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Visible light-induced highly selective transformation of olefin to ketone by 2,4,6-triphenylpyrylium cation encapsulated within zeolite Y†

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2,4,6-Triphenylpyrylium cation encapsulated within zeolite Y promotes highly selective transformation of olefins to ketones with molecular oxygen, under visible light (λ > 400 nm) irradiation at room temperature.

Selective transformation of olefins to ketones is one of the most important functional group transformations in organic synthesis.[1] Catalytic transformation processes driven by molecular oxygen (O_2) have attracted a great deal of attention;[2] however, most of the processes employ homogeneous catalysts which are rarely recyclable. Heterogeneous catalytic processes have also been proposed,[3] but they require relatively expensive oxidants such as H_2O_2. To the best of our knowledge, there is only one report of a successful heterogeneous catalytic system driven by O_2, which employs a Ru-bound Al_2O_3,[4] but it needs severe reaction conditions (550 K). Development of an economical heterogeneous system capable of promoting selective transformation of olefin to ketone with O_2 is now the focus of attention.

Photooxygenation is a promising process because it can be operated at room temperature. So far, photocatalytic processes using a semiconductor, titanium dioxide, have been studied extensively,[5] but the processes lack sufficient selectivity and require UV light for catalyst activation. Some homogeneous photosensitizers can promote oxygenation of olefins by visible light (>400 nm) activation, but the ketone selectivity is quite low.[6] 2,4,6-Triphenylpyrylium tetrafluoroborate (TPT) is one of these photosensitizers,[7] which is photoexcited by <470 nm irradiation. The excited TPT leads to an electron transfer (ET) from olefin to TPT and produces a radical cation of olefin (olefin$^{\bullet+}$), while producing neither singlet oxygen ($^1O_2$) nor superoxide anion ($O_2^{\bullet-}$). As a result of this, oxygenation proceeds *via* reaction of olefin$^{\bullet+}$ with O_2, thus inevitably promoting undesirable dimerization of olefin.

TP^+ cation can easily be immobilized onto a zeolitic support by a "ship-in-a-bottle" method.[8] Reaction of acetophenone and chalcone with zeolite Y leads to a formation of TP^+ within its supercage (13 Å diameter × 8 Å window),[8a] where Brønsted acid sites of zeolite act as the counterions. Bulky TP^+ cannot pass through the narrow window, thus affording TP^+ encapsulated within zeolite Y (TPY; Fig. 1A). Preliminary experiments revealed that TPY is applicable to several photoreactions, such as isomerization of *cis*-stilbene[8a] and decomposition of pollutants.[8d,e]

Herein, we describe that photoactivated TPY promotes *highly selective transformation of olefin to ketone with O_2*, while suppressing dimerization of olefin. This unprecedented activity is triggered simply by a structural feature of TPY: the small zeolitic cavity suppresses the formation of large dimers. This is a catalytic system achieving the highest ketone selectivity among those proposed so far.[2–7] Photooxygenation of olefins within zeolite have been studied extensively;[9] however, none of the systems achieves selective ketone production. Size-selective phototransformation of molecules is promoted within several zeolitic systems,[10] where substrate activities and product selectivities are controlled by the pores.[11] However, none of the systems had been utilized as a reactor for suppression of dimer formation leading to selective oxygenation of molecules.

TPY was prepared according to the literature procedure,[8a] where the amount of TP^+ within TPY is 6.8 wt% (0.22 mmol g^{-1} of TPY).‡ Photooxygenation was carried out by photoirradiation (>400 nm)[12] of a suspension of TPY in O_2-saturated MeCN with the respective olefins.§ Table 1 summarizes the results of photooxygenation of terminal olefins. Reaction of styrene **1** with TPT gives benzaldehyde **2** *via* C=C bond cleavage, along with a large amount of dimers (**3** and **4**) (77%). In contrast, TPY gives **2** with excellent selectivity (>99%) without the production of dimers. Reactions of TPT with α-substituted styrenes, such as

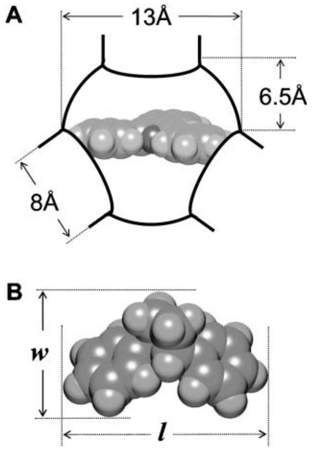

Fig. 1 (A) Schematic representation of TP^+ incorporated in zeolite Y supercage. (B) Maximum length (*l*) and its cross-sectional length (*w*) of molecule **3**.

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† Electronic Supplementary Information (ESI) available: DR UV–vis spectrum (Fig. S1); thermogravimetric profile (Fig. S2); relationship between average diameter of olefins and the ratio of k_q(TPY)/k_q(TPT) (Fig. S3); fluorescence decay profile (Fig. S4); $E_{1/2}^{ox}$ and k_q data (Table S1); photooxygenation results of β-substituted styrenes (Table S2). See DOI: 10.1039/b515137f

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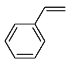
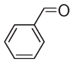
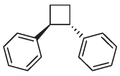
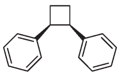
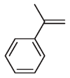
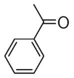
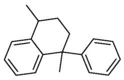
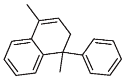
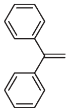
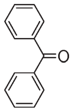
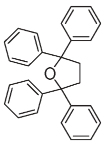
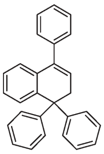
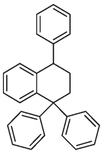
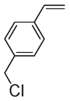
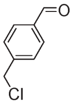
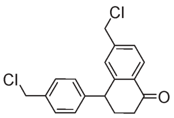
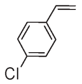
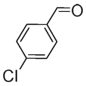
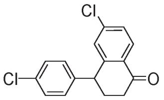
Table 1 Results of olefin photooxygenation on various sensitizers[a]

	Reactant conv. (%)	Product select. (%)			
		Ketone	Dimers		
	 **1**	 **2**	 **3**		 **4**
TPY	7.9	>99			
TPT	18.6	23	68		9
TPT + Y	12.1	26	67		7
	 **5**	 **6**	 **7**		 **8**
TPY	3.7	>99			
TPT	18.8	45	48		7
TPT + Y	18.5	48	44		8
	 **9**	 **10**	 **11**	 **12**	 **13**
TPY	6.2	>99			
TPT	25.4	73	18	8	1
TPT + Y	14.4	77	14	7	2
	 **14**	 **15**		 **16**	
TPY	9.3	>99			
TPT	52.1	49		51	
TPT + Y	25.8	56		44	
	 **17**	 **18**		 **19**	
TPY	4.2	>99			
TPT	18.0	51		49	
TPT + Y	14.6	60		40	

[a] MeCN, 15 ml; olefin, 750 μmol; O_2, 1 atm; photoirradiation time, 5 h; TPY or Y, 34 mg; TPT, 7.5 μmol.

α-methylstyrene **5** and 1,1-diphenylethylene **9**, also produce large amounts of dimers [(**7** and **8**) and (**11**, **12**, and **13**)], respectively. In contrast, TPY affords the corresponding ketones (**6** and **10**) with very high selectivity (>99%).

In the TPY system, material balance between olefins and ketones agrees reasonably well (>97%). When TPY recovered after the photoreaction was dissolved in hydrofluoric acid and extracted with CH_2Cl_2, GC analysis did not detect dimers or ketones. This implies that dimers neither adhered to the cavity wall nor were confined within the cavity, and therefore are *not formed within the cavity at all*. Use of TPT with zeolite Y (TPT + Y) for reactions of **1**, **5**, and **9** still produces dimers (Table 1), where the product distributions are similar to those obtained with only TPT. This rules out an acid site of zeolite as the factor for selective transformation.[13] Bulky TPT cannot pass through the small zeolite window;[8a] hence, in a TPT + Y system, ET from olefin to TPT and olefin$^{\bullet+}$ oxygenation by O_2 must occur in a bulk solution, as is also the case in the TPT system. In contrast, within TPY, olefin$^{\bullet+}$ formed *via* ET is stabilized as a charge-compensating cation of zeolite and hence its diffusion is much suppressed;[8a] therefore, olefin$^{\bullet+}$ oxygenation by O_2 must occur within the zeolite cavity. These suggest that suppression of the dimer formation within TPY may be attributable to the narrow zeolite cavity.

TP^+, of a planar structure with 13 Å length, is encapsulated on an equatorial plane of the spherical supercage (13 Å diameter), as depicted in Fig. 1A.[8a] Olefin$^{\bullet+}$ must therefore be formed and stabilized within the hemisphere space (13 × 6.5 Å). The size of dimers was checked to clarify whether dimers can form within this space. By MO calculations (MNDO-PM3),[11i] the maximum length (l) of molecules and their cross-sectional length (width, w) were determined (Fig. 1B). As summarized in Table 2, the widths of the dimers are clearly larger than the hemisphere height (6.5 Å), while the widths of the ketones are smaller. These findings clearly indicate that the narrow TPY hemisphere suppresses olefin dimerization, thus allowing selective ketone production.

TPY also promotes highly selective transformation of 4-chloromethylstyrene **14** and 4-chlorostyrene **17** to the corresponding aldehydes (Table 1), while both TPT and TPT + Y systems show much lower selectivity. As well known, these Cl-substituted aldehydes are indispensable materials in organic synthesis.[1,2e,3b,4] The present TPY system therefore has the potential to become a very powerful tool to synthesize these materials economically.

The disadvantages of TPY must be noted. (i) Conversions are lower than those obtained by TPT (Table 1). This is because ET from the olefin to TP^+ is suppressed by the narrow zeolite cavity. This is confirmed by fluorescence quenching experiments on TP^+: the quenching rate constants, k_q(TPY), by olefins are much lower (<17%) than k_q(TPT) (Table S1†). The ratio k_q(TPY)/k_q(TPT) tends to decrease with an increase in the size of the olefin (Fig. S3†), indicating that diffusion of larger size olefins is much more suppressed. (ii) Transformation of aliphatic olefins is not favored thermodynamically.[6,7] This is because ET from these olefins to TP^+ is poor due to the relatively positive oxidation potential of these olefins.[7a] (iii) Transformation of β-substituted olefins is unsuccessful (Table S2†). Reactions of *cis*- and *trans*-stilbene with

Table 2 Maximum length (l) and cross-sectional length (width, w) of molecules determined by MO calculations

	l/Å	w/Å		l/Å	w/Å
1	7.42	5.33	**11**[a]	11.24	11.14
2	6.61	5.39	**12**[a]	12.04	8.96
3[a]	9.91	6.53	**13**[a]	12.41	9.07
4[a]	8.16	7.71	**14**	8.89	5.42
5	7.46	5.54	**15**	8.06	5.49
6	7.44	5.33	**16**[a]	10.5	8.29
7[a]	9.72	7.01	**17**	8.48	5.36
8[a]	8.79	7.16	**18**	7.69	5.39
9	9.17	5.78	**19**[a]	9.80	8.10
10	8.98	5.93			

[a] Dimerized products shown in Table 1.

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TPY give isomerized olefins (>94%), while reaction with TPT gives **2** with >10% selectivity.[8a] Olefin$^{\bullet+}$ is stabilized within the cavity as a charge-compensating cation of zeolite.[8a] These diaryl olefins have relatively negative oxidation potential (Table S1†) and, hence, are stabilized more than monoaryl olefins. The strong stabilization may strongly suppress the C=C bond cleavage by O_2, thus leading to lower ketone production. Reaction of *trans*-β-methylstyrene with TPY affords allylbenzene (50%) together with **2** (Table S2†). This is because the carbocation of *trans*-β-methylstyrene is transformed into a more stable allylic cation *via* proton transfer catalyzed by acid sites within the zeolite.[14]

In conclusion, we found that TPY promotes the highly selective transformation of aryl olefins with a terminal C=C bond to the corresponding ketones with O_2 by visible light irradiation. This is triggered simply by suppression of dimer formation within the narrow zeolite cavity. The proposed system still contains several problems; we are now addressing issues (i) and (iii) by varying the cavity size and number of acid sites on the zeolite. Nevertheless, the proposed concept will contribute to the development of a more efficient photosensitizing system for selective transformation of molecules.

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Notes and references

‡ TPY was synthesized using HY zeolite (Tosoh Corp.; HSZ-331HSA; $SiO_2/Al_2O_3 = 6$; BET surface area, 650 $m^2\ g^{-1}$; particle size, 4 μm), as follows: a mixture of chalcone (100 mg) and acetophenone (50 mg) dissolved in isooctane (50 ml) was refluxed for 12 h with HY zeolite (1.0 g). The obtained yellowish solid was washed by Soxhlet extraction with CH_2Cl_2 for 18 h and dried under vacuum. The diffuse reflectance UV–vis spectrum of TPY is identical to the absorption spectrum of TPT dissolved in CH_2Cl_2 (Fig. S1†). The TP^+ content within TPY was determined by the loss of weight at 523–973 K on a thermogravimetric profile (Fig. S2†).

§ TPY (34 mg containing 7.5 μmol TP^+) was suspended in dry MeCN (15 ml) containing each olefin (750 μmol) within a Pyrex glass tube (id 10 mm; capacity, 20 ml), and each tube sealed using a rubber septum cap. TPY was dispersed well by ultrasonication for 5 min, and O_2 was bubbled through the solution for 10 min at 273 K to avoid the evaporation of solvent. The tube was photoirradiated with magnetic stirring by a 2 kW Xe lamp (USHIO Inc.) filtered through an aqueous $NaNO_2$ solution (3 wt%) to give light wavelengths of $\lambda > 400$ nm (light intensity at 400–470 nm: 477 mW m^{-2}). The solution temperature during photoirradiation was 313 K. The resulting solution was recovered by centrifugation and analyzed by GC-FID. For the TPT experiment, a MeCN solution (15 ml) containing TPT (7.5 μmol) was used for the reaction.

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