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

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ABSTRACT

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 leaching 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, process efficiency, as well as better quality control by eliminating the batch-to-batch variability [3]. Thus, the combination of (heterogeneous) catalysis and CF technology would be a very powerful tool for improving not only the efficiency of industrial processes, but also their sustainability and product quality.

For the synthesis of molecules of medium to high complexity, it is often necessary to employ solvents to dissolve the reactants in the liquid phase. In this regard, it is more desirable to employ heterogeneous

catalysts for commercial synthesis: As the catalyst remains in a different phase from the reaction mixture, it simplifies the workup procedure and facilitates catalyst discovery (reducing units of operation); furthermore, it is also highly amenable to CF operation. In such solid-liquid biphasic systems, however, catalyst leaching is a major concern. As the active material is irretrievably lost to the mobile phase, it will contaminate the product stream, negating the potential benefits of the CF process. 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

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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, τ . 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 (τ_1 and τ_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.

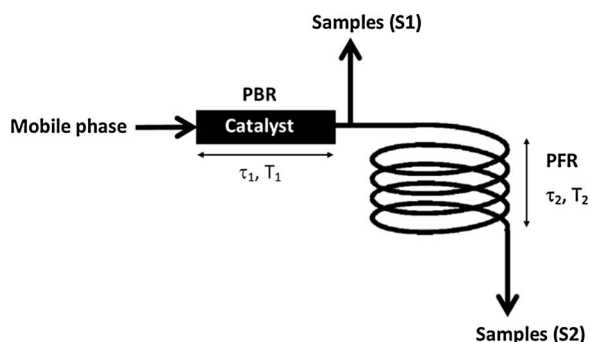


Fig. 1. Schematic of the tandem reactor system.

Table 1

Possible outcomes using the decoupled flow system (Fig. 1).

Case	Outputs	Conclusion
1	S1 = S2	No active catalyst leaching
2	S2 > S1	Leaching of active catalyst
3	S1 = S2, 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	S1 = S2, increasing with time	Activation of surface catalysis, no leaching of active catalyst
5	S2 < S1	S2 < S1 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 (Chemyx 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 \varnothing , 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 x 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-53II 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 \varnothing = 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 μ L, 7.4 mmol), iodobenzene (430 μ L, 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

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