

Monitoring Surface Processes During Heterogeneous Asymmetric Hydrogenation of Ketones on a Chirally Modified Platinum Catalyst by Operando Spectroscopy**

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Dedicated to the MPI für Kohlenforschung on the occasion of its centenary

Abstract: Surface processes occurring at the catalytic chiral surface of a cinchona-modified Pt catalyst during the asymmetric hydrogenation of activated ketones have been monitored for the first time using operando ATR-IR spectroscopy. Fundamental information about this catalytic system could be gained, including the chiral modification process of the catalyst, the surface interaction of reactant ketone with preadsorbed chiral modifier, the role of hydrogen as well as the influence of the product enantiomers in the catalytic cycle. The formation of a diastereomeric transient surface complex between ketone and chiral modifier was found to be related to the ketone consumption. Among the studied activated ketones, a correlation between stereoselection and the strength of the intermolecular hydrogen bond was identified. Dissociated hydrogen from the catalytic surface is found to play a crucial role in the formation of the diastereomeric surface complex.

Catalysis on chiral surfaces can offer an interesting alternative to homogeneous asymmetric catalysis with chiral transition metal complexes because of the inherent advantages regarding stability, handling, separation, regeneration, and recyclability of the solid catalysts.^[1] These properties make them also better amenable to continuous processes.^[2]

Among the various strategies for designing a heterogeneous enantioselective catalyst^[3] one of the most successful is to chirally modify a metal catalyst by addition of a strongly adsorbing chiral compound, the so-called chiral modifier. In the hydrogenation of activated ketones on Pt catalysts chiral modification of the catalytic surface with cinchona alkaloids leads to remarkable activity and enantioselectivity with an enantiomeric excess (*ee*) of up to 98%.^[4]

Unfortunately, the performance of this catalytic system is highly sensitive to the molecular structures of the ketone and chiral modifier, and even the nature of the solvent and the

hydrogen pressure can strongly influence the enantioselection.^[5] Mechanistic models reported in the literature widely agree upon the decisive role of a 1:1 modifier–reactant ketone diastereomeric surface complex.^[6] The molecular skeleton of the diastereomer cinchonidine (CD, Figure 1 A) with a basic tertiary amine function (quinuclidine, QN) connected by two chiral C atoms (C'8 (*S*), C'9 (*R*)) to a strongly adsorbing aromatic ring system (quinoline ring, Q) is nearly ideal for chiral modification of metal catalysts, providing strong stereocontrol in the Pt-catalyzed asymmetric hydrogenation of activated ketones, including, for example, the hydrogenations of ketopantolactone (KPL) to (*R*)-pantolactone, trifluoroacetophenone (TFAP) to (*R*)-phenyl trifluoromethyl ethanol ((*R*)-PTFE) and methyl benzoylformate (MBF) to methyl (*R*)-mandelate.^[6a]

Generally mechanistic models proposed for these reactions are based on competing enantioselective and racemic catalytic cycles^[7] as depicted in its simplest form in Scheme 1. However, more complicated schemes have also been pro-

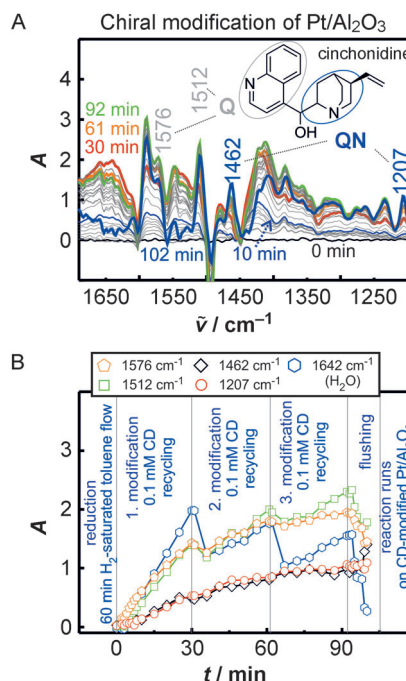
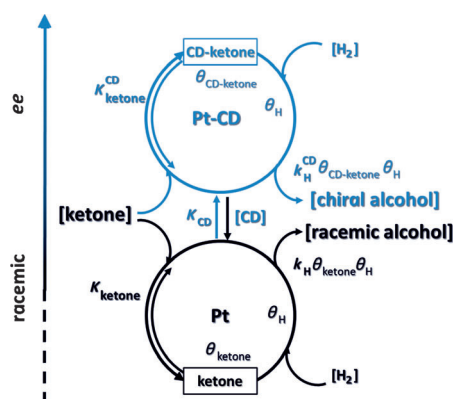


Figure 1. A) Surface spectra and B) transient profiles of CD adsorption onto the prerduced 5 wt % Pt/Al₂O₃ from toluene solution containing 0.1 mM CD for 3 × 30 minutes at 298 K. The recycle reactor volume was exchanged within 1 minute. Absorbance values are divided by 10^{−3}.

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Scheme 1. The two-cycle-two-step mechanism for the asymmetric hydrogenation of activated ketones on CD-modified platinum. Adsorption of CD onto the Pt surface creates chiral sites (Pt-CD) at which the prochiral ketone is stereoselectively hydrogenated by the formation of a diastereomeric surface complex (CD–ketone).

posed.^[8] According to the general mechanistic scheme, originally symmetric Pt sites (Pt) forming racemic product are transformed to asymmetric Pt sites (Pt-CD) by addition of CD to the liquid reaction solution. Interaction between reactant ketone and coadsorbed CD leads to the formation of a diastereomeric intermediate surface complex (CD–ketone) inducing the stereochemical control for the hydrogenation to the corresponding chiral product alcohol.

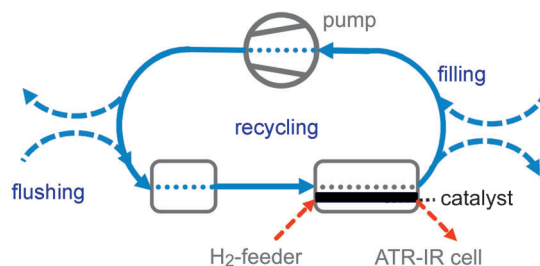
Up to date, most mechanistic studies of the surface processes relevant to asymmetric hydrogenation on chirally modified platinum catalysts have been carried out *ex situ*^[9] or under conditions relatively far from those encountered in practice.^[10] Recently, we investigated the adsorption–desorption behavior of TFAP and CD on the Pt catalyst applying modulation excitation spectroscopy and phase-sensitive detection revealing the formation of a diastereomeric complex between TFAP and CD involving a N–H–O-type hydrogen bond.^[11] In another *in situ* spectroscopic study on the asymmetric hydrogenation of KPL, we found evidence for an additional stereodirecting interaction between the alcoholic OH group of CD and a carbonyl C=O group of the cyclic α ketoester, which appears to be relevant for explaining the excellent enantioselection achieved with this substrate.^[12] While these *in situ* IR studies have been carried out in a similar chemical environment as encountered in the catalytic reaction, the methods applied captured only a snapshot of the surface at quasi-steady state and neither measurable catalytic turnover nor optical yield could be observed. This limitation leaves behind some uncertainty whether the observed species are actively participating or simply “spectators” in the catalytic cycle.^[13] The junction of spectroscopic and kinetic data would help to overcome this current limitation of the *in situ* techniques and speed up progress in the field.^[14]

With this in mind, we have made an effort here to monitor the surface processes occurring during the catalytic enantioselective hydrogenation of ketones on a CD-modified Pt catalyst under real working conditions. We studied the dynamic molecular interactions between reactants, products, and modifier at the catalytic solid–liquid interface using

operando ATR-IR (attenuated total reflection) spectroscopy. Our study simultaneously provides catalytic activity and molecular information about crucial interactions on the CD-modified technical 5 wt % Pt/Al₂O₃ catalyst in the presence of H₂ and the solvent toluene. Achieving essentially the same activity and *ee* as in a conventional semi-batch reactor, our analytical set-up provides spectroscopic data facilitating a molecular level understanding of the catalytic cycle under realistic working conditions.^[15] To accomplish monitoring of the catalytic process in the solid–liquid–gas system under actual working conditions a new ATR-IR reactor cell had to be designed providing excellent signal sensitivity (signals on the order of 0.00001 a.u. are detectable) suitable to probe the solid–liquid interface. The spectroscopic reactor cell (0.115 mL void volume) was implemented into a recycle loop (2.885 mL volume) in which the consumed hydrogen was continuously replaced mimicking a semi-batch reactor set-up with a recycling ratio greater than 7 (Scheme 2). In the focus of our study were the surface processes occurring during the chiral modification of the Pt/Al₂O₃ catalyst as well as the transient formation of the diastereomeric surface complex between coadsorbed CD and ketone substrate during the hydrogenation of KPL, TFAP, and MBF. Furthermore, the role of hydrogen, initial ketone concentration and the influence of chiral product alcohol in the enantiodifferentiating surface process were investigated.

The three operational modes applied in the operando study are highlighted in Scheme 2: flushing or filling of the recycle reactor system with H₂-saturated toluene solutions as well as recycling of the reaction mixture.

After reduction in flushing mode, 0.1 mM CD solution was admitted to the system and recycled for 30 minutes. Adsorption of the modifier on the prereduced catalyst is observable in the surface spectra in Figure 1A and the transient IR absorptions of a few assorted bands (1207 and 1462 cm^{−1}— δ (CH₂) of QN, 1512 and 1576 cm^{−1}—ring stretches of Q,^[16] 1642 cm^{−1}— δ (OH) of adsorbed water) are shown in Figure 1B. Clearly, accumulations of Q and QN moieties of CD followed at the solid–liquid interface obeyed different kinetics and at least two adsorption geometries coexisted. While the increase of Q absorption modes was readily observable after an initial delay, IR signals assigned to QN grew significantly slower. However, replenishing the CD solution after 30 and 61 minutes revealed strong adsorption of the CD surface species detected at 1207 and 1462 cm^{−1}. Particularly, toluene flushing after the modification process showed that signals originating from the aromatic ring system of CD must have been also masked by loosely bound species.



Scheme 2. The analytical set-up highlighting the three operational modes: filling, recycling, and flushing.

In contrast, the selected vibrational modes of the tertiary amine moiety must have originated from another stable surface species which appeared to reach saturation coverage after the 3rd modification and even resisted solvent flushing strongly.

Because a dipole moment change oriented parallel to a metal surface is cancelled out (Greenler's surface selection rule),^[17] in previous IR studies several coexisting adsorption geometries of the modifier could be identified and CD anchored with a flat-lying Q has been proposed to be the crucial species responsible for enantioselection.^[10] The stable CD species observed in our semi-batch reactor system most likely accumulated on Pt because of strong, nearly parallel adsorption of Q and the detected molecular vibration originating from wagging and scissoring of CH₂ of QN indicate a nonparallel, non/weakly adsorbed state of the interacting moiety. In the asymmetric hydrogenation of TFAP, premodification for only one run resulted in nearly half the *ee* compared to three runs (15 instead of 25 *ee* %, see Table S1) which is a strong indication that accumulation of this CD species (intensity at 1207 cm⁻¹ almost doubles after two additional runs) is connected to the enantiodifferentiating process.

The time-resolved surface plot presented in Figure 2 displays the vibrational changes on the CD-premodified Pt/Al₂O₃ catalyst induced by exchanging the solution in the recycle reactor with H₂-saturated toluene solution containing 5 mM KPL and recycling it for 5 minutes. The fast hydrogenation to pantolactone was evident from its growing absorption bands, for example, at 3548 and 1126 cm⁻¹ (ketone and alcohol liquid-phase spectra are shown in Figure S4). After toluene flushing, GC analysis of the effluent confirmed a ketone conversion (*X*) of 62 % (TOF 332 h⁻¹)

and an *ee* of 63 %. Repeating the hydrogenation run several times afforded the same *X* and *ee* indicating the absence of loss of activity within the time frame of reaction, despite only preadsorbed CD was present on the catalyst.

Upon admission of dissolved ketone the most interesting spectral feature is a broad and dynamic absorption band in the $\tilde{\nu}(\text{N-H})$ stretch region which is assigned to an intermolecular interaction between coadsorbed chiral modifier and reactant.^[18] The IR absorption peaking at 2730 cm⁻¹ originates from a hydrogen-bonded N-H-O vibration between the quinuclidine N atom of coadsorbed CD and the keto carbonyl O atom of KPL as depicted in the inset in Figure 2. Broadness and shape of the band indicate high flexibility and a dynamic nature of the observed bond which appears to get better defined during the 2nd and 3rd run. Replacing H₂ by D₂ confirmed the origin of the absorption band which shifted to 2310 cm⁻¹ in the surface spectra of the corresponding deuteration (additional hydrogenation and deuteration results provided in Figures S2 and S3) because of the isotope effect, indicating the formation of a N-D-O bridge. According to the transient spectroscopic data, rates of formation and consumption of this diastereomeric surface complex (CD-ketone in Scheme 1) lead to increase its surface concentration under the chosen reaction conditions, and hence to its detection as transient surface species.

The kinetic behavior of the observed active species can be better highlighted in the transient absorption profiles presented in Figure 3A. To corroborate the significance of the intermolecular hydrogen bond between modifier and ketone on the Pt catalyst as key interaction in the formation of the enantiodifferentiating surface complex, asymmetric hydrogenations have also been investigated on the CD-premodified catalyst for other important activated ketones, for example, TFAP and MBF. The obtained catalytic activities and enantioselectivities are in good agreement with values reported in the literature for MBF,^[19] TFAP,^[8b,19a] and KPL hydrogenations^[19a,20] at 1 bar H₂ pressure using toluene as solvent. For all three reactant ketones the kinetic sequence of the surface process can be described by the mechanism in Scheme 1: subsequent to modification of Pt adsorbed CD interacts with ketone leading to the formation of a relatively stable diastereomeric surface complex indicated by its characteristic N-H-O bond; after initial equilibration the surface coverage of the CD-ketone complex reaches a quasi-steady state and continuous alcohol product formation is observed at the solid-liquid interface. Toluene flushing and refilling of the reaction solution corroborated the different rates of formation and consumption of the observed species. Comparing the kinetic behavior among the different ketones, asymmetric hydrogenations of KPL and MBF lead to good enantioselectivities (both 62 *ee* % in the 3rd run) but the reaction is significantly faster for the keto-lactone (343 compared to 59 h⁻¹). While higher conversion of the ketone is reflected in the absorption profile of the corresponding alcohol, correlation of the N-H-O absorption bands to surface coverage of the CD-ketone complex is not straightforward and stereoselectivity is obviously not directly related to their peak intensities. Besides the extent of ketone accumulation at the CD-Pt sites, the orientation of the

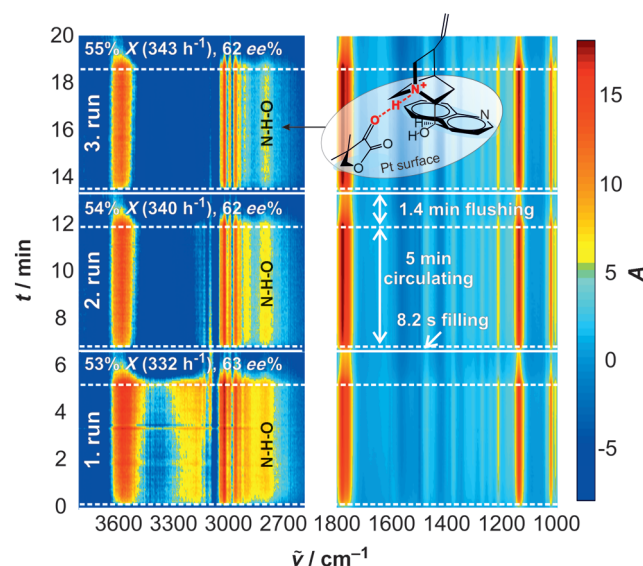


Figure 2. Time-resolved surface spectra of three hydrogenation runs (5 minutes recycling) of H₂-saturated toluene solution containing 5 mM KPL at 298 K on CD-modified Pt/Al₂O₃. The cycle volume was exchanged within 8.2 s with a flow rate of 22 mL min⁻¹. Conversion (TOF) and *ee* were determined by GC after the toluene flushing. Absorbance values are divided by 10⁻⁴ and 10⁻³ in the high and low wavenumber region, respectively.

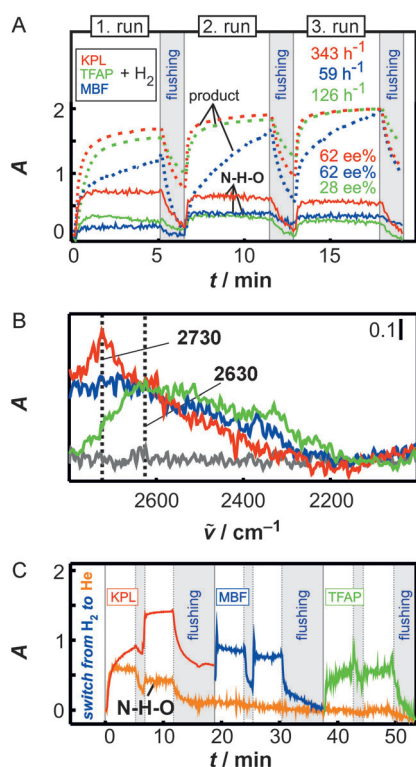


Figure 3. A) Transient monitoring of the CD–ketone surface complex (N–H–O band) during the asymmetric hydrogenation of 5 mm KPL (red), TFAP (green), and MBF (blue) at 298 K on CD-Pt/Al₂O₃. Alcohol product formations are also depicted. Turnover frequencies and *ee* values are shown for the 3rd run. B) Shape and peak position of the N–H–O absorption band. C) Transient monitoring of the N–H–O band formation (orange) after switching to He-saturated solution (H₂-Feeder switched off). Absorbance values are divided by 10⁻⁴.

intermolecular N–H–O bond with respect to the catalytic metal surface is also reflected in the intensity of this vibrational mode (surface selection rule)^[17] which might differ depending on the specific ketone.

Nevertheless, an interesting correlation of stereoselection with respect to the peak position of the N–H–O band is found which is depicted in Figure 3B. While for the α -ketoesters (62 *ee*%) the N–H–O band peaks at around 2730 cm⁻¹, its center is red-shifted in the presence of the α -trifluoro ketone (28 *ee*%). As the reduced masses of the atoms involved in the N–H–O bond formation are exactly the same, the bond strength (force constant) has to be lower for the trifluoro-activated ketone according to Hooke's law and simple harmonic motion. It can be assumed that a weaker interaction to the modifier at the asymmetric site is responsible for the decline of the enantiodifferentiation.

Another striking observation with respect to the formation of the intermolecular hydrogen bond was made in the absence of hydrogen. As seen in Figure 3C, after switching from H₂- to He-saturated solutions, the N–H–O band began to decrease. After removal of remaining surface hydrogen due to reaction, the surface complex formation was suppressed for all three ketones. The suppression of the intermolecular interaction in absence of H₂ as well as the observation of the shifted N–D–O band formation in the

deuteration on the CD-modified Pt (Figures S2 and S3) are strong indications that chemisorbed hydrogen is necessary for the formation of the intermolecular interaction. Obviously, surface hydrogen is able to interact with the quinuclidine N atom of CD to initiate the hydrogen bridge to the substrate even in aprotic toluene, which is in agreement with previous computational studies.^[21]

As illustrated in Figure 4A,B, and in accordance to the equilibrium involving the concentration of the transient CD–ketone complex in Scheme 1, the coverage of the diastereomeric surface complex increased at higher initial ketone concentration. Furthermore, the kinetic dependence of the quasi-equilibrated surface coverage of the modified sites on available ketone was reflected in the quicker initial increase of the N–H–O band at 50 mm TFAP. In contrast to KPL and MBF, in the hydrogenation of TFAP on the premodified catalyst the *ee* to (*R*)-PTFE increased incrementally with repeated hydrogenation runs from 25 % in the 1st run to 31 % in the 5th run (see Figure 4A and Tables S4 and S5 in the Supporting Information). Such a positive effect on enantioselection could be connected to a competitive adsorption between residing CD molecules from the modification process and TFAP at chirally modified sites or to potentially beneficial effects of formed chiral product alcohol.

To test the latter hypothesis, enantiopure trifluoro products were added to the feed. This addition caused a strong drop in conversion and enantiomeric excess, as indicated in Figure 4A. Interestingly, the desired right-handed product led

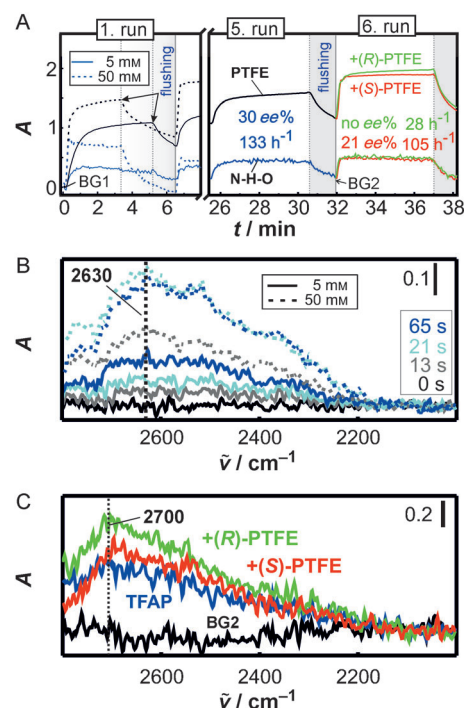


Figure 4. A) Transient monitoring (1st, 5th, and 6th run) of the CD–ketone surface complex (N–H–O band) during the asymmetric hydrogenation of 50 mm (dashed line) and 5 mm TFAP (solid line) as well as after addition of 5 mm (*R*)- (green) and (*S*)- (red) alcohol products in the 6th cycle at 298 K on CD-Pt/Al₂O₃. Alcohol product formations are also depicted. Shape and peak position of the N–H–O absorption band depending on B) the ketone concentration and C) chiral product addition. Absorbance values are divided by 10⁻⁴.

to a more prominent decrease than the undesired (*S*)-alcohol. The loss in enantioselection can be traced back to a similar interaction between acidic product alcohol and adsorbed modifier. The surface spectra in Figure 4C reveal that the right-handed stereochemistry in (*R*)-PTFE facilitates the interaction with the CD-modified site and the desired acidic alcohol product is more prone to block access to the asymmetric site by also forming an N–H–O type hydrogen bond. The signal indicative of the alcoholic N–H–O bond even appears at higher wavenumber (stronger bond) than the corresponding ketonic bond indicating that the bond formed with the product alcohol is strong enough to compete with that of available ketone. This contrasts with the hydrogenation of KPL and MBF where enantioselection was not significantly influenced by the corresponding alcohol (see Tables S2 and S3) and no interaction between CD and ester alcohols could be detected.

In conclusion, applying operando ATR-IR spectroscopy to the multiphase asymmetric hydrogenation of activated ketones on cinchona-modified Pt catalyst provides fundamental information about the interrelation between catalytic performance and molecular structure at the chiral catalytic solid–liquid interface. The spectroscopic data demonstrate the formation of a transient diastereomeric intermediate surface complex between adsorbed CD (chiral site) and reactant ketone at the catalytic Pt surface. Furthermore, the study confirms the formation of a N–H–O hydrogen bond interaction between coadsorbed CD and ketone which appears to be at the origin of enantioselection. Additionally, the direct involvement of hydrogen in the intermolecular hydrogen bridge is observed during the asymmetric hydrogenation in aprotic toluene. Fundamental information regarding the modification step, the role of the activated ketone, and hydrogen as well as the influence of chiral product alcohol could be gained. For the cinchona-Pt system, α -ketoesters appear to be more suitable substrates based on their stronger hydrogen-bond interaction with the modifier compared to trifluoro-activated ketones which is reflected by the higher achievable *ee* (up to 98%) with these substrates. In addition, the properties of the corresponding product alcohol also play a role for achieving efficient turnover at the asymmetric site and the proton donor ability of the trifluoro alcohol impedes optimum enantiodifferentiation.

Experimental Section

ATR-IR spectra were recorded on a Bruker 70v spectrometer equipped with a liquid-nitrogen-cooled MCT detector at 4 cm⁻¹ resolution. A film of 5 wt% Pt/Al₂O₃ catalyst (BASF-Engelhard 4759; platinum dispersion, 0.22, BET surface area, 168 m² g⁻¹)^[6b] was deposited on an ZnSe internal reflection element (IRE, bevel of 45°, 72 mm × 10 mm × 6 mm, Specac Ltd), and placed in a specifically home-built flow-through cell. Two two-position-four-way valves (VICI) allowed for admission of solutions from two different glass-bubble tanks as well as recycling of the reaction solution. The reactor cell and the periphery of the recycle reactor had a volume of 0.115 and 2.885 mL, respectively. By the use of a micro annular gear pump (HNP) a liquid flow rate of more than 22 mL min⁻¹ was achievable creating excellent mixing in the system. Prior to admission, solutions were saturated with hydrogen at atmospheric pressure. In addition, an in situ H₂-feeder built in-house allowed for maintaining the hydrogen

concentration during the hydrogenation. Details of the experimental procedure are available in the Supporting Information.

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