Biomass Utilization

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Solid Molecular Phosphine Catalysts for Formic Acid Decomposition in the Biorefinery

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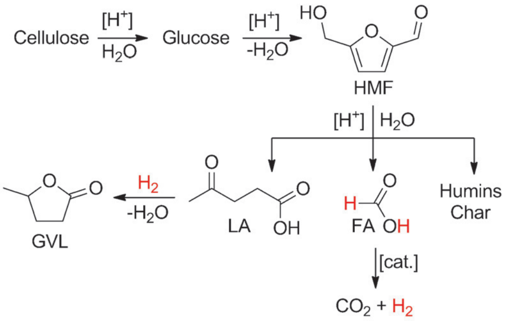
Abstract: *The co-production of formic acid during the conversion of cellulose to levulinic acid offers the possibility for on-site hydrogen production and reductive transformations. Phosphorus-based porous polymers loaded with Ru complexes exhibit high activity and selectivity in the base-free decomposition of formic acid to CO_2 and H_2. A polymeric analogue of 1,2-bis(diphenylphosphino)ethane (DPPE) gave the best results in terms of performance and stability. Recycling tests revealed low levels of leaching and only a gradual decrease in the activity over seven runs. An applicability study revealed that these catalysts even facilitate selective removal of formic acid from crude product mixtures arising from the synthesis of levulinic acid.*

Currently, many different routes for the sustainable production of fuels and chemicals from renewable resources such as biomass, CO_2, and solar energy are under intensive investigation. Perhaps, one of the most commercially viable routes is the conversion of cellulosic waste to levulinic acid (LA) (e.g. the Biofine process) (Scheme 1).[1]

LA is a useful platform chemical that offers several possibilities for valorization.[2,3] Hydrogenation yields γ-valerolactone (GVL),[4] which can be further converted to 2-MeTHF,[5] pentanoic acid,[6] and butenes.[7] These compounds find application as fuel additives, monomers, solvents, and fragrance intermediates. Likewise, the esters of LA are also useful as fuel components.[8] The synthesis of LA from cellulose proceeds via acid-catalyzed hydrolysis with the intermediacy of glucose and hydroxymethylfurfural (HMF). In the conversion of HMF to LA, formic acid (FA) is coproduced stoichiometrically.[9] The selective dehydrogenation of FA to H_2 and CO_2 provides an on-site hydrogen supply for reductive transformations, possibly in a one-pot fashion.[10] Catalytic FA decomposition is well known and can be achieved using a variety of transition metal complexes and supported metal catalysts. Particularly Ru/PR_3 and Ir/bipyridine complexes are highly active and selective for the synthesis and decomposition of FA.[11] They are typically studied in the context of hydrogen storage and fuel-cell applications.[12] Nevertheless, for the continuous decomposition of large volume streams of aqueous FA, heterogeneous catalysts are required. Recent reviews highlight that supported metal catalysts typically exhibit lower activities and selectivities than homogeneous catalysts.[13] Therefore, the immobilization of these complexes appears the most promising strategy for catalyst heterogenization. Zhao et al. studied Ru and Pd catalysts immobilized on SiO_2 functionalized with different heteroatom donor ligands (e.g., N, S, and P).[14] Turnover frequencies (TOFs) up to 960 h^{-1} were achieved at 80 °C for the Pd/S catalyst. Laurenczy et al.[15] tethered Ru/TPPTS on phosphine-modified MCM41 and reported TOFs up to 2780 h^{-1} at 110 °C. Stathi et al. immobilized Fe^{II} on phosphine-modified SiO_2 and obtained TOFs up to 7600 h^{-1} at 93 °C.[16] Bavykina et al. reported a biphenyl/pyridine-based CTF (covalent triazine framework) loaded with [Cp*Ir(OH)] for FA decomposition. At 80 °C, TOFs up to 27 000 h^{-1} were obtained.[17] These studies clearly demonstrate the high potential of immobilized catalysts. However, application under industrially relevant conditions requires materials that possess high corrosion resistance over a wide temperature range.[18] In this respect, porous organic polymers are clearly superior to organic/inorganic hybrid materials. For this purpose we have prepared phosphine-based cross-linked polymers as solid ligands for Ru complexes. The loaded materials were tested in the base-free aqueous decomposition of FA.



Scheme 1. Production of LA, its subsequent valorization, and on-site hydrogen production from FA.

Polymeric analogs of PPh_3 (pTPP), dppe (pDPPE), and 1,2-(diphenylphosphino)benzene (pDPPBe) were prepared using a previously developed method (Scheme 2).[19] The polymers were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), N_2 physisorption, transmission electron microscopy (TEM), and solid-state NMR spectroscopy (see the Supporting Information). The physical

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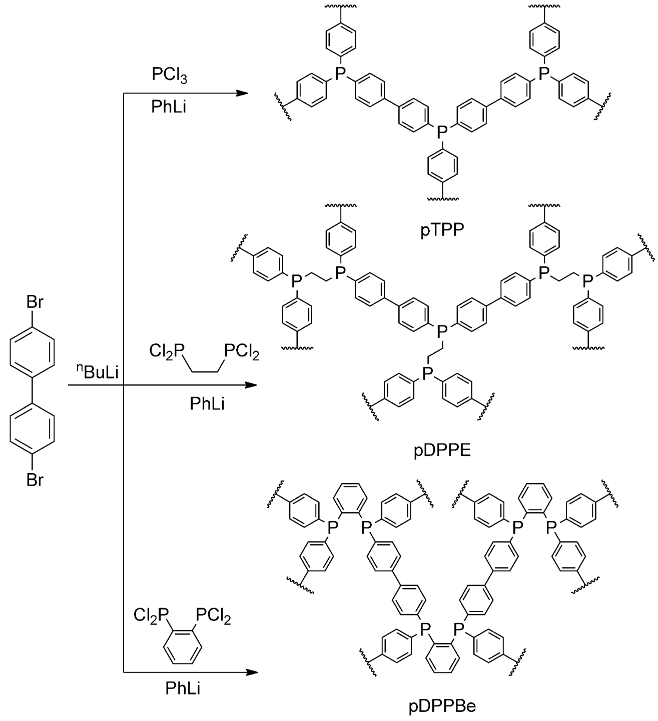

Scheme 2. Synthesis of phosphine-based cross-linked polymers.

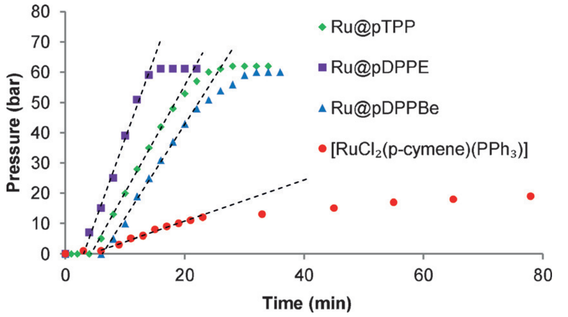

Figure 1. Reactor pressure of the Ru-catalyzed decomposition of aqueous formic acid at 160 °C (conditions: see Table 1.)

Table 1: Ru-catalyzed formic acid decomposition.[a]

Catalyst	FA conv. [%]	TOF [h^{-1}]	[CO]$_{(g)}$ [ppm]	[Ru]$_{(aq)}$ [ppm]	Ru loss [%]
blank[b]	2	–	n.d.	–	–
Ru/C[d]	24	810	7880	5.13	34.2
[RuCl$_2$(*p*-cymene)]$_2$[c]	23	750	3270	–	–
[RuCl$_2$(*p*-cymene) (PPh$_3$)]	30	2740	< 10	–	–
Ru@pTPP	99	15 050	67	0.22	0.7
Ru@pDPPE	99	22 900	13	0.19	0.6
Ru@pDPPBe	99	13 650	142	0.80	1.4

[a] Conditions: 50 mL Hastelloy autoclave, 15 mL aqueous solution (10 wt % FA, 2.17 M, 32.6 mmol FA), 0.022 mol % Ru, 160 °C. [b] 100 min. [c] 2.25 mg [RuCl$_2$(*p*-cymene)]$_2$, 80 min. [d] 15 mg Ru/C (5 wt %, 0.022 mol % Ru), 80 min.

and chemical properties of pDPPE and pDPPBe are quite similar to those reported previously for pTPP. The ^{31}P NMR spectra show that all phosphorus centers are trivalent and the ^{13}C NMR spectra confirm the proposed structures. All polymers are insoluble in common organic solvents, thermally stable (up to 340 °C), and XRD-amorphous, fluffy powders. The BET surface areas of pDPPE and pDPPBe range between 33 and 42 $m^2 g^{-1}$ and are somewhat smaller than that of pTPP (150 $m^2 g^{-1}$). TEM analysis shows that the materials are composed of polydisperse particles which are composed of coalesced smaller particles. In contrast to the particles of pTPP and pDPPBe, the particles of pDPPE are composed of clusters of discrete polydisperse spheres (see SI).

Previous studies on pTPP showed that leaching can be minimized by decreasing the metal loading;[19] therefore the polymers were loaded with 1 wt % [RuCl$_2$(*p*-cymene)] (MeOH, 2 days, RT). ICP analysis of the filtrates confirmed that approximately 95–99 % of the added complex was taken up by the polymers. The loaded materials (i.e., Ru@pTPP (P/Ru = 39 mol mol^{-1}), Ru@pDPPE (P/Ru = 51 mol mol^{-1}), and Ru@pDPPBe (P/Ru = 45 mol mol^{-1})) were tested in the base-free decomposition of aqueous FA at 160 °C (Figure 1, Table 1). A blank experiment run for 100 min gave only 2 % conversion, confirming that thermal decomposition is negligible. In the presence of Ru/C, conversion reached 24 % after 80 min and the pressure increased to 15 bar. Analysis of the gas phase revealed a large impurity of CO (7880 ppm) and ICP analysis showed that 34 % of the introduced metal had leached into solution. The performance of precatalyst [RuCl$_2$(*p*-cymene)]$_2$ was comparable to that of Ru/C with 23 % conversion after 80 min and the amount of CO was 3270 ppm. The monophosphine complex [RuCl$_2$(*p*-cymene)(PPh$_3$)] was also tested and gave a slightly better conversion of 30 % with a considerably improved H_2/CO_2 selectivity (CO < 10 ppm).

In contrast, the Ru-loaded polymers reached full conversion within 15–30 min in all cases (Figure 1). Following a short induction period of 4–6 min the pressure increased almost linearly, suggesting pseudo-zero-order kinetics. TOFs were estimated by using the pressure plots. The TOFs of Ru@pTPP (15 050 h^{-1}) and Ru@pDPPBe (13 650 h^{-1}) are comparable, whereas Ru@pDPPE exhibits a considerably higher TOF of 22 900 h^{-1}. CO concentrations of 67, 13, and 142 ppm were observed for Ru@pTPP, Ru@pDPPE, and Ru@pDPPBe, respectively. ICP analysis of the filtered reaction solutions confirmed low levels of Ru (0.2–0.8 ppm, equaling 0.6–1.4 % loss due to leaching). The ^{31}P NMR spectrum of the catalyst after the reaction showed no evidence of oxidation and only 1.5 ppm of phosphorus was detected in solution which confirms that loss of polymer through the filter is negligible. The obtained data clearly show that the polymer-supported catalysts are highly active and selective. Moreover they outperform the homogeneous analogue by an order of magnitude.

With these promising results in hand, Ru@pDPPE was chosen to study catalyst recycling in two ways (Figure 2). The first series of experiments was conducted following a start–stop procedure where a portion of pure formic acid was added after each run. The second method entailed a solvent-change procedure in which the catalyst was filtered and introduced into a fresh formic acid solution. All reactions were left until

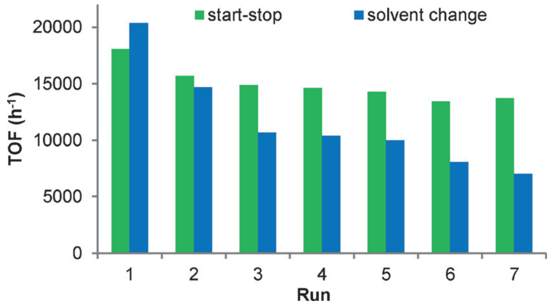

Figure 2. Recycling study of the Ru@pDPPE catalyst.

completion and a final TON of 30760 was achieved after seven runs for both series.

In the start–stop experiments, the TOF dropped significantly after the first run. After that, the rate decreased only slowly. At the end of the series still 76% of the initial activity remained, confirming that the supported catalyst is quite stable. The CO concentration slightly increased to 89 ppm and in the end 10% of the employed Ru had leached into solution. TEM images of the spent catalyst did reveal a few isolated Ru nanoparticles, but overall the catalyst was clean (see SI). Thus the data suggest that most of the metal remains molecularly dispersed on the polymer. In the solvent-change series the activity dropped rapidly in the first three runs. After this, the activity decreased more slowly and the CO concentration increased up to 318 ppm in the last run. Interestingly, the amount of leached Ru was consistently low (0.4–0.5%) during the first three runs. Therefore it is proposed that the steep decrease in activity stems from loss of the catalyst during the filtration procedure. After the fourth run, leaching increased (0.6–4.6%) and a cumulative amount of 11% was lost after the last run.

These results clearly demonstrate that the polymer-supported catalysts exhibit high activity and stability in clean dilute formic acid solutions. However, the conversion of cellulose to LA yields a complex mixture containing LA, FA, and H_2SO_4 as well as tar/chars and soluble humins. Insoluble by-products can be removed, for example, by filtration. Removal of H_2SO_4 with CaO yields $CaSO_4$, which in turn can be regenerated to CaO and SO_3. Suitable separation strategies for the other organic components include extraction or rectification. For example, LA can be extracted with organic solvents such as MeTHF. Alternatively, fractional distillation can be used to remove water/FA (azeotrope at 22% FA) and LA from the reaction mixture. Thus depending on the employed process design, different product streams can arise. Therefore, we chose to test the capability of the catalyst to work under various reaction conditions including different FA concentrations and the presence of sulfuric and levulinic acid, respectively. Finally, a crude mixture prepared via dehydration of glucose served as substrate for selective FA decomposition.

The influence of FA concentration was tested using Ru@pTPP (Table 2). The FA concentrations were set by varying the amount of water, while keeping the catalyst and FA amounts constant.

Table 2: Influence of formic acid concentration on the Ru@pTPP-catalyzed FA decomposition.[a]

FA conc. [wt%]	t [min]	FA conv. [%]	$[CO]_{(g)}$ [ppm]	Ru loss [%]
30	126	99	249	0.7
60	150	99	465	11.2
90	150	88	3108	31.3

[a] Conditions: 50 mL Hastelloy autoclave, 3 g (=97.8 mmol) FA, 75 mg Ru@pTPP (=0.0076 mol% Ru).

At 30 wt% FA, full conversion was observed after 126 min (TON 13160). The CO content of the gas phase was 249 ppm and 0.7% Ru leached. Compared to the data above (Table 1), the higher FA concentration led to a slight increase in CO production, but leaching was not affected. In contrast, at even higher FA concentrations both CO production and leaching increased severely. This suggests that at high concentrations the carbonic acid displaces the phosphine, leading to the formation of homogeneous species and possibly nanoparticles which exhibit significantly lower selectivity. Nevertheless, the data emphasize that up to 30 wt% FA can be tolerated without a significant effect on catalyst performance.

The influence of the presence of LA and H_2SO_4 was tested using Ru@pDDPE (Figure 3). With 0.33 equiv LA (with respect to FA) in 10 wt% FA solution, FA was rapidly converted, although the TOF decreased to 14000 h^{-1}. Leaching and CO formation were not affected. Also with 5 wt% FA and 1 equiv LA, the catalyst performed comparably and full conversion was achieved within 22 min. Interestingly, no GVL was observed during these reactions. The in situ conversion of LA was studied in a 24 h reaction and only 6% GVL was found afterwards indicating that Ru@pDPPE is not suitable for the hydrogenation of LA under these conditions. Nevertheless, FA could be selectively removed from a feed containing LA. In the presence of 2 wt% H_2SO_4 the reaction with 10 wt% FA was considerably slower and CO formation increased to 5042 ppm. Thus the data show that 2 wt% H_2SO_4 is detrimental for the catalytic activity and should be removed prior to FA decomposition.

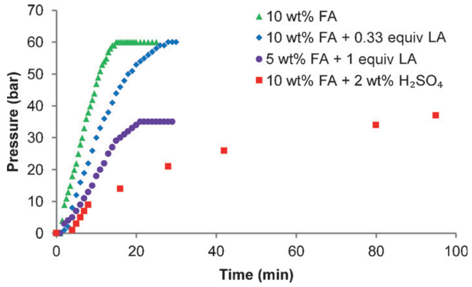

Figure 3. Effect of different contaminants on the Ru@pDPPE-catalyzed decomposition of formic acid.

Finally the conversion of FA in a crude LA synthesis mixture was attempted. For this purpose a glucose solution containing H_2SO_4 was subjected to 190°C for 30 min (Fig-

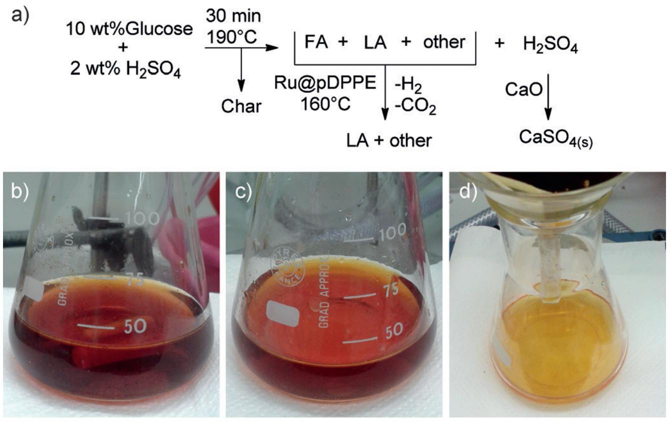

Figure 4. Application of Ru@pDPPE for the selective removal of FA from a crude LA synthesis reaction mixture. a) Reaction scheme; b) crude reaction mixture arising from LA synthesis after filtration; c) after addition of CaO and removal of $CaSO_4$; d) after FA decomposition and filtration of spent Ru@pDPPE.

ure 4a). The resulting mixture contained a large amount of char which was removed by filtration (Figure 4b). HPLC analysis showed that 81% of glucose had been converted to a complex mixture containing 2.4% LA and 1% FA. After removal of H_2SO_4 using CaO (Figure 4c), the mixture was used in the Ru@pDPPE-catalyzed decomposition of FA. The reaction was conducted for 24 h at 160°C, during which the pressure increased to 35 bar. Analysis of the gas phase revealed a relatively high amount of CO (2385 ppm). An additional 9% of glucose was converted during the second reaction and FA was completely removed. The amount of LA remained unchanged. A dark brown solid was recovered from the mixture and the filtrate had a light yellow appearance (Figure 4d). This suggests that further polymerization and precipitation of the soluble humins occurs and leads to a fouling of the catalyst. Nevertheless, these results affirm that the catalyst still performs in the presence of contaminants. Hence, it is proposed that the catalyst can be applied in downstream processing as well as at the end of the pipe.

In conclusion, it could be shown that phosphorus-based porous polymers are suitable ligands for the aqueous, base-free Ru-catalyzed decomposition of FA to H_2 and CO_2. The best results, in terms of TOF and selectivity, were obtained using a solid molecular analogue of DPPE. In addition it was shown that the polymeric PPh_3 catalyst outperforms its molecular analogue under the same conditions. Recycling tests confirm that the activity of the catalysts is stable over several runs and only minor leaching occurs. Variation of the FA concentration shows that the catalyst performs efficiently in solutions with 0–30 wt% FA. Also tests in the presence of LA and H_2SO_4 or with a crude product mixture prove that the catalyst is active and highly selective for FA removal. It is therefore proposed that Ru-loaded phosphorus-based polymers are promising catalysts for on-site hydrogen production in future biorefineries.

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