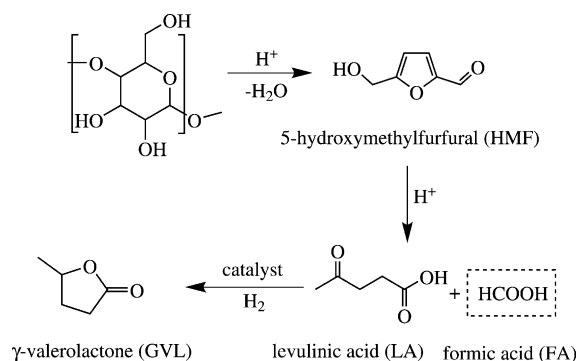


Hydrogen-Independent Reductive Transformation of Carbohydrate Biomass into γ -Valerolactone and Pyrrolidone Derivatives with Supported Gold Catalysts**

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Biomass and its derivatives provide renewable alternatives to fossil-fuel resources for the sustainable production of liquid fuels and valuable chemicals.^[1] The challenge for the effective utilization of these sustainable resources is to develop cost-efficient processing methods for the transformation of highly functionalized carbohydrates into value-added chemicals.^[2] Carbohydrates derived from lignocellulosic materials comprise the largest fraction of terrestrial biomass, and various strategies for their efficient use as a commercial chemical feedstock are currently being established with the aim to supplement and ultimately replace fossil fuels.^[3] In this respect, γ -valerolactone (GVL) has been identified as one of the most promising renewable molecules: it can be converted into a variety of intermediate chemicals, from which a diverse range of biofuels as well as commodity and fine chemicals can be generated.^[4] GVL can be obtained in high yield (> 99 %) by the catalytic hydrogenation of levulinic acid (LA, 4-oxopentanoic acid),^[5] which is accessible from lignocellulosic biomass by a simple and robust hydrolysis process.^[1c,6] Molecular hydrogen has generally been used for the catalytic hydrogenation of LA (Scheme 1);^[4,5] however, minimization of H₂ consumption would be preferable for the production of GVL from biomass,^[4d] especially when low-cost hydrogen is not readily available.

From both economic and engineering points of view, the development of new efficient methods for GVL production with formic acid (FA, formed in an equimolar amount with LA by the acidic hydrolysis of biomass) as an in situ source of hydrogen is much needed.^[7] This procedure can eliminate the need for an external source of hydrogen and thus has great industrial potential for the production of GVL from renewable biomass,^[8] especially if an efficient and reusable catalyst can be employed. Although the use of FA as a hydrogen donor in catalytic transfer hydrogenation reactions is a well-established method for the reduction of carbonyl function-



Scheme 1. Catalytic conversion of carbohydrate biomass into GVL.

alities,^[9] effective LA reduction with FA has proven to be very difficult, and many reported procedures require the use of FA in large excess or the addition of external hydrogen to enhance the activity of the catalyst.^[7,10] The most successful catalyst system reported to date is a RuCl₃/PPh₃ complex^[8a] that enables the conversion of a 1:1 neat mixture of LA and FA into GVL in high yield (up to 95 %). However, besides the inherent limitation of homogeneous catalysis for the development of a sustainable catalytic process, this system requires the strict absence of water and the addition of copious amounts of a base to improve the reduction kinetics and minimize deactivation. Given the high water content and the extremely high acidity of the products of biomass hydrolysis, these features may present serious drawbacks in terms of energy consumption and processing cost as well as additional handling problems. Hence, the successful development of an excellent reusable solid catalyst for base-free LA reduction solely with FA derived from biomass hydrolysis would represent a significant advance for this important transformation.

Supported gold nanoparticles (NPs) have recently emerged as versatile catalysts for a broad array of organic transformations, including a number of reactions involving hydrogen.^[11] Whereas much attention has been focused on several classical chemical reactions for green and atom-efficient organic synthesis,^[12] the potential offered by supported gold for catalytic biomass transformation, especially toward the sustainable synthesis of high-value-added fine chemicals, remains largely unexplored.^[13] Following the pioneering study by Ojeda and Iglesia,^[14] who showed that Au dispersed on alumina can selectively decompose HCOOH at 80 °C in the gas phase, we recently showed that supported gold acted as a highly efficient catalyst for the catalytic

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transfer reduction of carbonyl compounds by formate salts to give the corresponding alcohols under ambient conditions.^[15] The superior performance of Au catalysts for formate-mediated transfer reduction led us to investigate the possibilities offered by Au catalysts for LA reduction with FA as the hydrogen source. Herein we show that gold NPs deposited on acid-tolerant ZrO₂ serve as a highly efficient and robust heterogeneous catalyst for the generation of GVL from biomass, and more specifically for the selective reduction of LA with an equimolar amount of FA as the sole hydrogen source. Moreover, we show that with a single gold catalyst, it is possible to convert biomass-derived LA and ammonia or primary amines into 5-methyl-2-pyrrolidone or its derivatives^[16] in a one-pot catalytic process; this reaction only proceeds in the presence of FA as the reducing reagent.

We began our study by examining a diluted solution (pH \approx 2.0) containing equimolar concentrations (0.43 M) of LA and FA in the presence of a catalyst (Table 1), as we expected this setup to be the most straightforward for GVL production from biomass-derived LA. We initially studied the reduction of LA with FA over a catalyst derived from very small Au NPs (ca. 1.8 nm) supported on acid-tolerant ZrO₂ (catalyst denoted as Au/ZrO₂-VS; see details in the Supporting Information).^[17] Transmission electron microscopy (TEM) showed that a large fraction of the Au particles in this catalyst had a diameter between 1.2 and 2.5 nm (see Figure S1 in the Supporting Information). The time-course plot for the conversion of LA with FA in the presence of Au/ZrO₂-VS (0.1 mol %) at 150 °C is given in Figure S4, and the results

obtained after a reaction time of 6 h are compared with those obtained with other catalysts. Interestingly, when the Au/ZrO₂-VS catalyst was used, the 1:1 aqueous mixture of LA and FA was converted quantitatively into GVL (Table 1, entry 1).^[18] This result is remarkable, and the system has the added advantage that the catalyst can be reused at least five times with minimal decrease in the yield (95 %; Table 1, entry 2). Of yet further interest is the fact that the total turnover number (TON) based on five successive runs is as high as 7600, and is thus the highest TON value ever reported for the reduction of LA with FA (see Table S1). Importantly, when we used gold supported on ZrO₂ prepared by a routine deposition-precipitation (DP) method as the catalyst, which has a larger average gold-particle size (ca. 3.0 nm), a GVL yield as high as 95 % was still possible, although a longer reaction time was required (Table 1, entry 9). The reaction did not proceed at all with gold-free ZrO₂; thus, the presence of gold was essential for the high activity observed in the reduction of LA.

In subsequent experiments performed at 90 °C under otherwise identical reaction conditions, the Au/ZrO₂-VS catalyst exhibited very low activity (Table 1, entry 5). When the reaction temperature was raised to 120 °C, the yield of GVL improved dramatically from 15 to 79 % (Table 1, entry 6). At an elevated temperature of 180 °C, quantitative formation of GVL was observed within three hours (Table 1, entry 7). The catalytic reduction of LA to GVL has been carried out previously with a variety of homogeneous or heterogeneous Ru catalysts in high yield in the presence of a large excess of molecular hydrogen at high pressures (3–10 MPa) and low LA concentrations (7 wt %)^[7b] or in organic solvents rather than water.^[4b,5] Strikingly, in our case, GVL can also be produced in nearly quantitative yield from a concentrated aqueous solution of LA (50 wt %) only in the presence of FA produced in the original chemical hydrolysis step (Table 1, entry 8).^[19] The high activity of Au/ZrO₂-VS coupled with its excellent activity under highly acidic conditions in the absence of molecular hydrogen significantly improves the value of this gold-catalyzed LA reduction process in terms of economic considerations and sustainability.

A comparison with palladium, platinum, and ruthenium NPs supported on zirconia as reference catalysts showed gold to be far superior to other noble metals for the reduction of LA with FA (Table 1, entries 13–17). Since it has been shown that the choice of the support plays an important role in gold catalysis, we also evaluated gold supported on TiO₂ (Au/TiO₂). The use of this commercial catalyst resulted in the formation of the desired product GVL in moderate yield (Table 1, entry 10). In contrast, gold supported on silica (Au/SiO₂) and activated carbon (Au/C) were ineffective for the reduction of LA under similar reaction conditions (Table 1, entries 11 and 12). These results indicate that both the noble metal and the nature of the support play a role in the catalytic reduction of LA in the presence of FA as the sole hydrogen source. Among the various catalysts examined in this study, very small Au NPs deposited on ZrO₂ (Au/ZrO₂-VS) exhibited by far the best catalytic performance.

Table 1: Reductive transformation of LA into GVL with FA (1 equiv) in the presence of various catalysts.^[a]

Entry	Catalyst	<i>t</i> [h]	<i>T</i> [°C]	Yield of GVL [mol %] ^[b]	Selectivity [mol %]
1	Au/ZrO ₂ -VS	6	150	99	> 99
2 ^[c]	Au/ZrO ₂ -VS	6	150	95	> 99
3	Au/ZrO ₂ -VS	1	150	68	> 99
4	Au/ZrO ₂ -VS	3	150	86	> 99
5	Au/ZrO ₂ -VS	6	90	15	> 99
6	Au/ZrO ₂ -VS	6	120	79	> 99
7	Au/ZrO ₂ -VS	3	180	99	99
8 ^[d]	Au/ZrO ₂ -VS	6	150	99	> 99
9 ^[e]	Au/ZrO ₂	10	150	95	99
10 ^[f]	Au/TiO ₂	6	150	55	99
11	Au/SiO ₂	6	150	1	99
12 ^[g]	Au/C	6	150	trace	–
13	Pd/ZrO ₂	6	150	trace	–
14	Pt/ZrO ₂	6	150	trace	–
15	Ru/ZrO ₂	6	150	2	99
16 ^[h]	Pd/C	6	150	2	99
17 ^[h]	Ru/C	6	150	1	99
18	ZrO ₂	6	150	n.r.	–

[a] Reaction conditions: LA (18 mmol), FA (18 mmol), metal (0.1 mol %), water (40 mL), N₂ (0.5 MPa); n.r. = no reaction. [b] The yield was determined by GC with bis(2-methoxyethyl) ether as the internal standard. [c] Results for the fifth run with a recycled catalyst. [d] LA (60 mmol), FA (60 mmol), Au (0.1 mol %), water (4 mL), N₂ (0.5 MPa). [e] Au/ZrO₂ was prepared by a routine DP method. [f] Au/TiO₂ was purchased from Mintek. [g] Au/C was purchased from the World Gold Council (WGC). [h] Pd/C and Ru/C were purchased from Alfa Aesar.

During the reduction of LA over Au/ZrO₂-VS, the pressure inside the autoclave reactor increased rapidly from 0.5 MPa to a maximum value of approximately 6 MPa in the first half hour of the reaction. Significant FA decomposition leading to H₂/CO₂ formation could be responsible for this effect. To obtain information concerning the essential role of FA as the sole reducing agent, we performed several experiments to monitor the decomposition kinetics of FA in the absence of LA (Figure 1). Whereas blank controls indicated

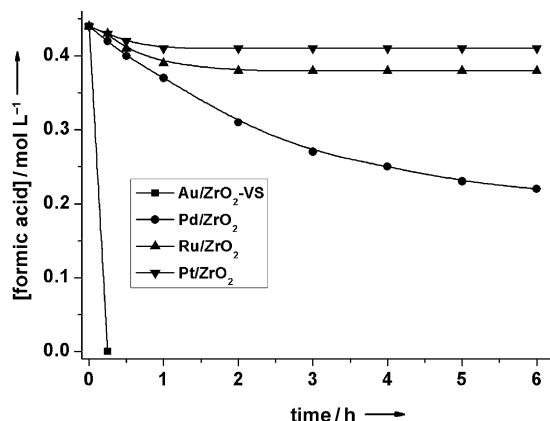


Figure 1. Activity of ZrO₂-supported metal catalysts for the decomposition of HCOOH in the absence of LA. Reaction conditions: 150 °C, FA (18 mmol), metal (0.1 mol %), water (40 mL).

that the FA concentration was constant at 150 °C in the absence of catalysts, FA decomposed upon the addition of Au/ZrO₂-VS to form H₂ and CO₂ in stoichiometric amounts (HCOOH → CO₂ + H₂). Importantly, in line with the catalytic data for LA reduction (Table 1), the rate of FA disappearance in the presence of Au/ZrO₂-VS was significantly higher than for all other samples.^[20] The lack of formation of CO over Au/ZrO₂-VS inferred that the FA dehydration pathway (HCOOH → CO + H₂O) is practically inhibited in this case. Indeed, clear CO formation at a level of 400–10 000 ppm was identified for the FA decomposition products over the Pd, Pt, and Ru catalysts (see Figure S6). As formic acid was recently identified as a convenient hydrogen carrier for fuel cells,^[21] the reactions described herein may also open the possibility of developing new versatile gold-based heterogeneous catalytic systems for the selective generation of CO-free clean H₂ from biomass-derived FA for energy-storage purposes.^[22]

To further understand the reaction pathways involved in the HCOOH-mediated reduction, we used H₂ at a pressure of 4.0 MPa for the hydrogenation of an aqueous solution of LA (0.45 M) at 150 °C. Whereas the hydrogenation performance of Au/ZrO₂-VS closely resembled that observed with FA as the reductant (see Figure S4), a surprisingly high rate was observed for LA hydrogenation catalyzed by platinum-group metals such as Pt and Ru (see Figure S7). Given the notorious low CO tolerance of platinum-group metals toward formic acid electrooxidation,^[23] we believe that the CO produced during FA decomposition may severely poison the Pt, Ru, or Pd catalysts during attempted LA reduction when

FA is used as the hydrogen source. Indeed, when we deliberately added CO (ca. 1000 ppm) to the direct-hydrogenation system, a strongly retarded LA hydrogenation was observed (see Figure S7). Taken together, these results demonstrate that the reduction of LA with FA does not proceed through gold-catalyzed transfer hydrogenation, but rather through a less straightforward hydrogenation of LA with H₂ generated in situ by FA decomposition. More specifically, the fact that the Au/ZrO₂-VS catalyst can substantially facilitate the crucial FA dehydrogenation appears to be the key factor for achieving high activity in the reduction of LA, although the aqueous hydrogenation of LA is the rate-determining step for the overall conversion of LA with FA in the presence of Au/ZrO₂-VS. The discovery of this unique catalysis by gold will open new routes for the hydrogenation or reduction/hydrodeoxygenation of biomass-derived intermediates to produce renewable fuels or value-added chemicals.

To demonstrate the utility of the Au/ZrO₂-VS catalyst in the context of biomass-derived substrates, we investigated the reduction of an aqueous mixture of LA and FA obtained by the hydrolysis of D-glucose. Through the acidic hydrolysis (catalyzed by 0.5 M H₂SO₄) of D-glucose (60 mL, 15 wt % aqueous solution), we obtained an aqueous solution containing LA (ca. 5 wt %) and FA (ca. 2 wt %). After partial neutralization and removal of insoluble solid by filtration (see the Supporting Information for details), the aqueous mixture was transferred into an autoclave containing Au/ZrO₂-VS (0.1 mol % Au) and heated at 150 °C for 8 h. Under these conditions, GVL was produced in 95 % yield. The overall yield of GVL from glucose was approximately 51 % (Table 2,

Table 2: Dehydration of carbohydrates^[a] and subsequent reduction of carbohydrate-derived LA with FA in the presence of Au/ZrO₂-VS.^[b]

Entry	Carbohydrate	Yield of LA [mol %] ^[c]	Yield of FA [mol %] ^[c]	Yield of GVL [mol %] ^[d]
1	glucose	54	58	51 (95)
2	fructose	61	67	60 (98)
3	sucrose	58	65	57 (98)
4	starch	52	60	50 (96)
5	cellulose	34	40	33 (97)

[a] Reaction conditions: carbohydrate (10.8 g), water (60 mL), H₂SO₄ (0.5 M), 170 °C, 1 h. [b] Reaction conditions: biomass-derived LA and FA (42 mL), Au (0.1 mol %), N₂ (0.5 MPa), 150 °C, 8 h. [c] Yield for the initial carbohydrate hydrolysis. [d] Overall yield for the two-stage conversion of the biomass-derived carbohydrate. The yield based on the conversion of LA is given in parenthesis.

entry 1). We thus demonstrated that the present gold-based technology can be used to convert glucose into GVL with high efficiency. Further improvements in the yield of GVL on the basis of carbohydrate conversion were possible when D-fructose was used instead of D-glucose. The highest GVL yield observed was 60 % at complete D-fructose conversion (Table 2, entry 2). Besides these monomeric C₆ sugars, a dimeric sugar (sucrose), a polymer (starch), and cellulose were also tested under the optimized conditions determined for D-glucose. In all three cases, near-complete conversion of

biomass-derived LA into GVL was observed (Table 2, entries 3–5); GVL was formed in 57, 50, and 33% overall yield, respectively, from biomass. These results are, to the best of our knowledge, unprecedented for the production of GVL from renewable biomass resources without the use of external hydrogen under heterogeneous reaction conditions.

Having established that Au/ZrO₂-VS is able to catalyze the selective reduction of biomass-derived LA to GVL without the use of an external H₂ supply, we explored the possibility of a one-pot conversion of LA and ammonia or primary amines into valuable and useful 5-methyl-2-pyrrolidones, which are currently derived from fossil resources,^[24] on the basis of the Au/ZrO₂-HCOOH-mediated reductive amination methodology. Pyrrolidones, in particular *N*-alkyl 5-methyl-2-pyrrolidones, have a wide variety of applications, for example, as solvents, surfactants, and important intermediates in the synthesis of pharmaceutical and agricultural bioactive compounds.^[25] They are also important constituents of a wide variety of cleaning agents and useful as ink or aerosol formulations.^[24] In the patent literature,^[25] it is reported that *N*-alkyl 5-methyl-2-pyrrolidones can be produced by the treatment of LA with molecular H₂ and ammonia or amines in the presence of a hydrogenation catalyst. However, the main drawbacks of this approach are the use of hazardous organic solvents, the requirement of a high excess of H₂, and limited selectivity for the formation of the expected product when aryl amines are used.^[25] We performed the one-pot reaction in water at 130 °C with LA (8 mmol), FA (8 mmol), NH₄OH or a primary amine (8 mmol), and Au/ZrO₂-VS. The results presented in Table 3 show that this one-pot procedure enables the conversion of LA into 5-methyl-2-pyrrolidone and its derivatives in high yield with excellent selectivity.

In summary, we have demonstrated that a highly active and robust catalyst based on gold deposited on acid-tolerant

ZrO₂ can be used to convert an equimolar aqueous mixture of levulinic acid and formic acid into GVL in excellent yield. Furthermore, through a one-pot process requiring only formic acid, ammonia or primary amines, and a single catalyst, it is possible to convert levulinic acid directly into the corresponding pyrrolidones. A preliminary study with glycerol showed that the present Au/ZrO₂-HCOOH-mediated procedure is not limited to the reductive transformation of levulinic acid (see Table S2). To the best of our knowledge, this system involving HCOOH-mediated gold catalysis is one of the most simple, efficient, ecologically friendly, and robust catalytic systems developed to date for the selective reductive transformation of biomass-derived compounds. The present findings open the possibility of developing new sustainable processes for the hydrogenation or reduction/hydrodeoxygenation of biomass-derived intermediates to produce renewable fuels or high-value-added chemicals without the use of an external hydrogen supply.

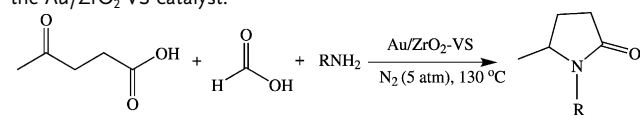
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Table 3: Production of pyrrolidone derivatives by the reductive amination of LA with primary amines (or ammonia) in the presence of FA and the Au/ZrO₂-VS catalyst.^[a]



Entry	Amine	<i>t</i> [h]	Conversion [mol %] ^[b]	Selectivity [mol %] ^[b]	Yield [mol %] ^[c]
1	benzylamine	12	98	99	97
2	hexylamine	12	100	95	95
3	cyclohexylamine	12	96	98	94
4	4-methylaniline	16	94	97	91
5	4-methoxyaniline	16	95	98	93
6	NH ₃ ·H ₂ O	16	90	95	85
7	4-chloroaniline	24	89	99	88
8	aniline	24	91	97	88

[a] Reaction conditions: LA (8 mmol), amine (8 mmol), FA (8 mmol), Au (0.05 mol %), water (0.56 mL), 130 °C. To improve the yield of the pyrrolidone, it is important to minimize the presence of free water in the reaction medium. [b] Conversion and selectivity were determined by GC with bis(2-methoxyethyl) ether as the internal standard. [c] GVL was the only side product.

- [1] a) B. Kamm, P. R. Grube, M. Kamm, *Biorefineries—Industrial Processes and Products, Vol. 1: Status Quo and Future Directions*, Wiley-VCH, Weinheim, **2006**; b) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098; c) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502.
- [2] a) A. L. Marshall, P. J. Alaimo, *Chem. Eur. J.* **2010**, *16*, 4970–4980; b) J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539–554.
- [3] a) A. Fukuoka, P. L. Dhepe, *Angew. Chem.* **2006**, *118*, 5285–5287; *Angew. Chem. Int. Ed.* **2006**, *45*, 5161–5163; b) N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. C. Liu, Y. Kou, *J. Am. Chem. Soc.* **2006**, *128*, 8714–8715; c) J. B. Binder, R. T. Raines, *J. Am. Chem. Soc.* **2009**, *131*, 1979–1985.
- [4] a) 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*, 227–239; b) L. E. Manzer, *Appl. Catal. A* **2004**, *272*, 249–256; c) J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, *Angew. Chem.* **2010**, *122*, 4581–4585; *Angew. Chem. Int. Ed.* **2010**, *49*, 4479–4483; d) J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* **2010**, *327*, 1110–1114.
- [5] a) L. E. Manzer, US Patent 0,055,270, **2003**; b) Z. P. Yan, L. Lin, S. J. Liu, *Energy Fuels* **2009**, *23*, 3853–3858.
- [6] a) S. W. Fitzpatrick, US Patent 5,608,105, **1997**; b) B. Girisuta, L. P. B. M. Janssen, H. J. Heeres, *Chem. Eng. Res. Des.* **2006**, *84*, 339–349.
- [7] a) R. J. Haan, J. P. Lange, US Patent 0,208,183, **2007**; b) H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horváth, *Top. Catal.* **2008**, *48*, 49–54.
- [8] a) L. Deng, J. Li, D. M. Lai, Y. Fu, Q. X. Guo, *Angew. Chem.* **2009**, *121*, 6651–6654; *Angew. Chem. Int. Ed.* **2009**, *48*, 6529–6532; b) L. Deng, Y. Zhao, J. Li, Y. Fu, B. Liao, Q. X. Guo, *ChemSusChem* **2010**, *3*, 1172–1175.
- [9] a) I. Kawasaki, K. Tsunoda, T. Tsuji, T. Yamaguchi, H. Shibuta, N. Uchida, M. Yamashita, S. Ohta, *Chem. Commun.* **2005**, 2134–2136; b) F. K. Cheung, A. J. Clarke, G. J. Clarkson, D. J. Fox,

- M. A. Graham, C. X. Lin, A. L. Crivillé, M. Wills, *Dalton Trans.* **2010**, 39, 1395–1402.
- [10] a) H. Heeres, R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta, H. J. Heeres, *Green Chem.* **2009**, *11*, 1247–1255; b) D. Kopetzki, M. Antonietti, *Green Chem.* **2010**, *12*, 656–660; c) J. C. Serrano-Ruiz, D. J. Braden, R. M. West, J. A. Dumesic, *Appl. Catal. B* **2010**, *100*, 184–189.
- [11] a) A. Corma, P. Serna, H. García, *J. Am. Chem. Soc.* **2007**, *129*, 6358–6359; b) L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2009**, *121*, 9702–9705; *Angew. Chem. Int. Ed.* **2009**, *48*, 9538–9541.
- [12] a) A. Corma, P. Serna, *Science* **2006**, *313*, 332–334; b) A. Grirrane, A. Corma, H. García, *Science* **2008**, *322*, 1661–1664; c) F. Z. Su, Y. M. Liu, L. C. Wang, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2008**, *120*, 340–343; *Angew. Chem. Int. Ed.* **2008**, *47*, 334–337; d) H. Sun, F. Z. Su, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2009**, *121*, 4454–4457; *Angew. Chem. Int. Ed.* **2009**, *48*, 4390–4393.
- [13] a) M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, *Angew. Chem.* **2004**, *116*, 5936–5939; *Angew. Chem. Int. Ed.* **2004**, *43*, 5812–5815; b) Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen, A. Riisager, *ChemSusChem* **2009**, *2*, 672–675; c) O. Casanova, S. Iborra, A. Corma, *J. Catal.* **2009**, *265*, 109–116; d) A. Villa, G. M. Veith, L. Prati, *Angew. Chem.* **2010**, *122*, 4601–4604; *Angew. Chem. Int. Ed.* **2010**, *49*, 4499–4502.
- [14] M. Ojeda, E. Iglesia, *Angew. Chem.* **2009**, *121*, 4894–4897; *Angew. Chem. Int. Ed.* **2009**, *48*, 4800–4803.
- [15] L. He, J. Ni, L. C. Wang, F. J. Yu, Y. Cao, H. Y. He, K. N. Fan, *Chem. Eur. J.* **2009**, *15*, 11833–11836.
- [16] a) L. E. Manzer, US Patent 7,227,029, **2004**; b) T. M. Lammens, M. C. R. Franssen, E. L. Scott, J. P. M. Sanders, *Green Chem.* **2010**, *12*, 1430–1436.
- [17] In a preliminary survey, ZrO₂ was found to be more suitable as a support for gold NPs owing to its excellent acid tolerance. In contrast, other oxide supports (e.g., Al₂O₃, Fe₂O₃, ZnO, and CeO₂) were leached or even dissolved under the reaction conditions.
- [18] No trace of 2-methyltetrahydrofuran (2-MTHF), a by-product which could raise a critical safety issue, was observed (see Ref. [7b]).
- [19] We confirmed that there was no leaching of gold or ZrO₂ under these highly concentrated and acidic conditions and thus verified the inherent stability of the Au/ZrO₂-VS catalyst in strong acidic media (see the Supporting Information for details).
- [20] The decomposition of FA in the presence of LA is slightly slower than in its absence, probably as a result of the high acidity of LA, which suppresses the decomposition of FA. Moreover, it was verified that there was no variation in the concentration of LA alone under all conditions examined. See the Supporting Information for details.
- [21] a) B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 4026–4029; *Angew. Chem. Int. Ed.* **2008**, *47*, 3962–3965; b) A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* **2008**, *1*, 751–758; c) B. Loges, A. Boddien, F. Gärtner, H. Junge, M. Beller, *Top. Catal.* **2010**, *53*, 902–914; d) K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. Smith, S. C. E. Tsang, *Nat. Nanotechnol.* **2011**, *6*, 302–307.
- [22] a) C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem.* **2008**, *120*, 4030–4032; *Angew. Chem. Int. Ed.* **2008**, *47*, 3966–3968; b) K. Morawa Eblagon, K. Tam, K. M. K. Yu, S.-L. Zhao, X.-Q. Gong, H. He, L. Ye, L.-C. Wang, A. J. Ramirez-Cuesta, S. C. Tsang, *J. Phys. Chem. C* **2010**, *114*, 9720–9730.
- [23] a) T. J. Schmidt, Z. Jusys, H. A. Gasteiger, R. J. Behm, U. Endruschat, H. Boennemann, *J. Electroanal. Chem.* **2001**, *501*, 132–140; b) S. Ha, R. Larsen, R. I. Masel, *J. Power Sources* **2005**, *144*, 28–34; c) N. C. Cheng, R. A. Webster, M. Pan, S. C. Mu, L. Rassaei, S. C. Tsang, F. Marken, *Electrochim. Acta* **2010**, *55*, 6601–6610.
- [24] W. Schwarz, J. Schossig, R. Rossbacher, H. Höke, *Ullmann's Encyclopedia of Industrial Chemistry*, online edition, Wiley InterScience, **2000**.
- [25] a) T. Werpy, J. G. Frye, Y. Wang, H. Zacher, US Patent 6,670,483, **2003**; b) L. E. Manzer, US Patent 6,818,593, **2004**; c) L. E. Manzer, US Patent 6,855,731, **2005**.