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Highly Selective Continuous Flow Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol in a Pt/SiO$_2$ Coated Tube Reactor

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Abstract: A novel continuous flow process for selective hydrogenation of $\alpha$, $\beta$-unsaturated aldehyde (cinnamaldehyde, CAL) to the unsaturated alcohol (cinnamyl alcohol, COL) has been reported in a tube reactor coated with a Pt/SiO$_2$ catalyst. A 90% selectivity towards the unsaturated alcohol was obtained at the aldehyde conversion of 98.8%. This is a six-fold improvement in the selectivity compared to a batch process where acetals were the main reaction products. The increased selectivity in the tube reactor was caused by the suppression of acid sites responsible for the acetal formation after a short period on stream in the continuous process. In a fixed bed reactor, it had a similar acetal suppression phenomenon but showed lower product selectivity of about 47–72% due to mass transfer limitations. A minor change in selectivity and conversion caused by product inhibition was observed during the 110 h on stream with a turnover number (TON) reaching 3000 and an alcohol production throughput of 0.36 kg g$_{Pt}^{-1}$ day$^{-1}$ in the single tube reactor. The catalysts performance after eight reaction cycles was fully restored by calcination in air at 400 °C. The tube reactors provide an opportunity for process intensification by increasing the reaction rates by a factor of 2.5 at the reaction temperature of 150 °C compared to 90 °C with no detrimental effects on catalyst stability or product selectivity.

Keywords: flow chemistry; hydrogenation; unsaturated aldehyde; platinum; tube reactor; alcohol; selectivity; stability; catalyst-coated

1. Introduction

Hydrogenation of cinnamaldehyde (CAL) is interesting not only due to wide applications of the valuable desired products [1–6], but also because it is a good model reaction to study structure-activity relationship of the catalysts [7,8]. The CAL molecule contains conjugated C=C and C=O bonds and an aromatic ring. The main catalytic routes of CAL hydrogenation in isopropanol (IPA) solvent are shown in Scheme 1. Hydrogenation of the C=O group leads to cinnamyl alcohol (COL), while hydrogenation of the C=C group forms hydrocinnamaldehyde (HCAL). Further hydrogenation of either COL or HCAL leads to the formation of hydrocinnamyl alcohol (HCOL). Other reactions such as aromatic ring hydrogenation or hydrogenolysis are possible, but these generally require considerably harsher conditions and are usually negligible [9,10]. The C=C hydrogenation is thermodynamically
favorable compared to the C=O hydrogenation [7,8,11]. Thus, hydrogenation of CAL to COL has been
viewed as one of the most challenging reactions in heterogeneous catalysis, primarily because of the
difficulty in selectivity control [7,8].

Various factors such as the type of metal [12–15], particle size [16], additives [17–20] and
supports [1,4,16,21–23] were found to influence the activity and selectivity of the catalysts in CAL
hydrogenation dramatically. In general, noble metals are used for the CAL hydrogenation because
of their high activity at low temperatures. The selectivity towards COL generally decreases in the
following order: Os > Ir > Pt > Ru > Rh > Pd [7]. Due to the scarcity of Ir and toxicity of Os, Pt is
the most promising catalyst for CAL hydrogenation.

The selectivity to COL improves as the particle size increases [7]. Because of the steric constraints
caused by the aromatic ring, the planar CAL molecule cannot adsorb parallel to a flat metal surface
(large particles) via the C=C bond, so the head-on (C=O) CAL adsorption is preferred and leads
to the hydrogenation to COL. Small particles which have high curvature do not show significant
steric constraints, so CAL can be adsorbed via both C=C and C=O bonds. Thus, the relatively large
nanoparticles (3–8 nm) have a higher selectivity towards COL compared to the smaller nanoparticles [7].
The selectivity towards carbonyl reduction can be further increased by the addition of a second metal
such as Fe, Co, Sn, Ge [7,8,17,20]. Additionally, the selectivity can be improved by optimising the
porosity of the support. Mesoporous supports with controlled porosity demonstrate a larger surface
area and stabilise the metal nanoparticles. Importantly, the pores of the catalyst support confine
the CAL molecules decreasing the probability of the C=C adsorption, and therefore increasing the
COL selectivity [11]. However, introducing porosity and a second metal inevitably increases the
complexity and costs of the entire process as well as compromises the catalyst reusability. For industrial
applications, simpler and cheaper catalysts are more desirable.

Traditionally, catalytic hydrogenation reactions are conducted in continuously stirred tank reactors
(CSTR), often needing elevated pressures and long reaction times [24–26]. These batch processes are highly
versatile but the discontinuous nature of the batch process requires a lot of non-productive operations
such as reactor cleaning and catalyst separation resulting in high labor costs [27]. Low heat and mass
transfer rates decrease the process efficiency and the product yield as well [28–30]. The presence of toxic
or hazardous compounds in large-volume, often pressurized vessels raises safety concerns and requires
notable infrastructure costs.

Scheme 1. The main reaction routes and side reactions during the catalytic hydrogenation
of cinnamaldehyde.
The problems of batch processes can be solved by a continuous flow operation which provides more efficient, safer and intensified processes [27–29]. Additionally, continuous flow processing benefits from the rapid removal of products and decreases the potential for catalyst poisoning which can reduce by-product formation [31]. The intrinsic problem of conventional micro-reactors with characteristic channel dimensions below 0.5 mm can be solved by increasing the channel diameter to the millimeter-range in milli-, or also called meso-, reactors. These systems offer all the benefits of conventional microreactors and enhanced scalability reaching up to a kilogram per day scale [32]. Therefore, the fine chemicals and pharmaceutical sectors have targeted a switchover from batch to continuous operation to improve process efficiency, atom economy and simplify scalability [28,33]. However, to the best of our knowledge, there are only a few reports that show limited success in cinnamaldehyde hydrogenation to cinnamyl alcohol in continuous flow with the highest selectivity towards unsaturated alcohol of about 60% [31,34,35].

In this paper, we aim to develop a new continuous process for selective hydrogenation of cinnamaldehyde to cinnamyl alcohol over a wall-coated catalyst tube reactor. We studied the effect of process conditions on the catalytic performance and stability of the reactors with a Pt/SiO$_2$ catalyst. The performance in a continuous tube reactor is compared to that in a batch reactor and a conventional fixed bed flow reactor.

2. Results and Discussion

2.1. Catalyst Characterization

Figure 1a presents characteristic scanning electron microscope (SEM) images of the catalytic coating in a tube reactor. The coating is uniform along the reactor length with a thickness of 28 ± 3 µm. The morphology of the coating (Figure 1b) shows that SiO$_2$ forms textured pillars with a diameter of 1.5 µm. The Pt loading of 12.5 wt % determined by energy-dispersive X-ray (EDX) spectroscopy analysis from several areas of the coating is in good agreement with the nominal loading of 12.0 wt %. When focusing the electron beam on the catalyst coating, we found no traces of Fe in the EDX spectra which indicates complete coverage of the silica support over the stainless reactor body and no Pt–Fe interactions.

![Figure 1. SEM (a) cross-sectional and (b) frontal images of the catalytic coating in a tube reactor.](image)

Figure 2 shows a representative transmission electron microscopy (TEM) image of the Pt/SiO$_2$ coating. The average size of the Pt particle is 4.3 ± 1.2 nm corresponding to a Pt dispersion of 28% [36]. The Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore-size distribution of SiO$_2$ and Pt/SiO$_2$ are analyzed using N$_2$ adsorption-desorption isotherms. Both samples show similar surface areas of 200 m$^2$ g$^{-1}$ and total pore volumes of 0.25 mL g$^{-1}$. A narrow pore size distribution ranging from 3 to 5 nm with a maximum around 4 nm is evident for mesoporous SiO$_2$ support (Figure 3). The pore size is reduced slightly after Pt loading with a distribution ranging from 3 to 4 nm and a maximum around 3.6 nm. The presence of suitable mesopores is beneficial in stabilizing
the Pt nanoparticles and improving the internal mass transfer in the coating which improves the COL selectivity [11,37,38].

![TEM image of the Pt nanoparticles supported on SiO2 with their diameter distribution.](image)

**Figure 2.** TEM image of the Pt nanoparticles supported on SiO2 with their diameter distribution.

![Barrett–Joyner–Halenda (BJH) desorption pore-size distribution for the SiO2 support and Pt/SiO2 catalyst studied.](image)

**Figure 3.** Barrett–Joyner–Halenda (BJH) desorption pore-size distribution for the SiO2 support and Pt/SiO2 catalyst studied.

Powder X-ray diffraction patterns of the Pt/SiO2 and SiO2 are shown in Figure 4. The (111) and (200) peaks are marked for the Pt nanoparticles. The average size of the Pt nanoparticles using the Scherrer method for the (111) peak was calculated to be 2.5 ± 1 nm which is comparable with the result of TEM analysis. The pattern also shows the presence of SiO2 (100) which may also include an amorphous content.

![Powder X-ray diffraction patterns (using Co Kα radiation) for the 12 wt % Pt/SiO2 catalysts and the SiO2 support.](image)

**Figure 4.** Powder X-ray diffraction patterns (using Co Kα radiation) for the 12 wt % Pt/SiO2 catalysts and the SiO2 support.
Small angle X-ray scattering (SAXS) measurements are shown in Figure 5. The main features (marked by *) are from the structure formed by the silica spheres. The silica spheres commonly pack with face centered cubic (FCC) and hexagonally close packed (HCP) structures [39]. The peaks are too broad to determine which of these is dominant here. Assuming an FCC structure with the (001) peak at \(q = 0.044 \text{ Å}^{-1}\) gives an average sphere radius \(\approx 8 \text{ nm}\). Between \(q = 0.1\) and \(0.3 \text{ Å}^{-1}\) there is an increase in intensity in the Pt/SiO\(_2\) compared to the SiO\(_2\) sample due to the scattering from the Pt nanoparticles. A model treating the Pt nanoparticles as a Gaussian distribution of spheres was used alongside a simple power law slope to account for the SiO\(_2\) scattering in the same \(q\) range. A unified fit method was used for fitting the power law slope developed by Beaucage and implemented within the Irena SAXS analysis package [40,41]. The power law slope was first fitted to the SiO\(_2\) only data in the \(q\) range from 0.1 to 0.3 \(\text{ Å}^{-1}\) and then used for fitting the Pt/SiO\(_2\) data in conjunction with a Gaussian distribution of Pt spheres. The overall fit for the Pt/SiO\(_2\) is shown in Figure 5 as the blue line, along with the fit without scattering from the Pt particles shown by the dashed line. From this fit the mean Pt particle diameter is 2.5 nm with a standard deviation of 0.48 nm, which is in good agreement with the TEM and XRD data.

![Figure 5](image-url)

**Figure 5.** Small angle X-ray scattering obtained from the 12 wt % Pt/SiO\(_2\) catalysts and the SiO\(_2\) support. The overall fit for the Pt/SiO\(_2\) is shown by the blue line and the fit without scattering from the Pt particles is given by the dashed line. The main features of SiO\(_2\) are marked by *.

Acidity of the Pt/SiO\(_2\) catalyst and SiO\(_2\) support was studied by pyridine temperature-programmed desorption (TPD). The materials held at 100 °C were dosed with the pyridine, flushed for 1.5 h with He followed by the temperature ramp (Figure 6). The silica support showed a small desorption peak with the maximum close to 170 °C. The low desorption temperature indicates weak pyridine adsorption on the SiO\(_2\) support. The low adsorption observed agrees with the literature data which showed that amorphous silica does not contain acid sites and weak pyridine adsorption is associated with the hydrogen-bonded pyridine molecules over the silanol groups [42–44]. However, the Pt/SiO\(_2\) catalyst showed much broader peaks centered at about 200 °C and 460 °C. The total amount of the pyridine adsorbed on the Pt/SiO\(_2\) catalyst compared to the SiO\(_2\) support increased substantially. The appearance of the peak centered at 460 °C indicates the formation of acid sites formed, likely at the vicinity of the Pt nanoparticles. The formation of new acidic groups on the Pt/SiO\(_2\) catalysts agrees with the literature data, but strongly depends on the catalyst preparation method [45–47].
Figure 6. Temperature-programmed desorption profile of pyridine from the Pt/SiO₂ catalyst and SiO₂ support.

2.2. Hydrogenation of CAL over the Pt/SiO₂ Catalysts in Batch and Tube Reactors

Firstly, the CAL hydrogenation was studied in a Pt/SiO₂ coated tube reactor by varying the residence time. Figure 7 shows that the CAL concentration decreased with the increasing residence time corresponding to a conversion change from 45.4% at 2.3 min to 99.2% at 10.5 min. The main reaction product was COL with its concentration increasing gradually with residence time. Interestingly, the alcohol selectivity remained around 90% under all conditions studied. The data show a high selectivity of the Pt/SiO₂ catalytic coating to unsaturated alcohol. The average turnover frequency (TOF) was 130 h⁻¹. The TOF numbers agree with the literature data for alkali-unpromoted hydrogenation of cinnamaldehyde over Pt catalysts [7,20,48,49]. The high selectivity observed might have been caused by the interaction with Fe from the reactor body as highlighted in recent publications [20,48,50]. However, the elemental EDX analysis showed no traces of Fe in the proximity of Pt likely due to the full coverage of the stainless tube with the silica support.

Figure 7. The outlet concentrations of the components obtained in the CAL hydrogenation as a function of residence time in the 5 m reactor coated with 190 mg 12 wt % Pt/SiO₂ catalyst. Reaction conditions: H₂ flow rate: 4–12 mL min⁻¹ (standard temperature and pressure, STP), liquid flow rate: 0.2–3 mL min⁻¹, inlet CAL concentration: 0.1 M in IPA, pressure: 10 bar, temperature: 90 °C.

The same catalyst was also used for hydrogenation in a batch reactor as shown in Figure 8. Rather higher concentrations of by-products were observed in the batch reactor. Along with the hydrogenation products such as HCAL, HCOL (Scheme 1), substantial amounts of acetals (diisopropyl acetal of hydrocinnamaldehyde, HCAL-IPA and diisopropyl acetal of cinnamaldehyde, CAL-IPA) were obtained. The acetals are formed by a reversible acid-catalyzed reaction of CAL and HCAL with
isopropanol [9,10,16,21]. It should be mentioned that the CAL-IPA concentration was considerably lower than HCAL-IPA although the CAL was present in a much higher concentration. The selectivity to the product of interest, COL, was only 15% which agrees with the literature for silica-supported Pt catalysts [51]. When acetals are formed, the C=O group becomes protected and its hydrogenation is not possible which results in a decreased selectivity towards COL (Scheme 1). Therefore, a significant difference in the selectivity pattern between the catalyst-coated tube reactor and the batch reactor is likely associated with the acetal formation.

The higher amount of HCAL-IPA compared to CAL-IPA was studied in a series of blank experiments with and without the catalysts as shown in the Supplementary (Figure S1). The data indicate that the acetal formation rate is negligible in the absence of the catalyst. This is expected considering that acetal formation is an acid-catalyzed reaction. In the presence of the Pt/SiO$_2$ catalyst, the concentration of acetals increased rapidly obviously because of the presence of acid sites on the catalyst.

A high formation rate of acetals was observed over a fresh Pt/SiO$_2$ coating in the tube reactor. After 0.5–1.5 h on stream, the acetal formation was almost fully suppressed indicating deactivation of the acid sites which catalyze the acetal formation. Due to the acid site deactivation, the acetal formation becomes negligible and the CAL hydrogenation proceeds with a much higher COL selectivity over the Pt/SiO$_2$ coating.

An obvious solution to avoid the acetal formation may lie with utilization of other solvents such as hexane or toluene. Gallezot et al. [7] indicated that there is little solvent effect on the cinnamaldehyde hydrogenation. However, a number of reports show either a considerably lower hydrogenation activity or even complete catalyst deactivation in non-polar solvents compared to alcohols [10,52]. Our results also confirm negligible catalyst activity when the solvent was switched to toluene. Therefore, we used only isopropanol in the subsequent experiments.

The activity and selectivity observed over the Pt/SiO$_2$ catalyst in the coated tube reactor was considerably higher than that of monometallic Pt catalysts such as Pt/SiO$_2$ [31], Pt/Ti [35] in the flow reactor and Pt/Graphite and Pt/C [12,23,53,54] in the batch reactors (Figure 9). The performance of Pt/SiO$_2$ coatings is comparable with that of bimetallic supported catalysts such as Pt-Co/SBA-15 [19]. A higher COL selectivity of above 90% was reported in CAL hydrogenation carried out in supercritical CO$_2$, however the conversion was below 50% [55,56]. While the selectivity above 90% was reported at full conversion over several catalysts such as Pt [24], Co [15] nanoparticles confined in metal-organic frameworks or bimetallic catalyst [20], their preparation is not straightforward and associated considerably higher catalyst costs. In addition, much longer residence time was needed (up to 48 h) in those experiments.

Figure 8. The outlet concentrations of the components obtained in the CAL hydrogenation as a function of residence time in a batch reactor. Reaction conditions: 0.1 g 12 wt % Pt/SiO$_2$, H$_2$ pressure 10 bar, 90 °C, 0.1 M CAL in IPA.
Circles represent continuous flow and squares represent batch reactors.

Figure 9. The selectivity to COL as a function of CAL conversion obtained in the current work over the 12 wt % Pt/SiO$_2$ catalyst in the tube (flow-this study, •) and batch (batch-this study, □) reactors compared with the literature data obtained in continuous flow reactors (Pt/Ti, ○ [35]; Pt/SiO$_2$, ◇ [31]) and batch reactors (Pt/G&C, ■ [12]; Pt-Co/SBA-15, ★ [19]; Pt/CNS, ♦ [23]; Pt/RGO, ♣ [53]; Pt/G, △ [34]). Circles represent continuous flow and squares represent batch reactors.

2.3. Long-Term Stability

High long-term catalyst stability is essential for the reactor operation under continuous flow. The reaction conditions were adjusted for the stability test to decrease liquid consumption and operate at 10–50% conversion range. The medium conversion range was selected to underline any deactivation phenomena. The results presented in Figure 10 show a minor loss of selectivity and increase in activity during the operation for over 110 h on stream. While the selectivity to COL decreased from 94% to 80% in 110 h, both the selectivity to the by-products increased gradually (for HCAL—from 4% to 12% and for HCOL—from 1% to 7%). The turnover number (TON), the ratio of the substrate molecules converted and the total amount of Pt in the catalyst, shows the practical longevity of the catalyst and reactor combination used. TON exceeded 3000 in 110 h compared to typical TON of 65 [48], 760 [6], 840 [49] in batch reactors as estimated from available literature data. Therefore, the TON value obtained over the Pt/SiO$_2$ catalytic coating is 1–2 orders of magnitude higher than the value observed in batch reactors. Even comparing with a more efficient magnetic catalyst separation technique in batch [57,58], the tube reactors provide higher catalyst utilization efficiency due to the continuous 24/7 operation with neither laborious catalyst separation steps nor idle time.

Figure 10. The stability test of the 5 m tube reactor coated with a 12 wt % Pt/SiO$_2$ catalyst. Reaction conditions: H$_2$ flow rate: 3 mL min$^{-1}$, liquid flow rate: 0.2 mL min$^{-1}$, CAL concentration: 0.8 M in IPA, pressure: 15 bar and temperature: 90 °C. Reduction was performed in the flow of isopropanol (1 mL min$^{-1}$) and H$_2$ flow rate (3 mL min$^{-1}$, STP) for 10 min. The duration of the reduction step on the plot is exaggerated for the presentation purposes.
Flushing with H₂ and IPA for 10 min under the same conditions after 110 h on stream recovered most of the activity and significantly increased the selectivity. However, a rapid deactivation was observed after the reduction step as the conversion reduced from 76 to 53% over the first 30 min after the reduction. This behavior agrees with previous reports describing a significant effect of hydrogen pre-activation step on the reaction kinetics. This also suggests a significant product inhibition of the catalysts [35].

The changes in the CAL conversion over time were also remarkable. The conversion decreased during the first 20 h on stream and then gradually increased up to 110 h and become even higher after the reduction treatment. The leaching study of the reaction products showed the Pt concentration in the final products was only 0.002 ppm. Low leaching observed demonstrates that Pt nanoparticles are confined in the mesoporous structure of the catalyst support (SiO₂) and confirms the high long-term stability of the coatings.

An additional study was performed at a higher temperature to explore a possibility for intensified process conditions. The details are reported in Supplementary (Figure S2). The activation energy for the CAL hydrogenation considering zero-order kinetics was determined to be 31.2 kJ mol⁻¹, which is in reasonable agreement with the literature data for a Pd/SiO₂ catalyst (30.1 kJ mol⁻¹) [59]. The conversion increased by a factor of 2.5 when changing the temperature from 90 °C to 150 °C allowing for process intensification.

Due to higher reaction rates at elevated temperatures, a shorter reactor (2 m) was used to study the long-term stability and explore possible regeneration of the Pt/SiO₂ catalytic coatings. In these experiments, the catalysts reduction and solvent treatment steps were repeated every 10 h to study their effect on catalyst performance. Finally, an oxidation treatment at 400 °C was performed after eight reaction-reduction cycles.

The activity and selectivity pattern of CAL hydrogenation performed at 150 °C follows the same trend as that at 90 °C (Figure 11). A combined reduction and solvent washing treatment can restore the selectivity significantly after every single cycle, however, the selectivity was slowly decreasing over time from 90 to 80%. Similarly, the conversion decreases with time in every cycle, however the reduction treatment restores or even increases the overall reaction rate. The notable effect of reduction and solvent washing demonstrates a strong product inhibition. The calcination treatment at 400 °C restores the selectivity which reaches the value observed over the fresh sample (90%) demonstrating excellent sintering stability and reusability of the catalytic coatings.

![Figure 11](image-url)  
**Figure 11.** The stability test of the 2 m tube reactor coated with a 12 wt % Pt/SiO₂ catalyst. Reaction conditions: H₂ flow rate: 3 mL min⁻¹, liquid flow rate: 0.2 mL min⁻¹, CAL concentration: 0.8 M in IPA, pressure: 15 bar and temperature: 150 °C. Reduction was performed in the flow of isopropanol (1 mL min⁻¹) and H₂ flow rate (3 mL min⁻¹, STP) for 10 min. Regeneration conditions: in air at 400 °C for 1 h. The duration of the reduction and calcination steps on the plot are exaggerated for the presentation purposes.
The stability test of a continuous fixed bed reactor packed with 190 mg 12 wt % Pt/SiO₂ catalyst was carried out under the same conditions (Figure 12). The results in Figure 12a explained why the selectivity of COL was much higher than that in the batch reactor. A fresh Pt/SiO₂ catalyst also produced high concentration of acetals at the beginning, but after 0.5–2.5 h on stream, the acetal formation was almost fully suppressed which results in a much higher COL selectivity in the flow reactors. The selectivity of COL increased from 47 to 72% in the first few hours and slowly dropped to 47% in 66 h, shown in Figure 12b. The range of the selectivity to COL is comparable to the other results produced in fixed bed [31]. The conversion decreased from 57 to 15% in 8 h and stabilized afterwards. Much lower conversion and selectivity were found compared with the performance of the catalyst-coated tube reactor. The likely reasons are the mass transfer limitations, broad residence time distribution associated with the possibility of liquid channeling [60–62].

![Figure 12](image_url)

Figure 12. The stability test of a continuous fixed bed reactor packed with 190 mg 12 wt % Pt/SiO₂. Reaction conditions: H₂ flow rate: 3 mL min⁻¹, liquid flow rate: 0.2 mL min⁻¹, CAL concentration: 0.8 M in IPA, pressure: 15 bar and temperature: 90 °C. (a) The outlet concentrations of the components obtained in the CAL hydrogenation as a function of time in stream. (b) The conversion of CAL and the selectivity to COL vs. Time on stream.

A combination of excellent catalytic activity, stability and selectivity in a tube reactor is promising for innovator pharma applications which are at gram to kilogram scale. The total production in 6 h over the Pt/SiO₂ coatings in the tube reactor was 7.5 times and 1.5 times higher compared to a batch reactor and a fixed bed reactor, respectively (Figure 13). The advantage becomes more significant over time because of required catalyst changeovers will further decrease the space–time yield in the batch reactor. A product throughput of 0.36 kg gₚt⁻¹ day⁻¹ was achieved in a single continuous flow catalyst-coated tube reactor. The best literature data reports a throughput of 0.13 kg gₚt⁻¹ day⁻¹ being obtained under much higher temperature and pressure [31,35]. There exists a possibility for further scale up to a 10 kg gₚt⁻¹ day⁻¹ by operating 32 tubes in parallel following the numbering up approach in a gas-liquid modular manifold [63,64]. A very low-pressure drop in the catalyst-coated tube reactor also allows increasing the reactor length by connecting the reactors in series. The main advantages of using the catalyst-coated tube reactors in the continuous flow process are higher throughout of product, the absence of catalyst separation from the products, negligible pressure drop, easy scalability, efficient energy utilization and safe operation.
3. Materials and Methods

3.1. Materials

Trans-cinnamaldehyde (CAL, 98 wt %) was purchased from Alfa Aesar (Heysham, UK) and stored under N\textsubscript{2}. Isopropanol (IPA, 99.5 wt %) used as a solvent was obtained from Fisher Scientific (Loughborough, UK) and tetradecane (99 wt %) as internal standard for GC analysis was ordered from Acros Organics (Linden, NJ, USA). The wall-coated Pt/SiO\textsubscript{2} tube reactors and identical powder Pt/SiO\textsubscript{2} catalyst were provided by Stoli Catalysts Ltd. (Stoli Catalysts Ltd., Coventry, UK). The detailed synthesis methodology is being patented (not yet public) [65,66] and cannot be disclosed. The coating was obtained by sol–gel method similar to the previously reported papers [67–69].

3.2. Materials Characterization

A typical tube reactor was a 5 m long with the 316 L stainless steel tubing (OD: 1.60 mm, ID: 1.27 mm) body coated with 190 mg of a 12 wt % Pt/SiO\textsubscript{2} catalyst (Figure 14). Several cross-sections of catalyst-coated tube reactor were studied using a Carl Zeiss Sigma scanning electron microscope equipped with an energy-dispersive X-ray detector (Oxford Instruments, Abingdon, UK). The catalyst tube was filled with a conductive resin to ensure that the coating layer is not damaged during the polishing. The Pt loading was determined by EDX taken at several areas along the coating.

Figure 13. The comparison of cumulative COL yield over the Pt/SiO\textsubscript{2} catalysts in batch, fixed bed and tube reactors at the same condition (0.1 g 12 wt % Pt/SiO\textsubscript{2}, CAL concentration: 0.1 M in IPA, pressure: 10 bar and temperature: 90 °C).

Figure 14. Photograph of a 5 m 1.27 mm ID Pt/SiO\textsubscript{2} coated tube reactor along with a pound coin for scale.
The specific surface area and pore volume were determined from nitrogen adsorption–desorption isotherms using a Micromeritics ASAP 2020 instruments (Norcross, GA, USA). For these experiments, the catalytic coating was mechanically removed from the tube, dried at 160 °C under vacuum for 5 h prior to the measurements. The powder obtained was also redispersed in acetone and applied on a carbon-coated copper grid. Several images with more than 100 Pt nanoparticles were obtained using a Jeol 2000FX transmission electron microscope (Akishima, Tokyo, Japan). From these images, the particle size distribution was obtained by ImageJ software (V 1.4.3.67) [70].

Powder X-ray diffraction (XRD) patterns were measured between 10–80° (2θ) on a PANalytical Empyrean diffractometer in Bragg–Brentano geometry with Co Kα radiation (1.7903 Å) (Malvern Pananalytical B.V., Almelo, The Netherlands). A beam knife was used to reduce the air scatter at low angles. Small-angle X-ray scattering (SAXS) measurements were made using a Xenocs Xeuss 2.0 equipped (Sassenage, France) with a micro-focus Cu Kα source collimated with Scatterless slits. The scattering was measured using a Pilatus 300 K detector with a pixel size of 0.172 μm x 0.172 μm. The detector was translated vertically and the images combined to form a virtual detector with double the number of pixels. The distance between the detector and the sample was calibrated using silver behenate (AgC_{22}H_{43}O_{2}), giving a value of 1.192(5) m. The magnitude of the scattering vector (q) is given by 

\[ q = 4\pi\sin\theta/\lambda \]

where 2θ is the angle between the incident and scattered X-ray and λ is the wavelength of the incident X-rays. This results in a q range for the detector of 0.01 Å⁻¹ to 0.5 Å⁻¹. The powder samples were mounted between two sticky Kapton windows. A radial integration as function of q was performed on the 2D scattering profile and the resulting data corrected for the sample absorption and background from the sample holder.

The temperature-programmed desorption (TPD) experiment was performed by placing the 50 mg powdered sample into a quartz tube 4 mm ID between 2 layers of quartz wool. The quartz tube was placed into a tube furnace and connected to a system presented in Figure 15. Prior to the measurements, the sample was calcined at 550 °C in the flow of 10 vol % O₂ in He in the total flow rate of 12 mL min⁻¹ (standard temperature and pressure, STP) and cooled down to 100 °C in the flow of He. Afterwards, pyridine was introduced by passing a flow of He 4 mL min⁻¹ (STP) through a vessel with liquid pyridine at the temperature of 14.7 °C for 30 min. The sample held at 100 °C was then purged with a He flow of 13 mL min⁻¹ (STP) for 2 h to remove the weakly adsorbed species followed by the temperature ramping to 550 °C at the heating rate of 8 °C min⁻¹. The gases from the quartz reactor passed through the PTFE tubing to minimize adsorption [71] into a quadrupole mass spectrometer that monitored the concentration of pyridine.

3.3. Hydrogenation in a Continuous Flow System

The continuous flow system used for the testing is schematically presented in Figure 16. The photograph of the system was shown in our recent paper [72]. The CAL solution (IPA as solvent)
was fed with a HPLC pump (Knauer P4.1S HPLC pump, Berlin, Germany). The H₂ gas was fed with a mass flow controller (Bronkhorst, Suffolk, UK). The reactor (tube or fixed bed) was placed in a convection oven (Carbolite Gero, Parsons Lane, Hope, UK). The pressure in the reactor was maintained by a back-pressure regulator (Equilibar, Fletcher, NC, USA). The system was operated in a fully automated mode with the samples taken for analysis into vials equipped with septa to minimize sample evaporation. The collection time was at least 3 times the liquid residence time to ensure a representative sample. The sampling was repeated at least twice for every measurement to ensure reproducibility. The analysis of liquid samples was performed by an offline gas chromatograph Shimadzu GC-2010 plus equipped with an Agilent DB-5 30 m 0.25 mm ID column and an FID detector (Kyoto, Kyoto Prefecture, Japan).

A reference fixed-bed study was performed in a glass column of 6.6 mm internal diameter (Omnifit, Kinesis Inc., Vernon Hills, IL, USA) filled with 190 mg of the same Pt/SiO₂ powder packed between 2 layers of glass beads (100 μm in diameter). The fixed bed was placed into the same system used for the tube reactors and operated by the same procedure.

Prior to the experiments, the catalyst was reduced in-situ in the H₂ flow of 10 mL min⁻¹ (STP) for 30 min at 50 °C. Leaching of Pt during the reaction was analyzed by concentrating about 1 L of the product solution to about 5 mL by evaporating the substances, extracting Pt with aqua regia on heating and analyzing the aqueous extract using the inductively coupled plasma-optical emission spectrometry (ICP-OES) using a PerkinElmer 5300 DV ICP-OES instrument (Waltham, MA, USA).

The CAL conversion was calculated by Equation (1), and the COL selectivity was calculated by Equation (2).

\[
X_{\text{CAL}} = 1 - \frac{C_{\text{CAL}}}{C_{\text{COL}} + C_{\text{HCAL}} + C_{\text{HCOL}} + C_{\text{others}}} \tag{1}
\]

\[
S_{\text{COL}} = \frac{C_{\text{COL}}}{C_{\text{CAL}} + C_{\text{HCAL}} + C_{\text{HCOL}} + C_{\text{others}}} \tag{2}
\]

where \(C_i\) represents concentrations of reactants and products which determined by the GC analysis.

Taylor flow with the alternating gas and liquid slugs was observed under all the conditions studied [73]. The average liquid residence time in the flow reactor was estimated by Equation (3).

\[
\tau_{\text{res}} = \frac{V_r}{F_L + \frac{F_g}{p}} \tag{3}
\]

where \(V_r\) is the reactor volume, \(F_L\) is the liquid flow rate, \(F_g\) is the gas flow rate (STP) and \(p\) is the reactor pressure.
The turn-over number (TON) was calculated by Equation (4).

\[
TON = \frac{C_{CAL,\text{in}} X_{CAL} F_L t}{n_{Pt}}
\]  

(4)

where \( C_{CAL,\text{in}} \) is the inlet reactant concentration of CAL, \( X_{CAL} \) is the average conversion during the time on stream (t), \( n_{Pt} \) is the total moles of Pt on the coating.

The turn over frequency (TOF) was obtained by Equation (5):

\[
TOF = \frac{C_{CAL,\text{in}} X_{CAL} Q}{n_{Pt} D}
\]

(5)

where \( D \) is the Pt dispersion, which was obtained by Equation (6) [36].

\[
D = \left( \frac{3.32 d_{Pt}}{d_p} \right)^{0.813}
\]

(6)

where \( d_{Pt} \) is the Pt atomic diameter and \( d_p \) is the nanoparticle diameter obtained from the TEM images.

### 3.4. Hydrogenation in a Batch Reactor

The batch hydrogenation was performed in a 160 mL stainless steel autoclave reactor (Parr) at a stirring rate of 1200 rpm under the same temperature, pressure and the substrate concentration as in the flow experiments. A total liquid volume of 100 mL was used. The Pt/SiO\(_2\) catalyst (0.1 g) was dispersed in isopropanol (IPA, 90 mL) and reduced in situ for 15 min in H\(_2\) at 90 °C. Then a 1.0 M CAL solution (10 mL) containing 0.1 M tetradecane (internal standard) was added. The reactor was pressurized to start the reaction. The liquid mixture was sampled periodically and analyzed by the same offline GC.

### 4. Conclusions

A selectivity of 90.0% to cinnamyl alcohol at a 98.8% conversion of cinnamaldehyde was achieved in a continuous flow tube reactor wall-coated with a 12 wt % Pt/SiO\(_2\) catalyst at 90 °C and a pressure of 10 bar. After a short period on stream, the formation of acetics was completely suppressed in the catalyst-coated tube reactor substantially increasing the selectivity to the target product. Both activity and selectivity were higher than that in the batch and fixed bed reactor at the same conditions. A turnover number of 3000 was reached in the flow reactor in 110 h and it enables to reduce catalyst costs by an order of magnitude. The change in the reaction rates over time demonstrated a strong product inhibition. The activity and selectivity were restored after a combined reduction and solvent flushing treatment performed in 10 h intervals. A calcination treatment of catalyst regeneration after eight reaction cycles completely restored the initial activity and selectivity. A product throughput of 0.36 kg g\(_{Pt}^{-1} \) day\(^{-1}\) was obtained in the single tube reactor. This value was three times higher than previously reported in literature. A possibility for further process intensification was demonstrated by the operation at higher temperature and even shorter residence times. The reaction rate was increased by 2.5 times at 150 °C without major decay in selectivity. Also the deactivation rates and catalyst leaching levels remained similar to that observed at 90 °C. Furthermore, the catalyst does not need to be separated from the substrates or the products by filtration or centrifugation after the completion of reactions, because it was coated inside of the reactor.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/2073-4344/8/2/58/s1](http://www.mdpi.com/2073-4344/8/2/58/s1), Figure S1. Acetal formation with CAL and HCAL. Figure S2. Increasing reaction rate with the reaction temperature.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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