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Occlusion of Grubbs' Catalysts in Active Membranes of Polydimethylsiloxane: Catalysis in Water and New Functional Group Selectivities

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Homogeneous catalysts exhibit terrific selectivities, and their reactivities can be readily tuned by altering the ligand or metal, but these catalysts are often difficult to remove after a reaction is complete and can be sensitive to solvents.[1] Heterogeneous catalysts are easily removed from a reaction medium and are easy to recycle, but their active sites are challenging to study and alter.[2] Although designing catalysts that combine the best aspects of homogeneous and heterogeneous catalysis is an active area of research, it has met with limited success. Typically, homogeneous catalysts are attached to surfaces or polymers which lower their selectivities or require additional synthetic steps that limit their applications.[3]

In this communication we report a new method to make homogeneous catalysts heterogeneous without requiring additional synthesis on the catalyst. We developed a new method to occlude the Grubbs' first and second generation catalysts in a slab of polydimethylsiloxane (PDMS) such that the reactions they catalyze occur within the slab.[4,5] The idea is simple: reagents dissolve in an aqueous solvent and diffuse into PDMS slabs to react with occluded catalysts.[6] Occluded catalysts are insoluble in the aqueous solvents used for reagents so they do not diffuse out of the PDMS slab. This method is exciting as it offers a chance to combine homogeneous and heterogeneous catalysis without modifying the catalysts, and the PDMS slab can function as an "active membrane" to exclude polar reagents to alter the reactivity of occluded catalysts.

Occluded PDMS slabs were readily prepared from commercially available, uncross-linked PDMS (Figure 1). We first cured PDMS by mixing its two components and heating at 65 °C for at least 12 h. These PDMS slabs were swelled in three batches of CH_2Cl_2 for 4 h to remove uncross-linked PDMS and Pt used as a cross-linking catalyst. The PDMS slabs were dried under vacuum, and a solution of the Grubbs' catalyst dissolved in CH_2Cl_2 was added to the PDMS slabs under an atmosphere of N_2. CH_2Cl_2 swelled the PDMS slabs and allowed the Grubbs' catalyst to diffuse into it. After removal of CH_2Cl_2 under vacuum, rinsing, and cutting the slabs into mm-sized pieces, the occluded catalysts were ready.

We carried out several ring-closing and cross metathesis reactions in H_2O to MeOH/H_2O mixtures as shown in Table 1. Conversions of these reactions were all 100% by ^1H NMR spectroscopy, and isolated yields were high.

This work is important since water was used as a green solvent for metathesis reactions with commercially available Grubbs' catalysts. Olefin metathesis in water is limited by the lack of solubilities of commercially available Grubbs' catalysts and by the low stabilities of ruthenium methylidenes. The first problem was partly addressed by Grubbs through the synthesis of water soluble ruthenium metathesis catalysts, but this catalyst requires extra synthetic steps that limit its potential uses.[7] The low stability of the ruthenium methylidenes that are generated in the catalytic cycle is a problem that is inherent to these catalysts.[8] These limitations have hindered the development of metathesis reactions in water such that there is only one report of cross metathesis with a homogeneous metathesis catalyst in water.[7] Ring-closing metathesis reactions are easier to catalyze than cross metathesis reactions, yet there are only a few reports of these reactions catalyzed by homogeneous catalysts in aqueous solvents.[7,9]

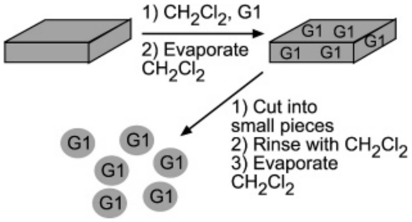

Figure 1. How the PDMS slabs were occluded with catalysts. A PDMS slab was swelled in CH_2Cl_2 with the Grubbs' first generation catalyst. The Grubbs' catalyst diffused into the PDMS slab with CH_2Cl_2. The CH_2Cl_2 was removed under vacuum and the PDMS slabs were briefly rinsed. The PDMS slabs were cut into mm-sized pieces and used in our reactions.

We addressed each of these limitations in our work. We used commercially available catalysts without modifying their structures or adding extra synthetic steps. In addition, we used aqueous solvents for reagents but the catalysts remained occluded in PDMS and were exposed to only minute amounts of water.[10] Thus, the ruthenium methylidene was stable, and we were able to carry out these reactions at temperatures up to 100 °C with low catalyst loadings. Our method solves the problems of not having to modify these catalysts while still using water as the solvent for olefin metathesis at low catalyst loadings. In addition, we showed that these catalysts could be recycled (see Supporting Information).

We believe these reactions occur in PDMS rather than the solvents because the catalysts are not soluble in aqueous solvents and the PDMS remained colored throughout the reaction while the solvent remained clear. To prove that the Grubbs' catalysts remained occluded in PDMS and metathesis did not occur in the solvent, we removed an aliquot of the reaction when the cross metathesis of $CH_2{=}CH(CH_2)_8CO_2H$ was at approximately 50% completion. The aliquot was placed in a Schlenk flask under N_2 and heated as before. The reaction did not proceed any further in this control experiment, but in the Schlenk flask with the remaining $CH_2{=}CH(CH_2)_8CO_2H$ exposed to occluded catalysts the conversion reached 100% by ^1H NMR spectroscopy. We repeated these control experiments and received the same result each time: the solvent did not contain catalysts and the metathesis reactions were occurring in PDMS.

Occlusion of metathesis catalysts provides a new opportunity to carry out functional group selective reactions since PDMS can be an "active" membrane. PDMS is very hydrophobic and although most organic reagents will diffuse into it, salts are poorly soluble. This difference in solubility of salts and organic reagents provides a chance to carry out functional group selective reactions as shown in Figure 2. Two dienes that readily undergo ring-closing metathesis

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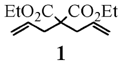
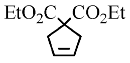
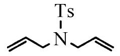
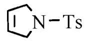
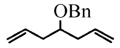
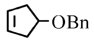
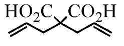
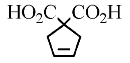
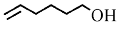
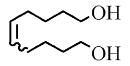
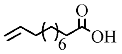
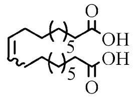
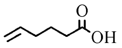
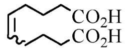
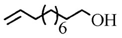
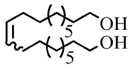
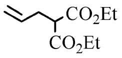
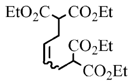
Table 1. Metathesis Reactions with Occluded Grubbs' First and Second Generation Catalysts

Substrate	Product	[a]Catalyst	[b]Time (h)	[c]Yield
 **1**	 **2**	2 (2%)	1	88%
Same as above		1 (2%)	2	85%
 **3**	 **4**	2 (1%)	2	98%
Same as above		1 (1%)	44	61%
 **5**	 **6**	2(6%)	17	79%
 **7**	 **8**	[d]2 (6%)	26	61%
 **9**	 **10**	2 (1%)	3	63%
Same as above		1 (1%)	12	64%
 **11**	 **12**	2 (2%)	4	87%
Same as above		1 (2%)	3	83%
 **13**	 **14**	2 (6%)	48	87%
 **15**	 **16**	2 (1%)	19	74%
 **17**	 **18**	2 (2%)	2	67%

[a] These reactions were run with either the first or second generation catalysts. The mole % of catalyst to substrate is shown in parentheses. [b] The time each of these reactions were run to 100% conversion by ^{1}H NMR spectroscopy. [c] Isolated yields are shown. [d] One equiv of *p*-toluenesulfonic acid to the substrate was added to the reaction.

were dissolved in 90% MeOH in H_2O with occluded Grubbs' second generation catalyst. In one reaction we added NaOH to deprotonate the acid on **7** and in another reaction we added *p*-toluenesulfonic acid (PTSA) to facilitate the diffusion of **7** into the PDMS. These reactions were run under identical conditions but yielded dramatically different results. In the reaction with NaOH we did not observe any of the cyclized products of **7**, but **5** cyclized.[11] When PTSA was added, both reagents cyclized. Thus, we were able to control the distribution of products by affecting the diffusion of reagent **7** into PDMS. These experiments are important since they demonstrate that occluded catalysts can demonstrate functional group selectivity without modification of the catalysts' structures.

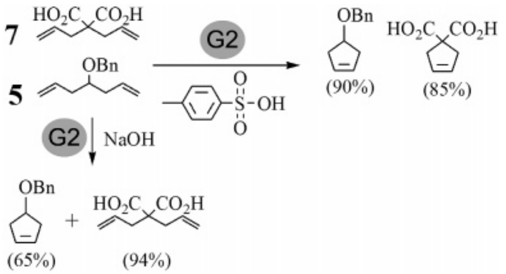


Figure 2. Functional group selective chemistry with occluded catalysts. These reactions were run under identical conditions with occluded Grubbs' second generation catalyst; they differed in the presence of an added base or acid. The base deprotonated the acid and kept **7** from diffusing into the PDMS and reacting. The numbers in parenthesis refer to the isolated yields.

Reactions of catalytically active Grubbs' first and second generation catalysts occluded in PDMS using aqueous solvents are described and show that Grubbs' catalysts are stable upon occlusion and can react by cross or ring-closing metathesis. Furthermore, the PDMS slab can act as an active membrane to impart functional group selectivity on occluded catalysts.

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Supporting Information Available: Experimental detail and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) To demonstrate how little water diffuses into PDMS, we cured crushed sodium bicarbonate into PDMS. The PDMS slab was immersed in water acidified to pH = 1 with HCl. After several months the sodium bicarbonate solid was clearly visible in the PDMS.

(11) In the reaction with NaOH, we did not observe any of the cyclized product of **7** by crude ^{1}H NMR spectroscopy.

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