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Spatial, temporal and quantitative assessment of catalyst leaching in continuous flow

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A B S T R A C T

Catalyst leaching is a major impediment to the development of commercially-viable processes conducted in a liquid-phase. To date, there is no reliable technique that can accurately identify the extent and dynamics of the leaking process in a quantitative manner. In this work, a tandem flow-reactor system has been developed, which allowed us to distinguish between surface-catalyzed reactions from those occurring in solution by comparing conversion at the exit of each reactor (S1, S2) corresponding to predominance of heterogeneous/homogeneous reactions (spatial) and two different residence times (temporal). A multiscale model is subsequently established to quantify the two types of reaction rate and simulate the catalyst leaching from a cross-coupling catalyst, PdEncat [30]; including: (1) a multi-particle sizes model for catalyst scale; and (2) a dispersion model for reactor scale. The results show that catalyst leaching occurs via more than one process, and that the homogeneous Pd-catalyst (leached from the immobilized catalyst and dissolved in the flow) dominates the reaction and possesses a much higher activity than the heterogeneous (immobilized) Pd-catalyst. Additionally, the change of leached Pd stream inside reactors can be predicted along with the axial direction and the reaction time through the reactor-scale dispersion model.

1. Introduction

Unquestionably, the modern chemical industry is powered by catalysis; the global demand for industrial catalysts is projected to exceed US$20 billion by 2020, with heterogeneous catalysts accounting for approximately 80% of the total market share [1]. In recent years, there has been much impetus to eschew the use of traditional batch reactors in favor of continuous flow (CF) technology, particularly in combination with catalytic processes, for the manufacturing of pharmaceutical products [2]. This is greatly championed by the ACS Green Chemistry Institute and the FDA, for reasons of promoting greater sustainability, improved efficiency of industrial processes, but also their product scale. This is especially problematic for the manufacture of consumer products (including pharmaceuticals), as the amount of impurities in the final product is strictly regulated [4].

Clearly, significant economic, safety and environmental benefits can be derived from effective strategies to mitigate catalyst leaching, by the design of more robust materials and processes. However, advances in this area are hampered by limited understanding of catalyst leaching [5], largely due to the lack of reliable and quantifiable methods for studying this phenomenon. Very often, leaching is determined by ex-situ quantification of metal content in the product using Inductively Coupled Plasma (ICP) spectroscopy. To determine whether the leached species participates in the catalytic turnover, additional experiments...
such as the three-phase test, mercury test or hot filtration can be performed, but these indirect and invasive methods can lead to ambiguous results [6]. Critically, none of these methods can determine how the catalyst leaches, nor can they distinguish relative rates of surface-catalyzed (heterogeneous) reactions from those occurring in solution due to leached species (homogeneous), particularly if both processes are taking place at the same time.

Recently, we have employed EXAFS spectroscopy as an in situ method to study dynamic changes in the structure of supported Pd catalysts in a packed bed, as they are subjected to a continuous flow of protic solvents. This allowed us to correlate oxidation state changes and structural rearrangement of nanoparticles with particle size, type of support and presence/absence of halide additives [7]. Herein, we will describe a novel approach to study catalyst leaching in real time under continuous flow conditions, using the Heck arylation reaction as a model for study. The novel aspect of this work is the ability to collect data and implement mathematical models to decouple and quantify catalysis occurring both on the catalyst surface and in solution due to leached species, thus enabling the time course of catalyst leaching to be delineated in a quantifiable way.

1.1. Construction of a continuous tandem flow reactor

For the purpose of studying the time course of leaching and the relative (heterogeneous and homogeneous) rates of reaction we have constructed a novel continuous tandem reactor system with intermittent flow diversion. In a catalytic CF reactor, the desired reaction is often achieved by passing a mobile phase consisting of reactants dissolved in a solvent through a heterogeneous catalyst confined in a reactor (e.g. as a packed bed, slurry, etc.), where the extent of reaction is dependent on the residence time, \( \tau \). By attaching an empty plug flow reactor (PFR) to a packed bed reactor (PBR) containing a heterogeneous catalyst, two different spatial regimes (heterogeneous and homogeneous) can be effectively decoupled (Fig. 1). The system is operated by delivering the mobile phase using a syringe pump, and the reaction progress is monitored simultaneously at two locations: where the product streams emerge immediately after the PBR (S1), and after the PFR (S2). Allowing for the residence time in the second reactor (to evaluate the same flow volume element), assessment of the catalyst activity and stability can be achieved by comparing the outputs at S1 and S2.

Using this setup, a matrix of outcomes can be perceived, with respect to catalyst stability, activity, and leaching behavior (Table 1): Single-pass conversions at sampling points S1 and S2 are dependent on the two residence times \( \tau_1 \) and \( \tau_2 \) and temperatures (T1 and T2) — these variables can be altered by changing the flow rate, the length of the reactors, and their temperature regimes. The data afforded by the system can then be used to derive rates of homo- and heterogeneous reactions, as well as the rate of catalyst leaching.

![Fig. 1. Schematic of the tandem reactor system.](image)

| Case | Outputs | Conclusion |
|------|---------|------------|
| 1    | \( S_1 = S_2 \) | No active catalyst leaching |
| 2    | \( S_2 > S_1 \) | Leaching of active catalyst |
| 3    | \( S_1 = S_2, \text{ decreasing with time} \) | Either: (i) loss of heterogeneous active sites due to inhibition/poisoning; or (ii) loss of catalytic sites due to leaching of inactive catalyst |
| 4    | \( S_1 = S_2, \text{ increasing with time} \) | Activation of surface catalysis, no leaching of active catalyst |
| 5    | \( S_2 < S_1 \) | \( S_2 < S_1 \) Reaction is reversible in the homogeneous phase (an unlikely outcome) |

2. Materials and methods

The notional system in Fig. 1 was realized using two syringe pumps (Chemxyx Nexus 6000) to deliver solvent or reaction mixture to the reactor through a 3-way ball valve. The pressure is monitored with a pressure gauge display inserted between the 3-way ball valve and the entrance (bottom) of the continuous plug flow reactor (PBR). The PBR consists of an aluminium block with drilled cylindrical bores to accommodate a quartz catalyst cartridge (4 mm inner Ø, 1 mm wall thickness) and cartridge heaters (1/4” x 3”, Under Control Instruments Ltd) powered and controlled with a PID controller (Sesto D1S-VR-200). A K-type thermometer is fitted to the side of the PBR to provide a feedback loop to the PID controller. Parallel slits (4 × 54 mm) in the aluminium heating block provide a direct view of the catalyst bed inside the cartridge. Either end of the block was fitted with appropriate Swagelok fittings: at the bottom of the PBR, connections to a 1/8” metallic tubing; at the top, connections to an outlet with an inserted K-type thermometer to measure the temperature of the fluid (RS-532II digital thermometer) this outlet is connected via 1/8” steel tubing to a three-way solenoid valve (the connection between the steel tubing and the valve was made with 1/8” PTFE tubing), one of the outlets of the valve is connected to a fraction collector (S1) and the other one is connected to a coil of 1/8” PTFE tubing (PFR, 1 m, internal Ø = 1/16”) that is submerged in an oil bath. The end of this coil is connected to the fraction collector (S2). The solenoid valve is controlled with a timer switch relay that allows the splitting of the flow between S1 and S2. Both reactor exit streams (S1 and S2) were collected using a multiple fraction collector (Spectra/Chrom® CF-2 fraction collector) at programmed intervals.

2.1. Leaching studies

A catalyst cartridge was prepared and mounted into the flow reactor. A 50 mL syringe was filled with DMF and loaded into the solvent syringe pump 1. Separately, a solution of methyl acrylate (670 µL, 7.4 mmol), iodobenzene (430 µL, 3.84 mmol) and triethylamine (1.02 mL, 7.4 mmol) in DMF (50 mL) was drawn up into a 50-mL syringe and mounted onto syringe pump 2. Both syringe pumps were connected to the reactor via the 3-way ball valve. At the start of each experiment, the reactor (PBR) was setup at r.t. and the coil (PFR) at the required temperatures (see cases I and II below). The system was flushed through with solvent (syringe pump 1) at a flow rate of 0.5 mL/min. The solenoid valve was switched on to direct the liquid flow to S2 only. Once the system is filled, syringe pump 1 was stopped and the 3-way ball valve was closed. If required, the heating controller was switched on and the PBR reactor was heated to 90 °C. At the end of this period, the ball valve was opened to allow syringe pump 2 to deliver the reaction mixture to the catalyst cartridge at 0.5 mL/min (t = 0), the solenoid valve was also switched on (50 Hz), splitting the flow between S1 and S2. The eluent was collected using a fraction collector (Spectra/Chrom® CF-2) every two minutes. Collected aliquots were analyzed by
RP-HPLC fitted with a UV detector (λ = 210 nm) and a C18 column.

In order to develop a kinetics model for the quantitative analysis, the reaction temperatures of the two reactors were varied to provide five datasets, which can be divided into two cases:

**Case I:** 1st (PBR) reactor @ r.t., 2nd (PFR) reactor @ 90/100/110/120 °C

**Case II:** 1st (PBR) reactor @ 90 °C, 2nd (PFR) reactor @ 112 °C

### 2.2. ICP analysis

Palladium residues in the collected solutions were determined using an ICP-OES (PerkinElmer OPTIMA 2000) instrument, calibrated with solutions containing 0.1, 1, 5 and 10 ppm of Pd (prepared from Palladium ICP/DCP standard solution from Aldrich, 10,000 µg/mL Pd in 6 wt.% HCl, diluted with and distilled water). The combined samples collected (S1 and S2) were evaporated under vacuum. *Aqua regia* was added to the residue to dissolve the Pd and diluted with distilled water before it was subjected to ICP analysis. The average of three measurements was taken for each of two separately prepared solutions.

### 2.3. Reactor modelling

In order to model the behavior of the two-reactor leaching system, the following scheme was adopted: Balances were derived for catalyst leaching and for the coupled flow reactors, resulting in a set of Ordinary Differential Equations (ODEs) representing various types of leaching processes; and a set of six Partial Differential Equations (PDEs) representing the coupled reactors. These systems of equations were implemented in Matlab using the numerical solver *Pdepe*. Curve fitting on the experimental data was subsequently performed using *Esymultin*.

Based on their respective goodness of fit, different leaching models were evaluated.

If, for example, the leaching process is controlled by the surface erosion of Pd particles (Fig. 2A) through interaction with a reactant, then the following ODE would be tested:

\[
\frac{dW_{\text{Pd}}}{dt} = -k_{\text{leach}}W_{\text{Pd}}C_1
\]

(1) This equation can also be used for particle size distributions where different particles leach at different rates. If, on the other hand, Pd leaching is caused by particle loss (Fig. 2B), then the following ODE would hold:

\[
\frac{dW_{\text{Pd}}}{dt} = -k_{\text{leach}}W_{\text{Pd}}
\]

(2)

In both cases, \(W_{\text{Pd}}\) weight of heterogeneous Pd; \(k_{\text{leach}}\) rate constant of leaching; \(C_1\): concentration of electrophilic reactant in first reactor.

Both reactors were modelled as dispersion reactors. The overall reaction was considered to have two contributions: one catalyzed by heterogeneous catalyst (immobilized Pd, \(W_{\text{cat}}\)) and the other by homogeneous catalyst (leached/dissolved Pd, \(C_{\text{hom1}}\) or \(C_{\text{hom2}}\)). Further assumptions were made:

1. Excess reactant concentration (methyl acrylate) is assumed to be constant. The reactant referred to in the model is iodobenzene.
2. The heterogeneous reaction can be described as a first-order reaction, i.e. \(r_{\text{cat}} = k_{\text{cat}}W_{\text{cat}}C_1\).

### 3. Results

As a proof-of-principle study, the Heck arylation reaction between iodobenzene and methyl acrylate was selected as a model reaction of a process known to be catalyzed by leached Pd species (Fig. 3) [8]. Using Pd EnCat™ 30 in a packed bed [9], a mobile phase of reactants was introduced at an initial flow rate of 0.5 mL/min, while samples at S1 and S2 were collected simultaneously using an auto-sampler, and fractional conversions were determined by HPLC analysis. The combined fractions were further subjected to ICP analysis to determine the total amount of Pd leached over the experimental period (90 min).

In the first experiment, the temperatures of the PBR and PFR were maintained at 90 and 110 °C, respectively. As shown in Fig. 2A, leaching of active catalyst is clearly evident by the greater conversion observed at the S2 output compared to S1 (corresponding to Case 1, Table 1). The total amount of leached Pd during the experiment corresponds to 0.26 mg, or 6.45% of the initial loading. The conversion profile shows that maximum productivity was recorded at the outset, which decayed rapidly with time [10].

Using the tandem reactor system, the catalytic activity of leached species in the solution phase, i.e. ‘homogeneous’ catalysis, can be independently assessed under catalytically relevant conditions. Indeed, leaching can be examined *even in the absence of surface-catalyzed reaction*: This is demonstrated by setting the temperature of the first reactor (T1) to ambient, while varying the temperature of the second reactor (T2) between 90 and 120 °C (Fig. 2B). Under these conditions, catalysis does not occur in the first reactor as no product is detected at S1. Thus, the catalytic activity observed at S2 can be attributed entirely to leached Pd in the homogeneous phase (0.14 mg, or 3.5% of initial loading, established by ICP analysis). This shows that Pd leaching from the surface can occur even in the absence of any catalytic activity, i.e. leaching due to the formation of reactive intermediates does not apply in this instance.

This approach provided experimental data that can be used to quantify the various dynamic parameters involved in the leaching process. In this preliminary work, five data sets were collected under the following conditions:

**A. Surface loss**

\[ \text{M(sol)} \text{ Mobile phase} \]

**B. Particle number loss**

\[ \text{M(sol)} \text{ Mobile phase} \]

---

**Fig. 2. Different modes of leaching.**
Case I: 1st reactor @ r.t., 2nd reactor @ 90/100/110/120 °C
Case II: 1st reactor @ 90 °C, 2nd reactor @ 112 °C

A minimal model was constructed (see Reactor modelling and further details in SI) which can yield homogeneous and heterogeneous reaction kinetics ($k_{\text{hom}}$ and $k_{\text{het}}$, respectively), as well as rate of Pd loss to the solution phase ($k_{\text{leach}}$). The model was calibrated and validated against the experimental data acquired in the two cases above. Curve fitting was performed simultaneously on the data sets with selection of appropriate initial and boundary conditions, including constraints such as total Pd loss, as determined by ICP. A least-squares method was applied for this non-linear fitting problem on scaled data sets to reduce computation time.

In Pd EnCat™ 30, Pd particles are encapsulated within a cross-linked polyurea matrix, and their particle size distributes within a certain range. In this work, a ‘one-particle size’ model was initially explored, assuming that particle size distribution (PSD) of Pd is very narrow and their leaching rates are approximately the same. However, the one-particle size model fails to fit any datasets of Case I. This led us to adjust the model to take into account a broader PSD, each with a different leaching rate ($k_{\text{leach}}$). This led to the development of a multi-particle sizes model, which simply divides the PSD into several classes of particles. By representing the PSD with three classes (size1, size2 and size3), good fitting to the experimental data was achieved, affording leaching constants ($k_{\text{leach1}}, k_{\text{leach2}}, k_{\text{leach3}}$) for the three particle sizes. Leaching rates were expressed as in Eq. (1) for the three classes. By fitting all reaction profiles simultaneously leaching rates as well as rate constants and activation energies can be extracted. The ‘three-particle model’ provided a good fit to the experiment data of Case I, where the second reactor ($S2$) was operated at four sets of reaction temperature, while the temperature of the first reactor was set to ambient (Fig. 4).

Since the model solves PDEs, i.e. the spatial distribution of Pd is calculated, it is possible to determine and quantify the loss of Pd (g min$^{-1}$) at the outlet of the two-reactor system. Indeed, the integral loss of Pd is used as a modelling constraint as it is independently measured using ICP (Fig. 5). By integrating the areas under the Pd loss curves, the total Pd loss (0.145 mg) is commensurate with the experimental value obtained by ICP analysis (0.14 mg).

The model also proved to be a good fit to the reaction data collected for Case II, where the temperature of the first and second reactors were set at 90 and 112 °C, respectively (Fig. 6). In this case, a loss of 0.261 mg of Pd at S1 and S2 can be simulated by the model (Fig. 7), corresponding to a total of 0.26 mg established by ICP.

All reaction parameters extracted from these fittings are listed in Table 2. In Case I, where the temperature of the first (PBR) reactor was kept at RT, $m1$ and $m2$ refer to the Pd wt% leached from nanoparticles of size1 and size2 ($W_{\text{cat1}}$ and $W_{\text{cat2}}$), respectively (while $W_{\text{cat3}} = W_{\text{cat}} - W_{\text{cat1}} - W_{\text{cat2}}$). In Case II, when the packed bed reactor was heated @ 90 °C, both size1 and size2 particles are eroded completely in the homogeneous phase over the course of the reaction (Fig. 2A). The dissolution time ($t_{\text{dissolution1}}, t_{\text{dissolution2}}$) can also be estimated. Combining with the rate expressions (Eq. (1)–(3)), three leaching rate constants can thus be obtained ($k_{\text{leach1}}, k_{\text{leach2}}, k_{\text{leach3}}$) corresponding to the loss of Pd from size1, size2 and size3 particles, respectively (Table 3).

3.1. Sensitivity analysis

Subsequent to the data fitting, a sensitivity analysis was performed. A sensitivity analysis can be useful to understand the change of response variables with respect to parameters (Eq. (4)) [11]. In order to compare the two cases, $P2_{\text{90°C}}$ and $P2_{\text{112°C}}$ (both have the similar variances) are selected as the representative response variables for Case I and Case II, respectively.

$$S_i = \frac{\delta R}{\delta \theta^i}$$  \hspace{1cm} (4)

4. Discussions

When the temperature of the 1st reactor was set to ambient (Case I), no conversion of iodobenzene to methyl cinnamate was detectable at the outlet of S1, i.e. both, surface-catalyzed (‘heterogeneous’) reaction and that occurring in solution due to leached Pd (‘homogeneous’) are negligible. By varying the temperature of the 2nd reactor (T2), turnover numbers between 34,000 and 159,000 were recorded, which can be attributed exclusively to the activity of the leached component, corresponding to average TOF’s of between 63 and 295 s$^{-1}$. Interestingly, these values are comparable to the catalytic activity previously reported by Corma et al. for Pd clusters containing 3–4 atoms for C–C coupling reactions [12], which leads us to speculate that very similar species are involved.

In Case II, where the temperature of the 1st reactor was set at 90 °C, the reaction outflow observed at S1 may be considered to be the result of heterogeneous and homogeneous contributions. Subsequent fitting revealed that $k_{\text{het}}$ is several orders of magnitude smaller than $k_{\text{hom}}$ (Table 2); to the extent that a reasonable fit can be obtained if $k_{\text{het}} = 0$. Conceivably, the surface-catalyzed process is negligible compared to that catalyzed by the leached species. The result is also in accord with the turnover numbers reported earlier by others, who concluded that many Pd-immobilized catalyst follow the ‘dissolution-redeposition’ mechanism, where homogeneous (dissolved) Pd species are active for the reaction while the heterogeneous (solid) source acts as a reservoir [13].

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Fig. 3. Reaction profiles obtained with Pd EnCat™ 30. A (Case II): S1 (red), S2 (blue). T1 = 90 °C, T2 = 110 °C. [Pd](leached) = 0.26 mg. B (Case I): T1 = 20 °C, T2 = 90 °C (blue circles). 100 °C (red crosses), 110 °C (green circles) and 120 °C (black crosses). [Pd](leached) = 0.14 mg. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Differences between the reaction time course profiles recorded at the outflows at S1/S2 in Case I and Case II (Fig. 2) are striking: The amount of product observed at the outflow at S2 decreases with time, and was found to be a more gradual process in Case I than in Case II, which allowed us to interrogate the leaching process through modeling. In this work, it was assumed that the Pd nanoparticles are spherical, with leaching occurring at its surface. Thus, the rate of Pd loss is expected to decrease as the volume of the sphere diminishes. In both cases, satisfactory fitting can only be obtained by applying a multiparticle leaching model, with a ‘three-particles’ leaching model providing the best fit [14]. Conceptually, the model may be interpreted as comprising of different Pd nanoparticles (Wcat1, Wcat2, Wcat3) with different leaching rates (kleach1, kleach2, kleach3). Alternatively, it may also be used to describe a system whereby different surfaces, edges or defects of nanoparticles lose Pd to the solution phase at different rates, due to differences in their surface energies. The results from the modeling (Table 3) show that a distribution of Wcat1: Wcat2: Wcat3 in a ratio of 47:6:47 was adequate with kleach1 > kleach2 > kleach3.

In Case I, leaching occurs slowly at ambient temperature, resulting in the gradual decline in product outflow at S2, as a result of leaching from three different sites/particles. In contrast, a very different reaction profile was recorded in Case II: When the temperature of the 1st reactor was set at 90 °C, the rate of leaching increase by an order of magnitude (Table 3). As a result, both Wcat1 and Wcat2, the main contributors to leaching, were completely or largely eroded/dissolved into the homogeneous solution over the time course of the experiment, with tdissolution times of 27.5 and 95.1 min, respectively (Table 2), giving rise to the maximum peak observed for product output, followed by a quick decay to a more gradual decline after 40 min (Fig. 2A).

The sensitivity analysis provides a quantitative assessment of the key parameters involved in determining the reaction profiles at S1 and S2. In Case I, parameters khom, Ehomo and Wcat1 (m1) are the most sensitive parameters (Fig. 7A). In this case, negligible product is produced by the surface-catalysed process in the 1st reactor at room temperature. Given that almost all the product is derived from leached (homogeneous) Pd catalyst in the 2nd reactor, it is perhaps unsurprising that khomo, Ehomo are the most sensitive parameter in Case I. Initial weight of size1 (Wcat1) and the weight percentage leached on size1 (m1) are major factors for the product outflow as well. The above-mentioned two parameters determine the leaching rate of size1, which is responsible for the sharp decrease of leached Pd species and further product.

In Case II, the response variable is sensitive to all the parameters except for khet (Fig. 7B). tdissolution (the time when size1 is totally dissolved) and Wcat10 are the two most sensitive parameters. Similarly, the above-mentioned two parameters determine the leaching rate of size1, which is responsible for the sharp decrease of leached Pd species and
further product. $t_{\text{dissolution}2}$ (the time when size2 is totally dissolved) and $W_{\text{cat}20}$ are also sensitive parameters, so size2 are important for the fitting of case II as well. In contrast, the sensitivity of case I has little relationship with $t_{\text{dissolution}2}$ and $W_{\text{cat}20}$, so size2 does not provide key parameters for the fitting of case I.

Although having the similar variance with $P_{290 \degree C}$ in cases I, $P_{112 \degree C}$ is more sensitive to parameters. In other words, case II is more difficult to fit compared with case I. Overall, the successful fitting of case I & case II largely depends on the homogeneous catalytic activity and how the initial weights and leached weights are distributed across the three particle sizes. Crucially, the fitting appears not to be influenced by heterogeneous catalytic activity.

### 5. Conclusions

In summary, we have demonstrated, for the first time, how to distinguish individual contributions from surface-catalyzed process from those occurring in the solution phase due to leached species. A model was successfully constructed to extract important parameters such as intrinsic reaction and leaching rate constants from the time-on-line data. The following conclusions can be drawn:

1) Product formation can be attributed almost entirely to catalysis occurring in the homogeneous solution due to leached species ($k_{\text{hom}}$); the surface-catalyzed reaction is negligible as changes in the $k_{\text{het}}$ and $E_{\text{het}}$ do not affect the outcome of the fitting of all data sets.

2) Intriguingly, the model requires the incorporation of multiple leaching processes, represented by $k_{\text{leach}}(1)$, $k_{\text{leach}}(2)$ and $k_{\text{leach}}(3)$, to account for the dynamics of product formation. This implies that leaching occurs via (at least) three different processes, and/or from three different sites, represented by Pd(1), Pd(2) and Pd(3). At this juncture, it is not possible to draw any definite conclusions, although these preliminary findings suggest that leaching is not a linear, first-order process.

With the above methodology, we provide a new tool to interrogate and characterize catalyst performance that has the potential to offer
unprecedented insights into the fundamentals of leaching processes. In the case of Pd EnCat™, we have calculated turn-over frequencies (TOF’s) of between 63 and 295 s⁻¹ for the homogeneous (leaching) component of the reaction at temperatures between 90 and 120 °C. Further work is underway to assess the reaction and leaching profile of other Pd catalysts. In the longer term, we hope to couple these kinetic experiments with surface-characterization techniques (such as Extended X-ray Absorption Fine Structure spectroscopy [7]) to provide a comprehensive structure-activity understanding of the catalyst leaching process. We anticipate that the insights provided by these studies will eventually lead to effective mitigation strategies against catalyst leaching, which will greatly enhance the sustainability of catalytic processes that are implemented under CF.

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