Visible-light induced solvent-free photooxygenations of organic substrates by using [60]fullerene-linked silica gels as heterogeneous catalysts and as solid-phase reaction fields

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Abstract—Novel recyclable heterogeneous catalysts generating singlet-oxygen under visible-light irradiation have been prepared by linking [60]fullerene to amino-functionalized silica gels. The catalysts facilitate various types of photooxygenations including Diels–Alder reaction, ene reaction, and oxidations of phenol and sulfide in a solid-solvent system and even in a solvent-free system. © 2006 Elsevier Ltd. All rights reserved.

Photooxygenation has been attracting considerable attention, since it is one of the important reactions that have been discussed as suitable for green and sustainable chemistry (GSC).[1] In particular, a photooxygenation with singlet-oxygen ($^1O_2$) formed via energy-transfer from an electronically excited dye molecule is known to be one of the cleanest ways to yield oxygenated products, and then the dye-sensitized photooxygenation is widely used for industrial applications, compared to those with $^1O_2$ formed by reactions of ozone with triphenyl phosphites, hypochlorite oxidations of hydrogen peroxides, thermal decompositions of endoperoxides (e.g., 9,10-diphenylanthracene peroxide), and so on.[2,3]

Although various photosensitizers such as Rose Bengal (RB),[4] methylene blue (MB),[4] porphyrines,[4] and fullerenes[5] are known to efficiently generate $^1O_2$ leading to photooxygenations, these dyes contaminate the product and have to be removed after the reaction by chromatography or distillation. Then, several heterogeneous catalysts such as RB-coated polymer beads and solid supports (clay and zeolite) have been developed,[6] since these catalysts can be simply filtrated out from the reaction solution and can be used recyclably. Latassa et al. reported photooxydation of sulfides under irradiation with a mercury lamp in MeOH by use of fullerene linking polysiloxane beads.[7,8] More recently, Jensen and Daniels also reported efficiently sensitized photooxygen-

ations using fullerene-coated beads in $CHCl_3$ under irradiation with light of wavelengths over 330 nm.[9] Additionally, Nagano et al. revealed that the $^1O_2$-producing ability of fullerene as a photosensitizer was considerably higher than those of common sensitizers, such as RB and MB.[10]

In recent times, design of a reaction without organic solvent has been the subject of considerable interest in the field of GSC.[11] However, solvent-free photooxygenations are hardly reported, although Griesbeck et al. more recently reported polymer-bound sensitizer systems using tetrastyrylporphyrine and protoporphyrin IX.[12] Furthermore, a solvent-free-photooxygenation system allows to elongate the lifetime of $^1O_2$ (~2700 s in air, cf. 3.3 μs in water; 640 μs in $CDCl_3$)[3,4] as well as to omit an air bubbling system. In particular, development of the photooxygenations under visible-light irradiation should be of interest from the viewpoint of GSC, since sunlight, which mainly consists of light with the range of visible-light frequencies, can be used as the light source. Hence, these considerations prompted us to
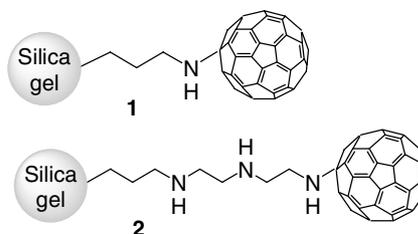
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investigate herein the solvent-free photooxygenation with a reusable heterogeneous catalyst bearing fullerene moiety under visible-light irradiation.

As a catalyst, which can be utilized both as an efficient heterogeneous photosensitizer and as a solid-phase reac-

tion field, two types of catalysts **1** and **2** were prepared by linking [60]fullerene (C_{60}) to commercially available amino-functional silica gels.[13] The C_{60} contents in catalysts **1** and **2** were estimated based on the amount of recovered C_{60} and the thermogravimetric analysis to be ca. 8.1 and 5.8 wt %, respectively. The UV–vis spec-

Table 1. Photooxydations with catalysts **1** and **2** with or without solvent under visible-light irradiation[a]

Substrate	Product[b]	Reaction conditions			Isolated yield[c] (%)
		Catalyst	Solvent	Reaction time	
3	**4**	1	CDCl$_3$	60 min	>97
		2	CDCl$_3$	60 min	70
		1	None	60 min	>97
		2	None	60 min	>97
		1[d]	None	60 min	>97
		1[e]	None	3 h	85
5	**6**	1	None	60 min	>97
		2	None	60 min	>97
		1	CDCl$_3$	60 min	>97
7	**8**	1	None	2 h	>97
		2	None	2 h	>97
		1	CDCl$_3$	60 min	>97
9	**10a** / **10b** / **10c**	1	None	60 min	>97 (41:31:28)
		2	None	60 min	>97 (50:25:25)
		1	CDCl$_3$	60 min	>97 (17:53:30)
11	**12a** / **12b**	1	None	12 h	>97 (42:58)
		2	None	12 h	50 (50:50)
		1	CDCl$_3$	10 h	>95 (50:50)
13	**14**	1	None	18 h	>70
		2	None	18 h	>36
		1	CDCl$_3$	90 min	>97
15	**16**	1	None	80 min	>97
		2	None	80 min	>97
		1	CDCl$_3$	80 min	>97
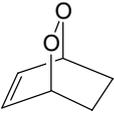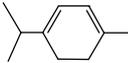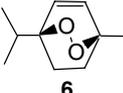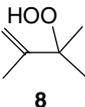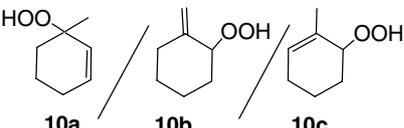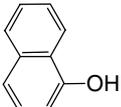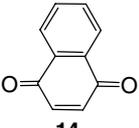
[a] Reaction conditions: catalyst **1** or **2** (100 mg); substrate (0.61 mmol); at room temp, under visible-light irradiation ($\lambda > 380$ nm, 500 W of Xe lamp); with air bubbling system only in the case of the solid-solvent system (5 mL of CDCl$_3$).
[b] Identified by NMR and GC mass spectroscopies.
[c] The value in parentheses is a ratio of the isomer estimated by the NMR analysis.
[d] Catalyst **1** recycled more than 50 times was used.
[e] A 300 W of halide lamp was used as a light source with the cut filter ($\lambda < 380$ nm).

$$10b \longleftarrow \text{Perepoxide } \mathbf{a} \xleftarrow{\;^1O_2\;} 9 \xrightarrow{\;^1O_2\;} \text{Perepoxide } \mathbf{b} \longrightarrow \begin{array}{c}10a\\10c\end{array}$$
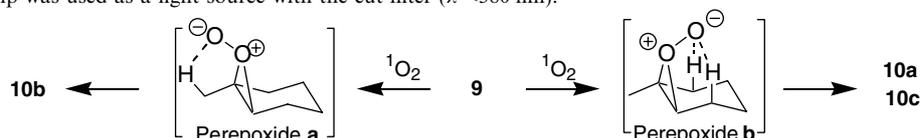
tra of catalysts **1** and **2** indicated that these catalysts clearly had fullerene moiety and that these absorption patterns of catalysts **1** and **2** were similar to that of C_{60} (solid state) itself (see Supplementary data).

The visible-light induced photooxygenations of several substrates were carried out by using catalysts **1** and **2** in the solid-solution system or in the solvent-free system (Table 1).[14] The Diels–Alder photooxygenation of cyclohexadiene **3** in the presence of catalysts **1** and **2** in $CDCl_3$ gave the corresponding product **4**, in which the yield in the case with catalyst **1**was higher than that with catalyst **2**, presumably due to the distinct amount of C_{60} between these catalysts. Meanwhile, the solvent-free photooxygenations of substrate **3** quantitatively proceeded with catalyst **1** and even with catalyst **2** for the same reaction time (60 min) to the cases in $CDCl_3$. In addition, the reaction smoothly underwent even by using catalyst **1** recycled more than 50 times and also took place even with a halogen lamp equipped with a filter, cutting radiation below 380 nm. Thus, these results imply that the present catalyst efficiently mediated a visible-light induced photooxygenation even in the solvent-free system, and then similar reactions with various substrates were also performed as shown in Table 1.

The solvent-free photooxygenations of α-terpinene **5** also smoothly proceeded by use of catalysts **1** and **2** to yield the oxygenated product (**6**), and the reaction efficiencies were also similar to the case in $CDCl_3$. The ene reaction of substrate **7** also readily took place, although the solvent-free reactions using catalysts **1** and **2** needed prolonged reaction time to quantitatively convert to product **8**, compared with the reaction in $CDCl_3$ (2 h vs 60 min). Interestingly, the solvent-free ene reactions of methylcyclohexene **9** both with catalysts **1** and **2** quantatively underwent for 60 min, although the reaction rate of photooxygenation of compound **9** with RB in the solution system is known to be extremely lower than that of compound **7** [$(k_{rel}$ of **9**)$/(k_{rel}$ of **7**) = 0.0041].[15] In addition, the total yields of endocyclic products **10a** and **10c** were higher than the case in solution, and it strongly implied that the intermediate giving **10a** and **10c**, perepoxide **b**, might be rather preferred in the solvent-free system to the intermediate giving **10b**, perepoxide **a**, probably due to more restricted molecular movement of the substrate in the solid-phase reaction field, compared with that in solution phase. Incidentally, in the similar reactions with RB and MB in solution the ratios of endo- and exo-cyclic products are 56:44 and 57:43, respectively.[16] The photooxygenation of citronellol (**11**), which is known to be industrially useful process for production of a fragrance, 'Rose Oxide', was also carried out in the present solvent-free systems by using catalysts **1** and **2**. As a result, the reaction also proceeded along with the similar production ratios of products **12a** and **12b** to the result of a common photooxygenation with RB in solution system.[17] Additionally, in the reaction using catalyst **2**, the total yield of products **12a–b** was 50% even in the reaction for 12 h. The oxidations of phenol **13** and sulfide **15** also proceeded in the solid-solution system as well as in the solvent-free system to give products **14** and **16**, although the reac-

tions of phenol **13** was hard to take place, compared with the similar case in $CDCl_3$.

In conclusion, various types of solvent-free $^1O_2$-photooxygenations were demonstrated to proceed under visible-light irradiation by using catalysts **1** and **2** prepared by conjugating C_{60} to amino-functional silica gels. Additionally in some cases, the catalyst efficiency of **1** was higher than that of **2**. The detailed investigations are now in progress and the results will be reported elsewhere.

Supplementary data

The UV–vis data and the photographs of catalysts **1** and **2** and C_{60} are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.12.081.

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8. Our reaction system was distinctly different from that of Latassa's reaction system. As described in the text, Latassa et al. reported photooxydation of sulfides under irradiation with a mercury lamp in MeOH by use of fullerene linking polysiloxane beads (Deloxan® DAP

beads (0.2–0.5 mm), namely a silicon polymer). On the other hand, the present catalyst prepared by linking of fullerene to amino-functionalized silica gels (40–60 μm), is able to be carried out in solvent-free photooxygenation by efficient utilization of silica gel part as a 'solid-phase reaction field'.

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13. Fullerene (100 mg) and 3-aminopropyl-functionalized silica gel or 3-(diethylenetriamino)propyl-functionalized silica gel (500 mg, Aldrich Co. Ltd.) were reacted in toluene (50 mL) at 60 °C for 8 h under Ar atmosphere. The resulting compound was filtrated, and then washed by hot toluene until the color of the toluene passing through the filter was clear to give the corresponding catalyst.
14. (a) In the typical solvent-free reaction procedure, a substrate (0.61 mmol) was charged with or without minimum amount of chloroform to catalyst **1** or **2** (100 mg). The resulting catalyst was dried and then irradiated with 500 W of xenon lamp (USHIO UXL-500D-O), which was located at 15 cm of the sample, attached with a filter cutting the light of wavelength below 380 nm at room temperature. After the reaction, the catalyst was washed well with chloroform or ethyl acetate. The obtained filtrate was evaporated in vacuo to yield the resulting product. (b) In the typical solid-solution reaction procedure, a substrate (0.61 mmol) was dissolved in 5 mL of $CDCl_3$, and then the catalyst (100 mg) was added to the solution. The mixture was similarly irradiated in a quartz cell with visible-light ($\lambda > 380$ nm), where air was passed through it continuously by using a bubbling system. After the reaction, the reaction mixture was filtrated and the catalyst was washed well with chloroform or ethyl acetate. Then, the resulting filtrate was concentrated under reduced pressure to afford the corresponding product.
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