Sustainable Chemistry

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Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone**

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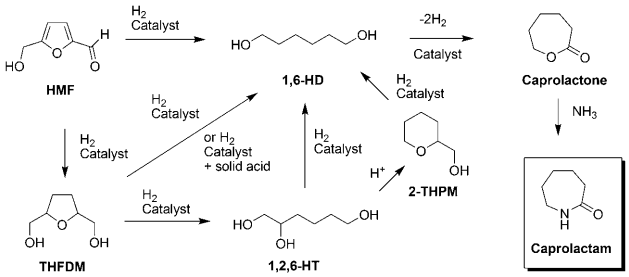
Lignocellulosic biomass is a very promising feedstock for the production of biobased chemicals.[1–8] The C_6 sugars (for example D-glucose, D-fructose, and D-mannose) in lignocellulosic biomass are interesting precursors for a broad range of chemicals with high application potential. Apart from fermentation to bioethanol[9] and reforming to CO/H_2,[10] the direct conversion of these sugars to useful platform chemicals is highly attractive.[1] Examples of such chemicals are levulinic acid[11] and 5-hydroxymethylfurfural (HMF).[12] HMF can be prepared in high yield from D-fructose,[13] although research is underway to convert D-glucose or even cellulose directly into HMF.[14] It can be converted into a range of derivatives with potential applications as a biofuel (furanics) and as building blocks for the polymer and solvent industry.[15]

Herein, we present our work on the conversion of HMF into caprolactam, the monomer for nylon-6, a widely used synthetic polymer with an annual production of about 4 million tons.[16] The proposed reaction for the conversion of HMF into caprolactone, via 1,6-hexanediol (1,6-HD), is shown in Scheme 1. The conversion of caprolactone into caprolactam by the reaction with ammonia is well-established and has already been used on a production scale.[17] A major breakthrough, needed in this research is the conversion of HMF to 1,6-hexanediol. For the feasibility of a bulk chemical process, it is absolutely essential that all conversions proceed with a selectivity in excess of 90%, and preferably even higher. High conversion is desirable, but not a prerequisite, and indeed many bulk processes, and in particular oxidations, are run at very low conversions to maintain a high selectivity. Four different routes were explored involving catalytic hydrogenation and hydrodeoxygenation reactions with various homogeneous and heterogeneous catalysts: 1) The direct hydrogenation of HMF to 1,6-HD; 2) a two-step sequence via 2,5-THF-dimethanol (THFDM); 3) a three-step synthesis via THFDM and 1,2,6-hexanetriol (1,2,6-HT); and 4) a four-step synthesis via THFDM, 1,2,6-HT, and tetrahydro-2*H*-pyran-2-ylmethanol (2-THPM). The last step in the sequence, namely the catalytic conversion of diols into lactones, is a known reaction,[18] but the conversion of 1,6-HD into caprolactone (5) rarely proceeds with high selectivity.[19] Probably the best method in terms of yield and selectivity is the oxidation with 30% H_2O_2 using heteropolyacids as catalyst which was reported twice and gave caprolactone in 70% and 98% yields, respectively.[19d,f] However, the use of H_2O_2 may be too expensive for a bulk caprolactam process. Herein, we report a version based on an Oppenauer oxidation that has never been used before on this substrate.[18c]



Scheme 1. Synthetic routes for the conversion of HMF into caprolactam.

The one-step hydrogenation reaction of HMF to 1,6-HD was performed under severe conditions (270 °C, 150 bar), with hydrogen as the reductant and a mixture of copper chromite and Pd/C (1:0.6) as the catalyst following a synthetic procedure reported by Utne and co-workers.[20] After 16 h reaction time, the HMF conversion was 100% and a mixture of products was obtained. The main product was THFDM; the desired product 1,6-HD was present in less than 4% yield. Use of just CuCr or Pd/C led to worse results. Rather worrying was that also some C_5 products, such as 1,5-pentanediol, were found. A possible pathway towards C_5 compounds is by decarbonylation of the aldehyde group. For this reason, it was deemed wiser to first hydrogenate HMF to THFDM under milder conditions and then hydrogenate this compound in a second step to 1,6-HD.

The catalytic hydrogenation of HMF to THFDM has been reported[21–27] using supported metal catalysts. A catalyst screening study was performed using a variety of catalysts and Raney-Ni (10 wt% catalyst intake, 100 °C, 90 bar hydrogen, 14 h) gave essentially quantitative yields of THFDM (*cis/*

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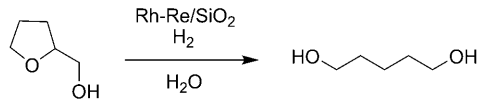
trans = 98:2). Good selectivities to the intermediate furandimethanol were also obtained using bimetallic Ni-Cu catalysts on zirconia and Ru on alumina, catalysts that have not been tested to date for this reaction.

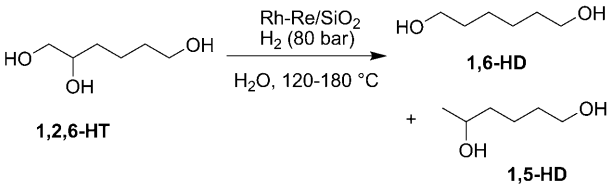
Hydrogenolytic ring opening of THFDM to 1,6-HD using a range of catalysts (various types of CuCr and CuZn catalysts, Pt/C, Ru/C, $NiCu/ZrO_2$, Raney-Ni) was explored in a batch autoclave setup at 260 °C and 100 bar pressure with 1-propanol as the solvent. The emphasis was on copper-containing catalysts, as Utne and co-workers reported a maximum 1,6-HD yield of 50% using a CuCr catalyst, although extreme conditions were applied (380 bar, 300 °C).[26] The best results in our screening study were obtained using a CuCr catalyst consisting of 75% $Cu_2Cr_2O_5$ and 25% CuO, giving a maximum selectivity to 1,6-HD of 41% at 41% THFDM conversion. Thus, although the hydrogenolytic opening of the tetrahydrofurfuryl ring of THFDM is possible the selectivity is still too low for further scale-up.

Recently, the Tomishige group reported the hydrogenolytic ring-opening reaction of tetrahydrofuran-2-ylmethanol using a $Rh-Re/SiO_2$ catalyst under mild conditions (120 °C and 80 bar hydrogen) to give 94% selectivity to 1,5-pentanediol at 57% conversion (Scheme 2).[28]



Scheme 2. Selective hydrogenolysis of tetrahydrofuran-2-yl-methanol by Tomishige et al.[28] Conditions: 120 °C, 80 bar.

A similar reaction using THFDM as the substrate could be envisaged to lead to the formation of 1,2,6-HT. In a subsequent step, a selective hydrogenolysis of the secondary alcohol group could lead to 1,6-HD. In the event, the hydrogenation of THFDM was carried out using a Rh-Re catalysts on a silica support (6.5 wt% Rh, 6 wt% Re). The reactions were carried out in water at temperatures between 80 and 180 °C. The initial pressure was 10 bar (1 h), and subsequently the pressure was increased to 80 bar for reaction times between 4 and 20 h (Table 1). The highest selectivity to 1,2,6-HT was 97%, and was obtained at 21% THFDM conversion (Table 1, entry 4). Higher temperatures and longer reaction times led to increased THFDM conversions, although the selectivity to 1,2,6-HT dropped. Byproducts are 1,6-HD and 1,5-hexanediol (1,5-HD). This result indicates that the diols are likely formed from 1,2,6-HT in a consecutive reaction pathway (Scheme 3).



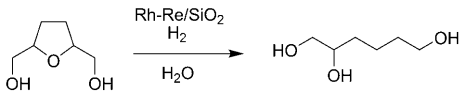
Scheme 3. Reaction of 1,2,6-HT to produce 1,6-HD and 1,5-HD.

Further reduction to 1-hexanol was not observed under the prevailing reaction conditions. The presence of the diols indicates that subsequent dehydroxylation of 1,2,6-HT is possible using the supported Rh-Re catalysts. In a next step, the hydrogenation of 1,2,6-HT was attempted with a variety of catalysts, including CuCr, CuZn, Pd, Ru, Rh, and the $Rh-Re/SiO_2$ catalyst, leading to mixtures of 1,6-HD and 1,5-HD (Scheme 3). The highest selectivity to 1,6-HD (73%) was obtained using the latter catalyst at 17% 1,2,6-HT conversion. The remainder is 1,5-HD. To date, we have not been able to suppress the formation of 1,5-HD by variation of the process conditions.

In an attempt to increase the selectivity to 1,6-HD, we added Brønsted acids to the hydrogenation reaction of 1,2,6-HT with the objective to selectively dehydrate the alcohol at the 2-position. Surprisingly this led to the formation of tetrahydro-2*H*-pyran-2-ylmethanol (2-THPM) in very high yields (Scheme 4).

Indeed, treatment of 1,2,6-HT with 0.6 mol% of trifluoromethanesulfonic acid in sulfolane at 125 °C for 0.5 h gave full conversion into 2-THPM in a very clean reaction. In view of the structural similarity between 2-THPM and 2-tetrahydrofuran-2-ylmethanol, we decided to subject the former to another hydrogenolysis reaction using the same $Rh-Re/SiO_2$

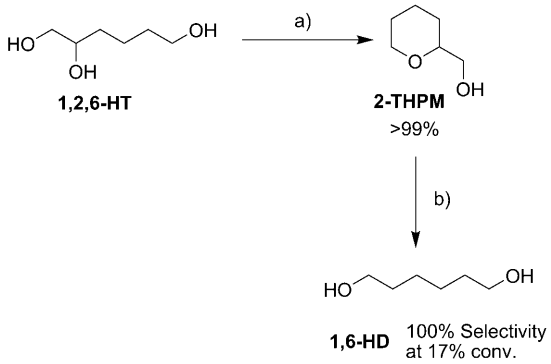
Table 1: The ring opening reaction of THFDM to 1,2,6-HT using $Rh-Re/SiO_2$ catalysts.[a]



THFDM 1,2,6-HT

Entry	*T* [°C]	*t* [h]	THFDM conv. [%]	Selectivity [%]		
				1,2,6-HT	1,6-HD	1,5-HD
1	120	4	55	77	15	5
2	120	20	81	61	28	10
3	180	4	83	54	30	15
4	80	20	21	97	0	0

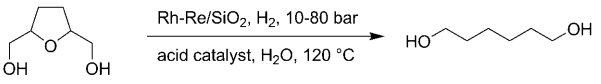
[a] Rh content 6.5 wt%, Re content 6 wt%, P_1 10 bar, P_2 80 bar, t_1 1 h, catalyst intake 25 wt%, 5 wt% THFDM in water.



Scheme 4. 1,6-HD production from 1,2,6-HT via 2-THPM. Conditions: a) TFSA, sulfolane, 125 °C, 30 min; b) $Rh-Re/SiO_2$, water, H_2 80 bar, 180 °C, 4.5 h.

catalyst. After 1 h at 10 bar and 3.5 h at 80 bar and 180 °C, 2-THPM conversion was 17 % and 1,6-HD was obtained with 100 % selectivity. This result finally gives us access to a high selectivity route from HMF to 1,6-HD involving THFDM, 1,2,6-HT, and 2-THPM as the intermediate products. A remaining drawback of this process to 1,6-HD is the number of steps. However, as both the hydrogenations of THFDM and of 2-THPM use the same catalysts and conditions an obvious next step was to try to combine the two hydrogenations and the ring closure to 2-THPM in a single process. In Table 2 we show the results of hydrogenating THFDM

Table 2: One-pot conversion of THFDM into 1,6-HD.

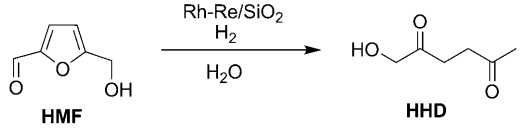


THFDM **1,6-HD**

Entry	Acid catalyst	*t* [h]	% conv	% selectivity		
				1,6-HD	1,5-HD	1,2,6-HT
1	sulf-C[a]	20	65	26	4	70
2	sulf-C[a]	4	22	9	1	90
3	zeolite 1[b]	20	82	39	9	52
4	zeolite 1[b]	4	37	15	4	81
5	zeolite 2[b]	20	92	61	12	27
6	zeolite 2[b]	4	38	18	5	77
7	zeolite 3[b]	20	87	47	7	46
8	zeolite 3[b]	4	29	9	2	88
9	Nafion SAC-13	20	100	86	14	0
10	Nafion SAC-13	4	57	21	5	74
11	Sulf-ZrO_2	20	88	49	9	42
12	Amberlyst-16	20	91	56	10	34
13	Smopex-101	20	93	60	10	30

[a] Sulfonated carbon (Sulf-C) was prepared by heating glucose at 400 °C for 15 h under N_2, followed by sulfonation with conc. H_2SO_4 during 15 h. [b] Zeolite 1 is SM-27, zeolite 2 is SM-55 (2 types of ZSM-5 silica from Alsi Penta);[30] zeolite 3 is CP-814E from Zeolyst (a type of beta zeolite).[30]

using the Rh-Re/SiO_2 catalyst in the presence of various solid acid catalysts. Full conversion was obtained after 20 h with Nafion SAC-13 with a very promising selectivity to 1,6-HT of 86 % (Table 2, entry 9). Other solid acids showed similar activities but led to slightly lower selectivities. Application of the Rh-Re/SiO_2-catalysed hydrogenation directly on HMF led to an unexpected result. Using 10 mol % of the catalyst at 120 °C on an aqueous solution of HMF at 10 bar for 1 h, followed by 17 h at 80 bar, led to full conversion and formation of 1,6-HD with only 7 % selectivity; furthermore, 1-hydroxyhexane-2,5-dione (HHD) was formed with 81 % selectivity (Scheme 5). Formation of this product from HMF

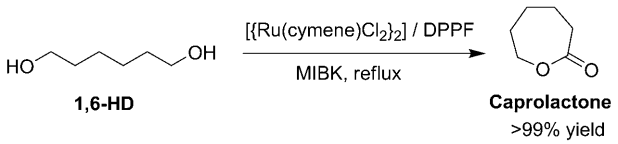


HMF **HHD**

Scheme 5. Reaction of HMF using Rh-Re/SiO_2. Conditions: 120 °C, 80 bar.

has been reported before during a hydrogenation under acidic conditions.[21]

Next we turned our attention to the conversion of 1,6-HD into caprolactone. This is essentially a one-pot two-step process in which the diol is first converted into the mono-aldehyde, which cyclizes spontaneously to the lactol, which is again dehydrogenated to the lactone. We were attracted by the method developed by Murahashi and co-workers, which is basically an Oppenauer oxidation using acetone as oxidant and a homogeneous Ru catalyst, $[H_2Ru(PPh_3)_3]$.[18c] They did report the formation of lactones from α,ω-diols, but the oxidation of 1,6-HD was not reported. In initial tests, we found that homogeneous ruthenium catalysts indeed outperformed a number of other catalysts based on iridium or titanium. Screening of ligands led us to the finding that the catalyst made in situ from $[\{Ru(cymene)Cl_2\}_2]$ and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) gave the best results. Thus, a solution of 1,6-HD in MIBK (methyl isobutyl ketone) was treated with this catalyst (1 mol %) at reflux temperature for 30 min. to give a virtually quantitative yield of caprolactone (Scheme 6).The use of MIBK instead of



1,6-HD **Caprolactone**
>99% yield

Scheme 6. Caprolactone production from 1,6-HD.

acetone allows much higher reaction temperatures (b.p. MIBK 117 °C) and thus faster rates. The only shortcoming of the method is the formation of stoichiometric amounts of the reduction product of MIBK, 4-methyl-2-pentanol. In an industrial setting this would need to be catalytically dehydrogenated back to MIBK, thus adding an extra step. A direct dehydrogenation of 1,6-HD to caprolactone without the use of an oxidant would be much preferred, but to date selectivities are too low.

In conclusion, we have identified a pathway that allows the conversion of HMF, which can be obtained from renewable resources such as D-fructose, into caprolactone with very good overall selectivity (95 % for the five-step process and 86 % for the two-step process). Using the one-pot conversion of THFDM into 1,6-HD, we can now convert HMF into caprolactam in only four steps, whereas the current caprolactam process needs six steps from benzene and ammonia. Furthermore, the current cyclohexane to cyclohexanone oxidation proceeds with very low conversion. Using this technology, 1.44 kg of HMF would be required (1.3 kg for the six-step process), 0.11 kg of H_2, and 0.17 kg of NH_3 to make 1 kg of caprolactam.

Note added in proof: While preparing this manuscript, we became aware of a paper by the Tomishige group describing the catalytic hydrogenation of tetrahydro-2*H*-pyran-2-ylmethanol using their Rh-Re catalyst.[29]

Experimental Section

Preparation of the Rh-Re/SiO_2 catalyst: An aqueous solution of $RhCl_3$ (302 mg,1.4 mmol) in water (10 mL) was added to silica (2 g, Wacker HDK T40; BET surface area 328 m^2g^{-1}, pore volume 0.742 cm^3g^{-1}) and stirred for 2 h at room temperature. After drying at 383 K for 13–14 h, this material was stirred with an aqueous solution of NH_4ReO_4 (193 mg, 0.7 mmol) in water (10 mL) for 2 h, followed by drying at 383 K for 13–14 h. Calcination in air at 773 K for 3 h gave a material with 6.5 wt% Rh and 6 wt% Re.

Hydrogenation of HMF to THFDM: HMF (500 mg, 4 mmol) dissolved in ethanol (30 mL) and Raney nickel catalyst (50 mg) were added to a 100 mL stainless steel autoclave (Parr). The reactor was flushed three times with nitrogen and subsequently with hydrogen. After flushing, the reactor was pressurized to 90 bar, and the reaction mixture was stirred and heated to 100 °C for 14 h. GC analysis showed 100% conversion and 99% selectivity to THFDM.

Hydrogenation of THFDM to 1,2,6-HT: THFDM (100 mg, 0.8 mmol), Rh-Re/SiO_2 catalyst (25 mg), water (2 mL), and a Teflon stirring bar were added to a 8 mL glass vial capped with a septum. The vial was then pierced with a small needle and placed in a stainless-steel autoclave. The lid of the autoclave was closed and stirring was started at 1000 rpm. After pressurizing three times with first nitrogen and then hydrogen, the autoclave was pressurized to 10 bar and the temperature was raised to 80 °C. After 1 h, the pressure was raised to 80 bar and the reactions were continued for 20 h. The autoclave was then allowed to cool to ambient temperature and the pressure was released. GC analysis showed 21% conversion and 97% selectivity to 1,2,6-HT.

Cyclization of 1,2,6-HT to 2-THPM: In a 100 mL three-neck round-bottom flask, 1,2,6-hexanetriol (3.354 g, 25 mmol) was dissolved in sulfolane (25 mL). Trifluoromethanesulfonic acid (13.3 μL, 0.15 mmol) was then added. The reaction mixture was heated to 125 °C for 30 min. GC showed full conversion with 2-THPM as the only product.

Hydrogenation of 2-THPM to 1,6-HD: 2-THPM (100 mg, 0.9 mmol), the Rh-Re/SiO_2 catalyst (10 mg), water (2 mL), and a Teflon stirring bar were added to a glass vial and hydrogenation was effected as described above for the hydrogenation of THFDM, except at a temperature of 180 °C. After 4.5 h, GC analysis showed 17% conversion and 100% selectivity to 1,6-HD.

One-pot hydrogenation of THFDM to 1,6-HD: The same procedure was used as described above for the hydrogenation of THFDM to 1,2,6-HT, but with an additional 15 mg of acid catalyst added (See Table 2).

1,6-HD to caprolactone: In a two-necked round-bottom flask with a condenser under an inert atmosphere, [{Ru(Cymene)Cl_2}$_2$] (0.02 mmol) and DPPF (0.022 mmol) were suspended in MIBK (5 mL) at room temperature. 1,6-HD (1.0 mmol), K_2CO_3 (0.2 mmol), and MIBK (25 mL) were then added, and the mixture was refluxed for 0.5 h. GC analysis showed 100% conversion of 1,6-HD with complete selectivity to caprolactone.

In all cases, samples were isolated by distillation or column chromatography and further analyzed by NMR and MS.

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[1] *Top Value-Added Chemicals from Biomass Vol. I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas* (Eds.: T. Werpy, G. Petersen), U. S. Department of Energy (DOE) by the National Renewable Energy Laboratory a DOE national Laboratory, **2004**.

[2] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044.

[3] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411.

[4] G. W. Huber, A. Corma, *Angew. Chem.* **2007**, *119*, 7320; *Angew. Chem. Int. Ed.* **2007**, *46*, 7184.

[5] J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem.* **2007**, *119*, 7298; *Angew. Chem. Int. Ed.* **2007**, *46*, 7164.

[6] *Catalysis for Renewables: From Feedstock to Energy Production* (Eds.: G. Centi, R. A. van Santen), Wiley-VCH, Weinheim, **2007**.

[7] *Sustainable Industrial Chemistry* (Eds.: F. Cavani, G. Centi, S. Perathoner, F. Trifirò), Wiley-VCH, Weinheim, **2009**.

[8] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cainey, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484.

[9] Special Issue on Lignocellulosic Bioethanol: Current Status and Perspectives, *Bioresour. Technol.* **2010**, *101*, 4743 – 5042.

[10] R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, *Appl. Catal. B* **2005**, *56*, 171.

[11] J. J. Bozell , L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenschwander, S. W. Fitzpatrick, R. J. Bilski, J. L. Jarnefeld, *Resour. Conserv. Recycl.* **2000**, *28*, 227.

[12] a) B. F. M. Kuster, *Starch/Staerke* **1990**, *42*, 314; b) J. Lewkowski, *ARKIVOC* **2001**, 17; c) R. J. van Putten, J. C. van der Waal, E. de Jong, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2011**, submitted.

[13] a) A. Gaseet, L. Rigal, G. Paillassa, J.-P. Dsalome, G. Fleche (Roquette Frères), FR2551754, **1985**; b) K.-I. Seri, Y. Inoue, H. Ishida, *Chem. Lett.* **2000**, 22; c) M. Bicker, J. Hirth, H. Vogel, *Green Chem.* **2003**, *5*, 280; d) C. Moreau, A. Finiels, L. Vanoye, *J. Mol. Catal. A* **2006**, *253*, 165 – 169; e) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* **2006**, *312*, 1933; f) C. Dignan, A. J. Sanborn (Archer Daniels Midland), WO2009/012445, **2009**.

[14] a) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597; b) S. Hu, Z. Zhang, J. Song, Y. Zhou, B. Han, *Green Chem.* **2009**, *11*, 1746; c) J. B. Binder, R. T. Raines, *J. Am. Chem. Soc.* **2009**, *131*, 1979.

[15] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982.

[16] Caprolactam": J. Ritz, H. Fuchs, H. Kieczka, W. C. Moran in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2002**.

[17] K. Weissermel, H.-J. Arpe, *Industrielle Organische Chemie*, 4th ed., VCH, Weinheim, **1994**.

[18] a) T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Green Chem.* **2009**, *11*, 793; b) J. Zhao, J. F. Hartwig, *Organometallics* **2005**, *24*, 2441; c) S.-I. Murahashi, T. Naota, K. Ito, Y. Maeda, H. Taki, *J. Org. Chem.* **1987**, *52*, 4319; d) Y. Lin, X. Zhu, Y. Zhou, *J. Organomet. Chem.* **1992**, *429*, 269.

[19] a) S. Oka, *Bull. Chem. Soc. Jpn.* **1962**, *35*, 986; b) T. Horlenko, D. R. Larkin (Celanese Corp), US3317563, **1967**; c) A. Tamura, Y. Fukuoka, Y. Suzuki, S. Yamamatsu, J. Nishikido (Asahi Chemicals), JP55024107, **1980**; d) Y. Ishii, T. Yoshida, K. Yamawaki, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 5549; e) H. M. Jung, J. H. Choi, S. O. Lee, Y. H. Kim, J. H. Park, J. Park, *Organometallics* **2002**, *21*, 5674; f) F. F. Bamoharrama, M. M. Heravi, M. Roshani, A. Gharib, M. Jahangir, *J. Mol. Catal. A* **2006**, *252*, 90.

[20] T. Utne, J. D. Garber, R. E. Jones (Merck & Co Inc), US3083236, **1963**.

[21] V. Schiavo, G. Descotes, J. Mentech, *Bull. Soc. Chim. Fr.* **1991**, *128*, 704.

[22] A. J. Sanborn, P. D. Bloom (Archer Daniels Midland), US7393963, **2008**.

[23] M. A. Lilga, R. T. Hallen, T. A. Werpy, J. F. White, J. E. Holladay, J. G. Frye, Jr., A. H. Zacher (Battelle Memorial Institute), US2007287845, **2007**.

[24] W. N. Haworth, W. G. M. Jones, L. F. Wiggins, *J. Chem. Soc.* **1945**, 1.
[25] R. A. Hales (Atlas Chemical Industries), US3040062, **1962**.
[26] T. Utne, R. E. Jones, J. D. Garber (Merck & Co Inc), US3070633, **1962**.
[27] T. J. Connolly, J. L. Considine, Z. X. Ding, B. Forsatz, M. N. Jennings, M. F. MacEwan, K. M. McCoy, D. W. Place, A. Sharma, K. Sutherland, *Org. Process Res. Dev.* **2010**, *14*, 459.
[28] S. Koso, I. Furikado, A. Shimao, T. Miyazawa, K. Kunimori, K. Tomishige, *Chem. Commun.* **2009**, 2035.
[29] K. Chen, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, *ChemCatChem* **2010**, *2*, 547.
[30] I. Melián-Cabrera, C. Mentruit, J. A. Z. Pieterse, R. W. van den Brink, G. Mul, F. Kapteijn, J. A. Moulijn, *Catal. Commun.* **2005**, *6*, 301.

