

DOI: 10.1002/cssc.201301027

# Enhanced Heterogeneous Catalytic Conversion of Furfuryl Alcohol into Butyl Levulinate

Piera Demma Carà,<sup>[a, b]</sup> Rosaria Ciriminna,<sup>[a]</sup> N. R. Shiju,<sup>\*,[c]</sup> Gadi Rothenberg,<sup>[c]</sup> and Mario Pagliaro<sup>\*,[a]</sup>

We study the catalytic condensation of furfuryl alcohol with 1-butanol to butyl levulinate. A screening of several commercial and as-synthesized solid acid catalysts shows that propylsulfonic acid-functionalized mesoporous silica outperforms the state-of-the-art phosphotungstate acid catalysts. The catalyst is prepared via template-assisted sol-gel polycondensation of

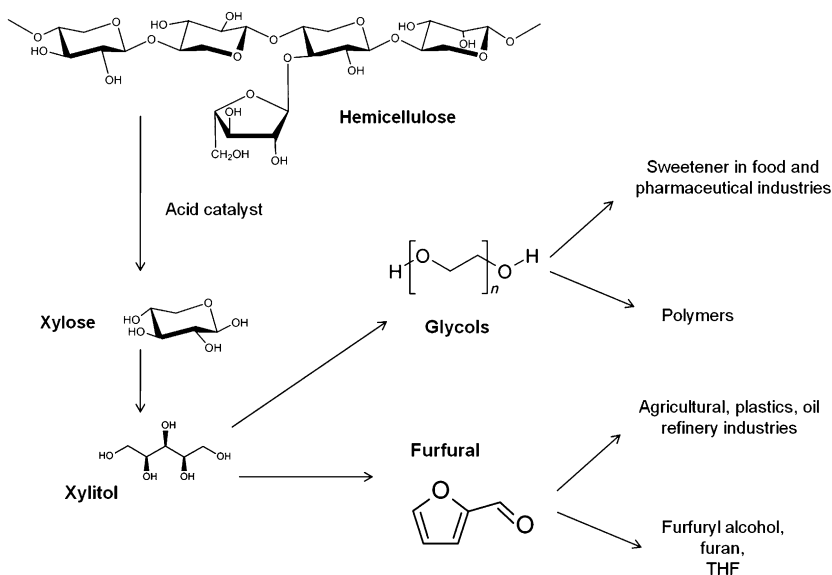
TEOS and MPTMS. It gives 96% yield (and 100% selectivity) of butyl levulinate in 4 h at 110 °C. Reaction profiles before and after a hot filtration test confirm that the active catalytic species do not leach into the solution. The catalyst synthesis, characterization, and mode of operation are presented and discussed.

## Introduction

The practical conversion of biomass into chemicals is an important challenge for today's chemists.<sup>[1]</sup> While biomass is no panacea, it can serve as a renewable resource for several key building blocks (so-called "platform chemicals"; see the example starting from hemicellulose in Scheme 1).<sup>[2–5]</sup> These should be chosen following two main criteria: (1) they should be available on a large scale at reasonable prices, and (2) they should utilize the built-in functionality of the original biomass molecules, thus minimizing the number of process steps.

In this context, we focus here on converting furfuryl alcohol, which is readily obtained from furfural by hydrogenation, into *n*-butyl levulinate (Scheme 2). Alkyl levulinates were identified already in 2004 as one of the top 10 biorefinery candidates.<sup>[6]</sup> *n*-Butyl levulinate, in particular, is

an FDA-approved flavor and fragrance, that also finds application in the solvent and plasticizer sectors.<sup>[7]</sup> The reaction fulfills the two conditions we stated above. Furfural is an important



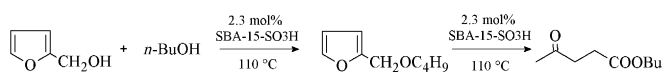
Scheme 1. Renewable chemicals obtained by hemicellulose hydrolysis and catalytic upgrade.

[a] P. Demma Carà, Dr. R. Ciriminna, Dr. M. Pagliaro  
Istituto per lo Studio dei Materiali Nanostrutturati, CNR  
via U. La Malfa 153, 90146 Palermo (Italy)  
E-mail: mario.pagliaro@cnr.it

[b] P. Demma Carà  
Dipartimento Sistemi Agro-Ambientali  
Università degli Studi di Palermo  
viale delle Scienze, 90128 Palermo (Italy)

[c] Dr. N. R. Shiju, Prof. Dr. G. Rothenberg  
Van't Hoff Institute for Molecular Sciences  
University of Amsterdam  
Postbus 94157, 1090 GD Amsterdam (The Netherlands)  
E-mail: n.r.shiju@uva.nl

biomass feedstock that is readily obtained from hemicellulose via hydrolysis and dehydration. Its global production (350 ktona<sup>-1</sup>), mostly located in China, is growing at >6% annual rate.<sup>[8]</sup> Biobutanol (1-butanol) is another versatile chem-



Scheme 2. Acid-catalyzed butanolysis of furfuryl alcohol to *n*-butyl levulinate.

ical currently obtained via the clostridial acetone–butanol–ethanol (ABE) biomass fermentation process. This process is competitive with the traditional oxo process, which starts from propylene.<sup>[9]</sup> Moreover, the butanolysis of furfuryl alcohol into butyl levulinate retains all the functionality of the reactants, so using a biomass derivative here makes “chemical sense” as well.

The acid-catalyzed ethanolysis of furfuryl alcohol is well-known.<sup>[10,11]</sup> Compared to this, publications on butanolysis are scant. To the best of our knowledge, only one report describes using a solid acid catalyst for converting furfuryl alcohol to alkyl levulinates. Using methylimidazolebutylsulfate phosphotungstate (5 mol%), Zhang and coworkers obtained a high *n*-butyl levulinate yield of up to 93% in 12 h.<sup>[12]</sup> That catalyst, however, is expensive and thus less practical, especially in biorefineries, that typically use low-cost feeds.

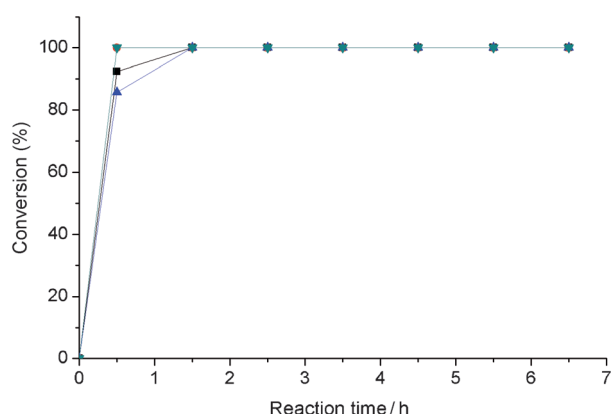
Herein, we study a number of solid acid catalysts, either commercially available or as synthesized in our laboratories. One of these, a hybrid sol–gel silica functionalized with sulfonic acid groups, proved to be an excellent catalyst for this condensation reaction. The results provide relevant guidelines for forthcoming practical applications.

## Results and Discussion

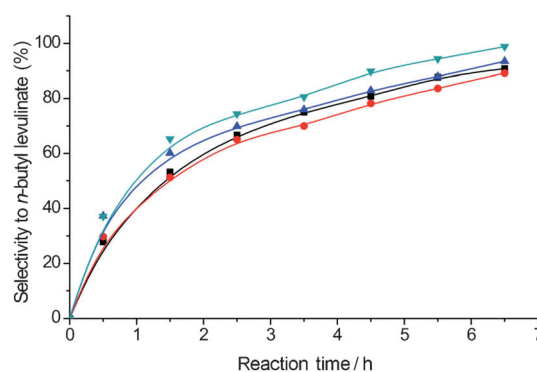
Details on the catalysts and their preparation are provided in the Experimental section. The solid catalysts tested in the butanolysis of furfuryl alcohol are grouped and described below. In the absence of catalyst no conversion of furfuryl alcohol was observed.

### Sulfonic acid-functionalized polystyrene resins

Figure 1 shows that furfuryl alcohol in the presence of different sulfonic acid resins (conventional macroporous Amberlyst and Purolite) is entirely converted in a very short time (0.5–1.5 h). The initial selectivity towards butyl levulinate, however, is poor (Figure 2). After 30 min, all resins gave a selectivity towards



**Figure 1.** Conversion of furfuryl alcohol in the presence of different sulfonic acid-functionalized polystyrene resins. Reaction conditions: furfuryl alcohol (0.177 mL); catalyst (0.05 g); *n*-butanol (6.17 mL); tetradecane (0.100 mL), 110 °C. ■: D5082, ●: D5081, ▲: Amberlyst 35, ▼: Amberlyst 70.



**Figure 2.** Selectivity of sulfonic acid-functionalized polystyrene resins in the conversion of furfuryl alcohol into butyl levulinate. Reaction conditions: furfuryl alcohol (0.177 mL); catalyst (0.05 g); *n*-butanol (6.17 mL); tetradecane (0.100 mL), 110 °C. ■: D5082, ●: D5081, ▲: Amberlyst 35, ▼: Amberlyst 70.

butyl levulinate between 30–40%. After 6.5 h, the selectivity reaches 99% for Amberlyst 70, 93% for Amberlyst 35, and 90% for D5081 and D5082.

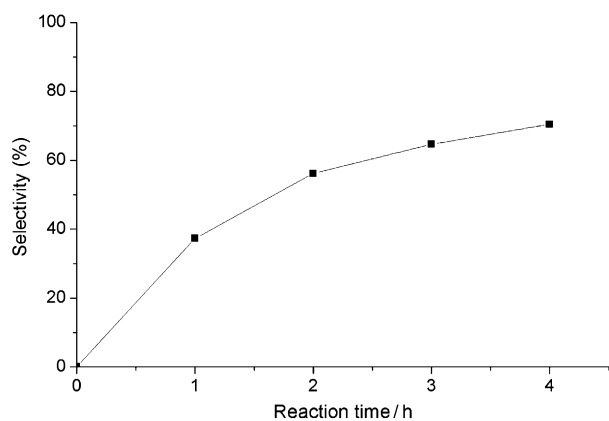
In general, the alcoholysis of furfuryl alcohol occurs in two steps: furfuryl alcohol first rapidly reacts with an alcohol to form intermediates (mostly 2-alkoxymethylfuran),<sup>[13]</sup> and then these intermediates are slowly converted into alkyl levulinate (Scheme 2). These results agree with the fact that D5081 and D5082 are functionalized at relatively low levels (1 mmol g<sup>-1</sup> and 2 mmol g<sup>-1</sup>, versus >5 mmol g<sup>-1</sup> for Amberlyst 15 and Amberlyst 70; approximately one sulfonic acid group per phenyl group in the resin). Amberlyst 35 is similar except that it has been “over-sulphonated” by 10–20%. The highest activity of Amberlyst 70 is ascribed to the increased strength of the supported sulfonic acid groups, through the interaction and activating effects of neighboring sulfonic acid groups.<sup>[14]</sup>

### Sulfonic acid-grafted silica gel and carbon

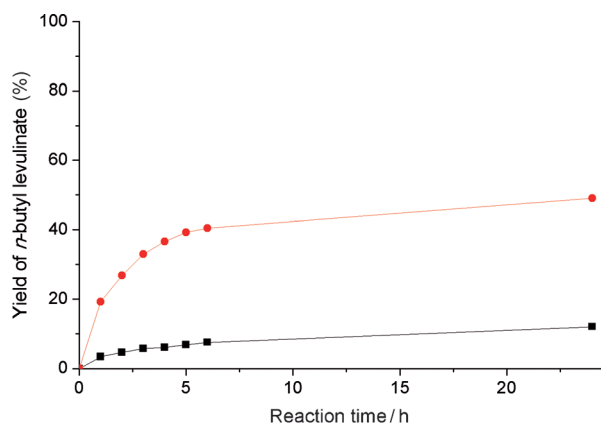
In the presence of sulfonic acid grafted silica gel, the conversion of furfuryl alcohol was complete in 1 h. The initial selectivity towards butyl levulinate, however, was low, similar to that with sulfonic acid resins. After 6 h, butyl levulinate is the main reaction product, but the 77% selectivity achieved is even lower than in the case of the acid organic resins (Figure 3). Sulfonated carbon was poorly active. After 6 h the conversion of furfuryl alcohol was almost complete (96%), but the selectivity for the desired product was only 16%, the rest was converted into secondary products.

### Zeolites and niobium oxide

Zeolites HZSM-5 (Si/Al ratio 50), and H-ferrierite (Si/Al ratio 55), despite stronger acid sites, showed poor activity, too (Figure 4). Even with a complete conversion of furfuryl alcohol into the intermediate of reaction, HZSM-5 gave only 19% yield of *n*-butyl levulinate after 1 h, with a slight improvement to 40% after 6 h. For H-ferrierite, the maximum yield of *n*-butyl



**Figure 3.** Selectivity of sulfonic acid-functionalized silica gel in the conversion of furfuryl alcohol into butyl levulinate. Reaction conditions: furfuryl alcohol (0.177 mL); catalyst (0.05 g); *n*-butanol (6.17 mL); tetradecane (0.100 mL), 110 °C.



**Figure 4.** Yield of *n*-butyl levulinate using HZSM-5 (red line) and H-ferrierite (black line) as catalysts. Reaction conditions: furfuryl alcohol (0.177 mL); catalyst (0.05 g); *n*-butanol (6.17 mL); tetradecane (0.100 mL), 110 °C.

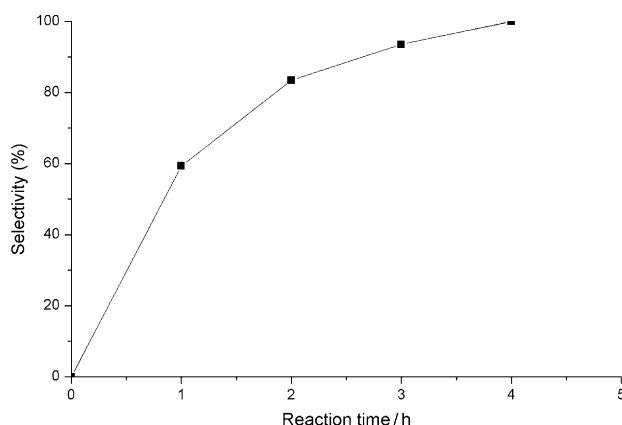
levulinate was 12%, after 23 h. The low activity may reflect the restricted pore sizes of microporous zeolites.

Further, we tested both niobium oxide hydrate and niobium oxide calcined at 400 °C. Niobic acid is an unusual solid acid, showing high acidic strength for certain reactions in spite of its relatively high water content.<sup>[15]</sup> In both cases no butyl levulinate was formed. The oxide in the hydrated form gave only 7% furfuryl alcohol conversion after 6 h. With calcined Nb<sub>2</sub>O<sub>5</sub> the conversion of furfuryl alcohol increased up to 62%. This points to the fact that conversion needs both Lewis and Brønsted acid sites.<sup>[16]</sup> We remind here that the acidity in these oxides depends on the calcination temperature, with both Lewis and Brønsted acid sites present at low calcination temperatures (400 °C) and only Lewis acidity being residual at high calcination temperature (700 °C).<sup>[17]</sup>

### Sulfonic acid-functionalized SBA-15

The most active and selective catalyst amongst those tested here was the sulphonated (arenesulfonic) mesoporous silica,

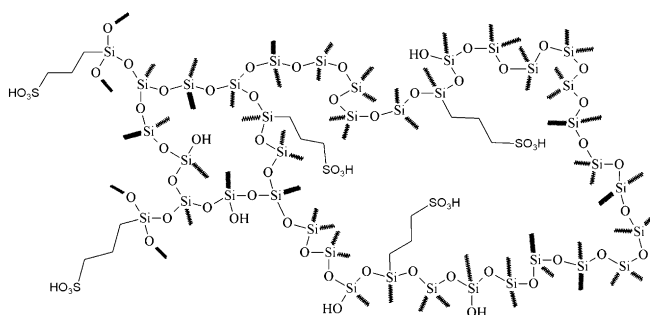
SBA-15-SO<sub>3</sub>H. This material is known for its excellent catalytic activity in the etherification of glycerol.<sup>[18]</sup> It was first synthesized in the early 2000s by Melero and co-workers.<sup>[19]</sup> Propylsulfonic acid-functionalized mesoporous silica (SBA-15-SO<sub>3</sub>H) was synthesized by sol-gel co-polycondensation of TEOS and 3-MPTMS in the presence of templating agent Pluronic surfactant. The process affords a periodic mesoporous organosilica that, compared to sol-gel mesoporous materials obtained without templating agents, exhibits long-range order and enhanced accessibility of the acid groups to the incoming reactants.<sup>[20,21]</sup> This material completely converted the furfuryl alcohol into intermediates in only 15 min. After 4 h the reaction was complete with 96% selectivity towards *n*-butyl levulinate (Figure 5).



**Figure 5.** Selectivity of sulfonic acid-functionalized SBA-15 in the conversion of furfuryl alcohol into butyl levulinate. Reaction conditions: furfuryl alcohol (0.177 mL); catalyst (0.05 g); *n*-butanol (6.17 mL); tetradecane (0.75 mL), 110 °C.

Such sol-gel entrapped catalysts act as molecular sponges, adsorbing and concentrating reactants at the cage (Scheme 2) surface. In agreement with the findings of Melero,<sup>[18]</sup> no significant degradation of the catalyst occurred, which is a crucial requirement for any forthcoming practical application (Scheme 3).

Given the excellent results above, we studied the influence of varying catalyst and *n*-butanol amounts in the SBA-15-SO<sub>3</sub>H-



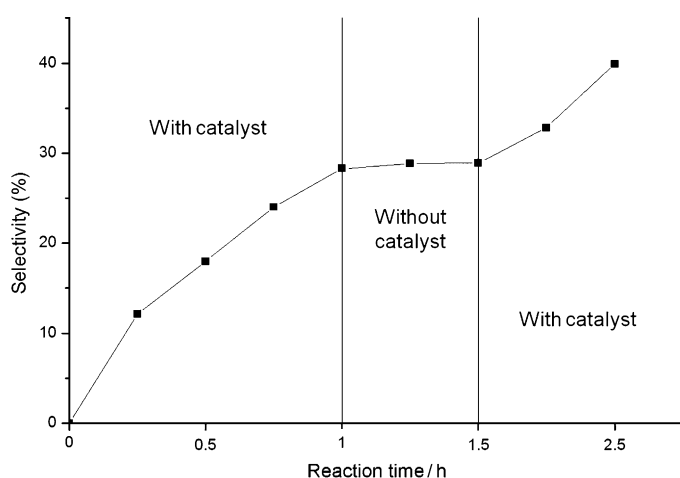
**Scheme 3.** Suggested representation of the structure of the sulfonic acid-functionalized SBA-15-SO<sub>3</sub>H, prepared by co-condensing TEOS and 3-MPTMS at 9:1 mol/mol.

Catalyst amount <sup>[a]</sup> [g]	<i>n</i> -Butanol [mL]	Yield <sup>[b]</sup> [%]
0.025	6.17	26
0.050	6.17	96
0.075	6.17	85
0.050	3	63
0.050	6.2	96
0.050	9	72

[a] Reaction conditions: Furfuryl alcohol (0.2 g, 0.33 M); i.s. tetradecane (0.058 g), 110 °C. [b] Furfuryl alcohol conversion is 100% in all cases; after 4 h reaction; GC analysis.

mediated alcoholysis of furfuryl alcohol. Results in Table 1 show that increasing the catalyst amount of 0.05 g up to 0.075 g has only a minor influence on the rate and the selectivity of the reaction. A lower amount of catalyst (0.025 g) reduces the selectivity to levulinate, indicating the need of a minimum number of catalytically active acid sites for levulinate formation. Keeping constant the amount of furfuryl alcohol, we then varied the amount of *n*-butanol, thereby changing also the concentration of furfuryl alcohol. Decreasing the volume from 6.2 mL to 3 mL, the selectivity to *n*-butyl levulinate after 4 h decreased to 77%. At higher concentration of furfuryl alcohol, the intermediate 2-butoxymethylfuran quickly formed. However the *n*-butyl levulinate yield was lower due to partial polymerization of furfuryl alcohol at higher concentration.<sup>[22]</sup> By increasing the volume of *n*-butanol from 6.2 mL to 9 mL, we inhibited the first step of the reaction by decreasing the furfuryl alcohol concentration. In both cases, the overall result was less *n*-butyl levulinate.

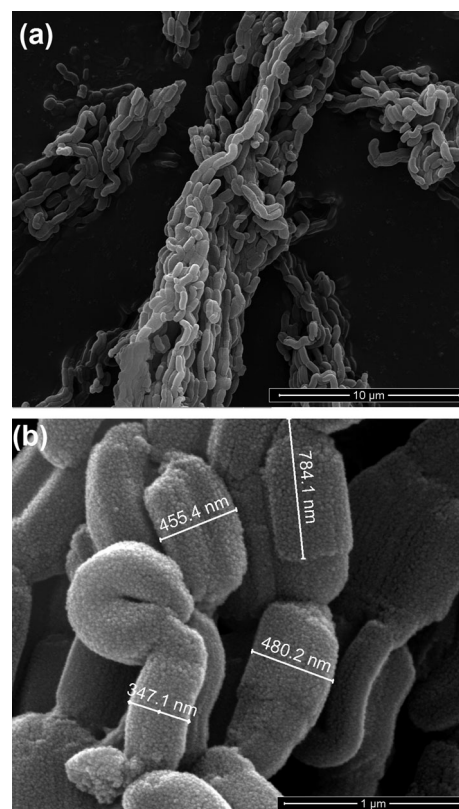
Finally, to exclude the possibility of homogeneous catalysis due to leaching of the organosilica-entrapped sulfonic acid groups, we carried out a hot filtration test. The solid catalyst was filtered out under hot conditions and the reaction was continued with the filtrate under same conditions. Figure 6



**Figure 6.** Results for the hot filtration test with SBA-15-SO<sub>3</sub>H. Reaction conditions: furfuryl alcohol (0.177 mL); catalyst (0.05 g); *n*-butanol (6.17 mL); tetradecane (0.75 mL), 110 °C.

shows that when the catalyst is removed from the reaction mixture, the reaction stops. When the catalyst is re-added, the reaction resumes with a similar rate. This proves that no active catalytic species leach into the solution.

The SEM investigation of the catalyst structure reveals that the sulfonic-modified SBA-15 material consists of many fiber-like domains of rather uniform size (430 nm on average) aggregated into macrostructures (Figure 7). Successful incorporation of sulfonic acid groups is clearly proved by the FT-IR spectrum (Figure 8).



**Figure 7.** SEM images of SBA-15-SO<sub>3</sub>H at different scale showing the aggregation of fiber-like domains. a) HV 20 kV, mag. 10 000 x, 10 μm; b) HV 20 kV, mag. 100 000 x, 1 μm.

The bands around 1220, 1070, 794 and 471 cm<sup>-1</sup> are assigned to the typical Si–O–Si banding and stretching vibrations of condensed silica network and the peaks around 960 cm<sup>-1</sup> correspond to non-condensed Si–OH groups. The peak at 698 cm<sup>-1</sup> is assigned to the bending vibration of the sulfonic acid group while the peaks at 1190 cm<sup>-1</sup> and 1036 cm<sup>-1</sup>, typical of –SO<sub>3</sub>H groups, are overlapped with the broad band of the silica framework.<sup>[23, 24]</sup>

## Conclusions and Outlook

Propylsulfonic acid-functionalized mesoporous silica prepared by the template-assisted sol–gel polycondensation of TEOS and MPTMS is an efficient catalyst for condensing butanol with furfuryl alcohol to butyl levulinate. The catalyst does not leach

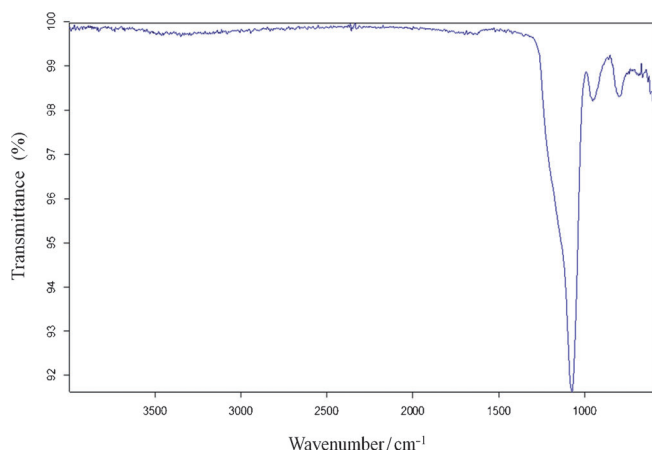


Figure 8. FT-IR spectrum of SBA-15-SO<sub>3</sub>H after removing surfactant.

into solution, and gives excellent yields and 100% selectivity after 4 h at 110 °C. Its activity and selectivity are much higher than those of sulphonated macroporous acidic resins such as Amberlyst 70. As the supply of furfural and biobutanol continue to increase, this catalyst and the related simple catalytic butanolysis route are good candidates for applications in biorefineries.

## Experimental Section

### Materials and instrumentation

Furfuryl alcohol (98% for GC), 1-butanol (99.8% for HPLC grade) and tetradecane (>99% for GC) were supplied by Sigma Aldrich. The silica gel for the synthesis of the functionalized mesoporous silica gels (SBA-15-SO<sub>3</sub>H), was supplied by Biosolve (60 Å, 0.063–0.200 mm). Tetraethoxysilane (TEOS, purity 98%), 3-mercaptopropyltrimethoxysilane (MPTMS, purity 85%), poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer Pluronic 123, and ethanol were supplied by Sigma Aldrich and used as-received.

The other catalysts tested were Amberlyst 70 and Amberlyst 35 (sulphonated macroporous polystyrene/divinylbenzene resin, Rohm and Haas), sulfonic acid-functionalized hypercrosslinked polystyrene resins in bead form (D5081 and D5082, Purolite International), niobium oxide hydrate (Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O) niobium oxide calcined at 400 °C, sulfonic acid-functionalized carbon, H-ZSM5 zeolites in protonic form (nominal Si/Al ratio of 55, Zeolyst International), and ferrierite in ammonium form (nominal Si/Al ratio of 55, Shell). The ammonium form was converted to the protonic form by heating to 500 °C at 5 °C min<sup>-1</sup> and calcining at this temperature for 4 h.

All experiments were carried out under reflux in a round-bottom flask equipped with a condenser and a heating plate, and analyzed by an Interscience Trace GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (VB-1, 30 m × 0.325 mm). When needed, by-products were identified by (GC-MS). FT-IR spectra were collected using a Bruker spectrometer. Morphology and size of the particles were determined by scanning electron microscopy (SEM) using an ESEM microscope (Philips, XL30) operating at 25 kV. The filtration procedure as a test for active species leaching is described in detail elsewhere.<sup>[25]</sup>

### Catalyst syntheses

#### Procedure for synthesizing sulfonic acid-functionalized silica gel

Sulfonic acid-functionalized silica gel was synthesized by grafting using a modification of a published procedure.<sup>[26]</sup> Silica gel (2 g) was added to toluene (20 mL) and heated to 115 °C with stirring for 1 h. Then, 3-mercaptopropyltrimethoxysilane (10.0 mmol, 2.0 g) was added and the stirring was continued at the same temperature for 24 h. The solid was filtered, washed with water (5 × 20 mL), and dried under ambient conditions overnight. It was then re-suspended in 33% H<sub>2</sub>O<sub>2</sub> (35 mL) and stirred for 1 h in a closed vessel at 60 °C. Note that oxidizing at this elevated temperature is advantageous in preparing these materials.<sup>[27]</sup> The solid was then filtered, and the cake was washed and re-suspended in 35 mL of 10% w/w H<sub>2</sub>SO<sub>4(aq)</sub> and stirred for another hour at room temperature. The final product was then filtered, washed with water (4 × 20 mL) and dried under ambient conditions overnight.

#### Procedure for synthesizing propylsulfonic acid-functionalized mesoporous silica (SBA-15-SO<sub>3</sub>H)

SBA-15-SO<sub>3</sub>H was synthesized following the co-condensation procedure described by Melero and coworkers.<sup>[28]</sup> The template, Pluronic 123 (4 g), was dissolved with stirring in 2 M HCl solution (125 g) at room temperature. The solution was heated to 40 °C and the required amount of TEOS added and stirred for 45 min. After this pre-hydrolysis period the required amount of MPTMS and 33% H<sub>2</sub>O<sub>2</sub> (20 mL) were added. The resulting mixture was stirred at 40 °C for 20 h and then aged without stirring for 24 h at 100 °C. The molar ratio of TEOS to MPTMS was 9:1. The solid product was then filtered and air-dried. The template was extracted with excess ethanol under reflux for 24 h (300 mL g<sup>-1</sup>), followed by washing with ethanol and drying at 100 °C.

#### Procedure for catalytic reaction

The SBA-15-SO<sub>3</sub>H catalyst (0.050 g; 2.3 mol% based on furfuryl alcohol) and 2.04 mmol of furfuryl alcohol were added to 5.0 g of 1-butanol in a round bottom flask and placed under reflux at 110 °C. Tetradecane was used as internal standard. Reactant conversion and product yields were monitored by GC.

## Acknowledgements

P.D.C. thanks Prof. Giuseppe Alonzo (University of Palermo and president of Italy's CRA) for co-mentoring on the conclusion of her PhD.

**Keywords:** alcohols · biomass · esterification · heterogeneous catalysis · solid acids

- [1] B. Kamm, P. R. Gruber, M. Kamm, *Biorefineries—Industrial Processes and Products*, Wiley-VCH, Weinheim, 2006.
- [2] P. Demma Carà, M. Pagliaro, A. Elmekawy, D. R. Brown, P. Verschuren, N. R. Shiju, G. Rothenberg, *Catal. Sci. Technol.* **2013**, *3*, 2057–2061.
- [3] Z. Strassberger, S. Tanase, G. Rothenberg, *Eur. J. Org. Chem.* **2011**, 5246–5249.
- [4] C. Caro, K. Thirunavukkarasu, M. Anil Kumar, N. R. Shiju, G. Rothenberg, *Adv. Synth. Catal.* **2012**, *354*, 1327–1336.



- [5] N. R. Shiju, G. Rothenberg, D. R. Brown, *Top. Catal.* **2010**, *53*, 1217–1223.
- [6] US Department of Energy, *Top Value Added Chemicals from Biomass, Volume 1, Results of Screening for Potential Candidates from Sugars and Synthesis Gas*, **2004**, Report NREL/TP-510-355532.
- [7] Market Publishers, Butyl Levulinate (CAS 2052-15-5) Market Research Report 2013, London, **2013**.
- [8] China is the biggest supplier of furfural in the global market, accounting for 80% of global capacity and 72% of world consumption. The other major commercial producer is Sasol in South Africa. For detailed information, see the market report: HIS Chemicals, *Furfural*, August 2011. <http://www.ihs.com/products/chemical/planning/ceh/furfural.aspx>.
- [9] B. P. Tracy, *mBio* **2012**, *3*, e00518–12.
- [10] a) K. J. Zeitsch, *The Chemistry and Technology of Furfuryl Alcohol and its Many By-Products*, Elsevier, Amsterdam, **2000**; b) J.-P. Lange, E. van der Heide, J. van Buijtenen, R. Price, *ChemSusChem* **2012**, *5*, 150–166; c) J.-P. Lange, W. D. van de Graaf, R. J. Haan, *ChemSusChem* **2009**, *2*, 437–441.
- [11] a) R. H. L. Hilford, K. R. Dagendam, US Patent 2.735.665, **1956**; b) C. C. Hsu, D. W. Chasar, US Patent 4.236.021, **1980**; B. Capai, G. Lartigau, US Patent 5.175.358, **1992**.
- [12] Z. Zhang, K. Dong, Z. K. Zhao, *ChemSusChem* **2011**, *4*, 112–118.
- [13] In detail, the GC-MS analysis gives 4 peaks for secondary products, two of which are small. MS analysis allows to identify only the intermediate, which is 2-alkoxymethylfuran. The remaining peaks give molecular ions at 259, 287, 244 as the result of the formation of larger molecules that could not be identified.
- [14] E. Andrijanto, E. A. Dawson, D. R. Brown, *Appl. Catal. B* **2012**, *115–116*, 261–268.
- [15] T. Okuhara, *Chem. Rev.* **2002**, *102*, 3641–3666.
- [16] K. Wilson, D. J. Adams, G. Rothenberg, J. H. Clark, *J. Mol. Catal.* **2000**, *159*, 309–314.
- [17] G. S. Nair, E. Adrijanto, A. Alsalmé, I. V. Kozhevnikov, D. J. Cooke, D. R. Brown, N. R. Shiju, *Catal. Sci. Technol.* **2012**, *2*, 1173–1179.
- [18] J. A. Melero, G. Vicente, G. Morales, M. Paniagua, J. M. Moreno, R. Roldán, A. Ezquerro, C. Pérez, *Appl. Catal. A* **2008**, *346*, 44–51.
- [19] J. A. Melero, G. D. Stucky, R. van Grieken, G. Morales, *J. Mater. Chem.* **2002**, *12*, 1664–1670.
- [20] a) R. Ciriminna, G. Palmisano, M. Pagliaro, *Chem. Rec.* **2010**, *10*, 17–28; b) M. Pagliaro, R. Ciriminna, G. Palmisano, *Chem. Soc. Rev.* **2007**, *36*, 932–940.
- [21] N. R. Shiju, A. H. Alberts, S. Khalid, D. R. Brown, G. Rothenberg, *Angew. Chem.* **2011**, *123*, 9789–9793; *Angew. Chem. Int. Ed.* **2011**, *50*, 9615–9619.
- [22] a) L. Pranger, R. Tannenbaum, *Macromolecules* **2008**, *41*, 8682–8687; b) A. Mija, P. Navard, C. Peiti, D. Babor, N. Guigo, *Eur. Polym. J.* **2010**, *46*, 1380–1387.
- [23] C. C. Chen, S. Cheng, L. Y. Jang, *Microporous Mesoporous Mater.* **2008**, *109*, 258–270.
- [24] X. Shi, Y. Wu, H. Yi, G. Rui, P. Li, M. Yang, G. Wang, *Energies* **2011**, *4*, 669–684.
- [25] A. V. Gaikwad, V. Boffa, J. E. ten Elshof, G. Rothenberg, *Angew. Chem.* **2008**, *120*, 5487–5490; *Angew. Chem. Int. Ed.* **2008**, *47*, 5407–5410.
- [26] P. F. Siril, N. R. Shiju, D. R. Brown, K. Wilson, *Appl. Catal. A* **2009**, *364*, 95–100.
- [27] E. Cano-Serrano, G. Blanco-Brieva, J. M. Campos-Martin, J. L. Fierro, *Langmuir* **2003**, *19*, 7621–7627.
- [28] D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* **1999**, *11*, 2148.

---

Received: September 25, 2013

Published online on February 12, 2014