Supplementary Material (ESI) for Green Chemistry

Electronic Supporting Information

Solvent-free Dehydrogenation of γ-Terpinene in a Ball Mill: Investigation of reaction Parameters

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Aluminas and silicas applied as milling auxiliaries

As indicated in Figure 1 of the manuscript different aluminas and silicas have been applied as grinding auxiliary in the solvent-free dehydrogenation of γ-terpinene (**1**) to *p*-cymene (**2**) initiated by ball milling. Table S1 provides particle sizes of all materials, the suppliers, and for the listed aluminas the surface properties. Employment of these materials as auxiliary afforded similar product yields either in presence or in absence of $KMnO_4$ as the oxidant. Due to this equality of the materials the median values are reported in Figure 1 of the manuscript.

Table S1: Milling auxiliaries applied for solvent-free dehydrogenation of γ-terpinene (**1**) to *p*-cymene (**2**) in a planetary ball mill.

auxiliary	particle size	pH-value	supplier	Y_2 [%][a,b]	Y_2 [%][a,c]
α-Al_2O_3 = alumina[d]	0.063-0.2 mm	acid	Merck	99	5
α-Al_2O_3(II)	0.05-0.2 mm	basic	Fluka	99	2
γ-Al_2O_3(III)	0.063-0.2 mm	basic	Merck	99	4
γ-Al_2O_3(IV)	0.063-0.2 mm	neutral	Merck	92	4
			Median:[e]	97	4
SiO_2(II)	0.063-0.2 mm		Fluka	99	10
SiO_2(III)	0.063-0.2 mm		VWR	95	8
SiO_2(IV)	0.04-0.063 mm		Machery-Nagel	95	10
SiO_2(V)	0.2-0.5 mm		Merck	95	10
			Median:[e]	96	9

[a] Batch (per beaker): 3.8 g auxiliary, 2 mmol **1**, 0.1 g H_2O; Ball milling: 2 milling beakers (ZrO_2, V = 45 ml), 6 milling balls (ZrO_2, d = 15 mm) per beaker; ν_{rot} = 800 rpm (13.3 Hz).

[b] With $KMnO_4$ (6 mmol) as oxidant.

[c] Without oxidant.

[d] Equal to the auxiliary "alumina" in the manuscript.

[e] Values reported in Figure 1 of the manuscript.

The modification in case of aluminas has been determined by XRD. All materials listed in *Table S1* have a purity of >95%, and are intended to use for chromatography.

Water as milling auxiliary

It was shown recently, that addition of water or the presence in form or physisorbed water on the milling auxiliary surface is beneficial for solvent-free transformation in ball mills.[1,2] However, reactions in presence of different amounts of water (0-0.4 g) added to the reaction mixture resulted in indifferent yields of *p*-cymene (**2**) from the dehydrogenation of γ-terpinene (**1**) initiated by ball-milling (Figure S1). Additionally, the water content has no significant influence on the product selectivity (> 98%). Nonetheless, doping the reaction mixture with water resulted in non-agglomerated free-flowing powders after treatment in the ball mill. Thus, the following work-up by extraction is strongly enhanced. Similar effects have been observed if $NaIO_4$ or $(NH_4)_4Ce(SO_4)_4$ are applied as oxidizing agents instead of $KMnO_4$.

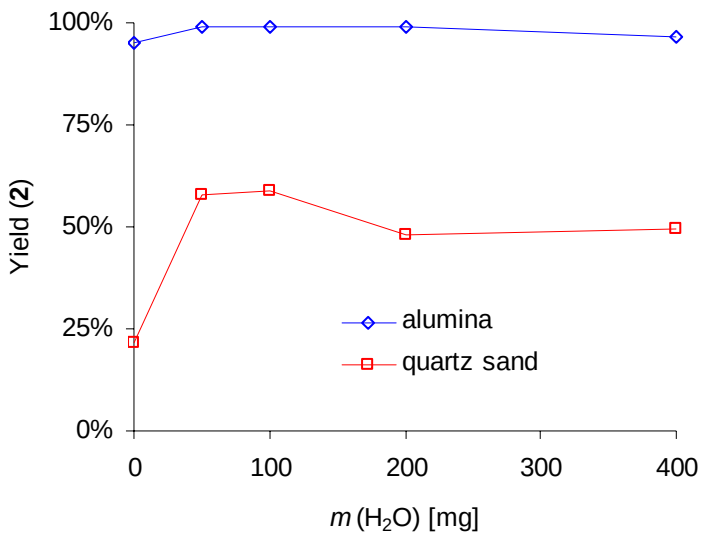

Figure S1: Influence of the water as auxiliary on the solvent-free oxidative dehydrogenation of γ-terpinene (**1**, 2 mmol) to *p*-cymene (**2**) with $KMnO_4$ as oxidant (6 mmol, 3.8 g auxiliary; Ball milling: 2 milling beakers (ZrO_2, V = 45 ml), 6 milling balls (ZrO_2, d = 15 mm) per beaker; ν_{rot} = 800 rpm (13.3 Hz), t = 5 min).

Variation of the liquid auxiliary from water to other organic solvents revealed insignificant changes in the performance of the reaction as indicated in Table S2. Observed differences in case of doping the reaction mixture with 0.1 g of acetone might count for a “solvent-effect” (quartz sand as grinding auxiliary). However, in general the yields and product selectivities are similar to the application of water. Independent from the solvent applied for his experiments the mechanical properties of the reaction mixtures are similar to those

experiments where water was employed. Thus doping the mixtures prior to reaction enhances the mechanical properties of the reaction, but no influence on the reaction itself could be determined for the transformation discussed herewith.

Table S2: Influence of different auxiliary solvents on the solvent-free oxidative dehydrogenation of γ-terpinene (**1**) affording *p*-cymene (**2**) in the presence of alumina or quartz sand as milling auxiliaries.[a)]

	alumina		quartz sand	
solvent	X_1 [%]	Y_2 [%]	X_1 [%]	Y_2 [%]
water	99	99	59	58
ethanol	92	93	74	73
toluene	99	95	54	53
THF	99	95	69	67
acetic acid	96	96	68	66
acetone	99	87	99	98
ethyl acetate	93	94	67	65
triethylamine	85	86	49	48

[a)] Batch (per beaker): 3.8 g auxiliary, 2 mmol **1**, 6 mmol $KMnO_4$, 0.1 g solvent; Ball milling: 2 milling beakers (ZrO_2, V = 45 ml), 6 milling balls (ZrO_2, d = 15 mm) per beaker; ν_{rot} = 800 rpm (13.3 Hz).

References

[1] M. Nüchter, B. Ondruschka and R. Trotzki, *J. Prakt. Chem.*, 2000, **342**, 720-724.

[2] F. Bernhardt, R. Trotzki, T. Szuppa, A. Stolle and B. Ondruschka, *Beilstein J. Org. Chem.*, 2010, **6**, No. 7.