

Olefin-Assisted Electrochemical Recycling of Homogeneous Hydrosilylation Catalysts in Nonpolar Media

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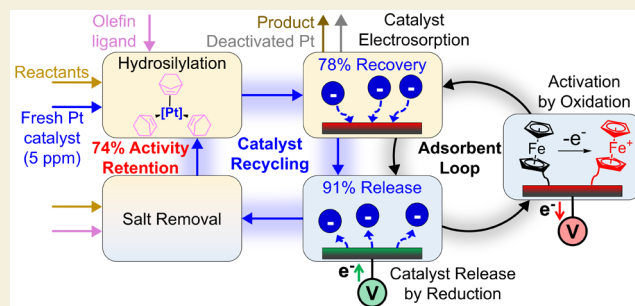
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ABSTRACT: Homogeneous platinum catalysts for hydrosilylation are essential for the chemical industry and society, through the production of commodities such as functional silicones. However, the high boiling points of the products and the low concentration of the homogeneous catalysts make the implementation of traditional separation methods difficult. Catalyst loss becomes a core sustainability and techno-economic challenge. In addition, the highly active platinum-based catalysts for hydrosilylation have remarkable susceptibility to deactivation upon reaction completion. Recently, redox-mediated electrosorption has been successfully demonstrated in a number of electrically conductive media as a separation platform. However, industrial hydrosilylation systems are carried out in highly nonconductive media. Therefore, developing an electrochemical recycling system in realistic, nonconductive hydrosilylation media can be transformative for sustainable homogeneous catalysis and chemical manufacturing. Here, we overcome these challenges for hydrosilylation catalyst recycling by introducing a strongly coordinating vinyl ligand and enabling the recycling of these Pt catalysts in solvent-free, nonpolar reactant media through two distinct loops for catalyst recycling and electrosorbent regeneration. The coordinating olefin ligand maintains catalytic activity after the reaction and prevents particle aggregation, a primary mechanism for deactivation. The Pt catalyst stabilized by the coordinated ligand can be reversibly adsorbed and released by the electrosorbent, demonstrating 100% catalytic activity retention and over 90% Pt release efficiency. A techno-economic analysis supports the economic potential of the electrochemical recycling system, with cost savings of >5k USD/kg_{Pt}. By combining chemical design and electrochemical engineering, we demonstrate the sustainable electrochemical recycling of industrially relevant hydrosilylation catalysts in practical nonconductive media.

KEYWORDS: electrochemical separation, adsorptive separation, homogeneous catalyst recycling, hydrosilylation, redox-responsive material



1. INTRODUCTION

Homogeneous catalysts make up 30% of the total catalyst market share owing to their remarkable turnover and selectivity.^{1,2} Hydrosilylation is a key process in the organo-silicon industry, with a market value of \$18 billion in 2021.³ Homogeneous platinum catalysts have dominated the hydrosilylation market for over 50 years, accounting for up to 30% of the final cost of a product.^{4,5} However, the separation and reuse of homogeneous catalysts from hydrosilylation products involve challenges, especially the low concentration of the catalyst (often down to the part-per-million range), and sensitive metal–ligand structures susceptible to activity loss during traditional thermal separations.^{6–8} In addition, the catalysts themselves can be highly sensitive to the solution environment during and after reaction completion. To overcome these challenges, we leverage a redox-active electrosorbent in combination with the introduction of a coordinating ligand for preventing catalyst deactivation, to enable an electrochemical recycling process for homogeneous

Pt catalysts from industrially relevant solvent-free, non-conductive hydrosilylation media.

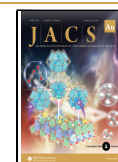
Developing a new recycling method for active Pt homogeneous catalysts in nonpolar hydrosilylation media is highly beneficial for chemical manufacturing to recover the intrinsic value from the platinum-group metals, extend the use of the catalyst for multiple turnovers, as well as reduce chemical waste, and improve sustainability. The high viscosity and boiling point of hydrosilylation products as well as the low Pt concentration make it expensive to apply traditional separation methods such as distillation,^{9–11} which also deactivates temperature-sensitive Pt homogeneous catalysts.^{7,12} Thus, recent advances in hydrosilylation catalysis have been

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focused on developing recyclable heterogeneous catalysts ranging from Pt- or Rh-based single-atom catalysts^{13–16} to ionic liquids (IL)-supported biphasic catalysts,^{17–19} which of the total turnover number (TON) over the recycling falls between 10^4 and 10^6 , comparable to hydrosilylation homogeneous catalysts. However, the direct recycling of a homogeneous catalyst from hydrosilylation has not been explored.

Another challenge for homogeneous Pt catalyst recycling is catalyst deactivation under regular reaction conditions, especially through nanoparticle formation.^{5,20} Terminal alkenes (e.g., 1-octene), the most commonly used olefins in industrial hydrosilylation,²¹ are weakly coordinating ligands to the Pt catalyst.⁵ This weak coordination is advantageous for high catalyst activity but lowers the Pt stability, leading to Pt particle formation, the main mechanism for catalyst deactivation.^{5,20} On the other hand, leveraging ligands that are excessively strongly binding can also result in catalyst activity loss. Thus, it is hypothesized that the addition of an olefin with moderately strong coordination to Pt can assist the adsorptive recovery of the active Pt catalyst without hampering the activity and, at the same time, provide a product that can remain within the reaction mixture without excessive downstream separations.

Electrosorption using redox-active polymers^{22–27} can provide a promising recycling platform for homogeneous catalysts owing to mild operation conditions and high selectivity of the redox binding site toward molecular targets.^{28–33} Redox-active materials such as polyvinyl ferrocene (PVF) have recently shown highly efficient separation of anions and pollutants from aqueous media^{28–30,34–38} as well as value-added molecules in organic media.^{32,33} In particular, a recent proof-of-concept study for the electrochemical recycling of homogeneous catalysts has demonstrated up to 100% homogeneous catalyst recovery and activity retention.³³ However, these electrosorption technologies have been investigated mainly in electrically conductive media, while most hydrosilylation reactions are conducted in nonconductive media. Thus, a successful electrochemical recycling method has to overcome the nature of the nonconductive media as well as the intrinsic catalyst stability challenges.

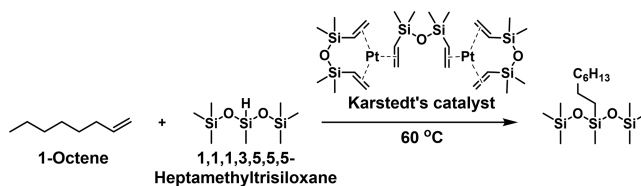
Here, we develop an electrochemical recycling system for a homogeneous Pt catalyst in solvent-free nonpolar hydrosilylation media to overcome the challenges for conductivity and intrinsic deactivation pathways. Two discrete loops of catalyst and electrosorbent recycling maintain the high catalyst activity in nonpolar hydrosilylation while leveraging the redox-switchable binding between the active Pt catalyst and ferrocenium (Fc^+) of PVF with 78% Pt recovery from nonpolar hydrosilylation of 5 ppm Pt. The judicious selection of an olefin ligand more strongly bound to Pt than 1-octene⁵ successfully balanced the catalyst activity and recycling efficiency by stabilizing the catalyst from aggregation after the reaction. The stabilizing effect significantly improved the ratio of the active catalyst in the electrosorption. A techno-economic analysis (TEA) shows that the recycling process cost is sensitive to the catalyst reusability and Pt uptake, but the cost savings at the current performance can already deliver over 5000 USD/kg_{Pt}.

2. RESULTS AND DISCUSSION

2.1. Proposed System for Hydrosilylation Catalyst Recycling

2.1.1. Selection of Hydrosilylation Reaction Conditions. 1-Octene and 1,1,1,3,5,5,5-heptamethyltrisiloxane were chosen as model hydrosilylation reactants due to their nonpolar properties as well as moderate reaction conditions³⁹ to investigate the capability of the electro-recycling system in electrically nonconductive media (Scheme 1). The solvent-free

Scheme 1. Hydrosilylation Model Reaction and Catalyst Used in This Work



mixture of the olefin and siloxane was used as a reaction medium for the catalyst recycling, being representative of industrial hydrosilylation that takes place in nonpolar solvents or even solvent-free reactant mixture owing to the high activity of the Pt homogeneous catalyst.⁴⁰ Karstedt's catalyst, the most common catalyst for hydrosilylation in the industry,⁴¹ was selected as a model Pt catalyst.

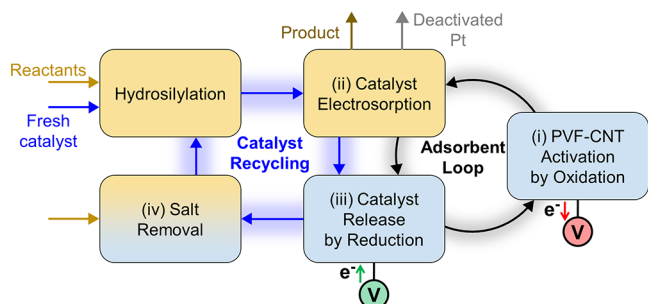
It must be noted that the reaction matrix was carefully selected to suppress Pt nanoparticle formation, which could hamper the recycling of the mononuclear-Pt active catalyst. A catalyst concentration below 50 ppm was maintained to keep a safety margin from the reported threshold of 125 ppm, which leads to activity loss.⁵ To confirm this design selection, an activity loss of the catalyst was observed when the concentration used was above 70 ppm under the model reaction conditions (Figure S4). We also chose to carry out the reactions under excess 1-octene conditions (a 2:1 reactant molar ratio), as excess silane or siloxane was reported to result in multinuclear Pt clusters in the literature.²⁰ When the reaction was carried out under excess siloxane (1:2 molar ratio), only 0.32% Pt was adsorbed on the PVF-carbon nanotubes (CNT) (Figure S5). The catalytic activity of Karstedt's catalyst in the solvent-free reactant mixture was found to be several orders of magnitude higher than with solvents (Figure S6), highlighting the necessity of catalyst recycling from electrically nonconductive hydrosilylation media for economic and industrial feasibility.

2.1.2. Electrosorbent for the Pt Homogeneous Catalyst. A PVF-CNT electrode was used as an electrosorbent. A strong charge transfer interaction between Fc^+ in PVF and anionic metal–ligand complexes is reported to be a key mechanism of redox-mediated electrosorption by PVF.^{33,34,38,42} The active Pt catalyst in the hydrosilylation catalytic cycle was also found to be anionic or highly polar based on the electrical conductivity increase over the catalyst concentration,³³ however, its exact molecular structure is not fully ascertained.⁵ PVF was synthesized by free radical polymerization ($M_n = 25,000$ and $M_w = 40,000$ by gel permeation chromatography⁴³). The PVF-CNT electrode fabrication was modified distinctly from the fabrication method reported in a prior work³³ (Supporting Information, Section S). A 2:1 mass ratio between PVF and CNT was used instead

of 1:1 to minimize the exposure of the CNT to avoid Pt nanoparticle nucleation, which causes the catalyst deactivation as CNT is known to provide Pt defect sites and strong interactions that facilitate nanoparticle formation.^{44,45} The PVF-CNT electrode was thermally cross-linked using 1,3-benzenedisulfonyl azide of 10 wt % to CNT, after optimization of the ratio (Figure S12), to avoid leaching in dichloromethane (DCM) or chloroform during the electrochemical recycling process.

2.1.3. Electrochemical Catalyst Recycling System. The developed electrochemical recycling for the homogeneous catalysts consists of four steps after the hydrosilylation is complete (Scheme 2), all performed in batch systems:

Scheme 2. Process Diagram of Electrochemically Assisted Catalyst Recycling^a



^aThe yellow boxes refer to electrically nonconductive hydrosilylation media, and the blue boxes to conductive media.

- Electrosorbent activation:** an electrosorbent is activated in a conductive media (with electrolyte) under its oxidation potential, to ensure the ferrocene units (Fc) in PVF convert into ferrocenium (Fc⁺). These ferroceniums then act as selective electrosorbing sites for the homogeneous catalyst. After the oxidation, the excess electrolyte was rinsed off the PVF-CNT electrode as the electrolyte layer immiscible to the hydrosilylation hampered the catalyst electrosorption on Fc⁺. With the electrolyte removal, the Pt recovery was 5.3 times higher (29.2%) than the nonrinsed PVF-CNT electrode (5.5%) (Figure S18).
- Electrosorption:** the PVF-CNT electrode was transferred to a nonconductive postreaction hydrosilylation medium where electrosorption of the spent Pt catalyst took place on the PVF-CNT interface.
- Release:** the Pt-adsorbed electrosorbent is transferred to a conductive electrolyte solution, and the Pt catalyst is released by applying a reductive potential to reduce the Fc⁺ sites.
- Salt removal:** a fresh hydrosilylation reactant medium is introduced to the electrolyte to remove the salt by precipitation and subsequent centrifugation. The recycled catalyst in the salt-free supernatant allows the hydrosilylation, and the PVF-CNT electrode gets reoxidized (back to (i)) for the next recovery cycle.

2.2. Stabilizing Hydrosilylation Catalysts through Olefin Ligands

To guide the design of a coordinating ligand that can optimally preserve activity, the hydrosilylation reaction was conducted in the presence of rationally selected vinyl ligands to investigate

their effect on the catalyst activity (Figure 1a). In addition to 1,3-divinyltetramethyl disiloxane, the original ligand of Karstedt's catalyst (DVS_i), norbornene (NB), and 1, 5-cyclooctadiene (COD) were selected due to their strongly coordinating properties to Pt catalyst in hydrosilylation^{5,46–48} (Figure 1b). The reaction was completed (>99%) in 30 min both with and without these additional olefin ligands (Figure S7). Although the turnover frequency (TOF) decreased (Table S2), the lifespan of the catalyst until deactivation was maintained up to 92% with NB (Figure S8). COD significantly slowed down the reaction rate (only 41% conversion at 30 min) and was excluded from further investigation due to the sluggish reaction.

We focused on the effects of NB and DVS_i ligands as they were found to protect the catalyst from deactivation during and after the reaction. Figure 1c shows the TOF retention of the catalyst ($\text{TOF}_{\text{second rxn}}/\text{TOF}_{\text{first rxn}}$) with varying the sitting time between the first and second batch reactions where the second reaction uses the catalyst spent in the first reaction (experiment details in the Supporting Information, 4.3). With no additional ligand, compared to the TOF in the first reaction, the TOF of the catalyst in the second reaction dropped by 66% within 20 min of sitting time. Furthermore, the catalyst continuously lost its activity and maintained only 4% activity compared with the pristine catalyst after 10 h. On the other hand, with NB, the TOF of the second reaction was maintained at 50% of the first reaction with 20 min of the sitting time, even increased up to 83% with 3 h of the sitting time, and then started to decrease. These increase and decrease in the catalyst activity over time were attributed to the changing number of NB attached to Pt. The activity decreases with a higher number of NB attached to Pt (maximum 3 NB per Pt²²). After the first reaction, the solution was in abundance of NB, making the catalyst activity slow. For the first 3 h, the catalyst activity increased as the number of NB attached to Pt decreased due to the NB consumption (Figure S9). Close to the complete consumption of NB by its reaction, the Pt that lost all NB ligands was likely to aggregate and lead to the activity decrease. The TOF retention in the second reaction decreased to 48% with 10 h of the sitting time. With DVS_i, the catalyst maintained its 100% activity at least up to 10 h after the first reaction, which suggests a much slower hydrosilylation of DVS_i than that of NB.

The stabilizing effect of NB on Pt was further supported by UV–vis absorption spectra and dynamic light scattering (DLS) data measured during the reaction. A Pt–Pt bond at 264 nm⁴⁹ appeared after the induction time in both reactions, with and without NB (Figure 1d). Without ligand addition, the number of multinuclear Pt nanoparticles increased rapidly during the reaction (10 min) and after the reaction completion, implying that Pt nanoparticles were constantly formed, attributed to the catalyst deactivation. However, the catalyst in the NB-containing hydrosilylation showed no change in Pt–Pt absorption during the reaction and a slight increase at 30 min. The slow increase in the absorption was found after reaction completion as NB was consumed. DLS measured during the reaction also showed faster nanoparticle growth without NB than with NB (Figure 1e). Without NB, 100 nm Pt particles were observed at 8 min and grew in size over time. On the other hand, smaller amounts of Pt particles were observed with NB than without NB and maintained the population until 12 min, followed by population and size growth still slower than without NB. These spectra

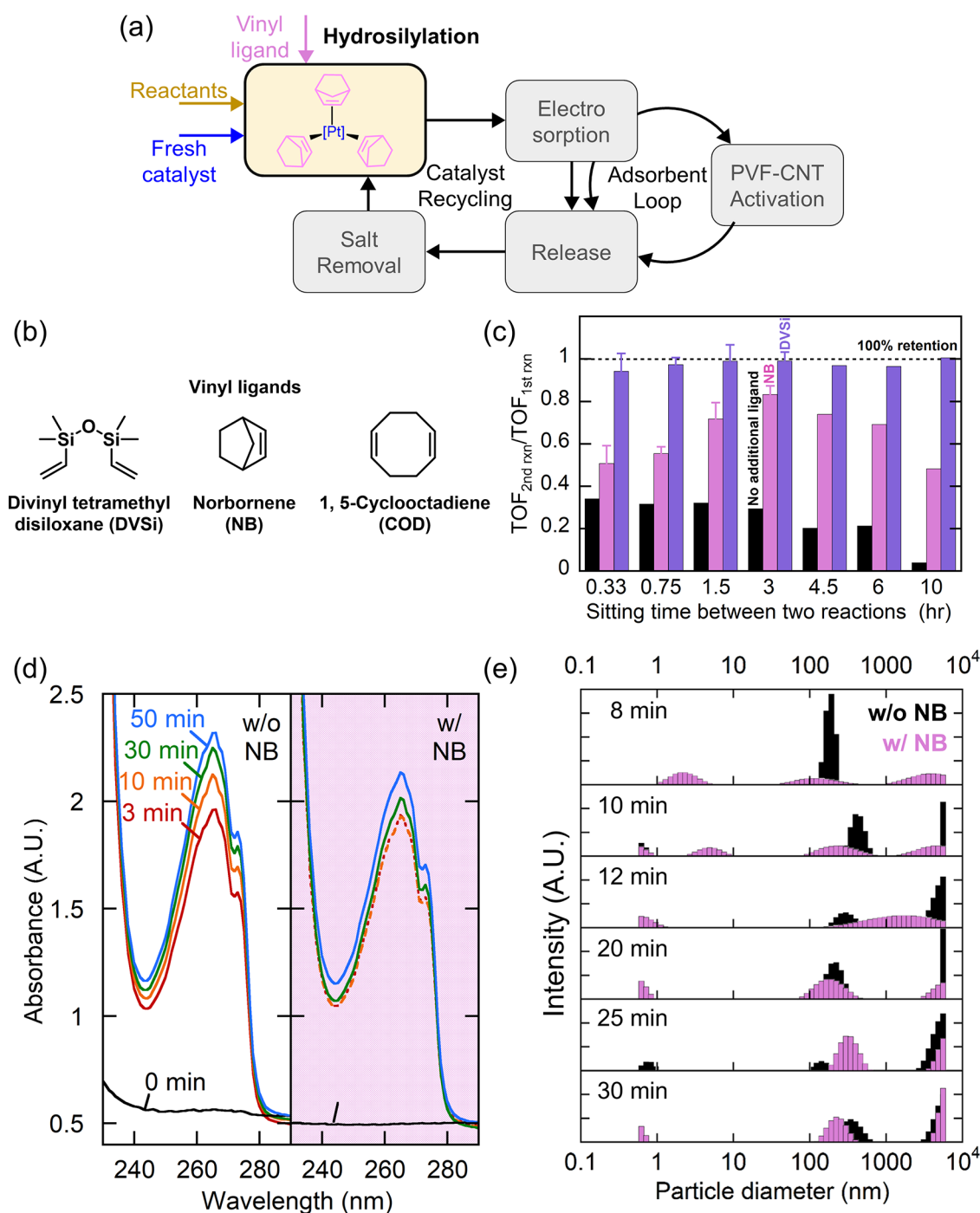


Figure 1. (a) Diagram of the electrochemical hydrosilylation catalyst recycling process, highlighting the hydrosilylation reaction step and introduction of stabilizing vinyl ligands. (b) List of vinyl ligands evaluated in this work for their catalyst stabilization effects. (c) TOF of the second reaction normalized by the TOF of the first reaction with no additional ligand (black), NB (pink), and DVSi (purple). The time on the *x* axis (0.33–10 h) represents the sitting time between the beginning of the first reaction and the second reaction. The standard deviation on the 0.33–3 h bars was from the replication. (d) UV–vis spectra showing the Pt–Pt bonding absorption peak at 265 nm over the course of the hydrosilylation without or with NB. (e) DLS spectra showing Pt nanoparticle growth in hydrosilylation without (black) or with NB (pink) containing 15 ppm.

observations prove that Pt nanoparticle formation is slowed by the presence of NB. In short, we found that the addition of strongly coordinating vinyl ligands protected the catalyst from aggregation (deactivation) and helped keep the catalyst active. This catalyst stabilizing effect was essential to enabling the various steps of the electrochemical homogeneous catalyst recycling system.

2.3. Performance of Electrochemical Catalyst Recycling

2.3.1. Catalyst Electrosorption. Electrosorption of the postreaction catalyst was investigated in nonpolar hydrosilylation media (Figure 2a). The solvent-free mixture of the olefin and siloxane was chosen as a model medium for the catalyst electrosorption because industrial hydrosilylation often takes place in nonpolar solvents or even solvent-free reactant mixture owing to the high activity of the Pt homogeneous

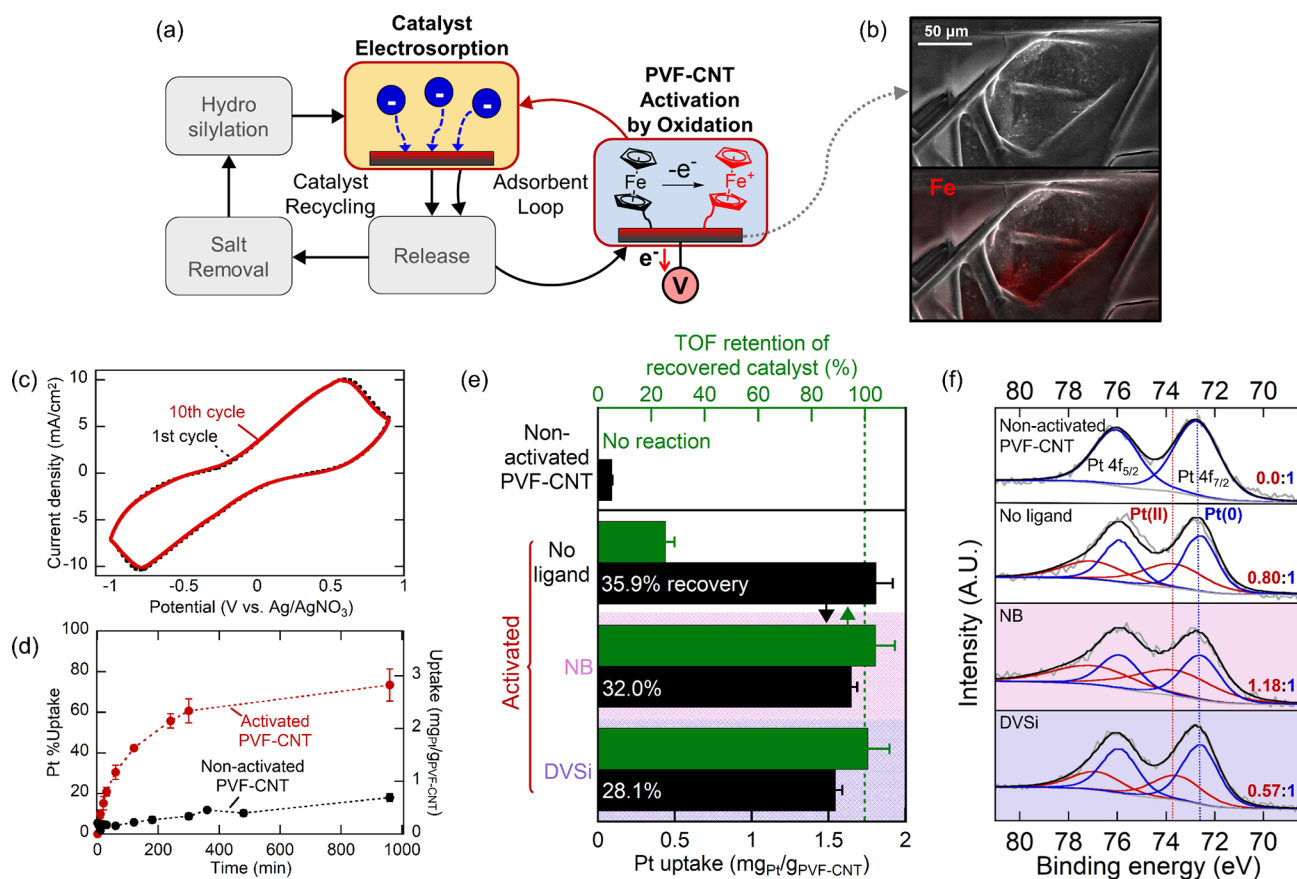


Figure 2. (a) Diagram of the electrochemical hydrosilylation catalyst recycling process, highlighting the activation and electrosorption step. (b) SEM (gray) and EDS mapping (iron in red) of PVF-CNT coated on carbon paper. (c) Cyclic voltammogram of a PVF-CNT electrode in 0.5 M TBAPF₆ DCM. (d) Pt recovery percentage with the activated PVF-CNT (red) and nonactivated PVF-CNT electrosorbent (black). (e) TOF retention of the recovered catalyst in nonconductive hydrosilylation media after electrosorption in the presence of no ligand (gray), NB (pink), and DVSi (purple) using nonactivated PVF-CNT or activated PVF-CNT. (f) Pt 4f XPS spectra of Pt adsorbed on PVF-CNT with the ratio between Pt (II) (red) and Pt (0) (blue). Pt 4f displays two different oxidation states of Pt with binding energies of 72.6 and 76.0 eV for Pt (0) and 73.6 and 76.9 eV for Pt (II).

catalyst.⁴⁰ Scanning electron microscopy (SEM) images with energy-dispersive X-ray spectroscopy (EDS) mapping of the iron of PVF showed PVF-CNT well-distributed on carbon paper (Figure 2b). The cyclic voltammogram (CV) of the cross-linked PVF-CNT indicated stable PVF-CNT immobilization without loss of charge capacity (Figure 2c and Figure S12c). The PVF leaching was below 0.5% during the electrosorption based on ICP-OES measurements of Fe leached in solutions (Figure S13). Neither redox activity of the hydrosilylation reactants nor charge transfer reaction between PVF-CNT and the reactants was detected within the potential window of PVF-CNT operation (Figure S15), which suggests that there would be no impact on the hydrosilylation by PVF-CNT throughout and after the recovery process. A PVF-CNT electrode activated at 0.6 V vs $E_{1/2}$, PVF-CNT showed that over 73% of Fc in PVF was oxidized (Figure S16).

The electrosorption performances of activated PVF-CNT and nonactivated PVF-CNT were compared to confirm the binding mechanism between PVF and the catalyst. After 16 h of adsorption in nonpolar hydrosilylation media, oxidized PVF-CNT adsorbed 78% of Pt while only 18% of Pt was adsorbed by neutral PVF-CNT (Figure 2d), proving the strong charge transfer between the active catalyst and Fc⁺.

The catalyst stabilizing effect of the vinyl ligands significantly improved the electrosorption of the active catalyst. The

catalyst after hydrosilylation with or without a vinyl ligand was adsorbed by and released from PVF-CNT in nonconductive hydrosilylation media (Figure 2e and Figure S20). Nonactivated PVF-CNT had little-to-no catalyst adsorption (0.09 mg_{Pt}/g_{PVF-CNT}), and the recovered Pt showed no catalytic activity (TOF = 0), confirming that the observation above that Fc⁺ sites is critical as the active catalyst binding. The catalyst uptake of activated PVF-CNT was similar among reactions in which no ligand was added (1.81 mg_{Pt}/g_{PVF-CNT}), and NB (1.65 mg_{Pt}/g_{PVF-CNT}) or DVSi (1.54 mg_{Pt}/g_{PVF-CNT}) was added. Studies were also carried out to ensure the NB ligand is not affected by the ferrocene oxidation process, by carrying out NMR control studies of NB before and after contact with oxidized PVF-CNT (Figure S19), as well as CVs across the potential range used in this study (Figure S28).

The lowest uptake of the catalyst, when DVSi was used as the stabilizing ligand, was attributed to its low polarity or bulkiness. DVSi is two times heavier than NB and has a bidentate nature, which may weaken the interaction between Pt and Fc⁺ due to steric effects. Without any additional ligand in hydrosilylation, the catalyst recovered by the activated PVF-CNT yielded only 25% retention of TOF, which implies that the recovered Pt had been mostly deactivated. However, the Pt

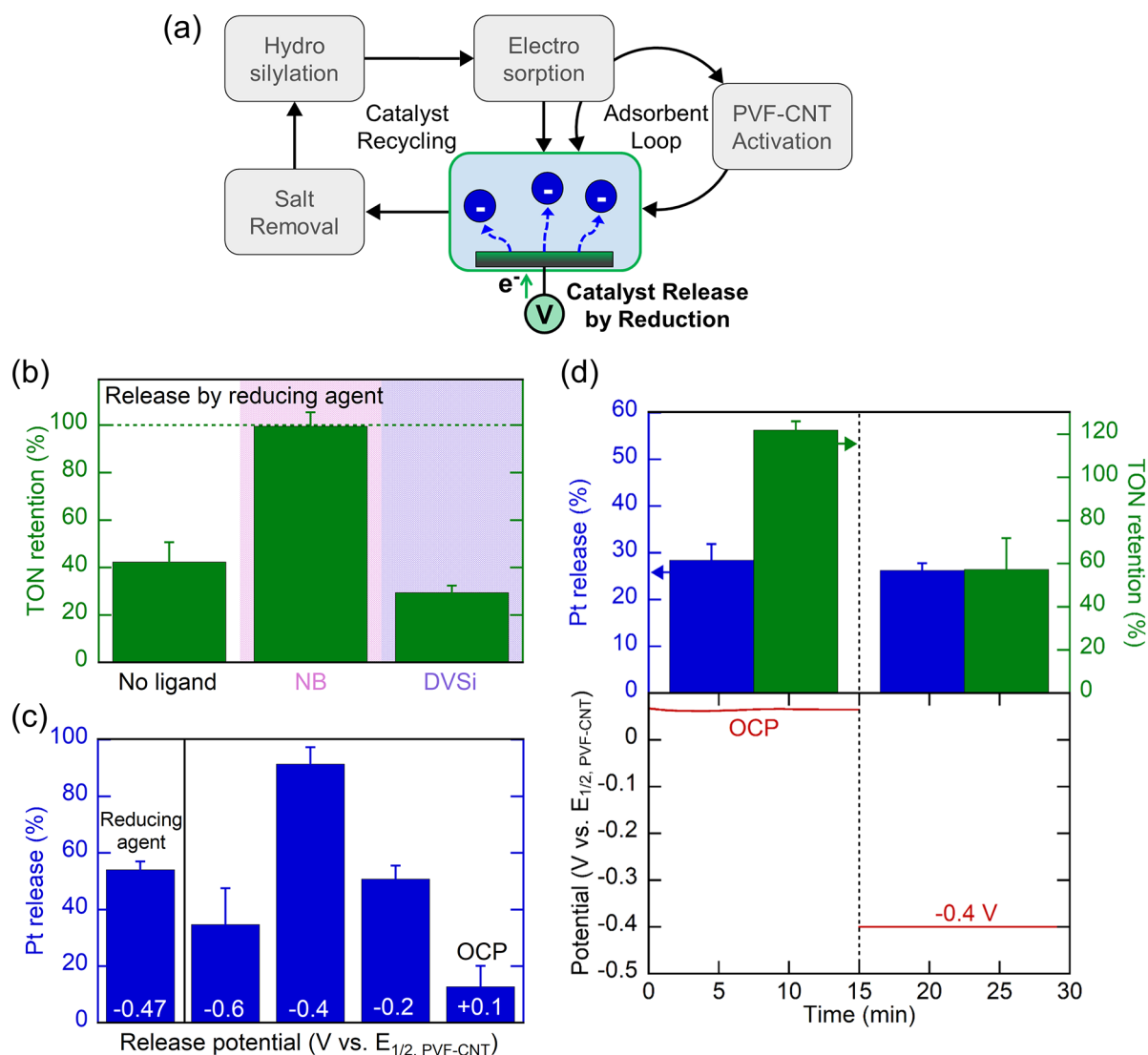


Figure 3. (a) Diagram of the electrochemical hydrosilylation catalyst recycling process, highlighting the electrochemical release step. (b) TON retention of the Pt catalyst released by the chemical reduction method using dmFc. (c) Release percentage of Pt at various applied potentials. In both panels (b) and (c), Pt was released in 0.45 M TBAPF₆ chloroform containing the reactants after the electro sorption from hydrosilylation in the presence of vinyl ligands (NB for panel (c)). Excess dmFc (2 equiv to Fc sites) was used for the chemical reduction. (d) Pt release percentage (blue) and TON retention (green) of Pt recovered by sequential release at OCP and -0.4 V. The potential applied to WE over time (red) is shown at the bottom.

recovered in the presence of NB and DVSi showed full retention of TOF (104% for NB and 101% for DVSi).

Pt 4f XPS spectra of the Pt catalyst adsorbed on a PVF-CNT electrode supported the catalyst stabilizing effect of the vinyl ligands (Figure 2f). The ratio between Pt (0) at 72.6 eV and Pt (II) at 73.6 eV was calculated by using peak integration. In nonactivated PVF-CNT, only Pt (0) was detected, which was deactivated Pt resulting in no catalytic behavior (TOF = 0). It should be noted that the Pt (0) species is not necessarily a dead catalyst or Pt aggregation as Pt of the active catalyst shifts between Pt (0) and Pt (II) in the catalysis loop of the Chalk-Harrod mechanism.⁵⁰ The ratio of Pt (II) to Pt (0) was the highest with NB (1.18), followed by no ligand (0.80) and DVSi (0.57), which was in close agreement with the TOF retention of the recovered catalyst in Figure 2e. In addition, Pt 4f XPS spectra of the catalyst in various conditions were obtained and suggested NB-attached active Pt species had higher binding energies than the original and deactivated

Karstedt's catalyst (Figure S17) although the exact speciation of Pt complexes could be challenging due to the low concentration at the ppb level.

2.3.2. Redox-Mediated Catalyst Release. After the catalyst electro sorption from the nonconductive hydrosilylation media, we investigated the release pathways of the adsorbed catalyst using both chemical and electrochemical reduction methods for the Fc⁺ binding sites (Figure 3a). Releasing a captured catalyst directly into nonpolar hydrosilylation reactant media would be ideal in the aspects of catalyst stability and process simplicity, but electrochemical reduction is challenging due to the lack of electrical conductivity of hydrosilylation media. Nonpolar hydrosilylation reactants such as silane and alkenes also hardly dissolve any salts.

Thus, the catalyst release into nonconductive hydrosilylation media by chemical reduction was first tested using decamethylferrocene (dmFc) as a reducing agent owing to

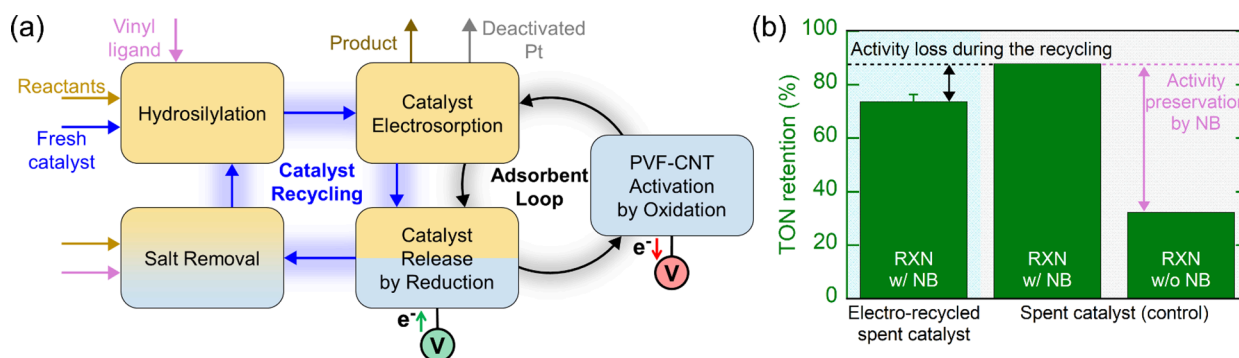


Figure 4. (a) Diagram of the full cycle for the catalyst recovery process, including hydrosilylation reaction, vinyl ligand addition, catalyst electrosorption and release, and salt removal. (b) TON retention of the recovered catalyst after the full recovery cycle, with the catalyst (spent in hydrosilylation with or without NB) directly taken from the product media into a fresh reactant mixture without any recycling steps.

its reduction potential -0.48 V lower than that of Fc.⁵¹ Regardless of the addition of a vinyl ligand, the chemical reduction achieved 38–43% Pt release, 1.4–3.5 times higher than that without dmFc (Figure S21). However, released Pt showed no catalytic activity with no ligand addition and only 48% activity retention with NB. This activity loss was attributed to the interaction between oxidized dmFc and released Pt.

The chemical reduction method was then tested in the presence of a supporting electrolyte (0.5 M TBAPF₆ chloroform), showing full catalyst activity retention after the NB-assisted recovery (Figure 3b and Figure S22). The catalyst recovered in the presence of no ligand or NB yielded TON retention of 42 and 99%, respectively, which agreed with the TOF retention of the recycled catalyst in nonconductive hydrosilylation media (Figure 2e). Thus, the catalyst stabilizing effect of NB was still present in the conductive media. On the other hand, Pt released after the DVS_i-assisted recovery only had 29% TON retention, implying that the catalyst recovered with DVS_i was more susceptible to deactivation by the ligand loss in the electrolyte than the catalyst recovered with NB. In addition, the life span of fresh Karstedt's catalyst in electrolytes was measured in the presence of the vinyl ligands and NB showed the highest TON (Figure S23). Owing to the higher Pt uptake, faster hydrosilylation kinetics, and better in-electrolyte stability of the catalyst with NB than with DVS_i, NB was selected for the rest of the recovery system study after further optimization of the NB concentration and catalyst electrosorption time (Figure S24).

Next, various potentials down to -0.6 V vs $E_{1/2, \text{PVF-CNT}}$ were applied to electrochemically release the adsorbed Pt by electrochemical reduction of Fc⁺ of PVF-CNT (Figure 3c). The Pt release was only 13% at the open circuit potential (OCP), implying that Pt was still strongly bound to an Fc⁺ site. The Pt release increased under a reduction potential (35% at -0.2 V vs $E_{1/2, \text{PVF-CNT}}$). The -0.4 V applied potential showed up to 91% Pt release, significantly higher than the chemical reduction (54%) (desorption kinetics in Figure S25). At -0.6 V, the release decreased to 51% because of the electro-deposition of Pt as shown on the catalyst CV measured during hydrosilylation (Figure S28) as well as in the previous work.³³ Reduction potential was found to affect the activity of the released catalyst, as a more negative potential decreased the TON retention (Figures S26). A high bias voltage was likely to cause the release of even deactivated Pt or affect the Pt ligand structure. Thus, a two-step sequential release (OCP and -0.4

V) was assessed to mitigate the activity loss and achieve high Pt release (Figure 3d). The sum of Pt release and the overall TON retention from the two steps were 55 and 91%, respectively. PVF-CNT electrosorbent maintained its redox capacity based on the comparison of CV before and after a recovery cycle as well as a charging–discharging test (Figures S27 and S32).

2.3.3. Catalyst Activity after the Full Recovery Cycle.

The full catalyst recovery cycle was conducted using a sequential release that included OCP in a fresh reactant mixture followed by chronoamperometry at -0.4 V in the electrolyte to maximize the catalyst activity (Figure 4a). Upon the Pt release, a fresh nonpolar reactant mixture was added and extracted the TBAPF₆ salt (>99.6%), followed by centrifugation. The hydrosilylation of the reactants in the supernatant took place by the recycled catalyst. The electro-recycled catalyst showed 74% TON retention (Figure 4b). This retention was only 14% lower than that of the spent catalyst, which was taken from the product media into a fresh reactant mixture, without undergoing electrosorption and release steps. The 14% activity loss was likely to be attributed to a combination of catalyst deactivation under the applied potential and potential Pt loss during salt removal. This high activity retention of the catalyst recycled from the nonpolar hydrosilylation was well comparable to the result (81%) in the fully conductive recycling system.³³ The electro-recycled catalyst activity was still significantly higher than that of the spent catalyst without NB in the reaction (TON retention = 32%), which demonstrates the importance of the catalyst stabilization by NB.

The electrochemical recycling process was also evaluated for hydrosilylation reactions with silanes containing different functional groups (e.g., $-\text{Cl}$, $-\text{O}-\text{R}$, and $-\text{C}_6\text{H}_5$) and showed Pt uptake ($0.43\text{--}0.86$ mg_{Pt}/g_{PVF-CNT}) and release (27–70%) comparable to those with the siloxane (Figure S29). However, the spent catalyst without the electrosorption and release steps had intrinsically low activity retention (6–10%) due to limited stability of the active catalyst in the electrolyte, while the electro-recycled spent catalyst in nonconductive media had much higher activity retention. Furthermore, the activity of the spent catalyst was found to be sensitive to the reaction condition such as the reactant ratio and temperature. While Pt uptake and release remained within the same order of magnitude, lowering the 1-octene fraction or running the reaction at ambient temperature led to low selectivity (3.9% with 1.5:1 with excess 1-octene) and activity retention (0.1–

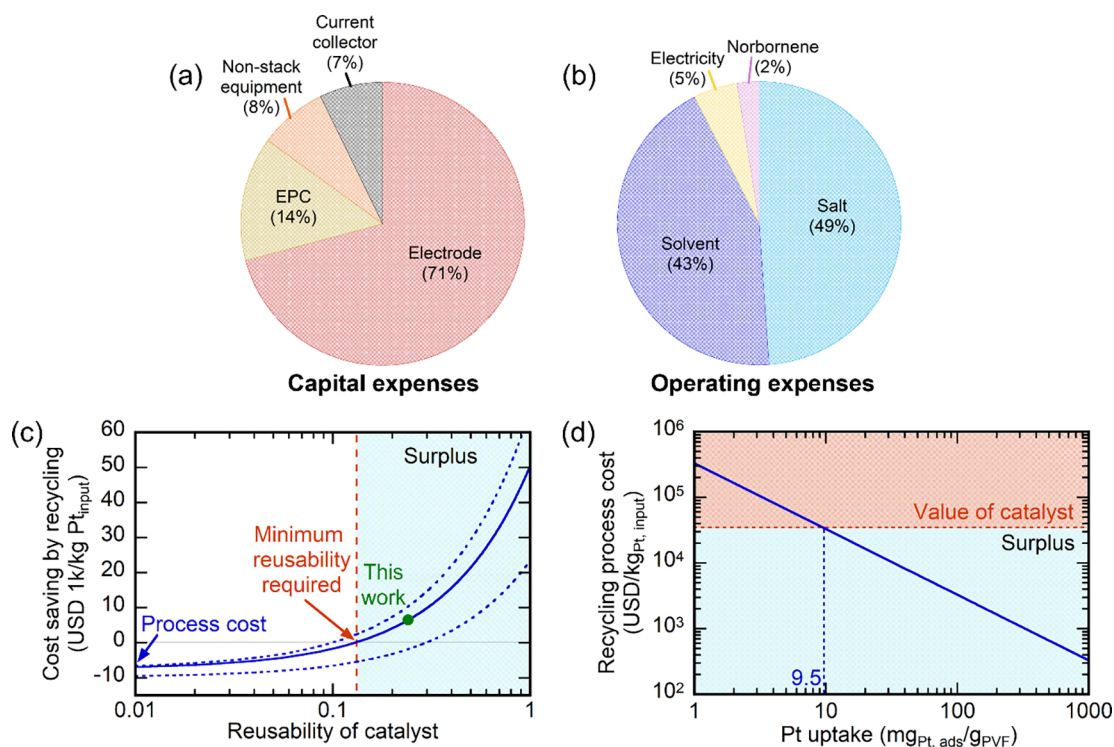


Figure 5. (a) Capital expenses and (b) operating expenses of the proposed electrochemical catalyst recycling process. (c) Cost saving by the process over the reusability of the catalyst with the Pt recycling ratio of 0.80 (reusability = the Pt recycling ratio \times the catalyst activity retention). The y-intercept represents the process cost, and the red arrow points to the minimum reusability required to achieve a surplus by the process implementation. Two blue dotted lines represent the upper and lower bound of the cost saving with varying price of the KC and solvent used in the process. (d) Recycling process cost over Pt uptake with the recycling ratio of 0.80 and the reusability of 0.60.

2.2%) of the spent catalyst (Figures S30 and S31). On the other hand, the electro-recycled catalyst in nonconductive media showed higher activity retention (13.0–28.9%). Therefore, the careful selection of stabilizing ligands and process optimization are needed for fit-for-purpose implementation and require the identification of the active catalyst structure under determined reactants and reaction conditions.

2.4. Techno-Economic Analysis

TEA was carried out on the electro-recycling process to provide its economic feasibility for industrial implementation. The cost of each component in both capital cost and operating cost was obtained with respect to the mass of PVF utilized in the system (USD/mg of PVF) and then converted to the cost with respect to the mass of the input Pt (methodology for TEA in the Supporting Information, Section 15).

The capital expenses consisted of electrode, engineering/procurement/construction (EPC), nonstack equipment (i.e., all other equipment besides electrochemical cells), and current collector (Figure 5a). It was assumed that the electrode needs replacement every 900 cycles (88 h) based on the charging–discharging performance of the PVF-CNT electrode (Figure S32), the current collector every 9000 cycles, and nonstack equipment every 90,000 cycles, approximately 1 year. The electrode accounted for 71%, the major portion of the capital expenses. Considering longer replacement periods of the nonstack equipment and corresponding EPC than 1 year, decreasing the cost for electrode materials is the key to lowering the capital expenses. The segmentation of the electrode cost showed that carbon cloth (as conductive support) and PVF took up 57 and 37% of the total cost, respectively (Figure S33a).

The operating expenses were divided into four components: salt (supporting electrolyte), solvent, electricity, and norbornene (Figure 5b). Adding fresh solvent for electrode rinsing and salt to make up for the loss of the electrolyte in conductive media accounted for 49 and 43%, respectively. Even after the capital and operating expenses were combined with the given replacement periods, the highest portions of the recycling process were the salt (47%) and solvent (42%) (Figure S33b). Thus, additional steps such as distillation for the purification of the solvent and the extraction of the salt may significantly decrease the overall recycling cost. Side products from the hydrosilylation of NB (only 0.1 mol % to 1-octene) are not likely to alter the chemical property of the main product, so their separation was not considered.

Figure 5c depicts the economic feasibility of our Pt recycling process based on the reusability of the catalyst. The reusability was defined as the recycling ratio ($Pt_{\text{recycled}}/Pt_{\text{input}}$) multiplied by the catalyst activity retention ($TON_{\text{recycled}}/TON_{\text{fresh}}$) to represent the fraction of the recycled active catalyst with respect to the fresh catalyst input (equations in the Supporting Information, Section 15.4). For example, if the process recycles all of the catalyst fed to hydrosilylation ($Pt_{\text{recycled}}/Pt_{\text{input}} = 1$) and the activity of the recycled catalyst is fully maintained ($TON_{\text{recycled}}/TON_{\text{fresh}} = 1$), the reusability would be 1. With the recycling ratio of 0.80, the process cost is 7461 USD/kg Pt_{input} and the minimum reusability required to have a surplus (catalyst price \times reusability $>$ recycling process cost) is 0.13.

After defining the relevant reusability from the entire electrochemical catalyst recycling tests (0.30 recycling ratio and 0.74 activity retention, giving the reusability of 0.22), it was determined through the TEA model that the recycling

process can save 5281 USD/kg Pt_{input} . In addition, we evaluated the impact of Pt uptake and solvent cost on the overall process expenses (Figure Sd and Figure S34). With the same recycling ratio and activity retention above, the minimum uptake of 9.5 mg_{Pt}/g_{PVF} would be required for the process to be economically feasible, while most solvents of similar polarity to chloroform can make the process cost cheaper than the value of the catalyst. Overall, the TEA analysis demonstrated a promising economic viability of the electrochemical recycling process for a Pt catalyst in hydrosilylation. Further optimization of separation variables and process modeling on a large scale will give more insight into the translation of this recycling process into industrial practice.

3. CONCLUSIONS

The electrochemically mediated recycling of a homogeneous Pt catalyst was achieved in solvent-free nonpolar hydrosilylation media for the first time. Selective redox-mediated electrosorption is combined with the judicious selection of an olefin ligand that avoids the instability of postreaction catalysts. The direct application of electrosorption is challenging in hydrosilylation matrices comprising nonpolar reactants due to the lack of ionic conductivity. Thus, by introducing two different loops for catalyst recycling and adsorbent charging–discharging, an electrochemically mediated catalyst recovery process was enabled in nonconductive hydrosilylation media, keeping the high activity of the catalyst while extending lifetime and reuse. The addition of a moderately coordinating olefin, norbornene, kept the Pt catalyst activity and improved the activity retention close to 100% after catalyst release.

This stabilizing effect was confirmed by XPS on Pt adsorbed on PVF-CNT as well as UV–vis and DLS spectra of the hydrosilylation media. The in-depth analysis of each recovery step (i.e., reaction, electrosorption, and release) identified key conditions to improve the overall performance of the recycling system. The electrochemical release showed up to 91% Pt release, and the full recycling procedure with the optimized conditions using NB resulted in 74% activity retention, 42% higher than that of the spent catalyst without NB in the reaction. Considering the concentration of NB (0.1 mol % to 1-octene) used in this study, the hydrosilylation of NB is not likely to affect the chemical property of the product, thus not immediately requiring an additional separation step for major applications. The TEA analysis supported the cost efficiency of our electrified separation technology with the cost saving of 5281 USD/kg Pt_{input} based on the highest performance achieved in this work.

Going forward, there are several directions for process optimization and eventual automation of the recycling process to reduce potential activity loss during the catalyst transfer between conductive and nonconductive media, along with any time-dependent loss. Implementation of these electrochemical systems in a flow-through electroswinging process can be a next step for the translation of these technologies for practical industrial implementation. In sum, we believe that the development of a fully operational electrochemical recycling process for hydrosilylation catalysts in industrially relevant media is an important step toward sustainable homogeneous catalysis in chemical manufacturing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.4c01071>.

Methods for hydrosilylation reactions, PVF-CNT electrode fabrication, electrochemical experiments, and catalyst recycling steps; analysis for hydrosilylation reactions and electrochemical recycling including NMR, XPS, and SEM; and techno-economic analysis (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Jemin Jeon** conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization, writing - original draft, writing - review & editing; **Ching-Hsiu Chung** formal analysis, investigation, methodology, writing - review & editing; **Shisang Roh** data curation, methodology, resources, validation; **Evan Bergman** methodology, resources, writing - review & editing; **Miao Wang** formal analysis, project administration, resources, writing - review & editing; **Xiao Su** conceptualization, funding acquisition, investigation, project administration, resources, supervision, writing - original draft, writing - review & editing.

Notes

The authors declare no competing financial interest.

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