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The Role of the Reactor Wall in Hydrothermal Biomass Conversions

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Dedicated to Prof. Herman van Bekkum on the occasion of his 80th birthday

Abstract: The processing of renewable feedstocks to platform chemicals and, to a lesser degree, fuels is a key part of sustainable development. In particular, the combination of lignocellulosic biomass with hydrothermal upgrading (HTU), using high temperature and pressure water (HTPW), is experiencing a renaissance. One of the many steps in this complicated process is the in-situ hydrogenation of intermediate compounds. As formic acid and related low-molecular-weight oxygenates are among the species generated, it is conceivable that they act as a hydrogen source. Such hydrogenations have been suggested to be catalyzed by water, by bases like NaOH, and/or to involve "reactive/nascent hydrogen". To achieve the temperatures and pressures required for HTU, it is necessary to conduct the reactions in high-pressure vessels. Metals are typical components of their walls and/or internal fittings. Here, using cyclohexanone as a model compound for more complex biomass-derived molecules, iron in the wall of high-pressure stainless steel reactors is shown to be responsible for the hydrogenation of ketones with low-molecular-weight oxygenates acting as a hydrogen source in combination with water.

Keywords: biomass · formic acid · high temperature and pressure water · reactor wall · reduction

Introduction

The processing of lignocellulosic biomass to platform chemicals and fuels is likely to provide a pivotal resource stream in the near future. Aqueous media are becoming increasingly attractive to induce "green" chemical conversions as water is an environmentally benign solvent. The use of high temperature and pressure water (HTPW) as a medium is particularly useful because of its unique properties in terms of heat- and mass-transfer, solvation power, and raised acidity/basicity.[1,2] Near the supercritical point, the physiochemical properties of water can be finely tuned by changing the temperature and/or pressure. Recently, many new reaction systems have been developed using such a water phase as a reaction medium and/or catalyst.[3,4] Compared to other thermochemical methods, hydrothermal treatments of biomass offer an advantage as they eliminate the need to dry wet biomass and as HTPW may simultaneously act not only as a solvent but also as a reactant and effective acid–base catalyst.[5] However, this approach gives rise to complex cascading reaction systems in which (ligno-)cellulosic biomass not only converts into a liquid biocrude oil and various water-soluble organic species (e.g., furans and catechols), but also partially degrades into corrosive low-molecular-weight oxygenates like formic acid. Therefore, a particularly attractive cascade to investigate is the decomposition of these problematic small oxygenates into carbon dioxide and hydrogen in such a way as to incorporate the hydrogen generated into the liquid products. Since one of the key targets in the conversion of biomass into synthetic fuels is the reduction in oxygen content of the liquid products, using the corrosive acids to do so would eliminate them as a problem and improve the quality of the fuels or fuel precursors simultaneously.

Within this context, a major reaction cascade is the reduction of aldehydes or ketones to the corresponding alcohols in the presence of small acids, for example, formic acid,[6] followed by their dehydration. Such reactions have been suggested to be catalyzed by water,[1,5,7] by bases like NaOH[8–10], and/or to involve "reactive/nascent hydrogen"[11–13] in HTPW. However, there is currently no consensus in the literature as to the precise way in which formic acid is decomposed and how any hydrogen generated is subsequently incorporated during the reduction of, for example, ketones.

The thermal decomposition of formic acid in dilute aqueous solutions involves two competitive reaction paths: decarboxylation, producing CO_2 and H_2, and decarbonylation/dehydration, producing CO and H_2O.[1,5,7,14–16] In contrast to the gas-phase decomposition by decarbonylation, the main route in the liquid phase under sub- or supercritical conditions is decarboxylation.[15–17] Ruelle et al.[18] have suggested first that water catalyzes the liquid-phase decarboxylation path (Figure 1). Later, Melius et al.[19] considered the potential catalytic effect of water in both the decarboxylation and

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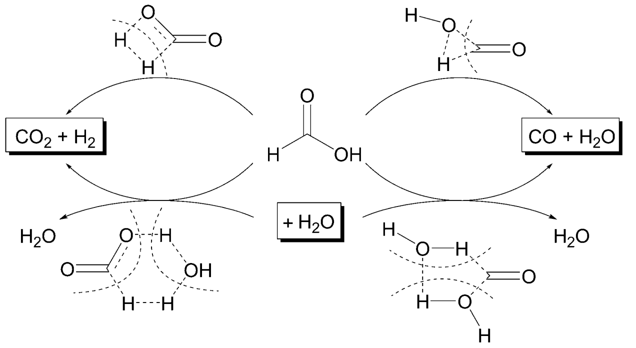

Figure 1. Molecular elimination mechanisms for the decomposition of formic acid; curved dotted lines indicate the eventual decomposition products.[20]

the dehydration reactions. The literature provides many studies on this topic,[20–25] taking into account the possible effects of density, surface-catalyzed reactions, and ionic or radical mechanisms. However, although all of the experimental results have confirmed that the decarboxylation is the main reaction path under supercritical or near-supercritical conditions, several inconsistencies regarding the mechanism of formic acid decomposition in the presence of water have not been fully resolved.

Hydrogen produced by the thermal decomposition of formic acid or HCOOX (X = Na or NH_4) via the decarboxylation route can be used for the hydrogenation of different functional groups.[11–13,26,27] The reductions of aldehydes, ketones, and nitroaromatics in HTPW using HCOOH, HCOONa, and $HCOONH_4$ have been performed in both batch-[26] and continuous-flow tubular reactors[27] without any co-solvent or added catalyst. Similarly, 2-propanol has been proposed as hydrogenating agent in different reactions under hydrothermal conditions without any additional metal catalyst.[28] Furthermore, Kleinert and Barth[11–13] reported a novel pyrolysis/solvolysis process of lignin conversion to liquid "oils". They showed that formic acid can serve as both hydrogen donor and reaction medium in the liquification process and that using alcohols as co-solvent can improve the yields and the hydrogen-to-carbon ratio of the products. The authors assumed that the high reactivity of the in situ-formed hydrogen is responsible for the lignin conversion into hydrogen-rich products without added catalyst. However, these and similar reports have not excluded the catalytic wall effect of the reactor experimentally.

Although many reports on HTPW processing can be found in the literature, fewer than ten publications[17,20,29–34] hint that the observed conversions are to some degree a result of wall-effects. Bjerre and Sørensen[17] have described experimental results using two different autoclaves (a new and a frequently used one) for the oxidative and non-oxidative decomposition of formic acid. They have found that the 'used' vessel resulted in a higher conversion of formic acid, higher yields of CO_2 and H_2, and a lower yield of CO. The authors attributed the differences in the results obtained from the two different reactors to the surface of the 'frequently used' reactor being rough and corroded and thereby influencing the reaction.

By examining the water–gas shift reaction under hydrothermal conditions, Brill and Miksa[35] have shown that the extremely toxic $Ni(CO)_4$ was formed by extraction of Ni from a slightly corroded 316 stainless steel (SS316) tube. These results are consistent with metals leaching from the reactor.

The first studies of the water–gas shift reaction under supercritical conditions and in the absence of any metals were performed by Potic[36a] and DiLeo,[36b] using small sealed quartz capillaries. Later, Savage[34,37,38] examined the non-catalytic gasification of cellulose and lignin using capillary quartz reactors as a metal-free environment, employing the same technique as had Potic and co-workers.[36] These results consistently show that the yields of the gases generated are strongly influenced by the presence of stainless steel, as the yields are lower in metal-free quartz reactors.

Shen et al.[39] recently published a hydrogen-transfer reduction process for ketones using formic acid as a hydrogen donor in HTPW. They attributed the catalytic effect to the water, as they found no difference in the conversion of ketones using a Teflon-lined batch reactor with and without added pieces of SS316 (their reactor's material). However, contact of the reaction mixture with metal parts of the reactor (stirrer, sampling tube, cap of the vessel, etc.) needs to be considered and was not mentioned in that paper. By contrast, Mondo et al.[40] more recently published findings that a 316 stainless steel reactor body is effective in the deoxygenation of sugar alcohols or levulinic acid and that the addition of 316 stainless steel powder to the reactor led to the formation of insoluble inorganic precipitates. The authors suggested that this effect is specific to aqueous Brønsted acidic solutions under a reducing atmosphere such as hydrogen. A promoting effect of the stainless steel has also been shown in hydrogenation reactions using supercritical carbon dioxide as a solvent at 50 °C.[41]

Thus, the literature is still unresolved in this field. While most attribute a catalytic effect to the HTPW under hydrothermal conditions, others do not exclude the effect of the reactor wall, yet are unable to define its role clearly. This study and the accompanying report[42] aim to resolve these issues and the role of the reactor wall more thoroughly. Through systematic study of a simple model compound system, it is demonstrated how the reactor wall plays an essential role in both formic acid decomposition and the eventual hydrogenation reactions. For simplicity and to allow straightforward reproduction of these results by other laboratories, cyclohexanone (**1**) was used as model compound and its hydrogenation to cyclohexanol (**2**), followed by the subsequent dehydration of the product **2** to cyclohexene (**3**) was investigated, using formic acid as a stoichiometric reductant and acid dehydration catalyst (Figure 2). The reaction was performed in both metal and metal-free reactors in HTPW.

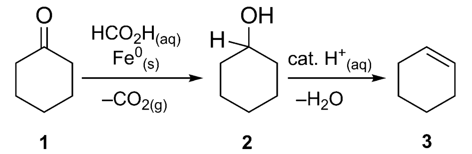

Figure 2. Formation of cyclohexanol (**2**) and cyclohexene (**3**) from cyclohexanone (**1**).

Results and Discussion

Cyclohexanone can be easily converted into cyclohexanol and cyclohexene in an aqueous solution of formic acid when using stainless steel (SS316) reactors. The variation of pressure (see Table 1, entries 1–10) by pre-pressurizing at the reaction temperature to 60–100 bar of nitrogen did not have any influence on the conversion or selectivity, whereas the variation in temperature, in addition to favoring cyclohexanol dehydration, results in a maximum cyclohexanone conversion apparently between 225 and 250 °C. This observation is consistent with the trends observed regarding the yields of gases during the decomposition of formic acid in supercritical water.[27] Therefore, a relative increase of formic acid should increase cyclohexanone conversion. As can be seen in Figure 3, this is indeed the case, with a plateau being reached at a formic acid/cyclohexanone molar ratio of about five. Notably, when using 2-propanol as hydrogen donor instead of formic acid, no conversion was observed, thus ruling out the Meerwein–Ponndorf–Verley (MPV) type hydrogenation mechanism.[43] Hydrogen gas is also not active under these conditions (Table 1, entry 11).

To investigate possible catalytic wall-effects of the stainless steel reactor in this system, the reactions were performed in a metal-free reactor, namely in a high-pressure sapphire NMR tube (with a titanium top) under the same conditions (taking care of the liquid-to-reactor volume ratios to ensure comparable pressures, see the Experimental Section). As no noticeable reaction in this metal-free environment was observed (Table 2, entries 1 and 2), neither using formic acid nor hydrogen gas as a hydrogen source, it is clear that the stainless steel in conventional autoclaves plays a crucial role under these conditions. Importantly, in the subsequent analysis by ^1H and ^{13}C NMR spectroscopy, using the still-sealed sapphire NMR tube, resonances due to formic acid could be observed, but none that were due to the formation of neither dissolved hydrogen, carbon dioxide nor carbon monoxide. The fact that a noticeable pressure build-up when opening the sapphire tube was also not observed is consistent with these NMR measurements.

To study the promoting effect of the reactor's material more fully, the metal-free sapphire reactor experiment was repeated in the presence of 316 stainless steel shavings (SSS). Both, the formation of cyclohexanol from cyclohexanone and noticeable additional pressure build-up inside the reactor, were observed when using formic acid, but no conversion was detected when using hydrogen gas as hydrogen source (Table 2, entries 3 and 4).

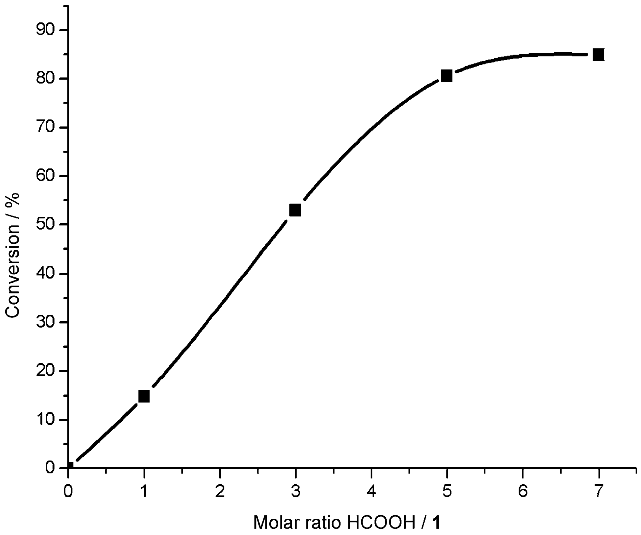

Figure 3. Effect of the amount of HCOOH on the conversion of **1**. Conditions: 250 °C, 80 bar, 4 h.

Table 1. The conversion of cyclohexanone (**1**) in aqueous formic acid in a 316 stainless steel reactor.

Entry	T [°C]	p [bar]	H-source	Conversion [%]	Selectivity [%]	
				1	**2**	**3**
1	200	60	HCOOH	72.5	10.2	89.8
2	225	60	HCOOH	89.0	4.4	95.6
3	250	60	HCOOH	50.6	3.7	96.3
4	200	80	HCOOH	73.5	10.0	90.0
5	225	80	HCOOH	82.2	4.7	95.3
6	250	80	HCOOH	85.2	2.5	97.5
7	200	100	HCOOH	71.0	9.4	90.6
8	225	100	HCOOH	89.8	3.6	96.4
9	250	100	HCOOH	81.7	2.6	97.4
10	225	80	–	–	–	–
11	225	80	H_2	–	–	–

Conditions: 0.2 mL of **1**, 0.2 mL of *n*-decane in 3 mL of aqueous acid solution, $t_{reaction}$ = 4 h. Molar ratio of H-source/water/**1** = 5:84:1. No formation of cyclohexane was detected.

Table 2. Reduction of cyclohexanone (**1**) with HCOOH in the presence of stainless steel shavings (SSS).

Entry	H-source	Amount of SSS [mg]	Conversion [%]	Selectivity [%]	
			1	**2**	**3**
1	HCOOH	0	1	100	–
2	H_2	0	0.0	–	–
3	HCOOH	550	20	66	34
4	H_2	550	0.0	–	–
5	2-propanol	550	0.0	–	–

Conditions: Molar ratio of H-source/water/**1** = 3:84:1, 250 °C, 4 h; although a direct measurement of the pressure was not possible, the conditions and volume ratios used mirror those used in the SS reactors, so approximately 80 bar pressure is assumed in each case.

These observations clearly demonstrate that the presence of a metal alloy, such as 316 SS or one or more of its components, is crucial for the reactions to occur. Importantly, despite the presence of 316 SS shavings, no conversion of cyclohexanone could be observed when using hydrogen gas as hydrogen source. This shows beyond doubt that 316 SS does not act as a hydrogenation catalyst under the reaction conditions, but that the metal surface and protons are involved in ketone reduction. Furthermore, these observations throw doubt on the role of water as a catalyst for formic acid decomposition. Although many studies have suggested water as a catalyst[18,19] for the decomposition of aqueous formic acid, these reports appear questionable now, at least for temperatures of up to 250 °C, as no decomposition of aqueous formic acid occurs in a metal-free environment.

However, water was observed to strongly promote the reaction of cyclohexanone with formic acid, either concentrated (water content 1.85 %, measured by Karl-Fischer titration) or dilute (water content 91.6 %), under otherwise identical conditions (Table 3), showing that additional water, although not necessary, is clearly beneficial.

Table 3. Comparison of the reactions with and without additional water.

Entry	Water	H-source	Conversion [%] **1**	Selectivity [%] **2**	**3**
1	+[a]	HCOOH	53	8.0	92.0
2	–[b]	HCOOH	29	7.9	92.2

[a] Molar ratio of H-source/water/**1** = 3:84:1. [b] Molar ratio of H-source/**1** = 3:1. Conditions: 250 °C, 80 bar, 4 h.

In the experiments above, the reaction mixture became pale green in the presence of stainless steel. To check whether the leaching of metals was influenced by the concentration of acid, 700 mg SSS were soaked in 3 mL diluted (2 M) and in concentrated formic acid (98 %) at room temperature. After 4 hours, no coloration could be observed in the case of the concentrated formic acid; however, a bluish-green color developed in the dilute solution. The control reaction carried out in the absence of formic acid did not result in any coloration of the reaction mixture. The corresponding trace metal analyses of the acid solutions are shown in Table 4.

The much more extensive leaching of metals in dilute acidic solutions is mirrored to some extent in the greater conversions that are observed in the presence of dilute acid, which is present when using ′additional water′ (see Table 3). This enhanced reactivity may be explained either by a greater supply of "fresh surface" to promote the reaction and/or by a greater concentration of reactive dissolved species originating from the wall's surface.

Table 4. The leaching of the most abundant metal components from 316 SS in concentrated and dilute formic acid solutions.

Metal	*c*(metal) [ppm] in conc. HCOOH	*c*(metal) [ppm] in 2 M HCOOH
Fe	61.7	17270
Cr	6.03	4068
Ni	1.13	1350

Concentrations of each metal were determined after leaching for 19 h at RT by inductively coupled plasma–atomic emission spectroscopy (ICP–AES).

To examine whether only one metal component of the stainless steel acts as an active species or whether a mixture of these metals is needed, the effects of the common constituents of 316 stainless steel were tested (Table 5) by repeating the sapphire tube experiments in the presence of powdered samples of each individual element under the same conditions as used to test the SSS. None of these powders (chromium, nickel, molybdenum, and carbon) were active in the formic acid-based reduction of cyclohexanone at 250 °C; however, the reaction did occur in the presence of iron or manganese (Table 6). As the ratio of Fe/Mn in 316 SS is approximately 35:1, it is reasonable to conclude that iron, rather than manganese, is the main reactive metal (although the involvement of manganese cannot be discounted completely). Again, regardless of the metal present, the use of gaseous H_2 as hydrogen source did not result in any reduction, which is consistent with the results obtained in the presence of SSS (Table 2).

Table 5. The principle components of 316 stainless steel.

Element	Fe	Cr	Ni	Mo	Mn	C
%	60–70	16–18	10–14	2–3	2	0.08

Table 6. Reduction of cyclohexanone (**1**) with HCOOH or H_2 in the presence of iron or manganese powder in the sapphire reactor.

Entry	Metal	H-source	Amount of metal [mg]	Conversion [%] **1**	Selectivity [%] **2**	**3**
1	Fe	HCOOH	570	55.4	37.5	62.5
2	Fe	H_2	530	0.0	–	–
3	Mn	HCOOH	250	4.8	100.0	0.0

Conditions: Molar ratio of HCOOH/water/**1** = 3:84:1, $[HCOOH]_{aq} = 2$ M, 250 °C, 80 bar, 4 h.

It has to be noted that the formation of by-products, such as iron formate(s) and oxide(s), were observed after the reaction when either SSS or iron powder was used under HTPW conditions. Analyzing the precipitates by X-ray diffraction (XRD) revealed that iron(II) formate hydrate, $Fe(OOCH)_2{\cdot}2H_2O$, which is easily oxidized to iron(III) formate hydrate under air, and magnetite (Fe_3O_4) were formed during the reaction. Moreover, according to the literature[44] $Fe(OOCH)_2{\cdot}2HCOOH$ is a green powder and can easily be converted into iron(II) formate dihydrate under these conditions.[45,46] This suggests that the green color observed during the treatment of the SSS with acid can be attributed to the presence of this compound. To test whether the iron formates and/or oxides formed during the reaction are active for the hydrogenation of cyclohexanone, they were prepared and tested separately in a metal-free NMR tube. No reaction was observed in any of these cases under HTPW conditions; thus, neither iron oxides nor iron formates promote the hydrogenation under the conditions outlined here. Notably, iron formate can decompose at higher temperature (above 250 °C)[45,46] which might explain the observations of CO and/or CO_2 during the investigation of the formic acid decomposition by other authors.[15–19,25]

In the case of manganese, a very vigorous reaction occurred (intensive gas production) when the metal was added to the acid solution. This rapid decomposition of formic acid to gaseous products in the presence of manganese results in the depletion of formic acid from the solution and, therefore, little formic acid is left to react with cyclohexanone, consistent with the low yields of cyclohexanol observed.

Conclusions

Cyclohexanone can be easily converted into cyclohexanol and mainly cyclohexene in an aqueous solution of formic acid in any of several common 316 stainless steel batch reactors, but no such reaction was observed to any degree in a metal-free sapphire reactor. However, reactivity can be induced in the metal-free reactor by adding metal shavings of stainless steel. Iron has been shown to be the likely principle actor in this reaction cascade. Furthermore, a dilute formic acid solution works more powerfully than a concentrated solution, corresponding to the extent of leaching observed. Although iron formates were isolated from the reaction, neither they nor common iron oxides promote these reactions. This clearly illustrates that the metal surface of the autoclave plays a crucial role under these conditions.

Therefore, any discussions regarding hydrogenations of (at least) ketones under HTPW conditions in the presence of small organic acids need to consider the wall-effect of the reactor. Furthermore, it can be surmised that in more complex systems, as are present in the case of the treatment of biomass under HTPW conditions, the reactor wall is likely to play a significant role. The role of the water, the fate of the iron, the composition of the hydrogen generated, and associated mechanistic considerations will be discussed more in detail in the accompanying report.[42]

Experimental Section

Cyclohexanone, cyclohexanol, *n*-decane, and formic acid (99 % purity) (all Sigma–Aldrich) were used without further purification. Quantitative analysis was performed on a Shimadzu GC-17 A Gas Chromatograph (GC) fitted with a Restek column (RTX5, 30 m × 0.25 mm × 0.25 μm) and equipped with an FID detector. Quantification was achieved by comparing integration values to those derived from standard curves (5 different concentrations) for the starting material and products, using authentic samples. In each GC run, *n*-decane was used as an internal standard. The injector and detector ports were maintained at 250 °C, and the analytes separated using a heating profile of 40 °C for 5 min (isothermal), followed by an increase to 130 °C at a rate of 10 °C min^{-1}. Retention times were: cyclohexene 5.7; cyclohexanol 11.1; cyclohexanol 11.4; and *n*-decane 14.5 min. All mass balances (relative to cyclohexanone) were ±10 % or better, most were ±5 % or better. Powder X-ray diffraction (XRD) measurements were made using a PANalytical X-Pert PRO MRD X-ray diffractometer equipped with a PIXcel detector, and using Ni-filtered $Cu_{K\alpha}$ radiation (λ 1.5419 Å) for the identification of the solid by-products formed during the reaction.

Hydrogenation of Cyclohexanone under HTPW Conditions in a Batch Reactor

Experiments were carried out in 15 mL 316 stainless steel standard batch reactors (AMTEC slurry phase reactor SPR-16) with individual pressure, temperature, and stirring control. Aqueous formic acid solutions (0.5–2 M, 3 mL) of cyclohexanone (0.2 mL) and of *n*-decane (0.2 mL) as an internal standard were measured into the vessels. The reactors were purged with nitrogen before being closed to remove the residual air, then heated up to 200–250 °C, reaching pressures of 40–80 bar. Additional nitrogen was added at the reaction temperature if the pressure had not reached the set value of 60, 80, or 100 bar. The reaction mixtures were stirred at the reaction temperature and pressure for 4 h. The reactors were cooled to ambient temperature, the residual pressure (20–40 bar) was released, and the reactors were opened. The reaction mixtures were separated by extraction with dichloromethane (2 × 45 mL) and dried over sodium sulfate. After filtration, the samples were analyzed by GC.

When H_2 was used instead of formic acid, the reactors were purged and pressurized with H_2 to 20 bar and then heated to the desired temperatures (200–250 °C), yielding pressures in the 40–80 bar range.

HTPW Treatment of Cyclohexanone in the Presence of Formic Acid in a Sapphire Tube

The metal-free experiments were carried out in a 7 mL sapphire high-pressure NMR tube (with a titanium top). Aqueous formic acid solutions (0.5–2 M, 2 mL) of cyclohexanone (120 mg) and *n*-decane (72 mg) as an internal standard were measured into the tube. It was purged with nitrogen, closed, and heated to the desired temperature in a sand bath. After a reaction time of 4 h, the sand bath was removed and the tube was air-cooled to ambient temperature. No pressure build-up was observed upon opening. The reaction mixture was extracted with dichloromethane (3 × 5 mL), separated, and the organic phase was dried over sodium sulfate. After filtration, samples were taken and analyzed by GC.

When H_2 was used instead of formic acid solution, the tube was purged then pressurized with 20 bar of H_2 before closing.

Hydrogenation of Cyclohexanone under HTPW Conditions in a Sapphire Tube

Dilute aqueous formic acid solution (0.5–2 M, 2 mL), cyclohexanone (120 mg), and *n*-decane (72 mg) as an internal standard were measured into the sapphire high-pressure NMR tube. Solid (250–550 mg) samples of stainless steel shavings or of iron, manganese, chromium, nickel, molybdenum, or carbon powder were added to the reaction mixture. The tube was purged with nitrogen, closed quickly, and heated to the desired temperature in a sand bath. The tube was not purged with nitrogen in the case of iron or manganese addition, as gas evolution was observed immediately after addition of the metal to the acidic solution. After a reaction time of 4 h, the sand bath was removed and the tube was air-cooled to ambient temperature. Significant pressure build-up was observed when using iron or manganese when it was opened. The reaction mixture was extracted with dichloromethane (3 × 5 mL), separated, and the organic phase was dried over sodium sulfate. After filtration, samples were taken and analyzed by GC.

Treatment of the SSS with Acid for ICP Analysis of the Metal Leaching

Two parallel experiments were carried out: SSS (700 mg) was soaked in diluted (2 M, 3 mL) and concentrated formic acid (98 wt %, 3 mL) at room temperature. After 4 h, no coloration was observed in the case of the concentrated formic acid; however, a bluish-green color developed in the dilute acid solution. The acid solutions were filtered and diluted to

25 mL with water. Quantitative analysis for the elemental composition of the three main elements present in 316 SS (Fe, Cr, Ni) was carried out using a Varian Vista AX ICP-AES equipped with a CCD detector.

Preparation of Iron(II) Formate ($Fe(OOCH)_2{\cdot}2\,H_2O$)

A 150 mL teflon-lined batch reactor was filled with formic acid solution (2 M, 28 mL), followed by addition of iron powder (1.3 g). The reactor was purged with N_2, quickly closed, and put into the oven at 250 °C for 16 h. After the reaction time, the reactor was cooled to room temperature, opened, and the white precipitate was quickly filtered under a N_2 atmosphere. The remaining solvent was removed under reduced pressure. The yield of iron formate was quantitative after the reaction. After 1 h in air, iron(II) formate dihydrate was spontaneously oxidized to iron(III) formate hydrate, $Fe(OOCH)_3{\cdot}x\,H_2O$, the change being observed as the white powder became brown. XRD measurements were performed to identify the products.[44,47]

Testing Iron Formates and Oxides for the Hydrogenation of Cyclohexanone

A 7 mL sapphire high-pressure NMR tube was filled with water (2 mL) or an aqueous formic acid solution (2 M, 2 mL). Cyclohexanone (**1**, 120 mg) and *n*-decane (72 mg) as an internal standard were added. Iron formate or oxide (magnetite or hematite) powder (250–350 mg) was added to the reaction mixture. The tube was purged with nitrogen, closed quickly, and heated to 225 °C in a sand bath. After a reaction time of 4 h, the sand bath was removed and the tube was air-cooled to ambient temperature. The reaction mixture was extracted with dichloromethane (3 × 5 mL), separated, and the organic phase was dried over sodium sulfate. After filtration, samples were taken and analyzed by GC.

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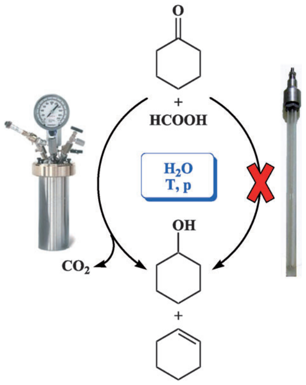
Biomass goes to the wall: The wall-effect of metal reactors is crucial in the high temperature and pressure water (HTPW) hydrogenation of cyclohexanone using formic acid as a reductant. Although it is possible to convert cyclohexanone into cyclohexanol and cyclohexene in a standard 316 stainless steel autoclave using HCOOH, it is impossible to do so in a completely metal-free environment, such as a sapphire high-pressure reactor. However, reactivity can be induced by adding metal shavings of stainless steel or iron.



Biomass Conversion

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The Role of the Reactor Wall in Hydrothermal Biomass Conversions