Communications

Photocatalytic Epoxidation of Olefins Using Molecular O₂ by TiO₂ Incorporated in Hydrophobic Y Zeolite

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ABSTRACT: Zeolite is an ideal host material for encapsulating nano-size metal catalyst species because of its defined microporous structure, prominent adsorption/condensation properties, high surface area, chemical/thermal stability, and transparency to light. In this study, TiO_2 photocatalyst was incorporated in highly hydrophobic Y zeolite and its photocatalytic activity was examined in the photocatalytic oxidation of olefins under UV-light irradiation using molecular oxygen as an oxygen source. TiO_2 nanoparticles incorporated in hydrophobic Y zeolite exhibited a markedly enhanced photocatalytic activity compared with bare TiO_2 owing to its excellent affinity toward organic moieties, which facilitates the mass transfer of organic substrates and allows them to efficiently access to the neighboring active TiO_2 surface.

Semiconductor photocatalysts such as TiO_2 have recently found emerging applications in selective organic synthesis including oxidation, hydrogenation, hydroxylation, amination and deoxygenation etc.[1-6] Among numerous studies concerning this issue, pioneering works have been done by Kanno et al. and Fox et al., who demonstrated photocatalytic oxygenation of aromatic olefins over semiconductor photocatalysts (TiO_2 and CdS).[7,8] Similarly, Ohno et al. have found that TiO_2 is photocatalytically active for epoxidation of alkyl olefins using O_2 as an electron acceptor under UV-light irradiation.[9,10] Epoxides are important starting materials for the synthesis of polymers and fine chemicals. Photocatalytic epoxidation of olefin compounds using molecular oxygen as an environmentally-benign oxidant and light as an energy source is considered one of the greenest oxidation processes. However, the yields of epoxides in these reports still remain low.

Since the discovery of porous silicate materials (e.g., zeolite and mesoporous silica), increasing attention has been directed toward their use as hosts for TiO_2 photocatalyst owing to their advantageous characteristics, such as adsorption/condensation properties, high surface area, chemical/thermal stability, and transparency to light; the defined geometry of the cavities and channels in the nanometer length scale can generate spatially isolated TiO_2 nanoparticles, and the high surface area can facilitate the adsorption and mass transfer of target organic substrates. A number of studies have witnessed that a combination of these porous silicate materials and TiO_2 photocatalyst allows to fabricate highly elaborated photocatalytic systems which enable efficient photocatalytic degradation of organic pollutants.[11,12] Our recent efforts have revealed that hydrophobic silicate support provides an improved catalytic efficiency for TiO_2 photocatalyst owing to its ability to adsorb and condense organic molecules from air/water systems.[13,14]

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Herein, we examine the photocatalytic epoxidation of olefins by using TiO_2 photocatalyst supported on highly hydrophobic zeolites. Hydrophobic zeolite is expected to greatly enhance the photocatalytic efficiency of TiO_2 owing to its efficient adsorption/condensation properties. In this study, ultrastable Y (USY) zeolite with extremely high hydrophobicity was chosen as a host for TiO_2, which was prepared from H^+-type Y zeolite with SiO_2/Al_2O_3 ratio of 5.8 (denoted as HY(5.8)) according to the method we previously reported.[15] The USY-supported TiO_2 photocatalyst (TiO_2@USY) was prepared by a conventional wet impregnation method using ammonium titanyl oxalate ((NH_4)$_2$[TiO(C_2O_4)$_2$]·$2H_2O$) as a Ti source, and the TiO_2 content was empirically fixed to be 10 wt.%.
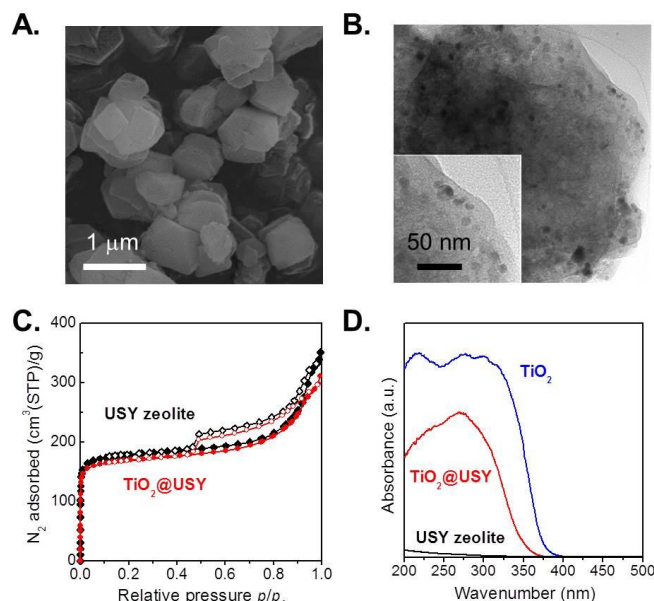

Figure 1. FE-SEM image (A), TEM image (B), N_2 adsorption-desorption isotherms (C) and diffuse reflectance UV-vis spectra (D) of TiO_2-incorporating USY zeolite, together with those of reference samples (USY zeolite and bulk TiO_2).

Figure 1A and 1B show FE-SEM and TEM images of TiO_2@USY, respectively. The FE-SEM image shows octahedral-like particles with the particle size less than 1 μm, which is characteristic of FAU-type zeolite. The TEM image clearly visualizes nano-size TiO_2 particles uniformly distributed within the zeolite. The average particle diameter of TiO_2 particles was estimated to be ca. 5 nm, which is obviously larger than the size of micropore channels of Y zeolite (the widest channel size is 1.3 nm). This suggests that most of TiO_2 particles are deposited on the exterior surface of zeolite. N_2

adsorption of TiO₂@USY identified microporous structures typical of FAU-type zeolite. The mean surface area (S_{BET}) and total pore volume (V_{total}) was estimated to be 705 m²/g and 0.56 cm³/g, respectively. These values are almost comparable to those of the original USY zeolite (S_{BET} = 782 m²/g, V_{total} = 0.58 cm³/g), verifying the preservation of zeolite structure even after the TiO₂ deposition and the incorporation of a small fraction of TiO₂ inside the zeolite cavity space (Figure 1C). XRD patterns also confirmed the structural retention of Y zeolite even after TiO₂ deposition (for XRD patterns, see the Supporting Information). In the XRD pattern, a broad peak assignable to (101) diffraction plane of anatase TiO₂ crystals was observed at 2θ = 25.4°. UV-vis spectra of TiO₂@USY exhibited a strong absorption at $\lambda < 370$ nm, which is different from that of bulk TiO₂ (Figure 1D). These results indicate the formation of anatase TiO₂ nano-particles which is likely caused by the confinement effect of USY zeolite frameworks, being consistent with the TEM observation.
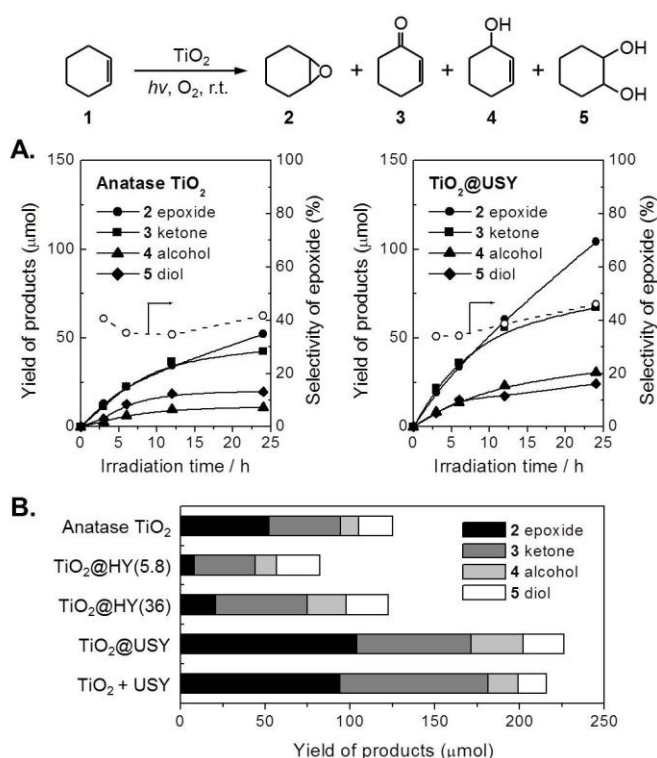

Figure 2. Time course of product yields in the photocatalytic oxidation of cyclohexene over anatase TiO₂ and TiO₂@USY (A). Comparison of product yields in the photocatalytic oxidation of cyclohexene over anatase TiO₂ and zeolite-supported TiO₂ photocatalysts after 24 h of UV-light irradiation (B).

Photocatalytic activity was examined by the photocatalytic oxidation of cyclohexene (**1**) under UV-light irradiation with a continuous flow of oxygen. Fig. 2A compares the reaction kinetics over bare anatase TiO₂ and TiO₂@USY photocatalysts. In both cases, the corresponding epoxide (**2**), ketone (**3**), alcohol (**4**) and diol (**5**) were formed with modest epoxide selectivities (34-46%) as increasing the UV-light irradiation time. A marked increase of product yields was observed by combining TiO₂ and USY zeolite, where the reaction rate was almost two times increased compared with that of TiO₂ alone; TiO₂@USY afforded 226 μmol of accumulated amount of products and 46% epoxide selectivity after 24 h of reaction, whereas bare TiO₂ gave 125 μmol of total products and 42% epoxide selectivity. The conversion of cyclohexene over sole USY zeolite (without TiO₂) was comparable to that of blank experiment, demonstrating that the reaction proceeds via a

photocatalytic process over TiO₂ surface. In addition, no products were obtained under Ar atmosphere, showing that the molecular oxygen is the oxygen source for this reaction. Concerning the reaction mechanism, Ohno et al. proposed that the olefins are initially oxidized to cation radicals by the photogenerated positive holes (h⁺) and subsequently the olefin cation radicals react with the photogenerated mono-oxygen (O⁻) species on the TiO₂ surface to afford the corresponding epoxide. Thus formed surface oxygen vacancy should be occupied with oxygen radical species created by the photogenerated electrons.[9,10] Compound **3** and **4** are considered as byproducts generated via a direct reaction between the olefin cation radicals and the oxygen radicals.

Fig. 2B compares the product yields over TiO₂ and those supported on Y zeolites with different SiO₂/Al₂O₃ ratios. Surprisingly, a drastic activity increase was observed as the SiO₂/Al₂O₃ ratio increased. No significant structural difference could be identified depending on the SiO₂/Al₂O₃ ratios (for structural parameters, see the Supporting Information), suggesting that there is little correlation between activities and zeolite structures. It has been long recognized that SiO₂/Al₂O₃ ratio of zeolite framework (i.e., Al content) directly affects the degree of hydrophilicity/hydrophobicity.[16] As the framework SiO₂/Al₂O₃ ratio increases, zeolite in principle tends to have hydrophobic nature. Our preliminary adsorption experiments also revealed that HI factor (Hydrophobicity Index defined by the adsorbed amount of water (at p/p_0=0.2) per the adsorbed amount of toluene (at p/p_0=0.2)) increased in the order of HY(5.8) (HI = 3.8) < HY(36) (HI = 4.6) < USY (HI = 76.8), indicating that the inside of USY zeolite micropore cavities is highly hydrophobic.[15] These facts indicate that the increased photocatalytic activity on TiO₂@USY is attributable to the ability of USY zeolite to efficiently adsorb and condense organic moieties rather than polar compounds such as acetonitrile. Such an activity enhancement was also attained by physically mixing TiO₂ and USY zeolite, indicating that the size of TiO₂ particles has little effect on the activity. USY zeolite is likely to facilitate the mass transfer of organic moieties and allow them to efficiently access to the neighboring TiO₂ surface, and thus resulting in higher photocatalytic efficiency. In addition, when Al-rich zeolites, HY(5.8) and HY(36), with more hydrophilic nature were used as supports, the epoxide selectivity was markedly reduced. This might be due to the subsequent ring-opening hydration of **2** to give **5** which is catalyzed by Al-related acid sites.

Table 1. Photocatalytic oxidation of various olefins using TiO₂@USY under UV-light irradiation[a]

Entry	Substrate	Time (h)	Yield (μmol)		Epoxide selectivity[c] (%)
			epoxide	others[b]	
1		24	104	122	46
2		24	443	0	>99
		72	1272	0	
3		24	272	57	83
		72	615	111	85
4		24	54	39	58
5		24	94	79	54
		72	215	100	68
6		24	70	58	55
		72	150	96	61

[a] *Reaction conditions:* photocatalyst (20 mg on a mass TiO₂ base), olefins (2 mmol), acetonitrile (20 ml), O₂ bubbling (3 mL/min), under UV-light irradiation (5 mW/cm²), room temperature. [b] Including the corresponding ketones, alcohols and diols. [c] Expressed by [produced amount of epoxide]/[produced amount of oxidized products].

Table 1 shows the scope of substrates for the photocatalytic oxidation of olefins over TiO$_2$@USY photocatalyst under UV-light irradiation. Various kinds of cyclic olefins and linear α-olefins were successfully converted to the corresponding epoxides with moderate to excellent selectivities. Among those, cyclooctene gave the highest conversion rate and the finest epoxide selectivity (>99%) (Entry 2). Cyclododecene also provided a high conversion rate with more than 80% epoxide selectivity (Entry 3). On the other hand, the photocatalytic oxidation of linear α-olefin molecules commonly showed moderate selectivities toward the corresponding epoxides (50-70%) (Entries 4-6). The remaining fractions were the corresponding aldehydes, ketones, alcohols, diols, and carboxylic acids. This difference in product selectivity is ascribed to the reactivity derived from the position of C=C bond. Another point that needs to be addressed is the acceptable molecular size of substrate. Given that the molecular diameters of cyclohexene, cyclooctene, and cyclododecene are 5.0, 5.7, and 7.6 Å, respectively, cyclododecene is incapable of entering the micropore of Y zeolite (ca. 7.4 Å). Considering the fact that cyclododecene was oxidized over TiO$_2$@USY, most of TiO$_2$ particles are present on the outer surface of zeolite, being consistent with the above characterization results.

In summary, we demonstrated that the photocatalytic epoxidation of olefins effectively proceeds over TiO$_2$ nanoparticles incorporated in highly hydrophobic Y zeolite under UV-light irradiation using molecular O$_2$ as an oxygen source owing to the ability of hydrophobic Y zeolite to efficiently adsorb and condense organic moieties. With the favorable affinity toward organic moieties and the confinement effect of metal species, hydrophobic zeolite can be utilized as an ideal host material for designing advanced semiconductor-based photocatalytic systems useful for selective organic synthesis.

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