

Homogeneous hydrogenation in supercritical fluids mediated by colloidal catalysts

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Abstract

As an intermediate form between homogeneous and heterogeneous catalysis, catalysts based on transition metal colloids have drawn a lot of attention in recent years. Mating advantages from different concepts of catalysis, they turn out to be highly active, selective, and, in addition, easily separated from other reaction components. Even though colloidal catalysts are widely used in conventional solvents, hardly anything is known about their reactivity in supercritical fluids such as supercritical carbon dioxide (scCO₂). Furthermore, scCO₂ is an especially attractive, non-toxic, and environmentally benign solvent for chemical reactions. When hydrogenations were conducted using polymer-supported colloidal Pd nanoparticles as catalysts in scCO₂, we found turnover frequencies (TOFs) as high as 4 000 000 h⁻¹ even at a reasonably low hydrogen pressures of 15 bar and temperatures of 50 °C. To our surprise, their reactivity turned out to be much higher than those of most other catalysts reported in the literature. The kinetics of their catalytic reactions in supercritical fluids has been investigated using in situ NMR in combination with a toroid cavity autoclave (TCA). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical carbon dioxide; Turnover frequency; Toroid cavity autoclave; Colloidal catalysis

1. Introduction

In recent years, catalytic reactions involving supercritical fluids have drawn substantial attention in both industrial applications and basic research [1,2]. Ever since the early work of Rathke et al. [3] and Jessop et al. [4], several advantages have been reported about catalysis in supercritical media, and individual hydrogenations and hydroformylations were conducted in supercritical fluids, whereby both heterogeneous

[5] and homogeneous catalysts have been used. [6–8] Especially, supercritical carbon dioxide (scCO₂) is valued as a modern solvent for it is environmentally benign, nontoxic, readily available, and inexpensive. Diffusivities in scCO₂ are higher and viscosities lower as compared to conventional organic solvents. Prominently, gases are completely and fast miscible with scCO₂ at all ratios. In addition, the dissolution properties vary with the supercritical density. (Fig. 1 shows the pressure dependence of the density of carbon dioxide at various temperatures above and below the critical temperature, T_c . In a typical experiment, the temperature is set to $T = 50$ °C, the pressure to $p = 150$ bar, yielding a density d of about 0.65 g/cm³.) Hence, subsequent separation of the start-

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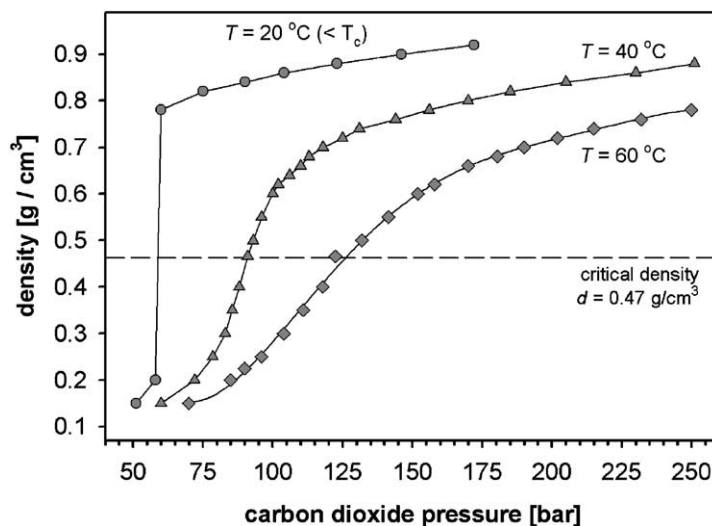


Fig. 1. Pressure dependence of the density of carbon dioxide, below and above the critical point. The typical working range for our experiments is $T \approx 50^\circ\text{C}$, $p \approx 150$ bar and, hence, $d \approx 0.65$ g/cm³.

ing materials, reaction products, and catalyst from the solvent CO₂ is easily achieved through temperature or pressure changes. Once a reaction is finished and the CO₂ has been vented, the only task left is to separate the catalyst from the product and, eventually, from remnant starting material. Colloidal catalysts dissolved in scCO₂ pose an interesting alternative, since they are readily extracted by ultra-filtration or vacuum distillation. Yet, colloidal catalysts are believed to show lesser activity in supercritical media, and so far their applications have practically been limited to bi-phasic systems [9]. Combining the two attractive concepts of modern homogeneous catalysis, namely using colloidal catalysts in combination with supercritical fluids as the solvent, it is possible to obtain products in high purity with only traces of remnant solvent or catalyst.

In this contribution, we report the fast and highly efficient, single-phase hydrogenation of alkynes in scCO₂ mediated by a polymer-supported colloid catalyst in which catalytically active, bimetallic Pd/Au nanoparticles are situated in block copolymer micelles of polystyrene-*block*-poly-4-vinylpyridine. The catalyst is obtained via living anionic block-copolymerization [10] with simultaneous reduction of suitable metal salts. Structural studies have shown that the

surfaces of the nanoparticle consist exclusively of Pd while Au forms the cores.¹

The reactions were carried out and investigated in situ with the toroid cavity autoclave (TCA) NMR technology according to Woelk et al. and Rathke et al. [12–14]. The TCA² is a cylindrical autoclave that also functions as a toroid cavity NMR detector. It allows us to quantitatively monitor the starting material and the products without disturbing or quenching the reaction, and to evaluate reaction rates and turn over frequencies (TOFs) accordingly [15]. Fig. 2 shows the time dependence of the NMR signals for the hydrogenation of phenyl ethyne to styrene and the hydrogenation of the latter to ethyl benzene (left axis). The curves follow classical A-to-B and B-to-C kinetics, which are nicely obtained applying the TCA and in situ NMR. The conversion (right axis, Fig. 2) is determined from

¹ Structure and properties of bimetallic colloids formed in polystyrene-*block*-poly-4-vinylpyridine micelles: catalytic activity in selective hydrogenation of dehydrolinalool. Characteristic data of the polymer: $M_n = 19\,400$, $M_w = 22\,500$, relative 4-vinylpyridine content $X_{4-vp} = 0.34$, micelle size 12 nm, bimetallic particle size 2 nm. The colloid catalyst is suspended in toluene with a Pd concentration of 6.6 mmol l^{-1} , see [11].

² A more detailed description of the TCA for in situ NMR in supercritical fluids will be given elsewhere, see [16].

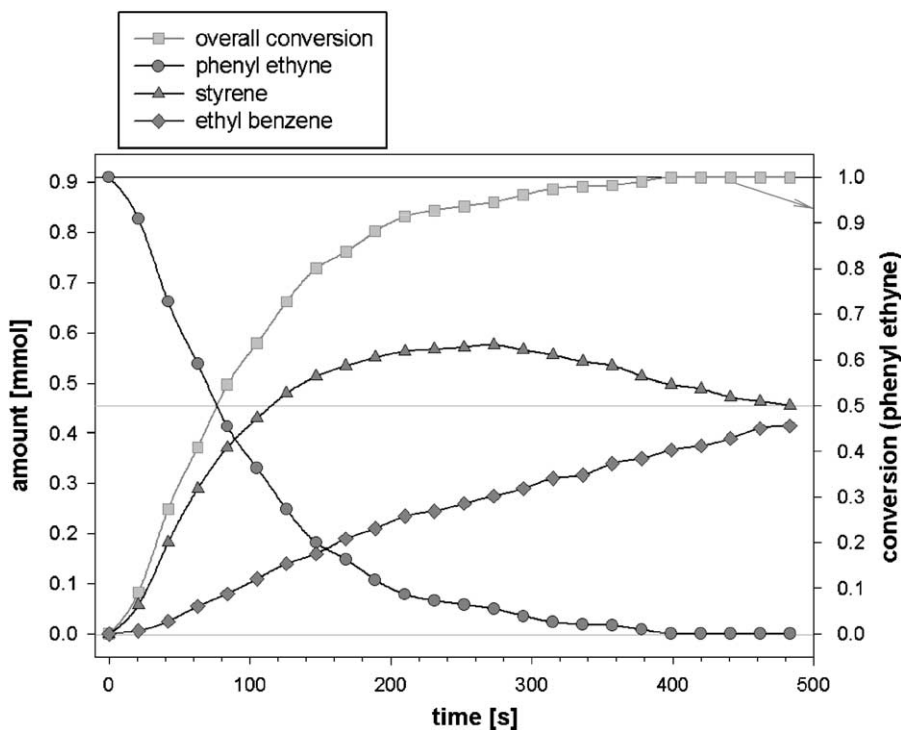


Fig. 2. Investigating the kinetic behavior of the colloid-catalyzed hydrogenation of phenyl ethyne applying in situ NMR and the TCA technology. The conversion (cubes, based on phenyl ethyne consumption) as well as the time dependence of phenyl ethyne (circles), styrene (triangles), and ethyl benzene (diamonds) are shown. Conditions: $p(\text{CO}_2) = 150 \text{ bar}$, $p(\text{H}_2) = 15 \text{ bar}$, $T = 50^\circ \text{C}$, $\text{SCR} \approx 6500$.

the consumption of the starting material phenyl ethyne. To outline the general utility of this method, only the first step of this reaction is used for the analysis of the TOF and to monitor the reaction progress.

Since this particular catalyst was originally developed for hydrogenation of alkynes, i.e., the stereoselective hydrogenation of dehydrolinalol to linalol (see footnote 2) in toluene at ambient pressure, the following substrates were used in this investigation: 1-hexyne, 3-methyl-3-hydroxy 1-pentyne, 3,3-dimethyl 1-butyne, phenyl ethyne, and 1-phenyl 3-propyne. This set was chosen to represent different electronic and sterical properties, which will allow us to obtain some indirect information about the catalyst site and the coordination of the substrate to the active site of the catalyst and about its efficiency toward different substrates. The substance 3-methyl-3-hydroxy 1-pentyne was chosen to mimic the dehydrolinalol hydrogenation. The experiments described in the following will demonstrate the very fast hydrogenation

of the substrate by this colloidal catalyst dispersed in scCO_2 . In our opinion, this example opens up new ways for modern catalysis, since this method yields products of high purity at very high reaction rates.

2. Experimental

For all investigated reactions, the procedure is as follows. The TCA (sample volume = 2.8 ml) was charged with 100 μl of the substrate (between 0.80 and 0.90 mmol, depending on molar mass of the substrate) and 20 μl of the colloid catalyst (0.132 μmol Pd) suspended in toluene. A substrate-to-catalyst ratio (SCR) of about 6500 is calculated from the nominal amount of Pd in the catalyst; however, for steric reasons, only a portion of Pd can be catalytically active at one time, i.e., several Pd atoms need to form an "active site" (vide infra). In the experiments with higher SCRs for the hydrogenation of 1-hexyne, the amount of catalyst

was reduced along with the increase of substrate. After the TCA is sealed, the reactive mixture is brought to a temperature of 50 °C and pressurized with CO₂ up to 150 bar using a supercritical-fluid-extraction and HPLC syringe pump (ISCO). After allowing for a few minutes for the dissolution of the reactive components, the main magnetic field of the NMR magnet is shimmed for optimized homogeneity. Thereupon, typical line widths of 1–2 Hz are achieved, even though the TCA is fabricated from a piece of a commercial (diamagnetic) copper alloy. Subsequently, hydrogen is added through an especially designed non-return valve, upon which the acquisition of the NMR spectra is started immediately. The pressures given for hydrogen do not represent the partial pressure within the supercritical mixture; rather, hydrogen is added to the carbon dioxide until a respective increase of the pressure (i.e., of 2–15 bar) is reached. This change in pressure is called the “hydrogen pressure” from here on. We wish to point out that this follows common practice in high-pressure catalysis. In addition, experiments conducted previously by our group we have shown that pressures of carbon dioxide and hydrogen are almost additive at this pressure level.

A macro program of the spectrometer provides for exact timing when acquiring consecutive spectra, which facilitates the analysis of the kinetics of the product formation. Typically, 50 spectra with an interim delay of 20 s are recorded. With the integrated

signal intensity of the alkyne proton of the substrates as a standard, NMR intensities were converted into concentrations.

3. Results and discussion

At a hydrogen pressure of 15 bar, a temperature of 50 °C, and a carbon dioxide pressure of 150 bar, our catalytic reactions reach TOFs of more than 4 000 000 h⁻¹ depending on the starting material, the hydrogen pressure, and the SCR. Accordingly, they are among the fastest known in catalysis. Considering the rather modest reaction conditions as employed here, these results are quite remarkable and *not* to be expected from current literature predictions in either homogeneous or heterogeneous catalysis. Fig. 3 depicts the results for all substrates used at a hydrogen pressure of 15 bar and 50 °C as a bar plot; the TOFs were determined from the time of 50% conversion of the starting material. This procedure to determine the TOF follows common practice. The use of initial rates for the calculation of the TOF, which is also widely used, would lead to much higher values. An SCR of about 6500 (i.e., 20 μl of colloidal catalyst dispersed in toluene, and about 100 μl of the substrate) has been used in all cases. Since the molar masses of the substrate are slightly different, the SCR varies accordingly around an average value of

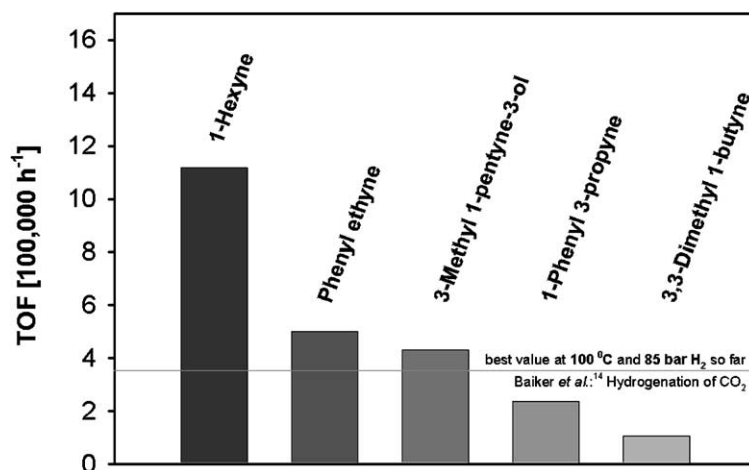


Fig. 3. Bar plot showing the TOF for the substrate used at a SCR \approx 6500. Conditions: $p(\text{CO}_2) = 150$ bar, $p(\text{H}_2) = 15$ bar, and $T = 50$ °C. The so far best TOF value ($360\,000\text{ h}^{-1}$) for the hydrogenation of CO₂ in scCO₂ as reported by Baiker et al. is shown as a line for reference.

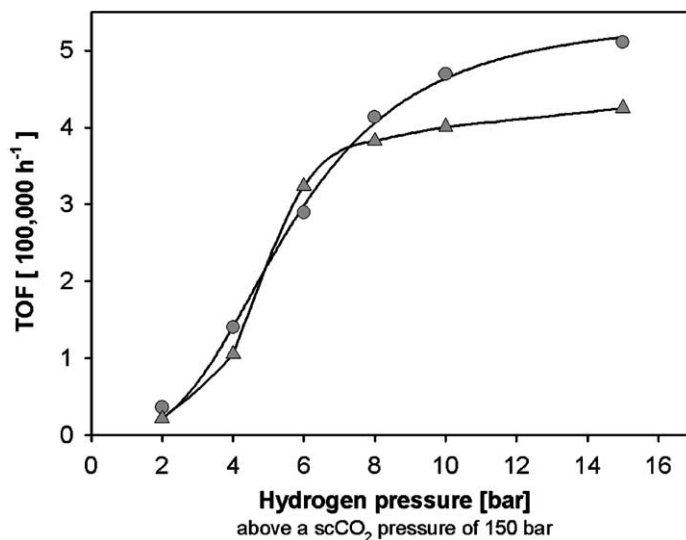


Fig. 4. Pressure dependence of the TOF for the hydrogenation of phenyl ethyne and 3-methyl-3-hydroxy 1-pentyne under the same conditions ($p(\text{CO}_2) = 150$ bar, and $T = 50^\circ\text{C}$, $\text{SCR} \approx 6500$).

6500. In addition, it is noted that, in the calculation of the TOFs, the smallest reasonable active site was assumed. From a comparison between the Pd atom diameter and the spatial demand of our relatively small reactive acetylenes, we assume that this smallest site consists of at least seven Pd atoms, i.e., of one central atoms that is symmetrically surrounded by

six other Pd atoms. Consequently, the TOFs reported here represent minimum values that could potentially be significantly higher, i.e., if an active site consists of more than seven Pd atoms [15]. A similar approach to visualize the catalytically active site on a surface of a nanoparticle was previously introduced by Besson et al. [17].

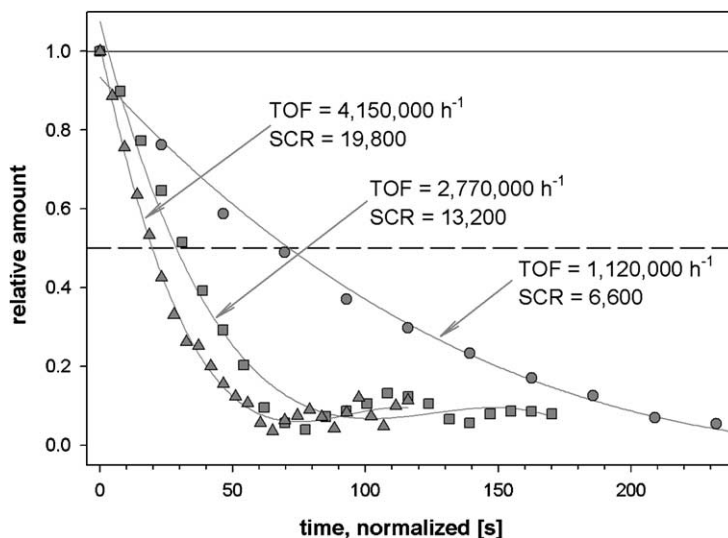


Fig. 5. Varying the SCR for the same substrate 1-hexyne. Conditions: $p(\text{CO}_2) = 150$ bar, $p(\text{H}_2) = 15$ bar, and $T = 50^\circ\text{C}$.

In the series of hydrogenations in which all five substrates described above were used, TOFs ranging from 100 000 to more than 1 000 000 h^{-1} were determined. Even our “slowest” reaction involving the

sterically hindered 3,3-dimethyl 1-butyne proceeded much faster than any other known, i.e., for almost any substrate in conventional solvents, such as hexane or benzene.

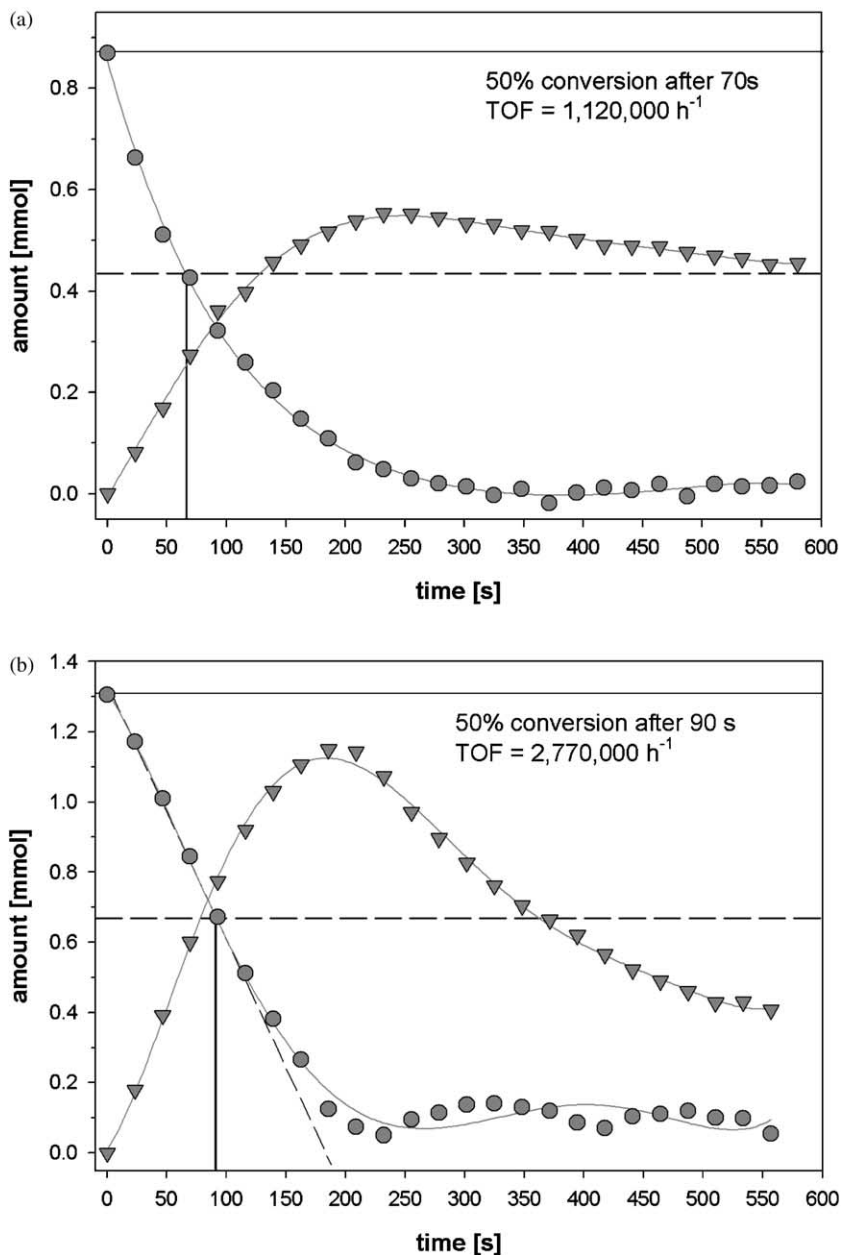


Fig. 6. Varying the SCR for the same substrate 1-hexyne. The change from first order kinetics (a) to zero-th order kinetics (b) is shown for two SCRs. The figure represents an expanded view of Fig. 5.

Fig. 4 shows the pressure dependence of the TOF for the hydrogenation of phenyl ethyne and 3-methyl-3-hydroxy 1-pentyne applying hydrogen pressures between 2 and 15 bar. Again, only the consumption of the starting material is monitored and used in calculating the TOF at 50% conversion. Increasing the hydrogen pressure to above 15 bar hardly increases the TOF in the reaction with either substrate, indicating that the concentration of hydrogen is not rate limiting.

Our investigations of the dependence of the TOF on the substrate and pressure raise the question, how to increase the reaction rate even further: does the catalyst operate at its maximum capacity and how is that determined? Following classical kinetics, a reaction that is limited by the concentration of only one component is of pseudo first order with respect to that component. Furthermore, saturation of the catalyst occurs at high substrate concentrations, and a change in reaction order is anticipated with respect to the substrate. Hence, varying the SCR changes the order of the reaction from first to zero-th order. Fig. 5 shows the consumption of the starting material 1-hexyne (where the highest TOF was reached before, see Fig. 3), for different SCRs of 6600, 13 200, and 19 800. It is noted that both axis of the graph have been normalized to allow for comparison of the three plots in one graph. As is outlined, the TOF rises from about 1 000 000 to over 4 000 000 h⁻¹. To examine the progress of the reaction more clearly, the plots for an SCR of 6600 and 13 200 are shown in Fig. 6a and b, respectively. It follows from Fig. 6 that the decrease of the concentration of 1-hexyne with time follows an exponential function for an SCR of 6600. By contrast, using an SCR of about 13 200, a linear change is observed for the time of the first six data points. This linear change indicates the change in pseudo reaction order. Fig. 6a and b also demonstrate the change in selectivity of the reaction, i.e., the time dependence of the formation of styrene is different for the two SCRs.

Further investigations revealed that the reaction seems to be partially inhibited by aromatic compounds, such as styrene, ethyl benzene, or toluene. Hence, we feel that the reaction has even more potential for optimization and may lead to further increased TOFs. For example, the substitution of toluene as the dispersing solvent or the variation of the reaction conditions are most promising.

4. Conclusions

The TOFs as determined here for these colloid-catalyzed hydrogenations in scCO₂ at a moderate hydrogen pressure (15 bar) are among the highest known in catalysis. They rank at least one order of magnitude above those reported for conventional solvents. Comparable but still up to an order of magnitude smaller values have so far only been reached in catalytic reactions conducted at higher temperatures, at much higher hydrogen pressures, or when carbon dioxide—i.e., the solvent—was directly hydrogenated [18]. In conclusion, we have identified and investigated an example of a highly efficient single-phase catalytic hydrogenation in scCO₂ mediated by a polymer-supported colloidal catalyst. It is conceivable and even highly likely that colloidal catalysts in scCO₂ will yield high TOFs in other catalytic cycles as well. Since for such high activity a high solubility of the catalyst in scCO₂ is crucial [18,19], it follows from our data that this originally in toluene dispersed colloid catalyst must become directly dispersed in scCO₂ during the course of this highly efficient hydrogenation.

After the reaction is completed, the catalyst can readily be recovered by ultra-filtration, hence, the catalyst may be reused many times. Consequently, colloid catalysis in combination with the modern and environmentally benign solvent scCO₂ can lead to ultra-fast catalytic reactions. Products demanding an especially high purity can be obtained through this elegant combination of a modern solvent with a modern catalyst. Lastly, it is noted that the colloid-stabilizing polymer did not need to be modified from its original formulation to enhance solubility in scCO₂, whereas most other homogeneous catalysts have to be adapted via functionalization with highly fluorinated alkyl moieties [1].

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