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Immobilization and Study of Homogeneous Catalysts in a Continuous Flow Reactor Using Inorganic Particles Coated with Polymer

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Abstract

We demonstrated that organometallic catalysts can be immobilized in a gas-phase packed bed reactor (PBR) by coating inorganic particles with a non-volatile polymer-catalyst solution. We validated the methodology through a case study on the ethanol coupling reaction (Guerbet reaction) catalyzed by a ruthenium pincer complex and on the hydrogenation of hexene catalyzed by an iridium complex. Our implementation of this technique serves to inspire the adoption of advanced reactor engineering strategies for the study of homogeneous catalysts.

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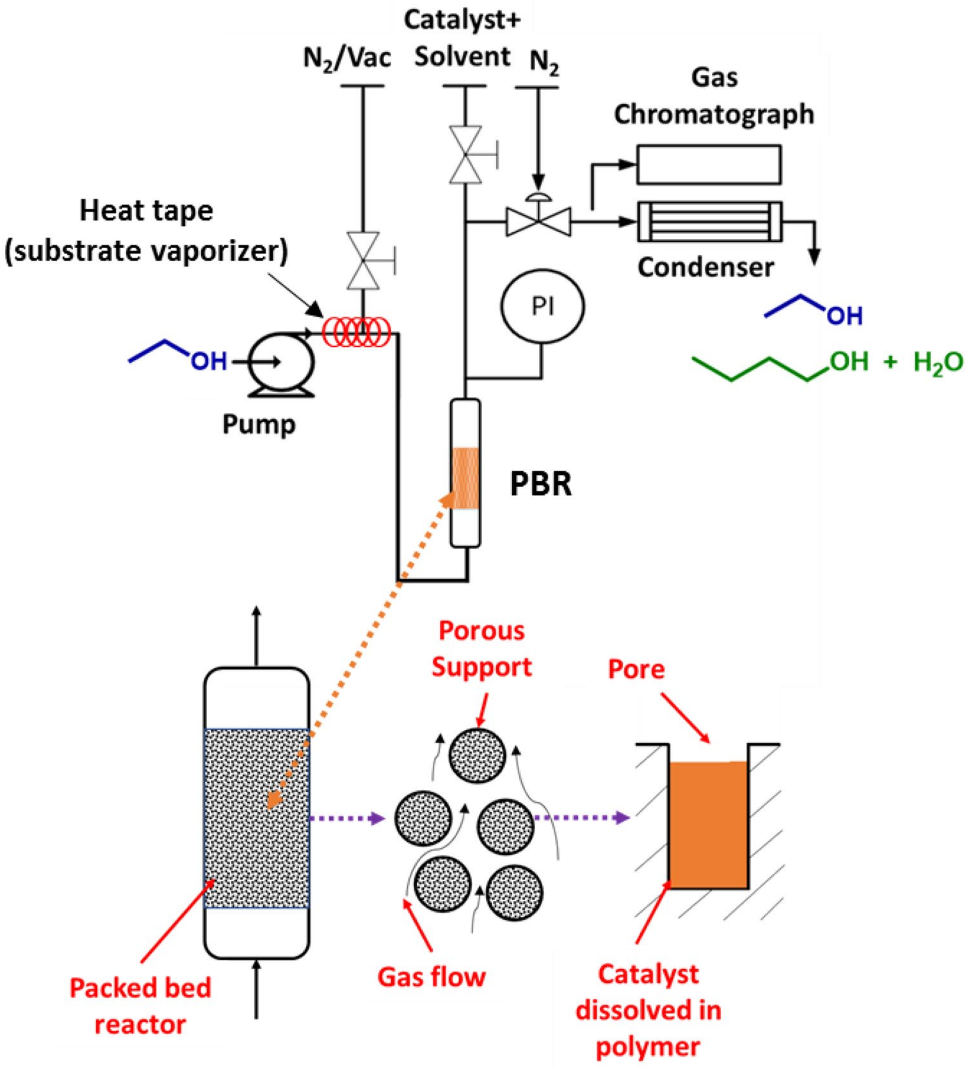
Graphical abstract



Keywords Organometallics · Immobilization · Flow chemistry

1 Introduction

The advantages offered by continuous reactors over classical batch reactors have long motivated scientific developments on the use of homogeneous catalysts in flow systems [1]. These advantages include facile and precise control over the reaction residence time, enhanced temperature regulation, improved chemical processing safety and catalyst recyclability. Moreover, flow setups are ideal for kinetic and mechanistic investigations as the reaction conditions can be tuned to maintain differential conversion under steady-state conditions. Homogeneous catalysts are traditionally maintained within a flow setup through their immobilization onto macroscopic supports. To do so, the organic ligand is modified to include a tethering group, which is used to anchor the organometallic complex [2]. Other approaches include the incorporation of organometallic molecules within metal-organic frameworks or the use of polymeric ligands [3–7]. All these methods are synthetically complex, and the ligand modification, oftentimes, has negative effects on the performance of the catalyst [8–11]. Thus, there is a need for the development of alternative immobilization strategies that do not require alteration of the ligand structure, and one such methodology is the supported liquid phase catalyst (SLPC).

In this strategy, a homogeneous catalyst is dissolved in a small quantity of solvent that is coated onto an inorganic

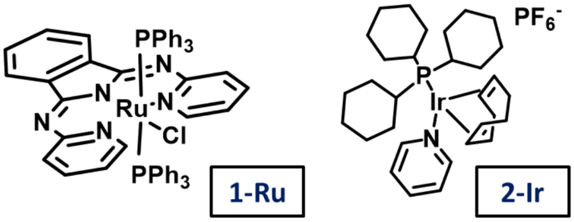
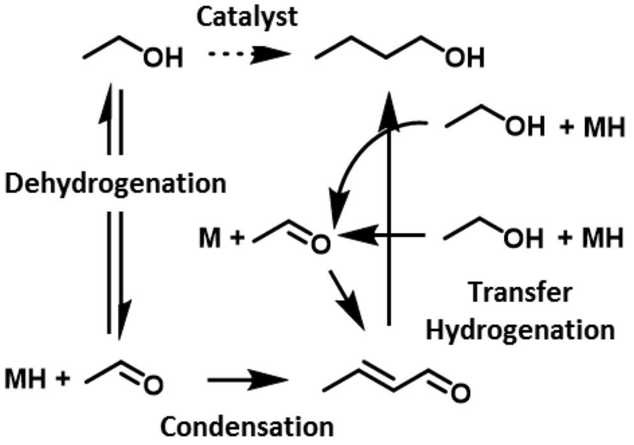


Fig. 1 Homogeneous catalysts studied in this work



Scheme 1 Previously proposed mechanism for the Guerbet reaction mediated by **1-Ru**

support to afford a catalytic reaction film [12–22]. The resulting solid material (the SLPC) is compatible with continuous flow operation similar to conventional heterogeneous catalysts. As this technique relies on physical absorption, no modification of the catalyst's chemical structure is required, and the simplicity of this approach served as our inspiration. Thus, we were interested in extending the SLPC strategy to new chemistries by immobilizing an ethanol coupling (Guerbet reaction) catalyst (**1-Ru**, Fig. 1) and a hydrogenation catalyst (**2-Ir**, Fig. 1) [23–25]. By using a low-volatility polymer solvent in the formulation of our SLPC, we retain the molecular catalyst within a packed bed reactor (PBR) at constant concentration while under a continuous flow of gaseous substrate. The substrates diffuse into the solvent layer to react while unreacted substrate and product diffuse out.

Herein, we detail the immobilization and study of organometallic catalysts within a PBR. In comparison to more recently popularized SLPC solvents such as ionic liquids, our use of a non-volatile polymer to coat inorganic particles offers a few advantages. First, polymers can be specifically designed to have a low inhibitory effect on an organometallic catalyst. Second, the wide array of polymer compositions, structures, and functionalities allow for fine-tuning of polarity which can affect the reaction. We decided to perform a case study on the Guerbet reaction (Scheme 1) to establish the SLPC methodology. This reaction is ideal for our process since the components of the ethanol coupling chemistry are volatile under the reaction conditions. Through a series of experiments, we demonstrate that the ethanol coupling reaction can be performed in continuous flow within a regime that is not mass transfer limited. The absence of mass transfer is critical for performing kinetic investigations. After the Guerbet case study, we used our SPLC technique to immobilize Crabtree's catalyst (**2-Ir)** for the hydrogenation of 1-hexene under flow conditions.

2 Experimental Procedure(s) and Setup

2.1 SLPC Synthesis

The synthesis of the SLPCs were performed under an inert atmosphere using a wet-impregnation technique. For the immobilization of **1-Ru**, basic alumina (Al_2O_3) is first dried in a heated oven (150 °C). Afterwards, basic Al_2O_3 is taken and stirred with sodium ethoxide (EtONa, co-catalyst) in ethanol for 1 h. This material is dried under vacuum to remove any trapped ethanol. The co-catalyst serves two functions: (1) as a condensation catalyst and (2) as an activator/initiator for the ruthenium complex [23]. Sole EtONa does not catalyze the (de)hydrogenation reaction, but both EtONa and **1-Ru** are required for (de)hydrogenation to proceed [26]. Next, the alumina-supported EtONa is mixed with PEG and the desired quantity of **1-Ru** in a solution of diethyl ether (Et_2O) for 1 h. Additional ligand (triphenylphosphine, PPh_3) can also be added in the prior step. Et_2O was used as the solvent as it dissolves, simultaneously, the catalyst and polymer without dissolving EtONa. This resulting slurry is dried under vacuum to remove the solvent, affording the SLPC. For the immobilization of **2-Ir**, the catalyst was heterogenized onto neutral Al_2O_3 in a single wet impregnation step using dichloromethane as the solvent. See the Supporting Information for additional detail on the SLPC synthesis.

2.2 Reactor Design and Build

We used a homemade PBR system equipped with a syringe pump for the delivery of liquid substrate, which is vaporized using resistive heating tape that is wrapped around the feed inlet. Nitrogen is used as a carrier gas for the vaporized substrate, and a mass flow meter is used to control its delivery. A cylindrical glass reactor containing the SLPC is loaded into a stainless-steel tube which is heated using an oven with controlled temperature. The reactor pressure is maintained at ca. One atmosphere, and the gaseous product flow is analysed using an in-line gas chromatograph equipped with an FID detector (Fig. 2). For hydrogenation reactions at room temperature, the syringe pump was removed, and 1-hexene

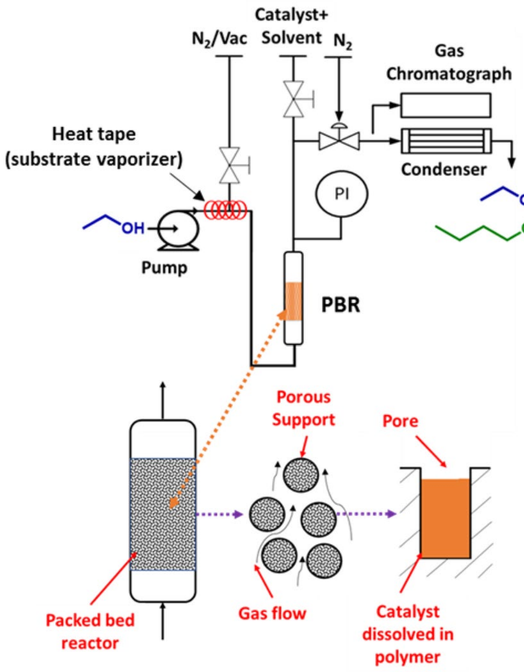


Fig. 2 Schematic of PBR design and SLPC methodology

was fed into the PBR by saturating a nitrogen gas stream whose delivery was controlled by a mass flow meter. This setup ensures that there is no condensation of 1-hexene in the reactor. The flowrate of hexene was determined gravimetrically. A second mass flowmeter was installed to control the co-feed of hydrogen gas. This mixed feed was then flown over the catalyst bed. See the Supporting Information for additional details on equipment and reactor design.

3 Results

3.1 Material Compatibility with 1-Ru

We have previously investigated the steady-state flow kinetics of **1-Ru** using a CSTR. Within this prior work, polyethylene glycol (PEG) was shown to be inert toward **1-Ru** under the reaction conditions. Moreover, additives with high acidity were shown to negatively affect catalytic activity [26]. Thus, to develop the SLPC containing **1-Ru**, we selected PEG (MW ~ 500 g/mol) as the liquid non-volatile reaction phase and basic Al_2O_3 as the inorganic support (silica was shown to inhibit the reaction see Supporting Information for details). To demonstrate **1-Ru** was compatible with basic Al_2O_3, we performed a series of ethanol coupling batch experiments that showed stable catalytic activity in the presence of the additive (linear increase of TON as a function of time, Fig. S3). Moreover, infrared (IR) spectroscopy revealed that characteristic stretches (1450–1600 cm^{-1}) of

Table 1 SLPC formulation and standard operating conditions for the study of 1-Ru

Catalyst composition	
Alumina	84.3 wt%
PEG	7 wt%
EtONa	7 wt%
1-Ru	1.7 wt%
Reactor conditions	
N_2 (g)	8 mL/min
EtOH (l)	4 µL/min
Pressure	16 psi
Residence time	0.64 s
Temperature	120 °C

the complexed isoindoline functionality present in **1-Ru** remained intact after impregnation of the catalyst onto the support (Fig. S4) [27]. A control IR spectrum of the bis(pyridylimino)isoindoline ligand was also collected that showed a characteristic N–H stretch for the non-deprotonated ligand located between 1600 and1650 cm^{-1} [27]. No peaks in this window were observed for the alumina-supported **1-Ru**. This spectroscopic data suggested that the catalyst structure remained unchanged when absorbed onto alumina. The addition of a PEG layer onto the support obscured these characteristic **1-Ru** IR signals, which prevented the spectroscopic characterization of the fully formulated SLPC. Finally, an extraction experiment was performed by placing the SLPC into a solution of benzene d-6, and an NMR analysis of the solution revealed no change in the ^{31}P resonance of the heterogenized and extracted ruthenium catalyst (Fig. S6). Thus, the combination of these experiments validated that the immobilization procedure does not alter the chemical structure of **1-Ru**.

3.2 Ethanol Coupling Reaction in the PBR

The residence time for the reaction was kept short to maintain ethanol conversions below 5 mol% (see Supporting Information for sample calculations). In this first experiment (see Table 1 for reaction conditions), butanol was identified as the major product of the reaction reaching a maximum TOF ($mol_{product}$ $mol_{\mathbf{1\text{-}Ru}}^{-1}$ h^{-1}) of 45 h^{-1} which corresponds to 3 mol% conversion of ethanol. Butanol formation continued for numerous hours (Fig. 3). In addition to butanol, trace quantities of butanal and crotonaldehyde were detected (> 0.01 mol%). Throughout the reaction, ca. 99 mol% of the substrate fed into the reactor was accounted for by the summation of these products and unreacted ethanol (near-quantitative closure of the mass balance). A control ethanol coupling reaction was also performed by removing PEG from the SLPC formulation. In this experiment, no butanol was detected (Fig. 3), confirming that the reaction occurred

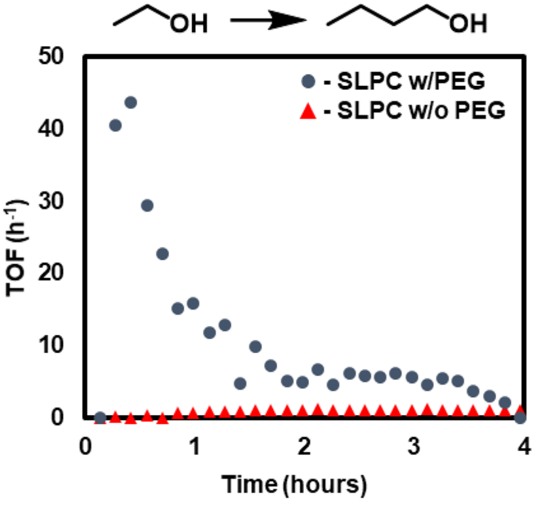


Fig. 3 EtOH and N_2 are fed into the reactor at 4 µL/min (l) and 8 mL/min (g) respectively at 120 °C and a pressure of 16 psi ($P_{EtOH} = 1.4$ psi). Circles (blue) indicate the activity of the SLPC in the presence of polymer (100 mg of SLPC, 7 wt% base, 7 wt% PEG, 1.7 wt% **1-Ru**). Triangles (red) indicate the activity of an identical catalyst, but in the absence of polymer

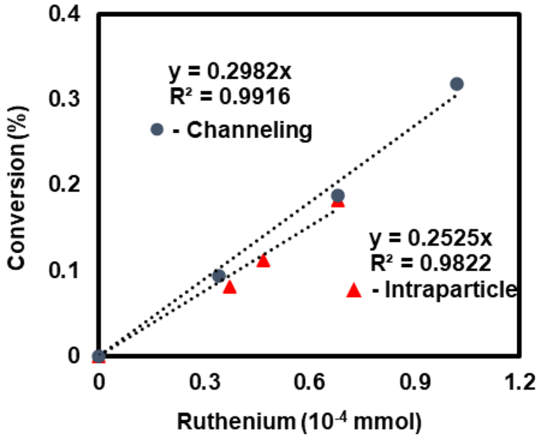


Fig. 4 EtOH and N_2 are fed into the reactor at 4 µL/min (l) and 8 mL/min (g) respectively at 120° and a pressure of 16 psi ($P_{EtOH} = 1.4$ psi). Circles (blue) show the data obtained while varying the total quantity of SLPC while maintaining a constant composition: 100, 200, and 300 mg (7 wt% base, 7 wt% PEG and 0.34 wt% **1-Ru**). Triangles (red) show data obtained while varying the concentration of catalyst material within three different batches: 200 mg SLPC with 0.34, 0.25, and 0.19 wt% **1-Ru** (7 wt% base, 7 wt% PEG)

within the polymer film and not on the support surface. However, in contrast to the stability observed in batch and in prior CSTR experiments (Fig. S3) [26], the activity of **1-Ru** decayed rapidly and reproducibly during the first hour of the reaction in the PBR (88% decay of the maximum conversion rate).

3.3 PBR Mass Transfer Studies

To use the SLPC methodology to investigate the kinetics of a reaction, it is essential to establish that the reaction proceeds without mass-transfer limitations. The mass transfer study discussed below is based upon the Koros–Nowak and Madon–Boudart criteria [28, 29].

First, we addressed intraparticle mass transfer considerations by performing catalysis with different concentrations of **1-Ru** in the polymer film. In the absence of mass transfer, the catalyst activity should be invariant to its concentration. This also implies that conversion should scale linearly with **1-Ru** loading. We synthesized three batches of SLPC with varying ruthenium loadings (0.34, 0.25, and 0.19 wt%), keeping the quantity of base and PEG constant (7 wt% base and 7 wt% PEG). The cumulative conversions obtained over 3 h were calculated (see the Supporting Information for sample calculations), and the conversion of the reaction was observed to scale linearly with the ruthenium loading (Fig. 4). Additionally, when changing the concentration of **1-Ru** in our material, we saw no change in the turnover frequency per mol of metal (Fig. 5). These observations establish that intraparticle mass transfer limitations are negligible under the reaction conditions studied.

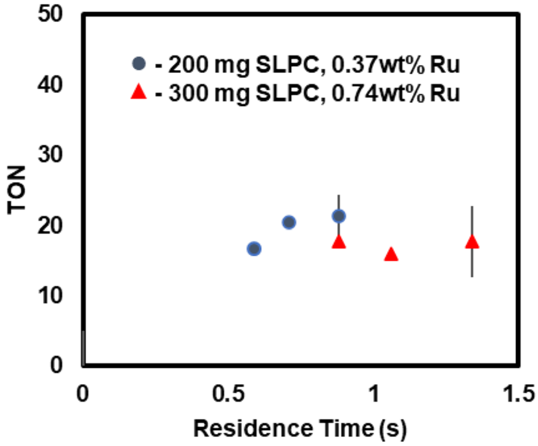


Fig. 5 The plost depicts total turnovers over 2.5 h of reaction time vs residence time over the bed at 120 °C and 16 psi. N_2 (g) flowrates were varied between 8 and 12 mL/min. EtOH (g) flowrates were varied between 2.2 and 3.3 mL/min. The partial pressure of EtOH was held constant at 3.5 psi. Two sets of experiments were conducted with varied catalyst composition and quantity. Circles (blue) show data obtained using 200 mg of SLPC (7.4 wt% PEG, 7.4 wt% base, and 0.37 wt% **1-Ru**). Triangles (red) show data obtained using 300 mg of SLPC (7.4 wt% PEG, 7.4 wt% base, and 0.74 wt% **1-Ru**). Standard deviations are reported based on three repeat experiments for a single batch of SLPC

Second, we probed for inhomogeneous contacting between the gaseous reagent stream and the inorganic particles (channeling effects). To accomplish this task, we varied the overall quantity of SLPC (100, 200, and 300 mg) while maintaining a constant composition under identical rection conditions. The cumulative conversion over 2.5 h of reaction time were calculated and plotted against the **1-Ru** content (Fig. 4). A linear and nearly identical scaling to that of our intraparticle studies was observed suggesting that the catalyst bed has uniform contacting with the reagent.

Finally, we tested for interparticle mass transfer effects by varying the reaction residence time. This was achieved by changing the ethanol and nitrogen flow rates while maintaining a constant ethanol partial pressure. In the absence of mass transfer limitations, the reagent flowrate should not affect the catalyst's activity (TON, $mol_{product}\ mol_{\mathbf{1\text{-}Ru}}^{-1}$), and indeed a constant TON of 18 is calculated regardless of residence time changes (Fig. 5). The reported errors for the TON are, however, relatively large (±3.5 TON). This large fluctuation was attributed to the rapid catalyst decay in the PBR (Fig. 3). Nonetheless, our systematic analysis revealed that the SLPC containing **1-Ru** was not limited by particle transport phenomena; and thus, the technique can be used to investigate the kinetics of the catalyst.

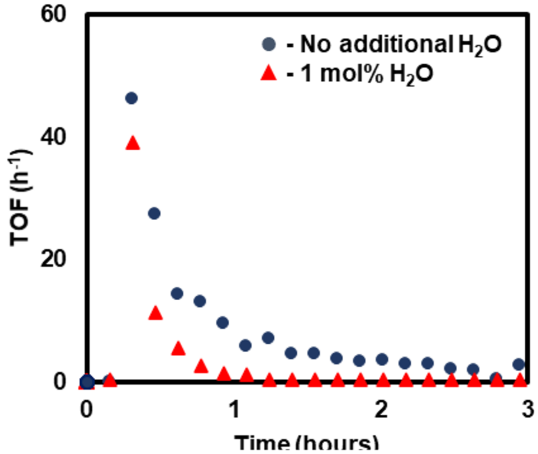


Fig. 6 EtOH and N_2 are fed into the reactor at 4 µL/min (l) and 8 mL/min (g) respectively at 120 °C and a pressure of 16 psi ($P_{EtOH}=1.4$ psi). Circles (blue) indicate the activity of the SLPC (200 mg of SLPC, 7 wt% base, 7 wt% PEG, 0.68 wt% **1-Ru**) in the absence of water. Triangles (red) indicate the activity of an identical catalyst, but in the presence of a water–ethanol feed (1 mol% water in ethanol)

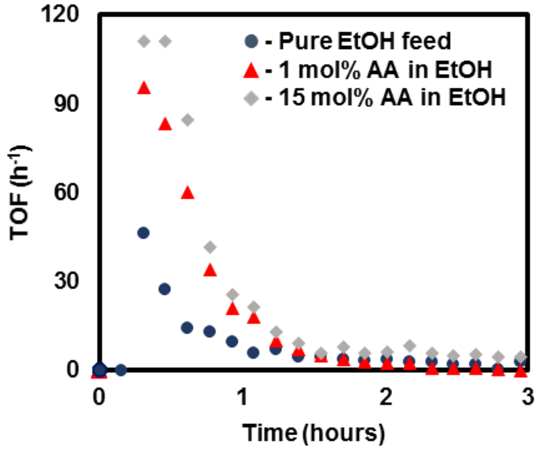


Fig. 7 EtOH and N_2 are fed into the reactor at 4 µL/min (l) and 8 mL/min (g) respectively at 120 °C and a pressure of 16 psi. Circles (blue) indicate the activity of the SLPC (200 mg of SLPC, 7 wt% base, 7 wt% PEG, 0.68 wt% **1-Ru**) in the absence of acetaldehyde. Triangles (red) indicate the activity of an identical catalyst, but in the presence of an acetaldehyde-ethanol feed (1 mol% acetaldehyde in ethanol). Diamonds (grey) indicate the activity in the presence of a feed that is 15 mol% acetaldehyde

3.4 Enhancing 1-Ru Catalytic Stability

The discrepancy in **1-Ru** catalytic stability between our batch, CSTR and PBR experiments led us to investigate the fundamental differences between these setups. First, we lowered the reaction temperature in the PBR based on the possibility that the reaction mixture was held at a lower temperature in batch and CSTR than recorded because only measurements of the bath temperature were noted. However, even reactions performed at 90 °C in the PBR resulted in almost complete catalyst deactivation after 2 h on stream (Fig. S10). Second, we considered the effect of the continuous evaporation of volatile products in the PBR as opposed to their accumulation in batch. We performed a series of experiments, cofeeding water (by-product of the aldol condensation) and acetaldehyde (product of ethanol dehydrogenation) into the PBR to compensate for their evaporation. Co-feeding 1 mol% H_2O in ethanol accelerated catalyst deactivation (Fig. 6) in the PBR. Feeding an acetaldehyde–ethanol mixture increased the butanol formation rate. A 1 mol% acetaldehyde feed doubled the butanol formation rate from 45 to 95 TOF h^{-1}; and a 15 mol% acetaldehyde feed resulted in a rate of 111 TOF h^{-1} (Fig. 7). The increased rate is not only consistent with a faster rate of aldol condensation (caused by the higher acetaldehyde concentration) but also with a faster rate of the subsequent hydrogenation reaction. However, the decay in activity was comparable to the deactivation observed when using ethanol as the sole substrate. Interestingly, C_4 unsaturated condensation intermediates were only detected while using a 15 mol% acetaldehyde feed. These products included butanal and crotonaldehyde which reached maximum rates of 39 and 9 TOF h^{-1}, respectively (see Fig. S11 for rate profile and mass balance). Only trace quantities of crotyl alcohol were detected in the vapor phase (>0.01 mol%). In our prior study of **1-Ru**, we determined that the Guerbet reaction proceeded through a rapid transfer hydrogenation step [26]. This prior conclusion is consistent with the low concentration of unsaturated C_4 intermediates (>0.7 mol% overall) detected in the PBR, in which C_4 intermediates are quickly converted

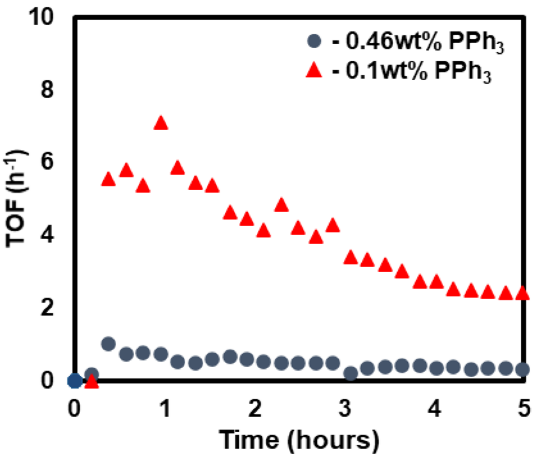


Fig. 8 The plot depicts the catalyst activity against reaction time. Nitrogen and ethanol were fed at 8 mL/min and 1.25 µL/min, respectively, into the reactor held at 120°C and 16 psi. The feed was vaporized and flown over the SLPC (300 mg SLPC, 7.4 wt% base, 7.4 wt% PEG and 0.36 wt% **1-Ru** and various **PPh_3** loadings)

to butanol under a high concentration of hydrogen transfer agent (ethanol).

Next, we attempted to increase the catalytic stability of **1-Ru** through the addition of PPh_3 (via wet impregnation, see SLPC Synthesis section above). A SLPC containing 0.1 wt% PPh_3 showed slower catalyst deactivation where only 42% of the maximum rate had decayed after 2 h (Fig. 8). However, this enhancement in stability coincided with a decrease in butanol formation rate. Further increasing the PPh_3 loading to 0.46 wt%, drastically decreased the rate of butanol formation (an average of 0.29 TOF h^{-1}) while only modestly improving stability (38% decay after 2 h). The low TOF was rationalized by the competition for coordination to the ruthenium center between PPh_3 and the substrate. The same decrease in activity was observed in batch experiments when using a high concentration of PPh_3 (Fig. S12).

These failed attempts to enhance the catalytic stability of **1-Ru** in the PBR led us to examine the conditions across our batch, CSTR, and PBR setups. Comparing amongst these systems, the ethanol concentration in the polymer solution and the ratio of co-catalyst to **1-Ru** are comparable in theory, however, the concentration of ruthenium in the PBR is nearly 100 times higher.[1] We hypothesize that the deactivation of **1-Ru** is particularly sensitive to its concentration which would be consistent with bimolecular deactivation pathways [30]. This decomposition pathway is, however, intrinsic to **1-Ru** and not related to the SPLC approach developed here.

3.5 Material Compatibility with 2-Ir

To showcase the universality of the SLPC approach, we performed a second chemical reaction using our supported-particle methodology. Specifically, we selected Crabtree's catalyst (**2-Ir**) for the hydrogenation of 1-hexene to hexane [25]. We first probed the catalyst's compatibility with different ingredients for the heterogenization in batch experiments (Table 2). Acidic supports (acidic alumina and silica) were shown to be detrimental to the catalytic activity, which is consistent with the catalyst's known sensitivity to acidic protons [25]. We selected neutral Al_2O_3 as the solid support, since **2-Ir** exhibited the highest activity in the presence of this additive (1030 TON, 46% conversion). **2-Ir**'s sensitivity to acidic protons led us to implement a dimethyl ether PEG (MW ~ 500 g/mol) as the polymer solvent. In batch experiments, we observed a significant increase in activity in the presence of the polymer in comparison to our control experiment (control 960 TON, PEG 2160 TON). The low activity in our control experiment is due to the poor solubility of **2-Ir** in neat hexene. In contrast, **2-Ir** was fully soluble in a PEG/hexene mixture (consistent with higher activity, 95% hexene conversion after 2 h). Ultimately, this experiment showcased that PEG did not deactivate **2-Ir**.

3.6 Olefin Hydrogenation in the PBR

After formulating a SLPC containing **2-Ir** (via wet impregnation, see SLPC Synthesis section above), we used the catalyst to hydrogenate 1-hexene in our homemade PBR. The reaction residence time was kept short (2.2 s) to maintain low conversions. Standard operating conditions are described in Table 3. A mixed feed of gaseous 1-hexene and hydrogen diluted by a nitrogen carrier gas was flown over a SLPC containing 0.69 wt% **2-Ir** at room temperature. Hexane formation was observed with a maximum TOF (mol_{hexane} $mol_{\mathbf{2\text{-}Ir}}^{-1}$ h^{-1}) of ~ 140 h^{-1} (maximum of 7 mol% conversion) reached after 5 min on stream (Fig. 9, see the Supporting Information for rate calculations). The activity of the catalyst decayed rapidly (89% decay in rate after 2 h). This rapid deactivation is consistent with instability of the catalyst reported in the literature (batch experiments) and thus is not attributed to the immobilization strategy [25, 31].

In this experiment, we showcased the conversion of 1-hexene to 1-hexane using **2-Ir** within a supported particle, accomplishing our primary goal. Because **2-Ir** operates under different reaction conditions and possesses a different intrinsic rate when compared to **1-Ru**, it would be necessary to reassess the transport limitations of the supported **2-Ir** catalyst before providing any kinetic analysis.

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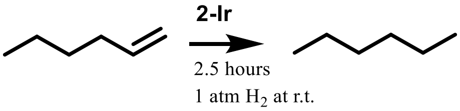
[1] For batch reactions, the [EtOH] in PEG is 0.87 M. This value was calculated using initial substrate loadings. Under flow in our PBR and CSTR, the [EtOH] is ca. 0.25 M. This value Was determined by simulating the VLE for a PEG/EtOH mixture in CHEMCAD(SRK).

Table 2 Batch hydrogenation of 1-hexene to hexane by 2-Ir in the presence of various additives



Entry	Additive	TON
1	Control	960
2	Basic alumina	1000
3	Neutral alumina	1030
4	Acidic alumina	400
5	Silica	770
6	Polyethylene glycol	2160

All reactions were carried out at room temperature in 0.74 mL of 1-hexene using 2 mg of **2-Ir** under 1 atm H_2. For reactions with additives, either 1000 mg of polymer or 200 mg of support was added to the batch reactor

Table 3 SLPC formulation and standard operating conditions for the study of **2-Ir**

Catalyst composition	
Alumina	90.31 wt%
PEG	9 wt%
2-Ir	0.69 wt%
Reactor conditions	
N_2 (g)	9 mL/min
H_2 (g)	2 mL/min
1-hexene (g)	0.12 mL/min
Pressure	17 psi
Residence time	2.2 s
Temperature	r.t

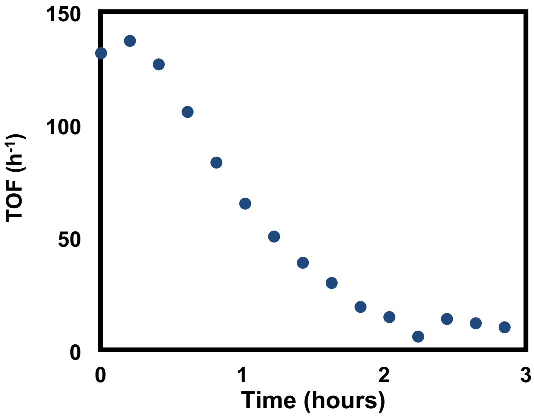


Fig. 9 The plot depicts the rate of hexane production against reaction time. A mixed vapor of N_2, H_2 and 1-hexene (9 mL/min, 2 mL/min and 0.12 mL/min respectively) are flown over the SLPC (300 mg Al_2O_3, 9 wt% PEG, and 0.69 wt% **2-Ir**) at room temperature

The evaluation of transport for the supported **2-Ir** catalyst was not performed in this work because the goal of this experiment was only to display the compatibility of the SLPC approach with other homogeneously-catalyzed reactions.

4 Summary and Conclusions

Our development of the SLPC methodology using polymer as solvent to immobilize organometallic catalysts (Guerbet reaction and hydrogenation of alkene) has permitted the implementation of two "as is" homogeneous catalysts in gas-phase packed bed reactor. The technique involves solvating the catalyst within a non-volatile solvent (PEG) which is subsequently absorbed into a porous inorganic support. In a first case study, we showed that the SLPC immobilization components did not alter the chemical structure of **1-Ru**. Moreover, a mass transfer investigation of an SLPC containing **1-Ru**, revealed a kinetically controlled reaction.

Significant decay in catalytic rate was observed for the ethanol coupling reaction in flow. This instability was, however, not attributed to the immobilization strategy but rather to the instability of the **1-Ru** at elevated concentration. Moreover, we also extended the SLPC methodology to the hydrogenation of 1-hexene where the catalyst was shown to be active for multiple hours on stream. Overall, our work aims to inspire the adoption and design of unique processes for the study of homogeneous catalysts.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10562-022-04056-6.

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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.

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Declarations

Conflict of interest There are no conflicts to declare.

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