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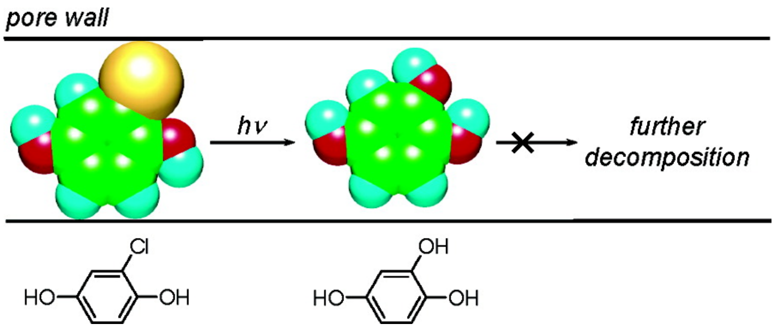

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COMMUNICATIONS

Titanosilicate Molecular Sieve for Size-Screening Photocatalytic Conversion

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Development of efficient and highly selective methods for photochemical organic synthesis is one of the biggest challenges in chemistry.[1] Photocatalytic version of organic synthesis on a heterogeneous catalyst is particularly attractive for practical applications because of the ease of catalyst recovery. Much investigation has so far been carried out on semiconductor (bulk) TiO_2, but this lacks sufficient product selectivity.[2] Practical use of bulk TiO_2 is limited mainly to a photocatalytic water treatment (decomposition of hazardous chemicals into CO_2 and H_2O).[3]

Titanosilicate molecular sieve is a silicious zeolite with titanium oxide [$Ti-O_x$; x (coordination number of Ti atom with oxygen atom) = 4−6)] species covalently linked into a porous SiO_2 framework.[4] This material has already been identified as an oxidation catalyst for organic substrates[5] and as an adsorbent for gaseous ones.[6] Application of the material as a photocatalyst has recently received much attention.[7] In this case, substrate reactivity and product selectivity depend strongly on the nature of the $Ti-O_x$ species. On the catalyst with low Ti content, the $Ti-O_x$ species exist in a tetrahedral coordination ($Ti-O_4$ species) and are highly dispersed in the SiO_2 matrixes. These "isolated" $Ti-O_4$ species, therefore, lack bulk semiconducting character and display photocatalytic activities quite different from those of bulk TiO_2, which consists of octahedrally coordinated (aggregated) $Ti-O_6$ species. On the $Ti-O_4$, some substrates are transformed selectively, for example, NO into N_2 and O_2, CO_2 with H_2O into CH_4 and CH_3OH, CO with CH_3OH into methyl formate, CO_2 with H_2 into CH_4, and propene with O_2 into propene oxide.[8] These unique activities of the titanosilicate molecular sieves are, however, inspired simply by the $Ti-O_4$ active species; structural advantages of the pore system on the catalyst are left unexploited.

Here, we report unprecedented "size-screening" photocatalytic activity of titanosilicate molecular sieves with the $Ti-O_4$ species, which promotes a selective conversion of molecules having a size close to the pore of the catalyst. This catalytic property is triggered by a combination of the $Ti-O_4$ active species and the pore system on the catalysts, when photoactivated in water with molecular oxygen (O_2). Size-selective conversion of molecules is promoted by several catalytic systems based on zeolites[5,9] (including photocatalytic systems[10]), which allow a preferential conversion of "either small or large molecules". The present photocatalytic system promotes a selective conversion of "appropriate" size molecules, while being inactive for too small or too large molecules. Some catalytic systems show such selectivity,[11] while none of the photocatalytic system does such. We highlight here a successful application of this unusual activity to a selective transformation of molecules that is associated with a size reduction of molecules, so-labeled "molecular shave" transformation.

We used two representative microporous titanosilicate, such as titanium silicalite-1 [TS-1; MFI structure; pore dimensions, 0.54 × 0.56 nm (sinusoid channel) and 0.52 × 0.58 nm (straight channel)][12] and titanium silicalite-2 (TS-2; MEL; 0.53 × 0.54 nm),[13] both containing 0.4 mol % Ti (= Ti/(Ti+Si) ratio).[14] Both catalysts exhibit a narrow absorption band at $\lambda < 290$ nm,[14] which is assigned to the LMCT (ligand-to-metal charge transfer) band from lattice oxygen (O_L^{2-}) to the titanium ion (Ti^{4+}),[15] suggesting that both consist of predominantly the isolated $Ti-O_4$ species.

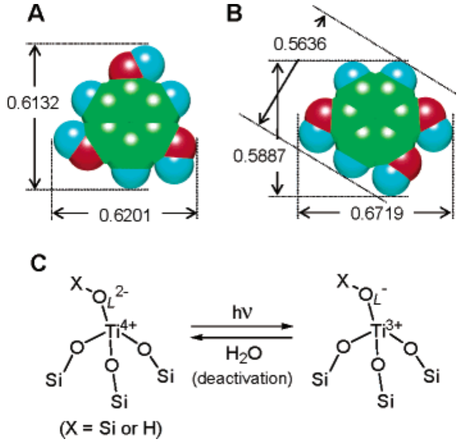

Figure 1. Maximum length, molecular width, and minimum width of (A) 1,3,5-trihydroxybenzene (**20**; EMW, 0.6132 nm) and (B) 1,2,4-trihydroxybenzene (**10**; 0.5762 nm). (C) Schematic representation of photoexcitation−deactivation process of the isolated $Ti-O_4$ species.

Measuring catalytic conversions of 25 kinds of phenol derivatives (**1**−**25**),[14] in water with O_2 under photoirradiation ($\lambda > 280$ nm; 0.5 h), revealed that the activity of TS-1 and TS-2 is rather lower than that of bulk TiO_2 (anatase); conversions of 17 kinds of these substrates are <3%, whose values are less than 20% of those obtained on bulk TiO_2. However, some substrates, such as **20** (1,3,5-trihydroxybenzene), demonstrate specifically high conversion (>10%) both on TS-1 and on TS-2, implying that some factor affects the catalytic activity. Considering the large internal surface area of the catalysts,[14] substrate conversion likely occurs inside the pore. We therefore hypothesized that substrate size may affect the catalytic activity. To evaluate whether a substrate can enter the pore or not and how it is oriented inside the pore, the substrate size must be determined. Molecules inside the pore align their long axis parallel to the pore wall and rotate about the axis.[16] By MO calculations,[17] maximum length of substrate parallel to the benzene plane was determined, and its perpendicular length was defined as molecular width (Figure 1A). For asymmetric substrates (Figure 1B), whose minimum width is smaller than the molecular width, we termed an average value of the molecular width and the minimum width as effective molecular width (EMW).[18] Relation between EMW and conversion of substrates on TS-1 and TS-2 is summarized in Figure 2A and B (open symbol). On both catalysts, conversion of substrates of <0.55 nm EMW is nearly zero, but obviously higher for substrates of 0.6−0.65 nm EMW, which is 10−18 and 12−21% larger than the average pore diameter of TS-1 (0.55 nm) and TS-2 (0.535 nm), respectively. However, substrates of >0.68 nm EMW show almost zero conversion on both catalysts. On bulk TiO_2

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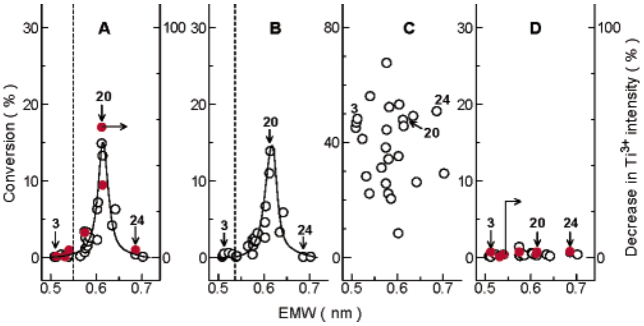


Figure 2. (Open symbol) Relation between EMW and photoconversion (0.5 h) of substrates (**1**−**25**) on (A) TS-1, (B) TS-2, (C) bulk TiO2, and (D) Ti−SiO_2. Substrates are (in the EMW order): **1**, hydroquinone; **2**, benzyl alcohol; **3**, phenol; **4**, 4-chlorophenol; **5**, *p*-cresol; **6**, 4-chlororesorcinol; **7**, 2-chlorophenol; **8**, 3-chlorocatechol; **9**, resorcinol; **10**, 1,2,4-trihydroxybenzene; **11**, 3-chlorophenol; **12**, 1,2,3-trihydroxybenzene; **13**, 2,5-dichlorophenol; **14**, 4-chlorocatechol; **15**, catechol; **16**, *m*-cresol; **17**, 2,6-dichlorophenol; **18**, 3,5-dichlorophenol; **19**, 2,4-dichlorophenol; **20**, 1,3,5-trihydroxybenzene; **21**, 2-chlorohydroquinone; **22**, 5-chlororesorcinol; **23**, 3,4-dichlorophenol; **24**, 2,6-bis(hydroxymethyl)-*p*-cresol; **25**, 2,4,6-trichlorophenol. (Red symbol) Relation between EMW and decrease in the Ti^{3+} intensity on (A) TS-1 and (D) Ti−SiO_2 in the presence of substrates, which were obtained by double integration of the Ti^{3+} signal on ESR spectra. The decrease in the Ti^{3+} intensity obtained with only H_2O is set as 0%. Substrates used are **3**, **5**, **7**, **10**, **20**, **21**, and **23**. The dotted lines denote average pore diameter of the catalysts.

(Figure 2C), such EMW-dependent profile is not observed. These impressive profiles for TS-1 and TS-2 imply a potential size-screening activity of the catalysts promoting selective conversion of appropriate size molecules.

On heterogeneous photocatalyst, substrate adsorption onto the catalyst surface is an important factor for the catalytic activity.[19] However, any relation between the amount of the substrates adsorbed and the substrate conversion is not observed for both TS-1 and TS-2.[14] Oxidation potential, HOMO level, and hydrophobicity (log *P*) of substrates also do not affect the catalytic activity.[14] The size-screening catalytic activity of TS-1 and TS-2 may be affected by the isolated Ti−O_4 species and/or the pore system on the catalysts. To check the former effect, when two catalysts, such as TiO_2-impregnated on a Ti-free silicalite-1 (TiO_2/S-1; 5 mol % Ti)[20] and TS-1 of high Ti content (TS-1^{high}; 5 mol % Ti) both containing Ti−O_6 species, were employed, no EMW dependence was observed.[14] When the latter effect was checked with a nonporous silica with Ti−O_4 species, prepared by a sol−gel method (Ti−SiO_2; Ti 0.4 mol %),[8e,21] almost zero conversion was obtained for all of the substrates (Figure 2D). These indicate that the size-screening activity of TS-1 and TS-2 is triggered by a combination of the isolated Ti−O_4 species and the pore of the catalysts.

In this photocatalytic system, the Ti−O_4 species $[Ti^{4+}-O_L{}^{2-}]$ on the catalysts are photoexcited to form charge-transfer excited state $[Ti^{3+}-O_L{}^-]^*$ (Figure 1C), which acts as the active species.[21] UV irradiation of TS-1 and Ti−SiO_2 catalysts in vacuo at 77 K gave rise to ESR signals assigned to Ti^{3+} and $O_L{}^-$ (Figure 3i, A and B). Upon addition of H_2O (56 mmol/g of catalyst) to both samples, the Ti^{3+} signals were decreased (Figure 3ii) because of the deactivation of $[Ti^{3+}-O_L{}^-]^*$ by H_2O (Figure 1C).[22,23] Further H_2O addition (0.5 mol/g of catalyst) led to a complete disappearance of the signal (not shown) on both catalysts. The present photoreaction system employs enormous quantity of H_2O (56 mol/g of catalyst), indicating that $[Ti^{3+}-O_L{}^-]^*$ is deactivated strongly. Upon addition of H_2O (56 mmol/g of catalyst) containing **3** (0.1 mmol/g of catalyst) of rather smaller EMW than that of the TS-1 pore (Figure 3iii), further decrease in the Ti^{3+} signal was scarcely observed for both catalysts, as compared to that obtained with only H_2O (Figure 3ii). Addition of H_2O containing **20**, of 11% larger EMW than that of the TS-1 pore, to the Ti−SiO_2 sample also did not show any signal change (Figure 3iv, B), but the addition to the TS-1 sample led to apparent signal decrease (Figure 3iv, A). However, addition of H_2O containing **24**, of 25% larger EMW than that of the TS-1 pore, still did not show any signal change for both catalysts. The Ti^{3+} signal was doubly integrated to obtain Ti^{3+} intensity, and the decrease in the intensity in the presence of substrates was plotted against EMW (Figure 2; red symbol), where the decrease in the presence of only H_2O is set as 0%. Surprisingly, the Ti^{3+} intensity profile on TS-1 (Figure 2A) agrees well with that for the substrate conversion (open symbol). For Ti−SiO_2 (Figure 2D), almost no decrease in the Ti^{3+} intensity is observed in the presence of any substrates, whose profile still agrees with the conversion profile. These indicate that the substrate conversion is closely related to the degree of the interaction between $[Ti^{3+}-O_L{}^-]^*$ and substrates.

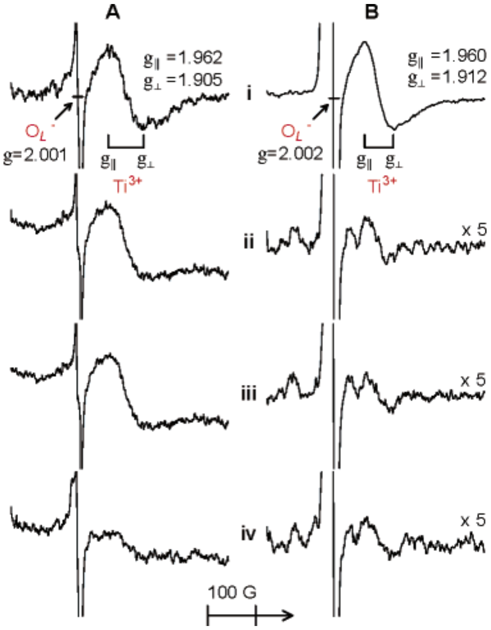
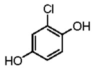
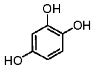
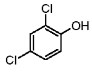
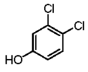


Figure 3. ESR spectra of (A) TS-1 and (B) Ti−SiO_2 obtained at 77 K with photoirradiation. The spectra were measured (i) in vacuo, (ii) with H_2O (56 mmol/g of catalyst), (iii) with H_2O (56 mmol/g of catalyst) containing **3** (0.1 mmol/g of catalyst), and (iv) with H_2O (56 mmol/g of catalyst) containing **20** (0.1 mmol/g of catalyst).

The above findings led us to assume the onset mechanism for the size-screening activity of TS-1 and TS-2, as follows. The excited state $[Ti^{3+}-O_L{}^-]^*$ species on the catalysts are deactivated strongly by H_2O, such that their lifetime is shortened significantly.[22] A slim molecule, of rather smaller EMW than that of the pore, diffuses smoothly inside the pore and is scarcely trapped by the short-lived $[Ti^{3+}-O_L{}^-]^*$. On the contrary, diffusion of a molecule of a size close to that of the pore is restricted by the pore wall, such that the “interlocked” molecule is trapped easily by $[Ti_3{}^+-O_L{}^-]^*$, resulting in high conversion. Zeolite framework is distorted in solution, and the pore structure changes elastically.[24] The molecules of ca. 10−20% larger EMW than that of the pore may, therefore, be interlocked more easily and allowed for the specifically high conversion (Figure 2A and B). However, a fat molecule of >20% larger EMW cannot enter the pore, thus showing zero conversion. To confirm the above, when reaction was carried out in acetonitrile, which scarcely deactivates $[Ti^{3+}-O_L{}^-]^*$,[25] no EMW dependence was observed.[14] However, the dependence became apparent with an increase in the H_2O quantity.[14] This indicates that the deactivation of $[Ti^{3+}-O_L{}^-]^*$ by H_2O is essential for the size-screening activity,

Table 1. Photocatalytic Transformation of 1,2,4-Trisubstituted Chlorophenols Promoted on Various Catalysts[a]

run	catalyst	substrate[b]	conv (%)	product[b]	select (%)
1	TiO_2	 **21**	99	 **10**	1
2	TS-1		67		85
3	TS-2		74		>99
4	TiO_2/S-1		47		<1
5	TS-1^{high}		82		<1
6	Ti/SiO_2		<1		N.D.
7	TiO_2	 **19**	92		2
8	TS-1		48		84
9	TS-2		41		86
10	TiO_2	 **23**	64		1
11	TS-1		37		80
12	TS-2		35		81

[a] Conditions: substrates, 20 μmol; catalyst, 10 mg; photoirradiation time, 2 h; H_2O, 10 mL; temperature, 313 K. [b] EMW: **10** (0.5762 nm); **19** (0.6051 nm); **21** (0.6149 nm); **23** (0.6431 nm).

and the activity is triggered by a combination of the short-lived $[Ti^{3+}-O_L^-]^*$ and the restricted diffusion of a molecule inside the pore. Zero conversion on Ti$-SiO_2$ (Figure 2D) is, therefore, attributed to the lack of the pore that regulates the motion of substrates.[26]

The size-screening catalytic activity, inspired by titanosilicate molecular sieves, is highlighted by their application to a selective transformation of 1,2,4-trisubstituted harmful chlorophenols (Table 1). Photoirradiation of bulk TiO_2 with **21** (run 1) afforded the corresponding trihydroxylated benzene derivative **10**, which is nontoxic and industrially valuable, as an initial product via a hydroxyl radical addition.[14] The yield of **10** is, however, significantly low (1%) because the sequential decomposition of **10** occurs on TiO_2.[14,27] The EMW of **21** (0.6149 nm) is 12 and 15% larger than the TS-1 and TS-2 pores, respectively, thus allowing effective photoconversion of **21** on both catalysts (>65%) (runs 2 and 3). On these catalysts, the substitution of $-$Cl by $-$OH also occurs, via reaction of **21** trapped on the O_L^- site with a superoxide anion formed by a reduction of O_2 on the Ti^{3+} site.[14] Astoundingly, excellent high selectivity of **10** was obtained on TS-1 (85%) and TS-2 (> 99%). Since the $-$OH is less bulky than $-$Cl, the EMW of **10** (0.5762 nm) is 6% smaller than that of **21** and is only 5 and 8% larger than the TS-1 and TS-2 pores, respectively, thus allowing relatively smooth diffusion of **10** inside the pores. Sequential reaction of **10** on the catalysts, therefore, scarcely occurs, thus affording **10** in high selectivity. These catalysts also promoted selective transformation of dichlorophenols (**19** and **23**) into **10** in high selectivity (>80%) (runs 8, 9, 11, and 12), where in both cases intermediately formed **21** is sequentially transformed into **10**.[14] The above findings demonstrate that the titanosilicate molecular sieves "shave" a molecule, interlocked inside the pore, into a smoothly diffusive slim molecule. In general, harmful chlorophenols are treated (detoxificated) by chemical[28] and photochemical[3,27] total destruction processes. The present molecular shave catalytic system enables the detoxification of chlorophenols and the synthesis of valuable phenol derivatives all at once, proving that this "green" photocatalyst may contribute to the development of an economically and environmentally friendly chemical process.

In conclusion, we have found the size-screening photocatalytic activity of titanosilicate molecular sieves. Various titanosilicate molecular sieves, of different pore sizes and structures, have so far been synthesized using a structure directing agent. The catalytic system based on titanosilicate molecular sieves has the potential to become a very powerful tool for photocatalytic organic synthesis.

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Supporting Information Available: Materials and methods, discussion, tables, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Double integration of the Ti^{3+} signal on ESR spectra (Figure 3ii) indicates that decrease in the Ti^{3+} intensity in the presence of H_2O (56 mmol/g of catalyst) is 12% (TS-1) and 82% (Ti$-SiO_2$), based on the intensity obtained in vacuo (Figure 3i). Surface hydrophilicity of Ti$-SiO_2$ is significantly higher than that of TS-1 (Supporting Information Table S1; monolayer adsorption capacity of H_2O). The strong Ti^{3+} deactivation on Ti$-SiO_2$ is, therefore, due to the enhanced access of H_2O to $[Ti^{3+}-O_L^-]^*$.
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(25) Relative Ti^{3+} intensity on TS-1, obtained by double integration of ESR spectra, is 1 (in vacuo), 0.99 [with acetonitrile (56 mmol/g of catalyst)], and 0.88 [with H_2O (56 mmol/g of catalyst)].
(26) A question arising is why the amount of substrates adsorbed on the catalyst surface does not affect the substrate conversion on TS-1 and TS-2 (Supporting Information Table S2), although the substrate adsorption may occur mainly inside the pore of high surface area and the strongly adsorbed substrate is likely to be trapped easily by $[Ti^{3+}-O_L^-]^*$. The substrate adsorption may occur mainly on the silicious surface of the catalysts because of very low Ti content. The substrate trapping by $[Ti^{3+}-O_L^-]^*$ is, therefore, not related to the degree of the substrate adsorption.
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