

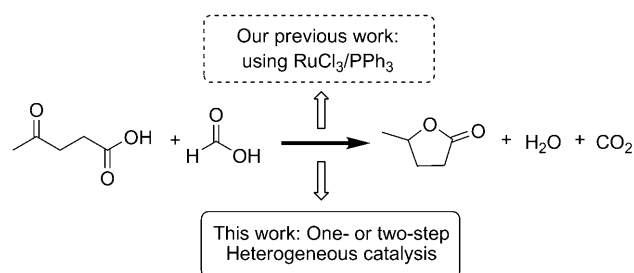
# Conversion of Levulinic Acid and Formic Acid into $\gamma$ -Valerolactone over Heterogeneous Catalysts

Li Deng,<sup>[a]</sup> Yan Zhao,<sup>[a]</sup> Jiang Li,<sup>[a]</sup> Yao Fu,<sup>\*[a]</sup> Bing Liao,<sup>[b]</sup> and Qing-Xiang Guo<sup>\*[a]</sup>

The current chemicals, materials, and energy base of our world depending on fossil resource will change drastically over the next decades.<sup>[1]</sup> Thus it is necessary to develop biomass-derived compounds to meet our practical demand for chemicals and liquid fuels. In this aspect,  $\gamma$ -valerolactone (GVL) has drawn increasing attention because of its benign properties and versatile functions.<sup>[2]</sup> It can be converted to monomers for the synthesis of nylon and polymer of high thermal stability.<sup>[3]</sup> As fuel additive, Horvath et al. demonstrated that GVL is a sustainable liquid with low volatility, minimum toxicity, and good stability.<sup>[2]</sup> Recently, two new directions for high-grade liquid fuel production have been proposed, both establishing a value chain based on pentenoic acid derived from GVL.<sup>[4]</sup> Combining hydrolysis of cellulose to levulinic acid (LA, precursor of GVL), hydrogenation to GVL, further hydrogenation to valeric acid and esterification, Lange et al. presented the synthesis of "valeric biofuels" and carried out a 250 000 km road trial run on the mixture of 15 vol% ethyl valerate and gasoline.<sup>[5]</sup> More importantly, Dumesic et al. have developed an integrated catalysis process to convert GVL to liquid alkenes without using external hydrogen or noble metals. However, they also suggested that though the process is efficient and inexpensive, the synthesis of GVL from biomass should be optimized in order to minimize the cost of GVL feed.<sup>[6]</sup> In our opinion, two key problems concerning GVL production need to be solved. First, LA should be obtained from cellulosic feed by a "green" dehydration process. Second, LA formed in aqueous medium should be reduced to GVL via a robust catalysis. Focusing on the second key problem, many efforts have been contributed to the hydrogenation of LA using high pressure H<sub>2</sub> and supported noble metal catalysts or homogeneous catalysts.<sup>[7]</sup> With the aim of replacing H<sub>2</sub> by formic acid which is a byproduct of LA, Horvath et al. developed a novel catalytic system in which excess formate was used for transfer hydrogenation of LA to GVL and 1,4-pentenediol catalyzed by [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru-(bpy)(H<sub>2</sub>O)]SO<sub>4</sub> in water.<sup>[8]</sup> More recently, Antonietti et al. found that transfer hydrogenation from formic acid to LA can be catalyzed by cheap sodium sulfate as a temperature-switchable

base under hydrothermal conditions.<sup>[9]</sup> Heeres et al. reported that fructose can be transformed to GVL with a medium yield in one step by using a catalyst system containing Ru/C, trifluoroacetic acid, and formic acid.<sup>[10]</sup> However, excess formic acid was still employed, which means that the hydrogen source could not be supplied solely from the dehydration process to produce LA. In the previous study, we have demonstrated a new route in which a simple RuCl<sub>3</sub>/PPh<sub>3</sub> catalyst can be used to produce GVL from 1:1 (molar ratio) aqueous mixture of LA and formic acid or the mixture arising from dehydration of glucose.<sup>[11]</sup> The success of using formic acid as hydrogen source not only avoids the external hydrogen supply but also generates usable high pressure CO<sub>2</sub> to mitigate the greenhouse gas emission.<sup>[6]</sup>

With the consideration of reducing the catalyst cost and simplifying the pretreatment for further conversion, improved methods employing heterogeneous catalysts have been developed in this work (Scheme 1). The previously examined aque-



**Scheme 1.** Transformation of LA with equimolar formic acid to GVL over heterogeneous catalysts.

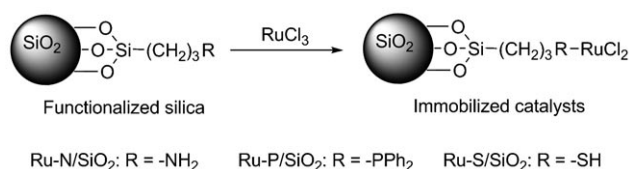
ous solution of LA and formic acid can be transformed to GVL, H<sub>2</sub>O, and CO<sub>2</sub> selectively in the presence of an immobilized Ru catalyst in one step. More importantly, in a two-step process, the efficiency of the whole catalytic process and the performance of recycle catalytic runs were improved obviously by using an immobilized catalyst for formic acid decomposition and Ru/TiO<sub>2</sub> for LA hydrogenation separately. Therefore, the heterogeneous catalysis makes the atom economic route more practical and sustainable.

We began our study by catalyst preparation via immobilizing RuCl<sub>3</sub> with functionalized silica according to Scheme 2. By anchoring noble metals on support, their loss can be minimized and catalyst separation can also be facilitated. Based on the observation of rapid increase of pressure inside the autoclave when formic acid was used as hydrogen resource, it is believed that the conversion of the mixture of LA and formic acid is carried out in two stages: 1) selective decomposition of formic acid catalyzed by the Ru-based complex at the beginning of

[a] L. Deng, Y. Zhao, J. Li, Prof. Y. Fu, Prof. Q.-X. Guo  
Anhui Province Key Laboratory of Biomass Clean Energy  
Department of Chemistry  
University of Science and Technology of China, Hefei 230026 (China)  
Fax: (+86) 551-3606689  
E-mail: fuyao@ustc.edu.cn  
qxguo@ustc.edu.cn

[b] Prof. B. Liao  
Key Laboratory of Cellulose and Lignocellulosics Chemistry  
Guangzhou Institute of Chemistry, Chinese Academy of Sciences  
Guangzhou 510650 (China)

Supporting Information for this article is available on the WWW under <http://dx.doi.org/10.1002/cssc.201000163>.



**Scheme 2.** Synthesis of immobilized Ru<sup>II</sup> catalysts.

the reaction and 2) the following hydrogenation of LA in the presence of high pressure H<sub>2</sub> and CO<sub>2</sub> as well as the catalyst.

Thus the three immobilized catalysts were tested in both reactions separately. The decomposition of formic acid was carried out in 4 M formic acid (HCOOH/HCOONa = 9:1) aqueous solution at 120 °C. Table 1 (entries 1–3) shows that the immobilized catalysts can decompose formic acid in water with high

Table 1. Transformation of LA and formic acid over heterogeneous catalysts.				
Entry	Catalysts	TOF of formic acid [h <sup>-1</sup> ] <sup>[a]</sup>	TOF of LA [h <sup>-1</sup> ] <sup>[b]</sup>	Overall TOF of LA [h <sup>-1</sup> ] <sup>[c]</sup>
1	Ru-N/ SiO <sub>2</sub>	1428	76	112
2	Ru-S/ SiO <sub>2</sub>	7357	142	173
3	Ru-P/ SiO <sub>2</sub>	3295	583 (453) <sup>[d]</sup>	447 (96%)
4	Ru/C	< 10	5345 (5638) <sup>[d]</sup>	69 (7%)
5	Pd/C	< 10	68	
6	Pt/C	< 10	16	

Reaction conditions: [a] 4 M formic acid (20 mL; HCOOH/HCOONa = 9:1) and catalyst (0.01 mmol, based on metal content) at 120 °C for 1 h. [b] LA (80 mmol), H<sub>2</sub>O (10 g), 4 MPa H<sub>2</sub> and catalyst (0.06 mmol; 0.01 mmol Ru/C) at 150 °C for 1 h. [c] LA and formic acid (80 mmol), H<sub>2</sub>O (10 g), NaOH (8 mmol), and catalyst (0.06 mmol) at 150 °C for 1 h; the value in parentheses is the yield of GVL obtained under the same conditions for 12 h. [d] The value in parenthesis is obtained under 4 MPa H<sub>2</sub> and 4 MPa CO<sub>2</sub>.

efficiencies. The highest turnover frequency (TOF) of formic acid was 7357 h<sup>-1</sup> using Ru-S/SiO<sub>2</sub> and even the worst one, Ru-N/SiO<sub>2</sub>, gives a TOF of 1428 h<sup>-1</sup> which is still much higher than the TOFs of LA for hydrogenation. The decomposition of formic acid in the presence of immobilized catalyst is carried out selectively and no CO was detected by GC (see the Supporting Information, Figure S7). Similar results were also reported by Laurency et al. with an aim of developing H<sub>2</sub> storage system.<sup>[12]</sup> On the other hand, 4 MPa H<sub>2</sub> was used for hydrogenation of 4 M LA aqueous solution at 150 °C. The hydrogenation performances of the three catalysts decreased in the order Ru-P/SiO<sub>2</sub> > Ru-S/SiO<sub>2</sub> > Ru-N/SiO<sub>2</sub>. The Ru-P/SiO<sub>2</sub>, which is a simulate of RuCl<sub>3</sub>/PPh<sub>3</sub> or [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>], showed the highest activity (TOF = 583 h<sup>-1</sup>) whereas the Ru-S/SiO<sub>2</sub> and Ru-N/SiO<sub>2</sub> gave TOFs of 142 and 76, respectively. Thus it is clear that the hydrogenation of LA in water is the rate determining step for the conversion of LA and formic acid in the presence of Ru-P/SiO<sub>2</sub> or Ru-S/SiO<sub>2</sub> or Ru-N/SiO<sub>2</sub>. Furthermore, Ru/C, Pd/C and Pt/C were also tested under 4 MPa H<sub>2</sub> atmosphere. Remarkably,

compared to the other catalysts, Ru/C showed excellent performance of hydrogenation giving a TOF of 5345 h<sup>-1</sup>. However, the yield of GVL from the mixture of LA and formic acid catalyzed by Ru/C was rather low (only 7% for 12 h), which could be attributed to its inability to catalyze the decomposition of formic acid for H<sub>2</sub> generation and the low efficiency of transfer hydrogenation at 150 °C. The TOF of formic acid over Ru/C was less than 10 h<sup>-1</sup> and only 1% of formic acid was converted after 12 h.

Regarding the fact that CO<sub>2</sub> derived from formic acid may promote the Ru-catalyzed hydrogenation of LA, a mixture gas of H<sub>2</sub> and CO<sub>2</sub> (1:1, 8 MPa) was employed for the hydrogenation test with Ru-P/SiO<sub>2</sub> or Ru/C. However, the TOFs of LA (Table 1, entries 3 and 4) indicated no obvious positive effect on both catalysts under the reaction condition in this study.

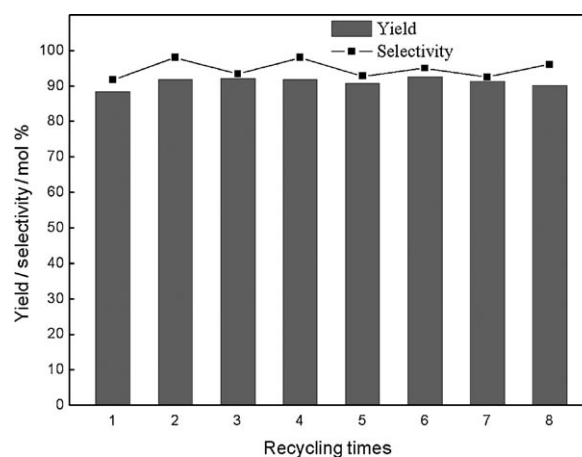
As we predicted, when using the Ru<sup>II</sup> catalysts for transforming the aqueous mixture of LA and formic acid, the overall TOFs of the combined reactions decreased in the same order as in LA hydrogenation. Compared to the other two catalysts, Ru-P/SiO<sub>2</sub> gave higher overall TOFs due to its better performance for LA hydrogenation. By prolonging the reaction time to 12 h, Ru-P/SiO<sub>2</sub> gave a yield of 96% which is the highest record in conversion of aqueous LA solution using equimolar formic acid and demonstrated that Ru-P/SiO<sub>2</sub> is a bifunctional catalyst. Moreover, only 42 µg ml<sup>-1</sup> Ru was detected in the resulting mixture, corresponding to 1.4% Ru leaching of fresh Ru-P/SiO<sub>2</sub>. According to a control experiment in which Ru-P/SiO<sub>2</sub> was separated from the mixture after 1 h and fresh formic acid was added, less than 1% of GVL was generated in the presence of the leached Ru species, indicating the reaction was catalyzed by Ru-P/SiO<sub>2</sub>, not by leached Ru species.

Based on combined transmission electron microscopy (TEM) microphotographs and energy-dispersive X-ray (EDX) spectroscopy, ruthenium is presented atomically in Ru-P/SiO<sub>2</sub> without detectable clusters or nanoparticles (see the Supporting Information, Figure S1). The X-ray photoelectron spectroscopy (XPS) revealed that the Ru species in fresh Ru-P/SiO<sub>2</sub> catalysts were present in the Ru<sup>II</sup> state, corresponding to the peaks with binding energies of 286.55 eV and 282.13 eV in 3d<sub>3/2</sub> and 3d<sub>5/2</sub> levels, respectively (Figure S2). The CP-MAS <sup>29</sup>Si NMR (CP = cross-polarization, MAS = magic angle spinning) measurements clearly showed that Ru-P/SiO<sub>2</sub> gave rise to a strong peak at 111.5 ppm and a weak peak at 65.2 ppm corresponding to the NMR signals of siloxane [Q<sup>n</sup> = Si(OSi)<sub>n</sub>(OH)<sub>4-n</sub>] and organosiloxane [T<sup>m</sup> = RSi(OSi)<sub>m</sub>(OH)<sub>3-m</sub>]. The T<sup>m</sup>/(Q<sup>n</sup>+T<sup>m</sup>) ratio was about 0.06. In addition, the CP-MAS <sup>31</sup>P NMR spectra of Ru-P/SiO<sub>2</sub> displayed two peaks at 38.7 ppm and 24.9 ppm corresponding to the -PPh<sub>2</sub> groups coordinated with Ru and free -PPh<sub>2</sub> groups. The relative integrated intensities of the two peaks were 0.82:1. Based on this value and total amount of -PPh<sub>2</sub> groups measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (0.39 mmol g<sup>-1</sup>), the amount of -PPh<sub>2</sub> groups coordinated with Ru was about 0.17 mmol g<sup>-1</sup>. Compared with the Ru content (0.14 mmol g<sup>-1</sup>), this suggested that most Ru species were anchored by the -PPh<sub>2</sub> groups. (see the Supporting Information for more details of catalyst characterization).

When Ru-P/SiO<sub>2</sub> was used repetitively for three times at 150 °C for 12 h, the yield of GVL decreased remarkably to 43%. The hydrogenation of LA was not completed over used catalyst. However, most formic acid could be converted to CO<sub>2</sub> and H<sub>2</sub> according to the pressure inside the autoclave although the reaction rate was lowered. Time needed to reach the maximum pressure increased from 20 min to 45 min by the used Ru-P/SiO<sub>2</sub>. The XPS clearly showed that after three catalytic runs, the Ru<sup>II</sup> species were partially reduced to Ru<sup>0</sup> state with binding energies of 284.85 eV and 280.75 eV in the 3d<sub>3/2</sub> and 3d<sub>5/2</sub> levels, respectively (see the Supporting Information, Figure S2).

To improve the durability and efficiency of the reaction system for practical applications, we attempted to combine the advantages of both Ru-P/SiO<sub>2</sub> and Ru/C in two stages by adding them together into the aqueous mixture of LA and formic acid. Unfortunately, the yield of GVL was only 30% after 6 h. We suspected the unreacted formic acid (or formate) poisoned Ru/C. Indeed, 50 mmol L<sup>-1</sup> formate or formic acid significantly inhibits the hydrogenation of LA catalyzed by Ru/C and the inhibition does not vanish until the concentration of formate is 10 mmol L<sup>-1</sup> (Table 2, entries 5 and 6). Thus the amount of formic acid should be controlled carefully for the following hydrogenation of LA. At this point, the concentration of the residual formic acid was analyzed by HPLC after decomposition in water at 150 °C for 1 h; as a result, 39 mmol L<sup>-1</sup> formate was observed (see the Supporting Information, Table S2).

Based on these results, a two-step transformation for GVL synthesis has been developed. In the first step, the mixture of LA and formic acid was subjected to Ru-P/SiO<sub>2</sub> at 170 °C for 1 h to decompose most formic acid. Then the resulting mixture from which Ru-P/SiO<sub>2</sub> was recovered was converted to GVL with 4.5 MPa H<sub>2</sub> (as the H<sub>2</sub> generated in situ) and Ru/TiO<sub>2</sub> which was tolerant to formic acid (Table 2, entry 7). As shown in Figure 1, the molar yield of GVL was over 88% via this two-step transformation. Moreover, recycle catalytic runs have also been performed with high efficiency and no severe deactivation of both catalysts was observed. The yields of GVL in eight recycle runs ranged from 88% to 93%. In principal, the aqueous mixture of LA and formic acid can be processed continu-



**Figure 1.** Two-step conversion of LA and formic acid to GVL in recycle catalytic runs. Reaction conditions: first step: LA and formic acid (80 mmol), H<sub>2</sub>O (10 g) and Ru-P/SiO<sub>2</sub> (0.05 mmol) at 170 °C for 1 h; second step: H<sub>2</sub> (4.5 MPa) and Ru/TiO<sub>2</sub> (0.01 mmol) at 170 °C for 2 h.

ously in a dual-bed (Ru-P/SiO<sub>2</sub> and Ru/TiO<sub>2</sub>) tubular reactor. Therefore, the two-step transformation seems more attractive and the further attempts of the continuous process are underway.

Finally, a safety issue around the formation of 2-methyl-tetrahydrofuran (2-Me-THF) from the over reduction of GVL was taken into consideration, because this unwanted byproduct readily generates peroxides which are dangerous during production, storage, transportation, and use.<sup>[13]</sup> According to the GC-MS analysis, the 2-Me-THF was not observed (< 2 mg L<sup>-1</sup>) under one-step or two-step reaction conditions. Even prolonging the reaction time to 12 h, no 2-Me-THF was detected from the two-step conversion (see the Supporting Information, Figure S6). Thus, the safety of the GVL production, storage, and further applications can be guaranteed.

In summary, we proposed the transformation of LA in water with equimolar formic acid to GVL over heterogeneous Ru-based catalysts without using the external H<sub>2</sub>. Ru-P/SiO<sub>2</sub> performs as a bifunctional catalyst with the capability to decompose formic acid and hydrogenate LA in one step giving 96% GVL. More importantly, an efficient two-step process has been developed by employing Ru-P/SiO<sub>2</sub> for decomposition and Ru/TiO<sub>2</sub> for hydrogenation. The two catalysts can be used repetitively for at least eight times without deactivation, indicating the two-step process is more practical for an industrial production of GVL. Furthermore, no hazardous 2-Me-THF is produced in this process.

## Experimental Section

All the catalytic experiments were carried out in a 50 mL autoclave made of zirconium alloy or a 50 mL stainless steel autoclave. Before each run, H<sub>2</sub> was used to exclude the air. The mixture of substrates and catalyst was heated to the desired temperature in 20 min with vigorous stirring. To recover the catalyst, the resulting mixture after reaction was filtrated. The used catalyst was added to the mixture of LA and formic acid directly for the next run. After

**Table 2.** Effect of formic acid on hydrogenation of LA to GVL at 150 °C.

Entry <sup>[a]</sup>	Catalysts	Time [h]	Hydrogen source	Molar yield of GVL [%]
1	Ru-P/SiO <sub>2</sub> +Ru/C <sup>[b]</sup>	3	Formic acid	21
2	Ru-P/SiO <sub>2</sub> +Ru/C <sup>[b]</sup>	6	Formic acid	30
3	Ru/C <sup>[c]</sup>	1	4 MPa H <sub>2</sub>	67
4	Ru/C <sup>[d]</sup>	1	4 MPa H <sub>2</sub>	2
5	Ru/C <sup>[e]</sup>	1	4 MPa H <sub>2</sub>	5
6	Ru/C <sup>[f]</sup>	1	4 MPa H <sub>2</sub>	49
7	Ru/TiO <sub>2</sub> <sup>[d]</sup>	1	4 MPa H <sub>2</sub>	63

[a] LA (80 mmol) and H<sub>2</sub>O (10 g). [b] Ru-P/SiO<sub>2</sub> (0.03 mmol) and Ru/C (0.03 mmol). [c] Ru/C (0.01 mmol). [d] Catalyst (0.01 mmol) and formic acid (2 mmol). [e] Ru/C (0.01 mmol), formic acid (1 mmol) or sodium formate (1 mmol). [f] Ru/C (0.01 mmol) and formic acid (0.2 mmol).

the reaction, the mixture was analyzed by GC–MS (Thermal Trace GC Ultra with a PolarisQ ion trap mass spectrometer) equipped with a TR-35MS capillary column (30 m × 0.25 mm × 0.25 μm). The concentration of formic acid was analyzed by a HPLC system consisting of a Waters 1525 pump, a Waters 5C<sub>18</sub>-PAQ column (4.6 × 250 mm) and a Waters 2414 refractive index detector. H<sub>2</sub>SO<sub>4</sub> (5 mM) was used as the mobile phase at a flow rate of 1 mL min<sup>-1</sup> or 0.6 mL min<sup>-1</sup>. The gas was sampled for analysis using a GC with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The components were determined by the external standard method using calibration gases (see the Supporting Information for more details).

## Acknowledgements

The authors are grateful to National Basic Research Program of China (2007CB210205), Knowledge Innovation Program of Chinese Academy of Science (KG CX2-YW-3306) and NSFC-Guangdong Joint Fund (U0834005) for the financial support.

**Keywords:** biomass · carbocyclic acids · heterogeneous catalyst · lactones · ruthenium

[1] A. Dadabhoy, P. Golitz, *ChemSusChem* **2008**, *1*, 4.

[2] I. T. Horváth, H. Mehdi, V. Fábos, L. Boda, L. T. Mika, *Green Chem.* **2008**, *10*, 238.

- [3] a) J. P. Lange, J. Z. Vestering, R. J. Haan, *Chem. Commun.* **2007**, 3488; b) L. E. Manzer, *Appl. Catal. A* **2004**, *272*, 249.
- [4] R. Palkovits, *Angew. Chem.* **2010**, *122*, 4434.
- [5] J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosse-link, *Angew. Chem.* **2010**, *122*, 4581; *Angew. Chem. Int. Ed.* **2010**, *49*, 4479.
- [6] J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* **2010**, *327*, 1110.
- [7] a) L. E. Manzer, US 0207878, **2002**; b) L. E. Manzer, K. W. Hutchenson, US 0254384, **2004**; c) R. A. Bourne, J. G. Stevens, J. Ke, M. Poliakoff, *Chem. Commun.* **2007**, 4632; d) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044; e) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411; f) F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, *Angew. Chem.* **2010**, *122*, 5642; *Angew. Chem. Int. Ed.* **2010**, *49*, 5510.
- [8] H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horváth, *Top. Catal.* **2008**, *48*, 49.
- [9] D. Kopetzki, M. Antonietti, *Green Chem.* **2010**, *12*, 656.
- [10] H. Heeres, R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta, H. J. Heeres, *Green Chem.* **2009**, *11*, 1247.
- [11] L. Deng, J. Li, D. M. Lai, Y. Fu, Q. X. Guo, *Angew. Chem.* **2009**, *121*, 6651; *Angew. Chem. Int. Ed.* **2009**, *48*, 6529.
- [12] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem.* **2008**, *120*, 4030; *Angew. Chem. Int. Ed.* **2008**, *47*, 3966.
- [13] V. Fábos, G. Koczó, H. Mehdi, L. Boda, I. T. Horváth, *Energy Environ. Sci.* **2009**, *2*, 767.

Received: June 11, 2010

Revised: August 4, 2010

Published online on September 24, 2010