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Efficient photocatalytic oxidation of benzene to phenol by metal complex-clay/TiO₂ hybrid photocatalyst

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Synthetic saponite containing a photosensitizing metal complex was complexed with colloidal anatase and used for the visible light photocatalytic reaction of aqueous benzene to phenol. The addition of phenol to the initial aqueous benzene solution was effective to improve the reaction yield and the product selectivity.

Phenol is an important chemical as precursor of plastics and drugs. Cumene process is the most famous industrial phenol production method, while there are several drawbacks; the production of acetone as by-products and the low yield of phenol. Accordingly, there has been a demand for an alternative process for efficient phenol production.¹ Photocatalytic oxidation of benzene using visible light is an ideal method due to the environmentally benign nature of visible light driven photocatalytic reaction. To meet the requirement for practical uses, visible light responsive photocatalysts, which lead high reaction yield and selectivity of phenol, are desired. As a new way to improve the reaction efficiency, phenol production from aqueous benzene solution was reported by using a gold nanoparticle supported layered titanate as visible light responsive photocatalyst.²

The photosensitization of titanium dioxide using dyes is a versatile way to achieve visible light responsive photocatalytic reactions.³ By designing the molecular structures, absorption in a wide range of wavelength have been tuned for the optimum uses of solar irradiation.⁴⁻⁹ Among possible candidate for sensitizer, ruthenium(II) poly(pyridyl) complexes have long been used to extend the photoresponse of TiO₂ into visible wavelength region.¹⁰⁻¹⁵ In addition to the direction for efficient sensitization, the stability of the dyes against the leaching and the decomposition, especially during the irradiation, is an important issue for the practical application.

We have reported improved stability of tris(2,2'-bipyridine)ruthenium(II) complex (hereafter abbreviated as [Ru(bpy)₃]²⁺) of [Ru(bpy)₃]²⁺-clay@TiO₂ hybrid under the irradiation if compared with that of an analogous ruthenium poly(pyridine) complex (tris(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) dichloride, abbreviated as Ru470) attached on the surface of a commercially available TiO₂ (AEROXIDE® TiO₂ P25, Nippon Aerosil Co., Ltd.).¹⁶ More recently, [Ru(bpy)₃]²⁺-clay@TiO₂ hybrid film was fabricated in a flow reactor to

construct flow reactor for photochemical reactions.¹⁷ This was achieved probably by the fact that the clay nanosheet separated [Ru(bpy)₃]²⁺ from TiO₂ with keeping the possible communication between photo-excited complex and TiO₂. In the present paper, we report the preparation of [Ru(bpy)₃]²⁺-clay@TiO₂ hybrid photocatalyst by a simple mixing of pre-synthesized [Ru(bpy)₃]²⁺-clay intercalation compounds and anatase nanoparticle. The application of the [Ru(bpy)₃]²⁺-clay@TiO₂ hybrid to promote the direct oxidation of aqueous benzene to phenol by visible light irradiation is also reported.

Hybrid photocatalyst was prepared from [Ru(bpy)₃]²⁺-clay intercalation compound, which was synthesized by cation exchange reaction of a sodium type synthetic saponite (Sumecton SA, Kunimine Ind. Co., Ltd., Cation Exchange Capacity (CEC) of 71 meq/(100 g of clay))¹, hereafter the sample is designated as SSA). Among available smectites, SSA was selected due to the purity, whiteness of solid and transparency of the suspension, and appropriate rheological property.¹⁶⁻²³ The loaded [Ru(bpy)₃]²⁺ amount was 7.1 meq/100 g clay in order to make stable suspension. The aqueous suspension of [Ru(bpy)₃]²⁺-SSA was mixed with an aqueous colloidal suspension of anatase (particle size of ca. 5 nm, the concentration of 0.21 g/L, Nissan Chemical Ind. Co. Ltd.), to obtain hybrid photocatalyst, [Ru(bpy)₃]²⁺-SSA@TiO₂. In our separate study on the photocatalytic flow reactor composed of [Ru(bpy)₃]²⁺-SSA@TiO₂ film, the composition of the catalysts was examined to obtain stable suspension as well as to achieve efficient reactions.¹⁷ In this study, the SSA:TiO₂ mass ratio of 2:9 was employed based on the previous examination. According to the XRD and TEM images reported in the previous reports,^{16,17} SSA was thought to be surrounded by TiO₂ nanoparticles.

Photocatalytic benzene oxidation on [Ru(bpy)₃]²⁺-SSA@TiO₂ was examined in aqueous suspension after the dissolved oxygen was removed by Ar bubbling. Reaction was done by visible light irradiation (the light source was San-Ei Electronic XES-502S solar simulator and the light intensity was 100 mW/cm²). The reaction was monitored by the concentration of benzene and phenol in the solution using high-performance liquid chromatography.

Figure 1(left) shows a chromatogram obtained after the visible light irradiation to aqueous benzene solution (32 mL of 1800 ppm benzene) for 5 h using [Ru(bpy)₃]²⁺-SSA@TiO₂ (6.92 mg TiO₂, corresponds to the concentration of 0.21g/L) as photocatalyst. The concentration of benzene decreased and that of phenol increased as shown by the chromatogram. Figure 1(right) shows the concentration of benzene (residual benzene)

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and phenol (formed by the visible light irradiation) during adsorption and photocatalytic reactions as a function of reaction time. From the results (Figure 1), the direct oxidation of benzene to phenol was confirmed, while the reaction yield was low, which need improvement.

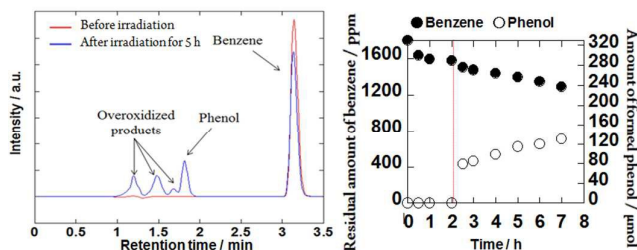


Figure 1 (left) Example of HPLC chromatograms of aqueous benzene/phenol mixture before and after the photocatalytic reaction under visible light irradiation. (right) Visible-light-induced catalytic oxidation of benzene in water with $[\text{Ru}(\text{bpy})_3]^{2+}$ -clay@TiO₂. The amounts of benzene and phenol in aqueous mixtures were denoted as (●) and (○), respectively. The light irradiation started after 2 h. The initial concentration of benzene is 1800 ppm (655 μmol).

In order to improve the reaction efficiency, we examined the oxidation of benzene to phenol in aqueous benzene/phenol solution. We have reported the possible modification of reaction efficiency by conducting the reactions under the designed reaction environments.^{2,23-26} For the visible light driven photocatalytic oxidation of benzene to phenol using gold nanoparticle supported layered titanate, the addition of phenol to the initial benzene solution promoted the benzene/phenol transformation (both reaction yield and the phenol selectivity).²

The chromatograms of the solution (the initial concentration of benzene 1800 ppm, phenol 1800 ppm) before and after the irradiation for 5 h are shown in Figure 2. From the data (Figure 2), the change in the concentration of benzene and phenol during adsorption and photocatalytic reactions was determined as a function of the reaction time as shown in Figure 3(a) show. It was shown that the efficiency of the oxidation of benzene to phenol was substantially improved (the benzene decomposition and the selectivity of phenol were 60 and 93%) if compared those achieved by the reaction from pure aqueous benzene solution (Figure 1). In order to confirm the effects of the addition of phenol, the concentration of phenol in the starting solution was changed to 18000 ppm. The changes in the concentration of benzene and phenol by the irradiation are shown in Figure 3(b). After the irradiation for 5 h, 51% of the

initial benzene was eliminated and 93% of the eliminated benzene was transformed into phenol.

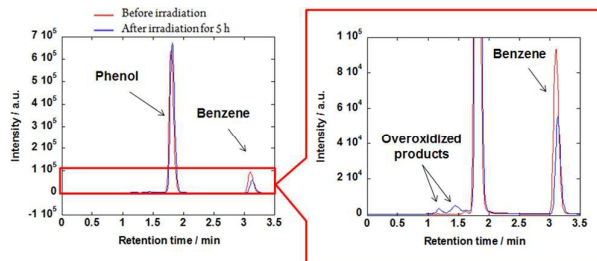


Figure 2 Examples of HPLC chromatogram of aqueous benzene/phenol mixture before and after the photocatalytic reaction under visible light irradiation. The amount of the initially added phenol is 1800 ppm.

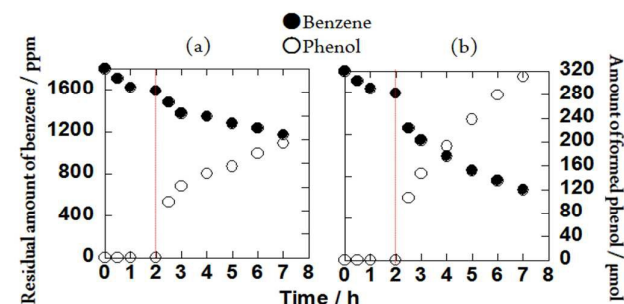


Figure 3. The change in the concentration of benzene (●) and phenol (○) in aqueous mixtures. The light irradiation started after the mixing for 2 h. The initial concentrations phenol are (a) 1800 and (b) 18000 ppm.

In order to modify the apparent reaction efficiency, the concentration of substrate, additive and catalyst was varied further. When a lower concentration (600 ppm) of benzene solution was used (phenol concentration was 83000 ppm), the yield of the benzene decomposition (60%) and the selectivity of phenol (93%) were very high. Under the conditions examined in the present study, the highest yield (72%) and selectivity (96%) of phenol were achieved when the initial benzene and phenol concentration were 600 and 83000 ppm, respectively, and the larger amount (0.42 g/L) of catalyst was used. The changes in the concentrations of benzene and phenol are shown in Figure 4. Table 1 summarizes the results on the photocatalytic reactions. Further optimization is possible by employing lower initial benzene concentration and larger amount of catalyst.

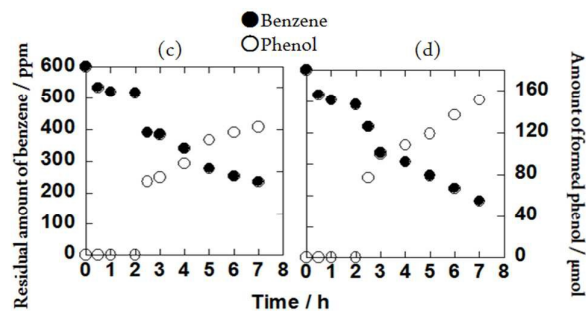


Figure 4 The changes in the amounts of benzene (●) and phenol (○) in aqueous mixtures. The light irradiation started after 2 h. The initial concentration of benzene and added phenol are 600 and 83000 ppm, respectively. The concentrations of TiO₂ are (a) 0.21 and (c) 0.42 g/L, respectively.

Concentration of TiO ₂ (g/l)	Initial benzene concentration (ppm)	Initial phenol concentration (ppm)	Amount of phenol formed (μmol)	Benzene conversion (%)	Phenol selectivity (%)
0.21	1800	0	130	28	70
		1800	194	35	85
		18000	311	51	93
0.42	600	83000	122	60	93
			151	72	96

Table 1. Photocatalytic oxidation of benzene on TiO₂ in the presence and the absence of phenol in the initial solution

If compared with reported oxidation of benzene to phenol,²⁷⁻⁴³ the present system possess such advantages as mild reaction conditions (visible light irradiation at room temperature), cheap source of oxidant (water) and cheap and eco-friendly catalyst (dye-clay-titania). Thus, the presently developed design of hybrid photocatalysts will be applied further; the photosensitizing dye is replaced by other cationic dyes with different absorption characteristics, which may lead visible light absorption and those with wider wavelength region and larger absorption coefficient, to lead better reaction efficiency. The adsorption characteristics of metal complex-clay can be used to achieve selectivity.⁴⁴⁻⁴⁷ The use of molecular catalysts immobilized in organically modified clays⁴⁸⁻⁵⁰ are also worth investigating. In addition, taking advantages of the development of titania nanoparticle preparation, various dispersed titania nanoparticle will be combined with photosensitizing dye-clay intercalation compounds.

Conclusions

In conclusion, a very simple hybrid photocatalyst composed of tris(2,2'-bipyridine)ruthenium(II) complex intercalated in the interlayer space of smectite clay and finite particles of TiO₂ was prepared and used as an environmentally benign photocatalyst for efficient direct oxidation of aqueous benzene to phenol. The photocatalytic reaction efficiency (both benzene decomposition yield and the selectivity of phenol formation) was substantially

modified when the reaction was conducted from aqueous phenol solution. The maximum yield of benzene decomposition and the selectivity of phenol were 72 and 96%, respectively, by visible light irradiation for 5 h, when the initial benzene and phenol concentrations are 600 and 83000 ppm.

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