process	−120 to −140 kJ/mol	−60 to −90 kJ/mol	−40 to −70 kJ/mol
Effect on γ-Al_2O_3	Minimal	Partial degradation	Loss of porous structure
Selectivity toward Pd	High	Medium	Low
Technological applicability	High	Limited	Limited

Table 1 presents a comparative study of acid systems used for the dissolution of palladium from spent γ-Al_2O_3-based catalysts.

The most effective system is HCl + NaOCl, in which palladium recovery proceeds through its oxidation and the formation of the stable chloride complex $[PdCl_4]^{2-}$. The process is characterized by high thermodynamic favorability (ΔG = −120 to −140 kJ/mol) and minimal impact on the support structure, which ensures high selectivity toward palladium.

When nitric acid is used, strong oxidative action with the formation of nitrate forms of Pd^{2+} is observed; however, reduced thermodynamic efficiency and partial destruction of γ-Al_2O_3 limit the practical application of this method.

Sulfuric acid exerts the most aggressive effect on the support, causing loss of its porous structure. The low thermodynamic efficiency of the process (−40 to −70 kJ/mol) and low selectivity toward palladium make this option the least preferable.

Web of Medicine: Journal of Medicine, Practice and Nursing
webofjournals.com/index.php/5

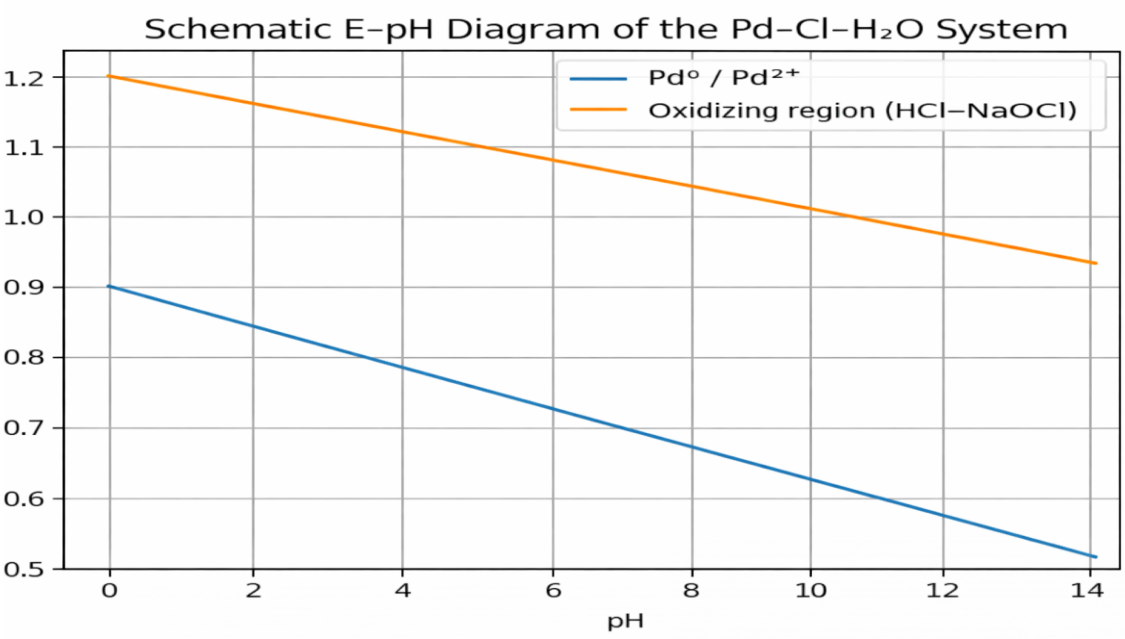
Licensed under a Creative Commons Attribution 4.0 International License.

6. Correlation of Thermodynamic Analysis with Experimental Data

Experimental data confirm a high degree of palladium recovery (95–98%) with minimal transition of Al^{3+} into solution. Preservation of the specific surface area and porous structure of γ-Al_2O_3 after leaching indicates the absence of support destruction.

In Fig. 1, the E–pH diagram for the Pd–Cl–H_2O system in the acidic region (pH < 1) and under oxidative potentials realized in the presence of NaOCl shows that the thermodynamically stable form of palladium is Pd^{2+} in the form of chloride complexes $[PdCl_4]^{2-}$. The stability region of metallic palladium Pd^0 is significantly narrowed. For γ-Al_2O_3, within the indicated pH and potential range, the thermodynamic stability region of the solid oxide phase is preserved, which explains the absence of support dissolution.

Figure 1



Conclusion

Chloride leaching using the HCl–NaOCl system is a selective, thermodynamically and kinetically justified method for palladium recovery from γ-Al_2O_3-based catalysts. The process is accompanied by negative Gibbs free energy values and stabilization of palladium in solution in the form of chloride complexes, while the alumina support retains its structural integrity.

References

1. Harjanto S. et al. Leaching behavior of palladium in chloride media. Minerals Engineering, 2014.
2. Kim B.S. et al. Chloride leaching of palladium from spent catalysts. Journal of Hazardous Materials, 2011.
3. Habashi F. Principles of Extractive Metallurgy. Vol. II. Hydrometallurgy. Gordon and Breach.
4. Greenwood N.N., Earnshaw A. Chemistry of the Elements. Butterworth-Heinemann.
5. Zhang W. Thermodynamic stability of palladium chloride complexes. Hydrometallurgy, 2017.

Web of Medicine: Journal of Medicine, Practice and Nursing
webofjournals.com/index.php/5

Licensed under a Creative Commons Attribution 4.0 International License.