

Porous Organic Polymers for Selective Palladium Recovery and Heterogeneous Catalysis

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Abstract: Palladium (Pd) recycling from waste materials is an important approach in order to meet the growing demand for Pd originating from its broad range of applications including in the automotive industry, electronics and catalysis. In this article, we discuss the design principles of solid-sorbents for efficient recovery of Pd from waste sources with a particular emphasis on porous organic polymers (POPs), which emerged as promising materials for Pd recovery due to their tunable chemical functionality, stability and porosity. We discuss the critical role of binding sites and porosity in the Pd uptake capacity, adsorption kinetics and selectivity. We also highlight the sustainable use of captured Pd within the polymer network as a heterogeneous catalyst for the cross-coupling reactions.

Keywords: Adsorption · Heterogeneous catalysis · Hierarchical porosity · Palladium recovery · Platinum group metals (PGMs) · Porous organic polymers (POPs)



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1. Introduction

Palladium (Pd), which is one of the platinum group metals (PGMs), has been extensively used in various applications including automotive industry, electronics, catalysis and many others. In

particular, Pd is widely used as a catalyst in the pharmaceutical industry for the cross-coupling reactions such as Suzuki-Miyaura, Sonogashira and Heck.^[1,2] The biggest use of Pd by a large margin is in the automobile industry, specifically in catalytic converters, which are essential for the conversion of harmful components in the car's exhaust.^[3] Hence, the demand for Pd is rather high, yet its low abundance creates supply problems. Mining is the general strategy to obtain palladium from the earth's crust. Pd is mainly produced by South Africa and Russia, which accounted for the 44% and 31% of global Pd supply in 2020, respectively.^[4] However, Pd mining has a significant environmental impact as it involves a series of high-temperature treatment steps (up to 1450 °C),^[5] which results in massive CO₂ emissions, estimated to be 3.88 tons per kg of Pd.^[6] Therefore, in an effort to address concerns arising from supply security and environmental impact of Pd production, recycling of Pd from various types of scrap has become an important research direction. The concept of Pd recycling is to extract Pd from the waste materials such as spent catalysts,^[7] automotive catalytic converters,^[8] waste electronics^[9] and used nuclear fuel.^[10] These materials contain varying amounts of Pd, *i.e.*, 2–7 g per one catalytic converter,^[3] average 0.04 g in one printed circuit board (PCB), 0.011 mg g⁻¹ in smartphones (g of smart phone),^[11] 165 mg L⁻¹ in high level liquid waste (HLLW) solution.^[10] Pd recycling technology, however, is still under development and only about 34% of the Pd supply originates from recycled Pd.^[4] In this direction, the development of efficient, low-cost Pd recycling technologies is necessary in order to meet ever-increasing demand for Pd. Compared to the Pd mining process, Pd recycling has a shorter production cycle and lower investment costs. Pd recycling involves pyrometallurgical or hydrometallurgical processes.^[7] The pyrometallurgical process segregates and concentrates the precious metals from waste materials through smelting in a furnace. However, given the high melting point of Pd (1550 °C), this process requires a high energy input, resulting in a high environmental impact. On the other hand, the hydrometallurgical process involves the dissolution of metals using cyanide, aqua regia (HCl/HNO₃) or strong concentrated acids (HCl and H₂SO₄).^[12] Afterwards, all the dissolved metals in the leaching solution need to be separated through either liquid–liquid or solid–phase extraction.

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The liquid–liquid extraction process uses organic extractants containing amine, oxygen, sulfur or phosphonium moieties.^[7] Generally, liquid–liquid extraction offers high selectivity and extraction efficiency but involves toxic solvents and shows poor recyclability due to the loss of organic extractants during the process. The solid-phase extraction process on other hand utilizes porous sorbents such as silica, polymers and zeolites and enables direct capture of Pd from waste solution.^[13] Considering its high recyclability, stability and ability to capture metals without using organic solvents, solid-phase extraction is the preferred method for Pd recycling over liquid–liquid extraction. When designing solid sorbents for Pd recovery, there are several parameters such as Pd adsorption capacity, efficiency, selectivity, uptake kinetics and recyclability that should be considered. In this vein, porous organic polymers (POPs) have emerged as promising alternatives over their crystalline counterparts, namely, covalent organic frameworks (COFs), and metal–organic frameworks (MOFs), owing to their high structural tunability, permanent porosity and stability under acidic conditions. These favorable features also enabled the application of POPs in CO₂ capture, separation^[14] and conversion,^[15] environmental remediation, heterogeneous catalysis,^[16] and precious metal recovery.^[17] In the context of Pd recovery, high surface area and well-defined binding sites are critical parameters for the selective targeting of Pd and recovery efficiency. Aside from surface area, pore size also plays an important role. Especially, hierarchical porosity, that is the combination of micro- (<2 nm), meso- (2–50 nm) and macropores (>50 nm), facilitates efficient mass transport,^[18] thus leading to improved adsorption kinetics. Conventionally, low-cost solid polymeric sorbents are preferred as they can be simply burned to recover Pd. In this direction, POPs can offer a sustainable pathway to use captured Pd as single-atom catalysts (SACs) for various chemical transformations. SACs are heterogeneous catalysts, in which all catalytically active metal species exist as isolated single atoms and stabilized by the support. SACs showed high catalytic performance in various organic transformations^[19] and in particular Pd-based SACs surpass catalytic performance of their homogeneous counterparts.^[20] Therefore, Pd-containing POPs are also actively researched for heterogeneous catalysis.^[21]

In this article, we discuss the design principles of efficient solid-sorbents for Pd recovery from waste sources with a particular emphasis on POPs and highlight critical factors to improve Pd recycling efficiency. Moreover, we also present the use of captured Pd within POPs as a sustainable pathway for the preparation of heterogeneous catalysts towards cross-coupling reactions.

2. Porous Materials for Palladium Recovery and Heterogeneous Catalysis

In solid-phase Pd extraction, the leaching solution from waste-materials is highly acidic and contains various metal ions (Pd, Cu, Ni, Fe, Zn and Cd). These ions exist as metal chloride complexes, *e.g.*, PdCl₄²⁻ (5.5 Å) and the nature of the complexes depends highly on the pH of the solution. There are two main pathways for Pd capture, namely the ligand-exchange mechanism and electrostatic interactions. Therefore, the design and understanding of binding sites are very important and, generally, polymers containing amine and oxygen atoms are used. In this section, we highlight selected examples of porous materials with a particular emphasis on their Pd binding sites and capture mechanisms.

2.1 COFs and MOFs for Pd Recovery

COFs are crystalline polymers with permanent porosity and generally synthesized through reversible covalent bond formation under solvothermal conditions. While this process is essential for the crystallinity, it also limits the stability of COFs. In a notable example, Wang and coworkers synthesized bipyridine-based COFs (TFBBPY-COFs, Fig. 1) and introduced -OH and -OMe groups in

close proximity to the imine bonds in an effort to improve water stability.^[23] In particular, TFBBPY-OH-COF can undergo a tautomerization reaction, first introduced by Banerjee and coworkers,^[22] thus substantially improving the stability of the resulting COF.^[23] The authors showed that both bipyridine and -OH/-OMe groups serve as binding sites for Pd(II). However, they observed higher Pd recoverability in the -OMe version, which was attributed to the intramolecular hydrogen bonding interactions in the -OH version, thus decreasing Pd binding affinity. In the same vein, Wang and coworkers demonstrated interlayer Pd²⁺ coordination of salicylaldehyde-based 2D COFs (COF-TzDa).^[24] The authors also used a tautomerization strategy to improve the water stability of their COFs. They showed that Pd(II) binds to the carbonyl group. Interestingly, they observed a clear correlation between interlayer spacing and Pd(II) loading, thus suggesting interlayer binding of Pd(II), which involves coordination with two oxygens from carbonyl groups of stacked COFs layer and two oxygens from the solvent molecules located within the pores.

As for the MOFs, Yun and coworkers reported Pd recovery using zirconia (IV)-based MOFs (Zr-MOFs).^[25] Zr-MOFs are stable in water as well as in acidic solutions owing to the presence of strong Zr-O bonds. The cationic Zr site of Zr₆ node (Zr₆O₄(-CO₂)_x)^[26] served as a binding site, wherein PdCl₄²⁻ replaced the -OH moiety of the Zr-node through an ion-exchange mechanism (from Zr-OH to Zr-Cl-Pd). The authors also revealed the critical role of pore size on the Pd adsorption kinetics and uptake capacity. The MOFs with larger pores of MOFs (18.4 Å of MOF-808, 16.4 Å of UiO-66) enabled much faster Pd uptake kinetics and higher Pd uptake capacity compared to the ones with smaller pores (5.6 Å of MOF-802). This result is expected considering the large kinetic diameter of Pd complex, 5.5 Å of PdCl₄²⁻. All Zr-based MOFs (UiO-66 (Fig. 1), MOF-808 and MOF-802) showed high Pd(II) selectivity from the spent catalyst leaching solution over Co(II), Ni(II), Cu(II) and Zn(II). Precise control over the pore size and geometry could be beneficial for size/shape-based separation of precious groups metals, *i.e.*, Pd and Pt separation.

2.2 POPs for Pd recovery

The synthesis of POPs involves irreversible bond formation, thus leading to mostly amorphous polymers. While this might

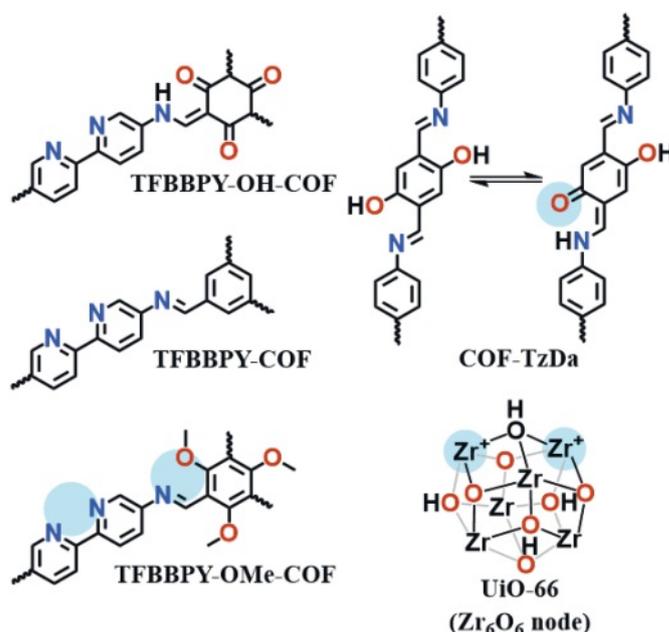


Fig 1. Selected examples of covalent organic frameworks (COFs) and metal organic frameworks (MOFs) for Pd recovery. Palladium binding sites are highlighted in blue.

seem like a disadvantage compared to their crystalline counterparts, high stability, scalability, surface area and structural tunability render them as highly competitive materials for Pd recovery. Yavuz and coworkers have reported a metal-free approach for the synthesis of a pyrazole-connected POP, COP-214 (Fig. 2).^[27] COP-214 showed a BET surface of $308 \text{ m}^2 \text{ g}^{-1}$ and maximum Pd uptake capacity of 103 mg g^{-1} . The N-site of the pyrazole moiety was identified as the Pd binding site through X-ray photoelectron spectroscopy (XPS) analysis before and after Pd capture. Noticeably, COP-214 showed exceptional Pd selectivity over precious metals (Pt, Ru, Rh, Sb, Ir) as well as the transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Cd, Ti, Pb, U). The most interesting point of this work is the high Pd/Pt selectivity. The authors attributed this result to the lower dissociation energy of Pd–Cl bond of PdCl_4^{2-} compared to that of PtCl_4^{2-} , thus leading to the preferential binding of Pd(II) over Pt(IV). In a similar approach, Ma and coworkers synthesized pyridine-based POPs bearing amino groups in *ortho* or *para* positions of the pyridine ring (POP-NH₂, POP-*o*-NH₂-Py and POP-*p*-NH₂-Py).^[28] As a Pd(II) binding site, the nitrogen atom of the pyridine moiety acts as a Lewis basic site, which was further reinforced by the neighboring amino groups. These POPs showed high Pd uptake capacities up to 752 mg g^{-1} along with fast Pd adsorption kinetics ($K_d = 1.1 \times 10^8 \text{ mL g}^{-1}$). Interestingly, the position of the amino group on the pyridine ring had a profound impact on the Pd(II) selectivity. The one with the *ortho* amino group, Pd-*o*-NH₂-Py, showed higher Pd selectivity from the metal mixture solution of Pd(II), Fe(II), Zn(II), Pb(II), Ni(II) and Cd(II) owing to the cooperative binding of pyridine and amino moieties.

Luo and coworkers reported the synthesis of conjugated-microporous polymers (CMPs) through Sonogashira-Hagihara coupling reactions by using a fluorinated-monomer, forming FCMPs.^[29] The introduction of electron-withdrawing groups reduced the electron density of FCMPs, which improved the $\pi^{\delta+}-\pi^{\delta-}$ interaction with PdCl_4^{2-} , thus leading to a maximum Pd(II) uptake capacity of 447.7 mg g^{-1} , albeit with a low selectivity owing to the lack of well-defined binding sites. As an alternative binding

mechanism, Feng and coworkers developed a cationic pyridyl triazine polymeric network (CPTPN). The authors showed selective Pd(II) recovery from high-level radioactive liquid waste (HLLW).^[30] The cationic pyridyl moiety acted as a binding site for Pd(II) through an anion exchange mechanism. Interestingly, CPTPN-Cl showed high Pd(II) and Ag(I) uptake from the metal-mixture solution owing to the AgCl precipitation. Thus, they exchanged the counter anion from Cl⁻ to NO₃⁻ to form CPTPN-NO₃, which showed high Pd(II) selectivity over Ag(I), highlighting the critical role of counter anions in charged POPs for selective Pd recovery.

In a notable recent advance, the Coskun group in collaboration with the research groups of Christophe Copéret and Maarten Nachtegaal under the auspices of NCCR Catalysis designed and synthesized porous polyisothiocyanurates, called covalent isothiocyanurate frameworks (CITCFs), through the trimerization of 1,4-phenyldiisothiocyanate under ionothermal conditions for selective palladium recovery.^[31] Contrary to the earlier reports, CITCFs feature S, which is a soft base, as a binding site for Pd(II), which is a soft acid. CITCFs showed surface areas up to $1589 \text{ m}^2 \text{ g}^{-1}$ and a hierarchically porous network structure. Notably, CITCFs showed the highest Pd uptake capacity, 909 mg g^{-1} , reported to date along with very fast Pd adsorption kinetics. The authors carried out XPS, extended X-ray absorption fine structure (EXAFS) and solid-state nuclear magnetic resonance (NMR) analyses to precisely probe the nature of the Pd(II) binding site as well as the binding mechanism. In line with the XPS analysis results, EXAFS analysis revealed Pd–S coordination bonding with an average of 2.9 ± 0.3 of S and 0.8 ± 0.2 of O atoms coordinated to Pd(II). The authors attributed the coordinating O atoms to H₂O molecules trapped within the pores. The authors also conducted selective Pd(II) capture test using wastewater conditioned solution of Pd(II), Ni(II), Zn(II), Fe(II) and Cd(II). CITCFs showed exceptionally high Pd selectivity in batch test and under practical conditions using a breakthrough test (Fig. 3). CITCFs also showed higher Pd(II)/Pt(IV) selectivity owing to the faster diffusion of PdCl_4^{2-} compared to the PtCl_6^{2-} . These results clearly show the

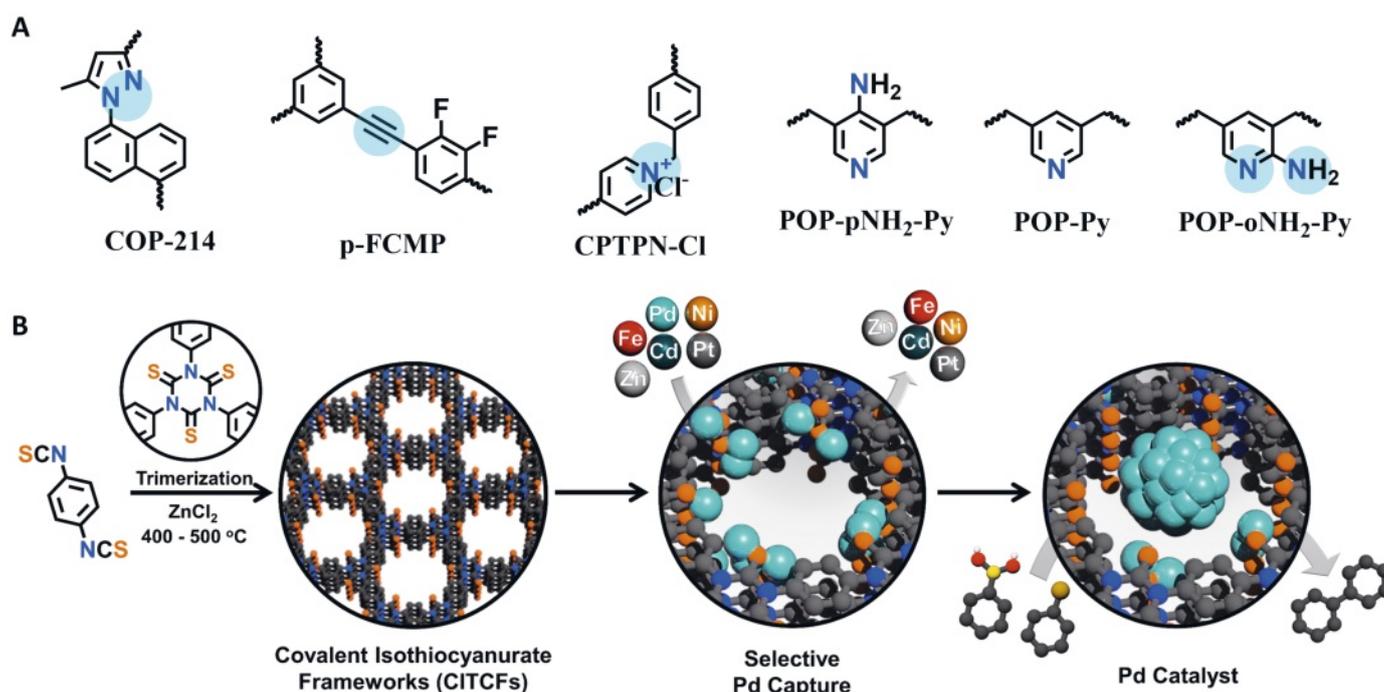


Fig 2. A) Examples of porous organic polymers (POPs) and their Pd binding sites. B) Chemical structure and graphical representation of the covalent isothiocyanurates frameworks (CITCFs) along with selective Pd(II) recovery and the use of captured Pd as a heterogeneous catalyst for the Suzuki-Miyaura cross-coupling reaction.

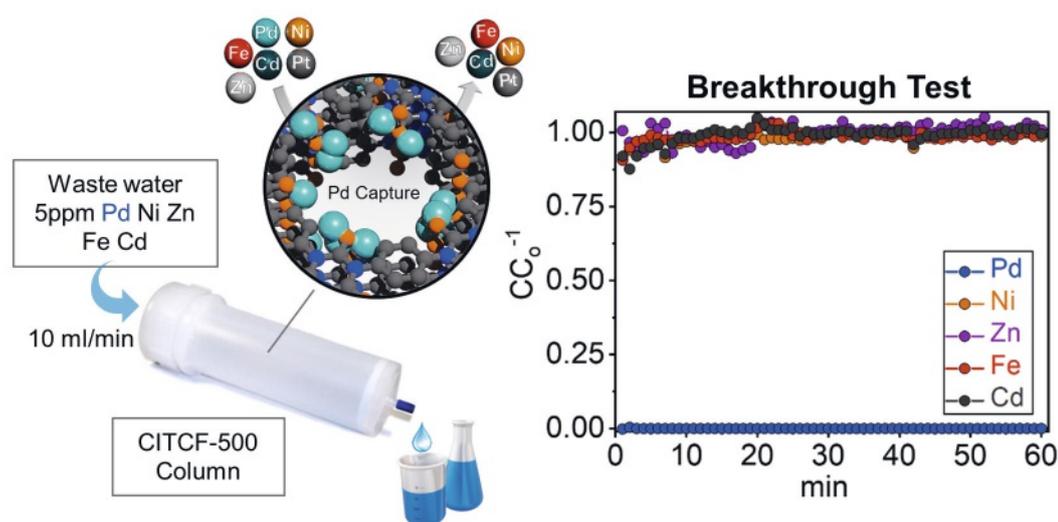


Fig 3. A) Graphical representation of breakthrough step-up and the test result using CITCFs.

impact of homogeneously distributed sulfur binding sites within the polymer network for efficient Pd recovery.

2.3 Recovered Pd for Heterogeneous Catalysis

The use of recovered Pd within the polymer network as an heterogeneous catalyst offers a sustainable approach for the catalyst development, which is rarely explored. Nevertheless, POPs have been shown to be excellent supports for Pd(II) and Pd NPs. In this direction, POPs containing amine,^[32] imine^[33] salen-porphyrin,^[34] phenanthroline,^[35] N-heterocyclic carbene (NHC),^[36] diisocyanate^[37] and phosphane^[38] as binding sites to coordinate and to stabilize the Pd atoms or Pd NPs have been studied. The lack of standard parameters such as catalyst loading, reaction temperature, solvent, turnover number, turnover frequency for catalytic tests, however, makes it rather challenging to properly compare and benchmark the performance of these polymers. In an effort to demonstrate the possibility of using recovered Pd for heterogeneous catalysis, Coskun and coworkers investigated the catalytic performance of CITCFs in the Suzuki-Miyaura cross coupling reaction.^[31] CITCFs showed high yields in the range of 78.0 and 99.9%, exceptional product selectivity and good substrate tolerance. Noticeably, the lack of Pd leaching and excellent recyclability of the catalyst revealed the ability of CITCFs to stabilize Pd(II) and Pd NPs within the pores. These results show the potential of POPs for Pd recovery and heterogeneous catalysis.

3. Outlook and Conclusion

Considering the massive environmental impact of Pd mining as well as the supply security issues, the recovery of Pd from waste sources is extremely important. The environmental impact of the process, however, should be assessed in detail. Solid-sorbents allow direct capture of Pd from an aqueous waste solution, naturally eliminating the use of toxic chemicals. In this direction, we showed the potential of porous organic polymers for efficient Pd recovery. The detailed understanding of the nature of the binding sites is essential to determine the binding mechanism and to control the selectivity towards Pd. It should also be noted that under practical conditions, metal solutions contain significantly excess amounts of transition metals compared to Pd, which could potentially interfere with the binding between Pd and the sorbent. While most of the porous materials involve N and/or O atoms as binding sites, the S atom has also been shown to be a rather efficient as a binding site. Other approaches relying on electrostatic interactions, however, suffer from low selectivity. High surface area along with the hierarchical pore structure also play a critical role in the uptake capacity and adsorption kinetics. While the initial examples are quite promising, we expect significant

research efforts in the coming years towards the development of new solid-sorbents for Pd recovery. The ideal sorbent should be low-cost and stable in a broad pH range. In addition, it should also combine high Pd uptake capacity, high selectivity, fast adsorption kinetics and high recyclability. The utilization of the captured Pd from waste conditions as an efficient heterogeneous catalyst in the cross-coupling reactions is a sustainable approach for the catalyst development and rather important to minimize environmental impact. Industrially, Pd recovery from heterogeneous sorbents is done by simply burning the low-cost organic polymeric host. Therefore, the transformation of POP-based solid sorbents into heterogeneous catalysts provide an alternative and high value application. By tailoring the binding sites, this approach can indeed be extended to selectively capture multiple metal ions to create bimetallic, trimetallic catalytic systems. All in all, the future of POPs in the areas of precious metal recovery and heterogeneous catalysis is rather promising.

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