Encapsulated molecular catalysts in polysiloxane gels: ruthenium cluster-catalyzed isomerization of alkenes†

Yukihiro Motoyama,[ab] Motonori Abe,[b] Kazuyuki Kamo,[b] Yusuke Kosako[a] and Hideo Nagashima*[ab]

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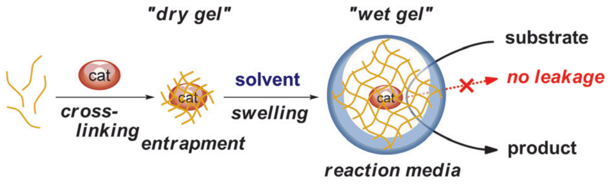
Novel ruthenium-encapsulating polysiloxane gels are prepared by treatment of polymethylhydrosiloxane with diols in the presence of ($\mu_3,\eta^2,\eta^3,\eta^5$-acenaphthylene)$Ru_3(CO)_7$, and act as reusable catalysts in the isomerization of alkenes without leakage of the catalyst species.

It is well known that homogeneous transition metal catalysts are useful for the efficient and selective transformation of organic molecules. Recently, the separation and recovery of catalysts from products and their reuse have been recognized as problems to be solved from an environmental point of view. The use of immobilized molecular catalysts on solid supports is one solution to these problems, and effective methods for attaching active metal species to organic polymers or inorganic oxides have been actively investigated.[1] During the course of our studies towards new access to the heterogenization of molecular catalysts, we were interested in enzymes physically enveloped in a polymer gel. Since the first paper reporting polyacrylamide gels to be useful for the entrapment of enzymes,[2a] gel-soaked enzymes have reportedly catalyzed several reactions without leaching of the enzymes.[2]

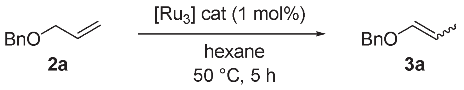
Our idea focuses on organometallic complexes possibly being immobilized in polymer gels similar to the enzymes. In metal-containing swelled gel, it is expected that substrate and solvents permeate through the gel membrane, and catalytic reaction takes place to form the product in contact with the organometallic species as shown in Scheme 1. Extraction of the wet gel with the solvent would result in facile isolation of the product, and the metal-containing gel would be reusable as the catalyst could be recovered as an insoluble, contracted dry gel. In this paper, we wish to report that this idea has actually been realized by catalytic cross-linking of polymethylhydrosiloxane (PMHS), leading to the self-encapsulation of the catalyst species.‡



Scheme 1 Simplified representation of catalyst-embedding polymer gel system for chemical transformation of the substrate.

The catalytic cross-linking of PMHS was previously discovered in the deoxygenative reduction of carboxamides with PMHS in the presence of a catalytic amount of a triruthenium carbonyl cluster (**1**).[4] The oxygen atom originating from the amide contributed to bridging the PMHS chains, and *ca.* 45% of Si–H groups in PMHS were converted to the Si–O groups with 55% of Si–H moieties remaining unreacted. This gave *O*-bridged polysiloxane gels containing ruthenium species ($[Ru_3]$@Si–O). All of the charged catalyst species (>99%) were immobilized in the polysiloxane gel. The ruthenium species in the gel was still active[5] and reusable for the reduction of carboxamides with PMHS to give the corresponding amines in good yields. This result implies the possible use of $[Ru_3]$@Si–O as a heterogenized molecular catalyst for other transformations. In fact, we found that the $[Ru_3]$@Si–O catalyzes the isomerization of alkenes, in which the product is obtained by filtration without contamination of the metallic species. However, the yield of the product is not high (Table 1, entry 1), because the Si–H moieties in the $[Ru_3]$@Si–O are reactive towards alkenes by catalysis of $[Ru_3]$@Si–O, which were grafted to the siloxane chain *via* hydrosilylation. This suggests that the Si–H groups in the $[Ru_3]$@Si–O must be converted to chemically inert groups (capping of Si–H groups).

Table 1 Isomerization of allyl benzyl ether **2a**[a]



Entry	Catalyst	Yield (%)[b]	*E* : *Z*[c]
1	$[Ru_3]$@Si-O	30	47 : 53
2	$[Ru_3]$@Si-EG	63	58 : 42
3	$[Ru_3]$@Si-EG_{cap}	>95	27 : 73
4	$[Ru_3]$@Si-BP_{cap}	>95	40 : 60

[a] All reactions were carried out with **2a** (1 mmol) and $[Ru_3]$ species (1 mol%) in hexane (3 mL) at 50 °C for 5 h. [b] Determined by ^{1}H NMR analysis. [c] Determined by GLC analysis.

The problem was solved by dehydrogenative silylation of PMHS with alcohols catalyzed by **1**. Thus, treatment of PMHS [*n* = 25.6 (average); Si–H = 4 mmol] with ethylene glycol (EG; 1 mmol) in the presence of **1** (0.01 mmol) at 50 °C for 2 h resulted in cross-linking of PMHS to form $[Ru_3]$@Si-EG. The

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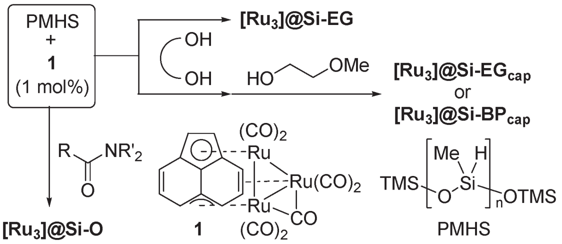
[a] *Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan. E-mail: nagasima@cm.kyushu-u.ac.jp; Fax: +81-92-583-7819; Tel: +81-92-583-7819*
[b] *Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

† Electronic supplementary information (ESI) available: Detailed experimental procedures and results, and characterization data of both the substrates and the products. See DOI: 10.1039/b809937e



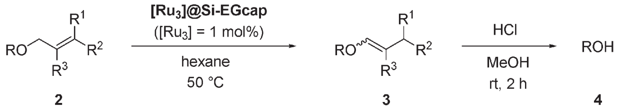
Scheme 2 Preparation of [Ru$_3$]@Si catalysts.

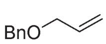
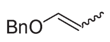
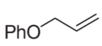
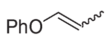
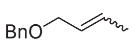
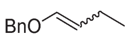
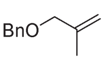
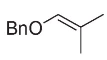
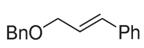
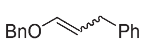
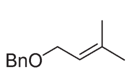
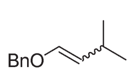
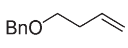
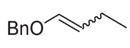
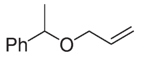
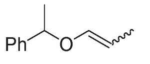
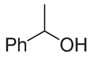
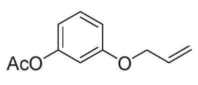
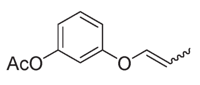
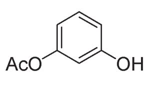
–O(CH$_2$)$_2$O– groups bridged the siloxane chain. The formed [Ru$_3$]@Si-EG contained unreacted Si–H groups, which were completely capped by treatment with MeOCH$_2$CH$_2$OH (2 mmol) to give [Ru$_3$]@Si-EG$_{\mathrm{cap}}$. Similar treatment of PMHS with 2,2′-biphenol (BP) followed by addition of MeOCH$_2$CH$_2$OH afforded Ru@Si-BP$_{\mathrm{cap}}$ (Scheme 2). NMR, IR, and ICP-MS analyses revealed that all of the Si–H groups in the gels reacted with alcohols and >99.9% of the [Ru$_3$] species were entrapped in the polysiloxane networks.§

The catalytic activity of [Ru$_3$]@Si-EG$_{\mathrm{cap}}$ and [Ru$_3$]@Si-BP$_{\mathrm{cap}}$ was proved by isomerization of allyl benzyl ether **2a**. A solution of **2a** in hexane was treated with [Ru$_3$]@Si-EG$_{\mathrm{cap}}$ (dry gel; [Ru$_3$] = 1 mol% to **2a**) to give two phases, liquid phase and swelled gel, in which the catalytic transformation of **2a** at 50 °C formed 1-propenyl benzyl ether **3a**. After 5 h, the mixture was filtered through a membrane filter under reduced pressure. The [Ru$_3$]@Si-EG$_{\mathrm{cap}}$ was recovered as a dry gel on the membrane filter, and the product was obtained from the filtrate in quantitative yields (Table 1, entry 3). The recovered [Ru$_3$]@Si-EG$_{\mathrm{cap}}$ is reusable (3 times) without loss of catalytic activity; the yield of **3a** in each recycle experiment was over 95%. ICP-MS analysis of the product in these recycle experiments showed the existence of only trace amounts of ruthenium species; the calculated catalyst leaching was 0.02% of the charged [Ru$_3$] in the first run, and 0.04% and 0.09% in the second and third runs, respectively. Similar results were obtained when [Ru$_3$]@Si-BP$_{\mathrm{cap}}$ was used as the heterogenized catalyst instead of [Ru$_3$]@Si-EG$_{\mathrm{cap}}$ (entry 4).

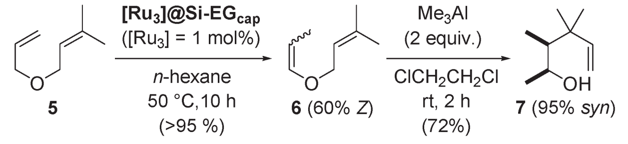
Table 2 shows the results obtained for the isomerization of other allyl and homoallyl ethers catalyzed by [Ru$_3$]@Si-EG$_{\mathrm{cap}}$

Table 2 Isomerization of various allyl ethers with Ru@Si catalysts followed by hydrolysis with HCl[a]



Entry	Substrate		Time/h	3, Yield (%),[b] (E : Z)[c]			4, Yield (%)[d]		
1		**2a**	5		**3a**	>95 (27 : 73)	BnOH	**4a**	93
2		**2b**	4		**3b**	>95 (27 : 73)	PhOH	**4b**	83
3		**2c**	10		**3c**	>95 (50 : 50)	BnOH	**4a**	93
4		**2d**	15		**3d**	>95 (–)	BnOH	**4a**	93
5[e]			15			>95 (–)			90
6		**2e**	12		**3e**	40 (48 : 52)	—		—
7		**2f**	24		**3f**	<1	—		—
8[e]		**2g**	24		**3c**	>95 (49 : 51)	BnOH	**4a**	71
9		±-**2h**	15		±-**3h**	>95 (12 : 88)		±-**4h**	90
10		(*R*)-**2h**	24		(*R*)-**3h**	>95 (<1 : >99)		(*R*)-**4h**	84[f]
11		**2i**	24		**3i**	>95 (26 : 74)		**4i**	85

[a] All reactions were carried out with **2** (1 mmol), [Ru$_3$] species (1 mol%) in hexane (3 mL) at 50 °C followed by hydrolysis with aq. HCl in MeOH at room temperature for 2 h. [b] Determined by ^{1}H NMR analysis. [c] Determined by GLC analysis. [d] Isolated yield. [e] [Ru$_3$]@Si-BP$_{\mathrm{cap}}$ was used. [f] Optical purity (>99.9% ee) was determined by chiral GLC analysis using SUPELCO β-DEX 120.



Scheme 3 Isomerization followed by alkylative Claisen rearrangement.

or [Ru$_3$]@Si-BP$_{cap}$.¶ Allyl, crotyl and methallyl ethers were completely converted to the corresponding vinyl ethers. In contrast, the reaction of cinnamyl ether **2e** gave an equilibrium mixture of **2e** and vinyl ether **3e**, and no isomerization took place in the reaction of sterically hindered prenyl ether **2f** (entries 6 and 7). Homoallyl ether **2g** underwent isomerization to give **3c** (entry 8). The double bond migration of (*R*)-**2h** (>99.9% ee) proceeded without loss of its optical purity (entry 10). In all of the above cases, treatment of the formed vinyl ethers with hydrochloric acid in methanol gave the corresponding alcohols in 71–93% isolated yields. In other words, double bond isomerization of allyl or homoallyl ethers catalyzed by [Ru$_3$]@Si-EG$_{cap}$ or [Ru$_3$]@Si-BP$_{cap}$ followed by hydrolysis provides a practical method for the deprotection of allyl and homoallyl ethers.[6] As an application, the allyl-selective deprotection of *m*-acetoxyphenyl allyl ether **2i** was achieved to give *m*-acetoxyphenol (**4i**) (entry 11).

Another interesting application of this isomerization is the selective preparation of a substrate for Claisen rearrangement. Allyl prenyl ether (**5**) was selectively converted to ruthenium-free prenyl 1-propenyl ether (**6**: *E* : *Z* = 40 : 60). A crude sample of **6** was then subjected to the alkylative Claisen rearrangement by treatment with Me$_3$Al[7] to give bishomoallyl alcohol **7** in 72% yield (Scheme 3).

In summary, the siloxane gels containing organoruthenium species, [Ru$_3$]@Si-EG$_{cap}$ and [Ru$_3$]@Si-BP$_{cap}$, have been demonstrated for the first time to be a new type of heterogenized molecular catalyst. They are easily available by simply mixing the catalyst, cross-linker, capping reagent, and PMHS. This is in sharp contrast to tedious procedures for conventional catalysts which are prepared by anchoring a ligand to a support followed by complexation with transition metals.[8]‖ It is important that success of the present catalytic isomerization without catalyst leaching and facile separation of the product is first achieved by the special feature of [Ru$_3$]@Si-EG$_{cap}$; substrates, products, and solvents rapidly permeate through a gel membrane,** whereas the [Ru$_3$] species is immobilized in the polymer networks throughout the reaction. We now envision construction of inner structures of the siloxane gels by the appropriate choice of both cross-linker and capping reagents. Investigations in this line and application of the resulting gels to chemo- and stereoselective reactions are underway.

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Notes and references

‡ Occluded homogeneous catalysts in polydimethylsiloxane (PDMS) derivatives were reported: zeolite-filled PDMS membranes,[3a] silica-filled PDMS films,[3b] elastomeric type PDMS membranes,[3c] hybrid siloxane films,[3d] and PDMS slabs.[3e]

§ Preparation of [Ru$_3$]@Si-EG$_{cap}$ and [Ru$_3$]@Si-BP$_{cap}$: to a solution of ($\mu_3,\eta^2,\eta^3,\eta^5$-acenaphthylene)Ru$_3(CO)_7$ (**1**) (6.5 mg, 0.01 mmol) and PMHS [M_w = 1500–1900; n = 25.6 (average); Si–H = 4 mmol] in tetrahydropyran (0.7 mL) was added 1 mmol of either ethylene glycol (EG) or 2,2′-biphenol (BP), and then added 2 mmol of 2-methoxyethanol and the mixture was heated at 50 °C. Dehydrogenative silylation proceeded smoothly and [Ru$_3$]@Si-EG$_{cap}$ and -BP$_{cap}$ were formed as a wet gel after 2 h. The wet gel was washed with ether and then dried under reduced pressure to afford the corresponding dry gel. The Si–H groups remaining in the siloxane gels were less than 1% (determined by IR). ICP-MS analysis of the ether solution revealed that it contained only 0.4 μg of ruthenium (<0.04% of charged [Ru$_3$] species); >99.96% of [Ru$_3$] species were immobilized in the polysiloxane networks. IR (KBr) ν 1272 (Si–Me), 1030 (Si–O) cm^{-1}.

¶ A solution of allyl ether (1 mmol) in *n*-hexane (3 mL) was added to the dry [Ru$_3$]@Si catalyst ([Ru$_3$] = 1 mol%), and it was stood at 50 °C without stirring. After the reaction was complete, the vinyl ether formed was obtained by filtration and washing the gel with hexane (10 mL). Treatment of the vinyl ether with aq. HCl in MeOH at room temperature for 2 h gave the deallylated alcohol, which was purified by silica gel column chromatography.

‖ The facile access to the catalyst immobilization is comparable to the "Polymer Incarcerated" method, which is a physical entrapment of catalysts in polystyrene derivatives, see ref. 9.

** The diffusion velocity of organic molecules through the gel membrane is very fast. For example, dry [Ru$_3$]@Si-EG$_{cap}$ (*ca.* 500 mg) absorbed 1.5 mL of hexane. Addition of DME (1.5 mL) to the resultant gel gave two phases, liquid phase and swelled gel. At this time, the liquid phase contains only DME. After 5 min, the ratio of DME : hexane in the liquid phase attained equilibrium in a ratio of 46 : 54. See ESI.†

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