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Layered Silicate as an Excellent Partner of a TiO_2 Photocatalyst for Efficient and Selective Green Fine-Chemical Synthesis

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Supporting Information

ABSTRACT: When the partial oxidation of benzene to phenol, which is one of the most important reactions in chemical industry, was conducted using TiO_2 in the presence of a phenol-philic adsorbent derived from a layered silicate, phenol was recovered in unprecedentedly high yield and purity. This resulted from the fact that the adsorbent captured the generated phenol promptly, selectively, and effectively to prevent the overoxidation, after which the captured phenol could be easily eluted.

Fine-chemical synthesis by solar-driven photocatalysis, especially using environmentally benign reactants such as molecular oxygen or water, is one of the most compelling objectives in modern chemistry. Thanks to its abundance, nontoxicity, and high photostability, TiO_2 is a promising photocatalyst for this purpose. However, organic substrates tend to be overoxidized to undesired byproducts such as carbon dioxide on TiO_2 because of the presence of highly oxidizing species. Accordingly, the design of novel photocatalysts has been extensively investigated;[1−5] however, photocatalytic activities for desired partial oxidations are still insufficient for practical applications. The use of titanosilicate zeolites composed of a silica framework and highly dispersed TiO_2 is a green methodology for photocatalytic partial oxidations.[6] However, the presence of micropores (with aperture diameters below 1 nm) often goes hand-in hand with diffusion limitations that adversely affect the photocatalytic activity and limit the available organic substrates. In this communication, we describe a conceptually new methodology to attain a high photocatalytic activity for desired partial oxidations even using TiO_2. As an example partial oxidation, the oxidation of benzene to phenol was conducted. Phenol, which is currently produced from benzene by a three-step cumene process, is one of the most important commodity chemicals in industry. Because the cumene process is energy-consuming, has a low phenol yield, and produces unwanted byproducts, extensive efforts have been made to develop catalysts for direct benzene oxidation.[7−18]

One of the main difficulties in partial oxidations of organic substrates on TiO_2 is that the desired products are easily overoxidized. During the photocatalytic oxidation of benzene on TiO_2 with water containing dissolved O_2, once phenol is generated, it is promptly overoxidized to hydroxyphenols (e.g., catechol and hydroquinone) and finally oxidized to carbon dioxide as a result of the presence of highly oxidizing radical species such as hydroxyl radical.[19] We expected that during the photocatalysis, a coexisting adsorbent that can promptly and selectively adsorb phenol from a mixture of water, benzene, and phenol would separate the photocatalytically formed phenol from TiO_2 to prevent such overoxidation (Figure 1). Layered inorganic solids, such as layered clay minerals, have been widely investigated as adsorbents because of their large surface areas derived from the nanometer-thick layers assembled naturally in a layer-by-layer manner and their surface reactivities (ion exchange, hydrogen bonding, etc.).[20] Magadiite ($Na_2Si_{14}O_{29}$, denoted as Na-mag) is a naturally occurring layered silicate that can be readily synthesized by a simple hydrothermal reaction.[21,22] The layered silicic acid derived from magadiite via a cation-exchange reaction of the interlayer sodium ions with protons ($H_2Si_{14}O_{29}$, denoted as H-mag) has been known to take up various polar organic molecules (e.g., alcohols) in the interlayer space via hydrogen-bonding interactions with the surface silanol groups.[23,24] In this study, we prepared Na-mag and H-mag and investigated their adsorption of phenol in the presence of water and benzene (from an aqueous benzene solution).

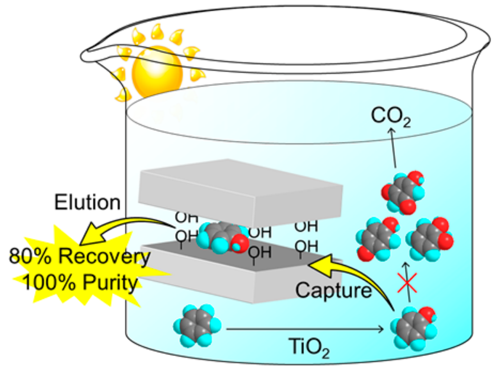

Figure 1. Scheme for effective and selective recovery of phenol by a phenol-philic adsorbent, layered silicic acid (H-mag), during the photocatalytic oxidation of benzene in water over TiO_2 under solar irradiation.

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The time-dependent adsorption of phenol on H-mag from an aqueous mixture of benzene and phenol (Figure 2a) showed that phenol adsorption occurred on a scale of minutes. The adsorption isotherm of phenol on H-mag from the aqueous mixture with benzene (Figure 2b) was an H-type isotherm according to the Giles classification,[25] indicating strong adsorbent−adsorbate interactions. These results revealed that H-mag could promptly and selectively adsorb phenol from water even in the presence of benzene. On the other hand, pristine Na-mag hardly adsorbed phenol from the aqueous mixture with benzene (Figure 2b), presumably because of competition with water, which strongly interacts with the sodium ions in the interlayer space.

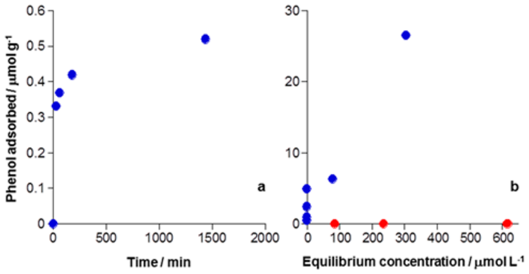

Figure 2. (a) Time-dependent phenol adsorption from water containing benzene by H-mag. (b) Adsorption isotherms of phenol from water containing benzene for Na-mag (red circles) and H-mag (blue circles). The initial concentrations of phenol and benzene were 0.05−3 and 600 ppm, respectively.

Photocatalytic benzene oxidation on TiO_2 was conducted using water as the solvent and oxidant and dissolved O_2 as the oxidant under simulated solar irradiation ($\lambda > 320$ nm) in the absence or presence of Na-mag or H-mag. We used flaky TiO_2 with a size of a few square millimeters rather than fine TiO_2 particles, which allowed us to easily remove TiO_2 from the reaction mixture after the photocatalysis and thus to elute possibly captured products only from the adsorbent. The results of the photocatalytic oxidations were summarized in Table 1. When TiO_2 alone was used, significant amounts of products of phenol overoxidation (e.g., catechol, hydroxyquinone, and 1,2,3-trihydroxybenzene) were detected in the chromatogram of the supernatant of the reaction mixture after the photocatalysis (Figure 3a), giving 4% phenol selectivity at ca. 80% benzene conversion after photoirradiation for 24 h (Table 1). However, when H-mag was present under identical photoirradiation conditions, phenol and the overoxidized products were hardly detected in the supernatant despite benzene conversion of ca. 80% (Figure 3a), and only phenol was detected in the chromatogram of the eluate obtained from H-mag using aqueous ethanol (Figure 3b). In this case, phenol was recovered with 100% selectivity (purity) at ca. 80% benzene conversion (Table 1). It should be noted here that phenol was hardly detected in the reaction mixture at any point during the course of the photocatalysis (Figure 3c). These results showed that H-mag adsorbed the newly-formed phenol so promptly and selectively that phenol was hardly overoxidized, allowing it to be recovered selectively and efficiently. The adsorbed phenol was stabilized as a result of the separation of phenol from the TiO_2 surface;[26] it is probably difficult for oxidizing radical species generated on TiO_2 to diffuse inside H-mag before they are deactivation. On the other hand, phenol was considerably less effectively recovered when Na-mag was used instead of H-mag (Table 1). On the basis of the fact that phenol was detected in both the reaction mixture and the eluate from Na-mag (Figure 3a,b), Na-mag adsorbed phenol via relatively weak interactions and released it in a repetitive manner during the photocatalysis. We cannot rule out the possibility that variation in the nature of the reaction medium (pure water, water/H-mag dispersion, water/Na-mag dispersion), such as its hydrophobicity or hydrophilicity, affects the photocatalytic performance of TiO_2.[27]

Table 1. Photocatalytic Oxidations of Benzene on TiO_2 with or without Adsorbent[a]

	in supernatant after photocatalysis			in eluate[b]	
adsorbent	amount of phenol formed (µmol)	phenol selectivity (%)[c]	benzene conversion (%)[d]	phenol recovered (µmol)	recovery selectivity (%)[e]
none	4.9	4.1	77.4	–	–
H-mag	0.3	0.2	76.2	119.2	100
Na-mag	26.6	22.7	76.1	13.0	100

[a] Benzene, 154 µmol; water (saturated with O_2), 20 mL; flaky TiO_2, 60 mg; adsorbent (if present), 60 mg; simulated solar irradiation time, 24 h. [b] Solution obtained after washing the adsorbent with 100 mL of aqueous ethanol (1:1 v/v). [c] [formed phenol]/[reacted benzene] × 100%. [d] [reacted benzene]/[added benzene] × 100%. [e] Based on HPLC results.

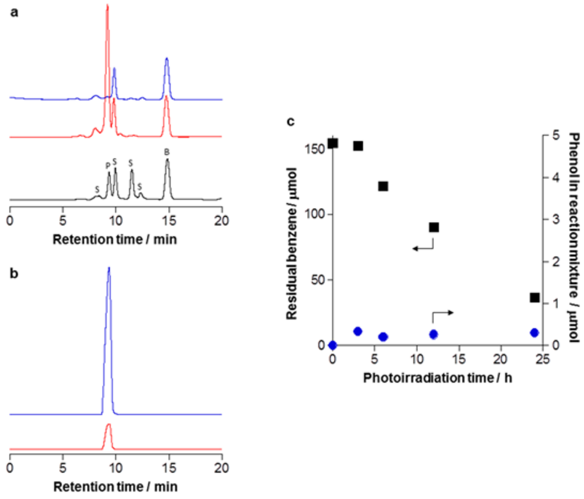

Figure 3. (a) HPLC chromatograms of aqueous benzene after photocatalysis under solar-simulator irradiation using TiO_2 in the absence (black line) or the presence of Na-mag (red line) or H-mag (blue line). Peaks B, P, and S are assigned to benzene, phenol, and the products of phenol overoxidation, respectively. (b) HPLC chromatograms of eluates obtained after the recovered Na-mag (red line) or H-mag (blue line) was washed with aqueous ethanol. (c) Time courses of the amounts of benzene (black squares) and phenol (blue circles) in aqueous benzene during the photocatalysis of TiO_2 with H-mag.

The presently observed phenol production (recovery) activity was considerably higher than those reported for catalytic and photocatalytic processes for direct benzene oxidation,[9−18] although the present process required only abundant, safe materials and reagents (TiO_2, silicate, water, O_2, and ethanol). The present activity was also much higher compared with that on a titanosilicate zeolite (65% phenol selectivity at <20% benzene conversion under UV irradiation for 24 h),[6] which can be explained by the fact that nonporous TiO_2 does not limit the diffusion of benzene and phenol. To date, the combination of TiO_2 and layered silicates [e.g., TiO_2-incorporated (pillared) layered clays[28] and TiO_2 supported on the particle surface of layered clays[29]] has been investigated for the decomposition (complete oxidation) of organic substrates, where the layered clays play a role in concentrating the organic substrates near the catalyst surface. However, this is the first report to demonstrate an important role of layered silicates as a partner of TiO_2 for the partial oxidation of organic substrates. Adsorbents based on layered inorganic solids can be tailor-made for a wide variety of organic molecules with varied size and structure by intercalation reactions.[20] In combination with recent progress in the design of TiO_2 with higher sunlight absorption for photocatalysis,[30] the large-scale production of phenol and other fine chemicals in an environmentally and economically benign fashion is expected upon optimization of the reaction conditions (e.g., light intensity, the kind and amount of the added adsorbents, reactors, etc.).

In summary, we have reported that phenol was recovered with unprecedentedly high efficiency and selectivity (purity) when the photocatalytic oxidation of benzene in water over TiO_2 under simulated solar light was conducted in the presence of a layered silicic acid (protonated magadiite). We expect that the combination of layered silicates with TiO_2 will open a door to green fine-chemical synthesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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