Supplementary Information

Metathesis in water conducted by tailor-made encapsulated Grubbs' catalyst

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1. General

¹H and ¹³C NMR spectra were recorded with a Bruker Avance III 500 HD (measuring frequency: ¹H NMR = 500.2 MHz, ¹³C NMR = 125.8 MHz) spectrometer in CDCl₃ or D₂O solution. Chemical shifts are referenced to the residual peaks of the solvent [CDCl₃: 7.26 ppm (¹H NMR), 77.16 ppm (¹³C NMR)] (H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512). HPLC experiments were carried out on a Machery-Nagel NUCLEODUR® C18 Gravity-SB (5 µm) column.

2. Particle size

In our first experiments with dispersed Grubbs' second-generation catalyst in sodium alginate we revealed that the particle size of raw commercial Grubbs' catalyst is not convenient, since it led to clogged needles during encapsulation procedure. Therefore, we determined the particle size of raw catalyst with a Malvern Mastersizer 3000 particle size analyser to give an average particle size of $177\pm28 \ \mu m$ (Figure A). After we crushed the catalyst particle aggregates with a spatula to reduce their particle size and enhance the distribution in alginate, particle size was reduced about 50% ($92\pm15 \ \mu m$). Since the application of ultrasonics for the reduction of particle size is a common method, we ultrasonicated the catalyst to reduce the particle size even more. For that, Grubbs' catalyst was dispersed in sodium alginate and ultrasonicated with a Hielscher UP200Ht ultrasonic homogeniser. During ultrasonication, the mixture was cooled with ice to prevent catalyst deactivation by heat. Using this method, we reduced particle size to 40% compared to manual crushing ($54\pm7 \ \mu m$).



Figure A. Average particle size Dx (50) of raw, crushed and ultrasonicated Grubbs' catalyst. (means \pm standard deviations; n = 5; different letters above bars indicate significant differences according to ANOVA with Tukey's *post hoc* test at p < 0.05).

After that, we conducted the ring-closing metathesis with ultrasonicated catalyst in alginate amide with substrate **1**. The reaction rate was reduced by 70% compared to crushed catalyst, which can be explained by ultrasonics that create high pressure and temperature peaks in the medium, thus irreversibly deactivating the catalyst. Therefore, we applied the manual crushing method for all experiments, since with this particle size the problem of clogged needles disappeared.

3. Experimental data

Reaction rates presented in the full paper for non-encapsulated (Figures 1,2) and encapsulated catalyst (Figures 2,3,5) are listed in Table A and B, respectively.



Table	A.	Reaction	rates	of	experiments	with	non-encapsulated	catalyst	presented	in
Figures	s 1-2	2.								

Bead material	Solvent	Substrate	Catalyst loading (mol%)	Reaction rate $[\mu mol \cdot min^{-1}]$
-	water-tBuOH (3:1)	1	0.5	0.456 ± 0.054
-	water	1	0.5	2.64±0.20
-	tBuOH	1	0.5	0.073 ± 0.004
-	dichloromethane	1	0.5	3.58±0.17
-	acetone-water (2:1)	1	0.5	0.347±0.075
-	water	3	0.5	0.92±0.14
-	water	5	0.5	25.25±0.93

Bead material	Solvent	Substrate	Catalyst loading (mol%)	Reaction rate [µmol · min ⁻¹]
calcium alginate	water	1	0.5	0.047 ± 0.002
calcium alginate	water	3	0.5	0.095±0.035
calcium alginate	water	3	0.5	no reaction
calcium alginate	water-tBuOH (3:1)	1	0.5	0.031±0.005
calcium alginate	acetone-water (2:1)	1	0.5	0.013±0.003
calcium alginate	methanol-water (2:1)	1	0.5	no reaction
calcium alginate	water-Tween	1	0.5	0.006±0.002
alginate amide	water	1	0.5	0.108±0.041
alginate amide	water	3	0.5	0.146±0.082
calcium alginate	water	1	2.5	0.192±0.082
alginate amide	water	1	2.5	0.333±0.081
calcium alginate	water	3	2.5	0.083±0.004
alginate amide	water	3	2.5	0.357±0.034
calcium alginate	water	1	5.0	0.214±0.055
alginate amide	water	1	5.0	0.502±0.011
calcium alginate	water	3	5.0	0.097±0.016
alginate amide	water	3	5.0	0.398±0.096

Table B. Reaction rates of experiments with encapsulated catalyst presented in Figures 2,3,5.

3.1 Turnover frequencies (TOFs; Figure 6)

The given TOFs in Figure 6 were calculated as follows: Using 0.25 mmol substrate results in 6.25 µmol catalyst (2.5 mol%). For the reaction with substrate **1** (in alginate amide), dividing the reaction rate of 0.333 µmol \cdot min⁻¹ by 6.25 µmol results in a TOF of 0.05328 min⁻¹ (3.20 h⁻¹). A TOF of 0.05712 min⁻¹ (3.43 h⁻¹) was calculated for the reaction with substrate **3** (in alginate amide). To evaluate these TOFs, for example, a study showed that with encapsulated Rucatalyst on mesoporous silica (SBA-1) a TOF of 3.78 h⁻¹ (0.063 min⁻¹) was achieved for substrate **1** (H. Yang, Z. Ma, T. Zhou, W. Zhang, J. Chao, Y. Qin, *ChemCatChem* **2013**, *5*, 2278). Hence, our TOFs are of a similar order of magnitude.

4. Preparation of octyl-grafted alginate amide

Octyl-grafted alginate amide was synthesised according to an adapted reported procedure (W. Hu, J. Li, H. Hou, H. Yan, Y. Feng, X. Mi, Q. Lin, *Asian J. Chem.* **2013**, *25*, 9904). Sodium alginate (3.0 g) was dissolved in water (90 ml), resulting in a 3.33% w/v solution. EDC \cdot HCl (0.73 g) was added to this solution and pH was adjusted to 3.4 with HCl_(aq) (0.5 M). After diluting the solution with 30 ml water (resulting in 2.5% w/v), octyl amine (5.1 ml) was added. Then, the reaction mixture was stirred for 24 h at 35 °C. By adding ethanol (300 ml) after the reaction time, the product was precipitated. The mixture was centrifuged, washed with ethanol (5 x 20 ml) and dried for three days at room temperature. After milling the chunky solid in a ball mill, a fine white powder (2.72 g) was obtained.

In the following, protons are assigned to the octyl group:

¹H-NMR (500.2 MHz, D₂O, 296 K): $\delta = 0.87$ (t, ³ $J_{H,H} = 5.4$ Hz, 3H, CH₂(CH₂)₆CH₃), 1.29-1.67 (m, 12H, CH₂(CH₂)₆CH₃), 2.99 (t, ³ $J_{H,H} = 7.2$ Hz, 2H, CH₂(CH₂)₆CH₃) ppm.-

The analytical data are in accordance to those reported (W. Hu, J. Li, H. Hou, H. Yan, Y. Feng, X. Mi, Q. Lin, *Asian J. Chem.* **2013**, *25*, 9904).

¹H NMR spectra revealed introduced octyl groups (0.8-1.7 ppm):



5. NMR spectra













6. HPLC analysis

The analysis of conversion for the calculation of reaction rates required a fast and highthroughput analysis method. Therefore, we chose to perform this analysis *via* HPLC. Samples of relevant substances were analysed alone and subsequently together to develop a suitable method. With this method, it is possible to determine substrate / product ratios, <u>after calibrations</u> <u>with defined substrate / product ratios</u> were performed. We evaluated our method to be suitable for our application by preparing mixtures of substrate and product with different ratios. We also considered possible substrate or product decomposition and therefore measured the samples again after a week, showing no change in the substrate/product ratio.



6.1 Calibration for substrate 1







% Product	% Substrate	Integral product	Integral substrate	Integral product Integral substrate
10	90	93461	833431	0.100832675
20	80	223467	820364	0.214083506
30	70	325568	685275	0.322075733
40	60	442500	590197	0.428489673
50	50	577333	512053	0.529961832
60	40	702399	425637	0.622674276
70	30	810785	322669	0.715322369
80	20	940400	218895	0.811182658
90	10	963087	98838	0.90692563



6.2 Calibration for substrate 3







% Product	% Substrate	Integral product	Integral substrate	Integral product Integral substrate
10	90	431506	4689562	0.084260939
20	80	972699	4599650	0.174558162
30	70	1419116	4100777	0.257091215
40	60	1915876	3508647	0.353187921
50	50	2565353	3236215	0.4421827
60	40	2709190	2253780	0.545880793
70	30	3212803	1758093	0.646322715
80	20	3572563	1158503	0.755128548
90	10	4001874	516878	0.885614878



6.3 Calibration substrate 5







% Product	% Substrate	Integral product	Integral substrate	Integral product Integral substrate
10	90	513920	760803	0.403162099
20	80	930498	681538	0.577219119
30	70	914291	659005	0.581130951
40	60	1130630	573525	0.663454909
50	50	1403551	500701	0.737061586
60	40	1597640	436846	0.785279427
70	30	1703478	337681	0.834564088
80	20	1868813	333482	0.848575236
90	10	2023814	186952	0.915435645
100	0	-	-	Manually set to "1"



6.4 Example for determination of substrate-product-ratios:

Non-encapsulated catalyst (0.5 mol%) in water, substrate 1, repetition 1/3







Time / min	Integral product	Integral substrate	Integral product Integral substrate	Conversion / %
5	51956	962717	0.051204674	5
10	122164	848692	0.125831225	12
20	128490	359430	0.263342351	26
40	362824	525759	0.408317512	40
60	308581	303604	0.504064948	49
120	331003	183138	0.643798102	63
240	251988	62357	0.801628784	78
360	187221	27959	0.870066921	85
1440	181019	4383	0.976359478	95



The initial reaction rate was calculated within the first 60 minutes.

6.5 Chromatogram for calculation of conversion after 24 h reaction time with substrate 1 and 2.5 mol% catalyst in alginate amide



6.6 Chromatogram for calculation of conversion after 24 h reaction time with substrate 3 and 2.5 mol% catalyst in alginate amide

