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Supporting Information

Snβ-zeolite catalyzed oxido-reduction cascade chemistry with biomass-derived molecules.

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Catalyst synthesis and catalytic tests

The catalytic materials were synthesized as described in literature.[1] Commercial β zeolite (CP814e, Zeolyst International, SiO_2/Al_2O_3 = 25) was dealuminated by stirring the zeolite powder overnight in an aqueous HNO_3 solution (55 ml per gram of zeolite, at 353 K), an acid concentration of 7.2M was used. Afterwards, the powders were filtered, washed with water and dried at 333 K. Before grafting, the powders were dried at 423 K to remove excess of physisorbed water. The dealuminated zeolite was contacted with $SnCl_4.5H_2O$ (27 mmol/g of zeolite) in dried isopropanol (100 ml/g of zeolite) and placed in a reflux setup under N_2 atmosphere. After 7 hours, the mixture was filtered in air, rinsed with dry isopropanol, dried at 333 K and calcined (3 K/min to 473 K, dwell 6 hours, 3 K/min to 823 K, dwell 6 hours). The material is denoted as Sn/DeAlβ. Hydrothermal Snβ was synthesized following procedures described in literature.[2]

Materials containing both Sn and Al were synthesized by changing the acid concentration during dealumination to 3.6M instead of 7.2M. This ensured a presence of 0.29wt% of Al in the material. Other steps and parameters are kept constant.

Catalytic tests were performed in magnetically stirred and closed glass reactors of 10 ml, which were placed in a copper heating block. Temperature control is carried out in a reference glass reactor containing only solvent. For Baeyer-Villiger reactions, 1.11 mmol of ketone was added to 50 mg of catalyst in 5 ml of dioxane. 50 wt% aqueous H_2O_2 solution was added in a molar H_2O_2/ketone-ratio of 2 (0.114 ml). Ethylcyclohexane was used as the internal standard for chromatographic analysis and quantification. For reactions with per-acid, 2,22 mmol m-CPBA was used as the oxidans instead of H_2O_2. The catalytic reactions were performed at 363K. Meerwein-Ponndorf-Verley reactions were performed at 373K. 15 mg of catalyst was added to a 2-butanol solution containing 1 mmol of ketone. The solvent was used in a 2-butanol/ketone ratio of 50 (4.6 ml). 1,4-dioxane was used here as the internal standard. For each reaction, aliquots of the sample were taken at regular time intervals through a rubber septum and were quantitatively analyzed with an Agilent 6850 GC, equipped with a HP-1 column and FID detector. Identification of these products was based on retention time analysis and confirmed by GC-MS (Agilent 6890 GC with HP5-MS column and Agilent 5973 Mass Selective Detector). Turnover frequency was calculated as $mole_{product}.h^{-1}.mole_{Sn}^{-1}$. Mole Sn present in the materials was determined by EPMA analysis. Absence of extraframework SnO_2 species was verified with DR UV-vis analysis, combined with ^{119}Sn MAS NMR, XRD and EXAFS Analysis.[1, 3] Accessibility of the Sn-sites was verified with (quantitative) pyridine and cyclohexanone-probed FTIR measurements. Both techniques showed a clear correlation between amount of cyclohexanone adsorbed and number of Sn-sites present in the materials. It can therefore be concluded that these S)sites are all accessible for substrates The combination of all these techniques allows a comparison between the materials based on the TOF during reaction. To exclude a limitation in substrate availability or catalyst deactivation, turnover frequencies were determined at initial conversion points after 30 minutes of reaction. Selectivity was determined near full conversion (reached after 6h).

Cascade reaction:
Catalytic cascade tests were performed in the same reactor setup as described above, heating and temperature control are also identical. 50 mg of catalyst and 1 mmol alcoholic substrate were added to 4.6 ml of 2 butanone. The mixture was heated to 373 K and allowed to react for 3h. At the 3h point, 2 mmol H_2O_2 was injected in the reactor to start the BV reaction. The mixture was stirred for another 3h.

Hot filtration test:
A typical BV reaction was started. After 30 minutes of reaction, a sample of reactant medium was taken and filtered to remove any heterogeneous catalyst particles. The sample was placed in a reaction vial, and set in reaction conditions. Both the filtrate and the original reaction vial were allowed to react and samples were taken at regular time intervals through a rubber septum.

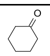
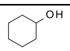
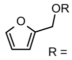
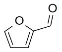
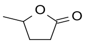
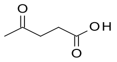
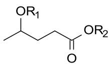
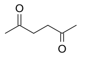
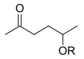
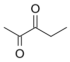
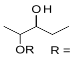
Efficiency H_2O_2:
To test the efficiency of the H_2O_2 use, a reaction was set up using a H_2O_2/ketone ratio of 0.5. After 6 hours of reaction, the yield of ε-caprolactone was determined and efficiency was calculated as yield/0.5. To test the efficiency in utilization of H_2O_2, The catalysts were used in a reaction with a H_2O_2/substrate-ratio of 0.5. After 6 hours, yields of 34 and 30% were found for the hydrothermally synthesized and the post synthetic material respectively, corresponding to a similar H_2O_2 efficiency of 68 and 60%. These values are unexpectedly low, as an efficiency of 86% was reported for Sn-MCM-41 materials.[4] Possibly, the used H_2O_2 did not contain the claimed concentration (50%) of H_2O_2. Therefore, these absolute value of this test should be taken with extreme caution. The ratio between PS and HT materials, however, indicates that both materials have a similar H_2O_2 efficiency.

Reagent suppliers and purity:
Tin chloride pentahydrate (98%), nitric acid (65%), cyclohexanone (99%), furfural (99%), 2,5-hexanedione (98%), levulinic acid (98%), cyclohexanol (99%), 2-methyl cyclohexanone (98%), 3-methyl cyclohexanone (97%), 4-methyl cyclohexanone (99%), 4-ethyl cyclohexanone (97%), 4-propyl cyclohexanone (99%), 4-tert butyl cyclohexanone (99%), 2-ethoxy cyclohexanone (98%), 1,4-dioxane (99.8%), 4-tert butyl cyclohexanol (98%) and 2-ethyl cyclohexanol (99%) were purchased from Sigma Aldrich. Zeolite beta, CP814E, was purchased from Zeolyst international, purity unknown. 2-butanol (99%) and 2,3-pentanedione (97%) were purchased from Acros organics. 4-propylcyclohexanone (95%)) and 4-propylcyclohexanol (98%) were purchased from TCI Europe. 2-butanone (99%) was purchased from Fisher Scientific.

Additional graphs and tables

MPV with various biomass-derived carbonyl compounds like furfural, levulinic acid, 2,5-hexanedione and 2,3-pentanedione was explored. Furfural is a product derived from hemicellulose[5], while levulinic acid and 2,5-hexanedione are usually produced from carbohydrates like cellulose and inuline.[6-8] 2,3-Pentanedione can be obtained from lactic acid.[9, 10]
Upon testing the carbonyl compounds, we noticed a diverse substrate reactivity, but also that MPV in presence of both Snβ types tolerates various functional groups such as furans, carboxylic acids and diketones. For instance, furfural is fairly reactive and can be selectively converted to furfuryl alcohol, a precursor for levulinic acid,[11] and its ether derivative (entries 2A and B, Table 1). When performing the reaction at higher temperatures, significant amounts of γ-valerolactone were analyzed (entries 3A and B). Formation of γ-valerolactone is a consequence of the domino pathway involving two MPV reactions, a ring-opening and lactonization reaction, as was recently demonstrated.[12] To improve the yield, a PS-Snβ containing also Brønsted acid sites (to catalyze the ring-opening steps) was readily prepared according to a reported procedure (experimental details in supporting information),[3] forming PS-Snβ with an atomic Si:Al:Sn zeolite composition of 101:1:2. A γ-valerolactone yield of 30% was obtained in presence of the latter catalyst (entry 3C). The direct conversion of levulinic acid with 2-butanol to γ-valerolactone though is difficult to achieve (entries 4A and 4B) in line with earlier reports.[12] MPV of bio-derived diones yields the respective alcohols and ethers. The conversion of 2,5-hexanedione is slow, but the reaction is substantially faster and more selective in presence of PS-Snβ (entries 5A and B in Table 1). 2,3-pentanedione is converted unprecedentedly fast in presence of both catalysts, with catalytic turnover frequencies (TOFs) over 100 h^{-1} (entries 6A and B).

Table S1: Catalytic results of MPV in presence of PS- Snβ (1.57 wt% Sn) (A), HT-Snβ (1.26 wt% Sn) (B) and PS- Snβ with Brønsted acidity (1.57 wt% Sn, 0.29 wt% Al) (C). Conditions: 15 mg catalyst, 1 mmol substrate, 50 mmol 2-butanol (50:1 molar ratio of solvent to substrate molar ratio), 373 K. [a] Turnover frequency (TOF) was calculated after 30 min of reaction. [b] Yield and selectivity (Sel.) were calculated after 6 h. [c] Sum of products with R = H and C_4H_9. [d] Reaction at 393 K, 2.1 mmol furfural in 5 ml 2-butanol, Fur:Sn = 100:1, 24 h.[12].

Entry	Substrate	Product	TOF[a] (h^{-1})	Yield[b] (Sel. Sum H+R)) (%)	Product molar ratio (%) R=
1A			96	89 (99)	/
1B			78	84 (99)	/
2A		 R = H or C_4H_9	62	71 (90)[c]	H: 55.9%, C_4H_9: 44.1%
2B			45	35 (88)[c]	H: 99%, C_4H_9: 1%
3A[d]			/	16 (17)	/
3B[d]			/	4 (6)	/
3C[d]			/	30 (32)	/
4A		 R_x= H or C_4H_9	6	9 (95)[c]	R_1:H; R_2:H: 33.8% R_1:H; R_2:C_4H_9: 24.5% R_1:C_4H_9; R_2:H: 41.6% R_1: C_4H_9; R_2:C_4H_9: 0%
4B			<1	1 (9)[c]	R_1:H; R_2:H: 88.0% R_1:H; R_2:C_4H_9: 12.0% R_1:C_4H_9; R_2:H: 0% R_1: C_4H_9; R_2:C_4H_9: 0%
5A		 R = H or C_4H_9	16	19 (84)[c]	H: 32.2%, C_4H_9: 67.8%
5B			<1	<1 (44)[c]	H: 100%, C_4H_9: 0%
6A		 R = H or C_4H_9	105	37 (68)[c]	H: 58.6%, C_4H_9: 41.4%
6B			130	41 (82)[c]	H: 59.8%, C_4H_9: 40.2%

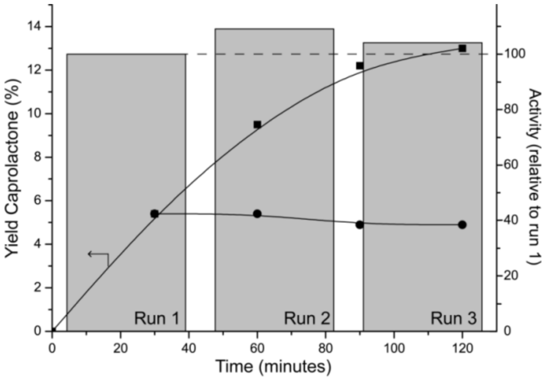


Figure S1 Results of a hot filtration test (bottom and left axis) and from 3 consecutive runs (right axis) with Sn/DeAlβ in a Baeyer-Villiger oxidation of cyclohexanone. The square points show the reaction with heterogeneous catalyst, the dots show the reaction after filtration of the heterogeneous particles. The striped line indicates the 100% activity of the first run in the consecutive run test.

Table S2 Catalytic result of stability tests in Meerwein-Ponndorf-Verley (entries 1-3) and Baeyer-Villiger (entries 4-5) reactions. MPV reactions were performed in 2-butanol at 373K with cyclohexanone using the Sn/DeAlβ catalyst. BV reaction were performed with cyclohexanone in 1,4-dioxane at 363K. [a]Productivity and TOF were calculated after 30 min of reaction. [b]Sample was calcined in air at 823K.

	Entry	run	Sn-content	Initial Productivity[a]	Initial TOF[a]	Selectivity
			wt%	$g_{product}.h^{-1}.kg_{catalyst}^{-1}$	$Mole_{product}.mole_{Sn}^{-1}.h^{-1}$	%
MPV	1	fresh	1.57	1277	96	>99
	2	3th	1.57	627	48	>99
	3 [b]	4th	1.57	1249	96	>99
BV	4	fresh	1.57	742	49	98
	5	3th	1.57	772	51	98

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