Photocatalytic Decomposition of 4-Nitrophenol over Titanium Silicalite (TS-1) Using Hydrogen Peroxide as an Oxidant

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Abstract: Titanium silicalite (TS-1) having Si/Ti ratio of 26.3 was synthesized and used as a photocatalyst for decomposition of 4-nitrophenol (4-NP) in water. The photocatalytic activity of TS-1 for decomposition of 4-NP was found to be greatly affected by H₂O₂. In the absence of H₂O₂, TS-1 exhibited only small catalytic activity irrespective of pH. In the presence of H₂O₂, on the other hand, TS-1 showed a marked increase in photocatalytic activity. Especially, in acidic conditions, the addition of H₂O₂ in reaction solution resulted in a remarkable enhancement of photocatalytic activity. It seemed that titanium-hydroperoxide species are formed by the interaction of framework titanium in TS-1 with H₂O₂ and ·OH radicals are formed easily from titanium-hydroperoxide species under UV illumination. In this experimental condition, most of the 4-NP molecules and ·OH radicals are likely present in tiny volume of the TS-1 pore. As a result, in the presence of H₂O₂, the photocatalytic decomposition of 4-NP over TS-1 can be enhanced due to the efficient formation of ·OH radicals and the close proximity of ·OH radicals to the reactant molecules.

Keywords: titanium silicalite, photocatalyst, decomposition, 4-nitrophenol, hydrogen peroxide

Introduction

Heterogeneous photocatalytic decomposition of organic pollutants is a promising process for air and water decontamination. A wide range of organics can be oxidized into CO₂ and H₂O on illuminated semiconductor photocatalyst at ambient temperature and pressure. Band gap excitation of semiconductors generates electron-hole pairs that can initiate redox reactions that oxidize the adsorbed organic molecules. An efficient semiconductor photocatalyst must have suitable band-gap energy and chemical stability over long irradiation time, and TiO₂ is known to be the most active photocatalyst for organic oxidation [1-3]. Putting titanium within the zeolite cavity or the zeolite framework, as in titanium silicalite (TS-1), may have advantages because zeolites have nanoscale pores, high adsorption capacities, and ion-exchange capacities [2,3]. Titanium silicalite has the MFI structure, which is the same structure that ZSM-5 and silicalite zeolites have.

Yamashita and coworkers [2] found that titanium oxides anchored in the Y-zeolite cavity by an ion-exchanged method had high and unique photocatalytic activity for the direct decomposition of NO into N₂, O₂, and N₂O at 275 K, and high selectivity for N₂ formation. They attributed the high activity to highly dispersed tetrahedral titanium oxide species. The specific photocatalytic activities, normalized by the amount of TiO₂ in the catalyst, were much higher than for bulk TiO₂.

Anpo and coworkers [3] used titanium oxide species anchored within Y-zeolite cavities for photocatalytic reduction of CO₂ with H₂O. The titanium oxide species that were highly dispersed within the zeolite cavities existed in a tetrahedral coordination, and they had high selectivity for CH₃OH formation. In contrast, catalysts with aggregated, octahedrally-coordinated titanium oxide and powdered TiO₂ catalysts had high selectivities for CH₄ formation.

Yamagata and coworkers [4] used titanium silicalite...
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(TS-1) having a Si/Ti ratio of 33.2 as a photocatalyst for CO₂ reduction to CH₄ with H₂. They concluded that all Ti atoms in the TS-1 framework acted as photocatalytic sites.

Yamashita and coworkers [5] used titanium oxide dispersed within zeolite cavities and in the zeolite framework (TS-1, Si/Ti = 85) as photocatalysts for CO₂ reduction by H₂O to produce CH₄ and CH₃OH at 328 K. They observed that Ti-mesoporous molecular sieves exhibit much higher photocatalytic activity for CH₃OH formation compared to powdered TiO₂. The high activity was attributed to both the high dispersion of Ti-oxide species and the large pore size.

Recently, Lee and coworkers [6] prepared TS-1 zeolites having Si/Ti ratio of 5, 12.5 and 50, and used them for photocatalytic oxidation (PCO) and decomposition (PCD) of acetic acid. It was found that the TS-1 zeolites were effective catalysts at room temperature for both PCO and PCD of acetic acid. They observed that the product distribution and rates of PCO and PCD varied with Si/Ti ratio in TS-1.

In the current study, titanium silicalite (TS-1) was prepared by in-situ crystallization and used as photocatalyst for decomposition of 4-nitrophenol (4-NP) in water. TS-1 is of interest because it has outstanding catalytic activity and selectivity in the oxidation of various organic compounds using H₂O₂ as an oxidant and it has been used for other photocatalytic reaction as described above. Photocatalytic decomposition of nitrophenols is of interest because they are some of the most refractory pollutants present in industrial waste water. Although extensive mechanistic study has been done for oxidation of organics using H₂O₂ as an oxidant on TS-1 and some gas phase photocatalytic reaction were carried out on TS-1, photocatalytic reaction in aqueous solution using TS-1 as catalyst has not been reported. Thus, in this study, special attention is paid to the photocatalytic properties of TS-1 in aqueous solution using H₂O₂ as an oxidant. The photocatalytic properties of this catalyst were then compared with those of bulk TiO₂ catalyst.

Experimental

Catalyst Preparation and Characterization

Titanium silicalite (TS-1) catalyst was prepared by in-situ crystallization [6]. To obtain high dispersion of Ti within the MFI framework, clear synthesis solutions were used. The Si source was tetraethyl orthosilicate (TEOS) and the Ti source was tetraethyl orthotitanate (TEOT). Tetrabutylammonium hydroxide (TPAOH) was used as the template. The 0.02 mol of TEOT was diluted with 3 mol of 2-propanol while stirring, and 1 mol of TEOS was then added and the solution was stirred for 30 min at room temperature. A solution of water (36 mol) and TPAOH (0.5 mol) was then added to the mixture, which was stirred for an additional 2 h at room temperature to obtain a clear, homogeneous gel. The gel was crystallized in an autoclave at 448 K for 5 days. The zeolite was separated from the liquid phase by centrifugation, dried at 373 K, and then calcined at 773 K for 8 h. The Si/Ti ratio in the synthesis mixture was 50. Degussa P-25 TiO₂ was used as a reference TiO₂ catalyst. X-ray diffraction (XRD) analysis of the TS-1 sample was performed on a Philips X’pert diffractometer using Cu Kα radiation. Surface area measurement was carried out using Quantachrome Autosorb and diffuse reflectance spectroscopy (DRS) was performed on Varian Cary 100 with polytetrafluoroethylene (PTFE) as standard. The Si/Ti ratio in the final solid product was determined using Shimadzu XRF-1700.

Measurement of Distribution Coefficient

The distribution coefficients of 4-NP were measured from pH 2 to 10 to monitor the interaction between the catalyst and 4-NP in the dark. The pH was controlled with H₂SO₄ or NH₄OH. The catalyst of 1 g/L was added into 0.726 mmol/L 4-NP solution. After reaching equilibrium under stirring for 1 h, the catalyst was filtered at 10000 rpm with a Hanil Supra 21 K centrifuge. The concentration of 4-NP in solution was measured by using a Shimadzu UV-240 UV-visible spectrophotometer.

Photocatalytic Experiments

The photocatalytic reactor consists of 500 mL annular quartz body with sampling port and gas inlet and outlet ports. The cooling water in a quartz cylindrical jacket round the lamp was used to keep the reaction temperature constant (30±2 °C). Prior to illumination, the reaction suspension was stirred continuously in dark for 1 h to ensure adsorption/desorption equilibrium. The suspensions were illuminated by using a 500 W high pressure Hg lamp. During the illumination, the suspension was magnetically stirred and bubbled with air. The concentration of catalyst was 1 g/L. The initial concentration of 4-NP was 0.726 mmol/L.

The pH of the reaction solution was adjusted with H₂SO₄ or NH₄OH as required. When H₂O₂ was used as an oxidant, a required amount of H₂O₂ was also added to the suspension.

Samples were taken out at given time intervals and filtered at 10000 rpm with a Hanil Supra 21 K centrifuge. The analysis of concentration of 4-NP in filtered solution was performed by means of Shimadzu UV-240 spectrophotometer.
Results and Discussion

Characterization of Catalyst

Figure 1 shows the XRD pattern of TS-1 catalyst, which matches that reported for the pure MFI structure with good crystallinity. The Si/Ti molar ratio in final crystallized product was found to be 26.3, which is lower than that in synthesis mixture (Si/Ti=50). It was reported that, at a fixed crystallization temperature, the titanium content of the crystalline product is always lower than that of precursor mixture because the solution is enriched in titanium during synthesis [7]. The maximum mole fraction of titanium in TS-1 was reported to be 0.025 (corresponding to a Si/Ti molar ratio of 39) [8]. Above that value, the excess is extra framework titanium, which is usually present as anatase particles. Since the TS-1 synthesized in the present work has Si/Ti mole ratio of 26.3, it should have some extra framework titanium, and thus the XRD pattern for the catalyst seems to be a combination of TS-1 and anatase patterns.

Figure 2 shows the diffuse reflectance spectra of TS-1 and TiO₂(P-25). The absorption bands at about 230 and 310 nm have been assigned to isolated framework titanium and anatase, respectively. As shown in Figure 2, TS-1 shows almost no band at around 310 nm, indicating that a large amount of titanium atoms were incorporated into framework and the amount of the extra framework titanium was very small.

The distribution coefficient (D) of 4-NP measured as function of pH is presented in Figure 3. The point of zero charge (PZC) of TiO₂ occurs at pH 6.4 [9]. Therefore it is expected that the PZC of TS-1 occurs below pH 6.4, because SiO₂ is more acidic than TiO₂. In basic solution, 4-NP (pKₐ=7.15) is predominantly present in the deprotonated form and, thus, at the pH below 6, D value was nearly constant. At the pH above 6, on the other hand, D decreased with the increase in pH.

Photocatalytic Decomposition of 4-NP in the Absence of Hydrogen Peroxide

In the absence of catalyst or UV illumination, the decomposition of 4-NP was not observed. Actually, under acidic conditions, the concentration of 4-NP decreased dramatically after the addition of TS-1 in the solution. However, the addition of strong adsorbent, such as t-butyl alcohol, restored the concentration of 4-NP in the solution, indicating that the 4-NP was replaced by t-butyl alcohol. From this observation it was confirmed that in the dark only the adsorption of 4-NP occurred and any reaction of 4-NP over TS-1 did not take place at room temperature.

Figure 4 shows photocatalytic decomposition of 4-NP over TS-1 and TiO₂ in the absence of H₂O₂. In the case of TiO₂, the adsorption of 4-NP in the dark and reaction rate were almost identical at pH 3 and 10. It has been demonstrated that pH has a significant effect on the photodecomposition rate of various organic compounds [10,11]. It was reported that the highest photocatalytic decomposition rate of 4-NP over TiO₂ can be obtained at near the PZC of TiO₂, and at both low and high pH, photodecomposition rates are quite slow [11]. In the present work, accidentally, the photocatalytic decomposition rate of 4-NP over TiO₂ was found to be nearly identical at both pH 3 and 10.

In the dark, the adsorption of 4-NP on TS-1 was quite different at pH 3 and 10. At pH 3, 4-NP can adsorb easily on positively-charged TS-1, whereas at pH 10 deprotonated 4-NP molecules adsorb less on the negatively-charged TS-1. The photocatalytic decomposition rate of 4-NP over TS-1 was found to be quite slow at both pH 3 and 10. TS-1 is known to have remarkable catalytic activity in selective oxidation of organic compounds under mild conditions [7,12]. However, it can catalyze
the reaction only in the presence of H₂O₂ as an oxidant [12]. It is also seen in Figure 4 that, in the absence of H₂O₂, TS-1 has very low photocatalytic activity for the decomposition of 4-NP in aqueous solution, even considering its low titanium content.

**Photocatalytic Decomposition of 4-NP in the Presence of Hydrogen Peroxide**

Figure 5 shows the photocatalytic decomposition of 4-NP over TS-1 and TiO₂ in the presence of H₂O₂ (11 mmol/L) at pH 3. In the presence of H₂O₂, TS-1 showed a marked increase in photocatalytic activity.

Photocatalytic reactions have been reported to exhibit appreciable rate increase when H₂O₂ is added to aqueous photocatalyst slurry [13]. Such enhancements can be explained by several facts, that is, H₂O₂ is a better electron acceptor than molecular oxygen (reaction 1) and H₂O₂ may be split photolytically to produce ·OH radical directly (reaction 2).

\[
e^+ + H_2O_2 \rightarrow \cdot OH + OH^-
\]

\[
H_2O_2 + h \nu \rightarrow 2 \cdot OH
\]

The reaction (1) results in lowering the electron-hole recombination and thereby increasing the efficiency of hole utilization for photocatalytic oxidation. The reaction (2) gives additional ·OH radicals and the ·OH radical is widely thought to be required to initiate photocatalyzed decomposition of various organic compounds.

It is worth to note that the results over TS-1 and TiO₂ in Figure 5 are obtained by using same catalyst loading (1 g/L). Thus, if we compare the titanium content in TS-1 (Si/Ti=26.3) with that in TiO₂, it could be seen that, in the presence of H₂O₂, the titanium in TS-1 acts as much more active photocatalytic site as compared with that in TiO₂ (P-25).

However, the way in which H₂O₂ enhances the photocatalytic activity of TS-1 is ambiguous, because the addition of H₂O₂ leads to extraordinary enhancement of the photocatalytic activity of TS-1. In order to clarify the role of H₂O₂ in the enhancement of photocatalytic activity of TS-1, the effect of oxygen concentration on the photocatalytic decomposition of 4-NP over TS-1 was monitored, and the results were illustrated in Figure 6.

Oxygen is known to be one of efficient conduction band electron traps and form H₂O₂ through successive reactions over photocatalyst. As can be seen in Figure 6, the improvement of photocatalytic activity of TS-1 by increase in oxygen concentration is much smaller compared to that by the addition of H₂O₂, suggesting that more efficient trapping of conduction band electron is not main factor for the enhancement of photocatalytic activity of TS-1 by the addition of H₂O₂.

It was reported that photocatalytic degradation of 4-NP is governed by ·OH radical reaction [11]. Thus, it can

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**Figure 3.** Change in the distribution coefficient of 4-nitrophenol as a function of pH.

**Figure 4.** Photocatalytic decomposition of 4-nitrophenol over TS-1 and TiO₂ in the absence of H₂O₂.

**Figure 5.** Effect of H₂O₂ on the photocatalytic decomposition of 4-nitrophenol over TS-1 and TiO₂ at pH 3.
be assumed that the enhancement of photocatalytic activity of TS-1 by the addition of H₂O₂ is mainly attributed to more efficient formation of ·OH radical. However, the reaction (2) can occur irrespective of the presence of photocatalyst. As a consequence, direct split of H₂O₂ to form ·OH radical can not explain the enhancement of photocatalytic activity of TS-1 by the addition of H₂O₂.

In this experimental condition, therefore, it seems that there is another route of formation of ·OH radical via H₂O₂ over TS-1. It was reported that unstable hydroperoxodic species are easily formed by the interaction of framework titanium in TS-1 with H₂O₂ [12,14]. In this work, white TS-1 powder became light yellow when TS-1 was immersed in aqueous solution of H₂O₂, indicating the formation of titanium-hydroperoxide by the direct interaction of TS-1 with H₂O₂ [15]. Karlsten and Schöpf [16] reported that the O-O bond length in the titanium-hydroperoxide species formed by interaction of TS-1 with H₂O₂ is 1.52 Å and it represents a remarkable activation of O-O bond compared to H₂O₂. Therefore, it could be deduced that under UV illumination ·OH radical can be formed more easily from titanium-hydroperoxide species compared to H₂O₂.

Figure 7 presents the effect of H₂O₂ concentration on the photocatalytic decomposition of 4-NP over TS-1 at different pH. At pH 3, the addition of 5.5 mmol/L of H₂O₂ dramatically increased the reaction rate, resulting in rapid decrease of 4-NP concentration to almost zero. Thus the further increase in H₂O₂ concentration (11 mmol/L of H₂O₂) revealed similar result. These results may suggest that in acidic conditions adsorbed H₂O₂ molecules decomposed easily under UV illumination to participate in the reaction. At pH 10, the reaction rate increased with increasing H₂O₂ concentration until 11 mmol/L. However, it was found that the reaction rate with 11 mmol/L of H₂O₂ at pH 10 is still lower than that with 5.5 mmol/L of H₂O₂ at pH 3. Considering above results, it can be said that, at lower pH, the increase of reaction rate by the addition of H₂O₂ is more remarkable. Tozzola and coworkers [14] claimed that the titanium-hydroperoxide species formed by interaction of TS-1 with H₂O₂ can be transformed in basic conditions into a more stable form. This fact may suggest that in acidic conditions titanium-hydroperoxide species can decompose more easily to form ·OH radical. This result may also support above hypothesis that ·OH radical can be formed from titanium-hydroperoxide species.

One may think that the amount of reactant adsorbed on catalyst and the concentration of reactant in solution can also affect the reaction rate, because the adsorption of 4-NP on TS-1 varied significantly with pH, as can be seen in Figure 7. Figure 8 demonstrates the effect of initial concentration of 4-NP in the absence of H₂O₂. The change of initial concentration of 4-NP resulted in big difference in the amount of 4-NP adsorbed on catalyst and the concentration of 4-NP in solution at the beginning of illumination. As can be seen in Figure 8, however, the photocatalytic reaction rate was not changed considerably with initial concentration of 4-NP, indicating that adsorption of 4-NP on catalyst and the concentration of reactant in solution are not main factors for the difference in reaction rate presented in Figure 7.

Considering above results, it can be said that ·OH radicals can be formed easily from titanium-hydroperoxide species and these ·OH radicals seem to play an important role in photocatalytic decomposition of 4-NP over TS-1 because most of the 4-NP molecules and ·OH radicals are likely present in tiny volume of the TS-1 pore under present experimental conditions. As a result, in the presence of H₂O₂, the photocatalytic decomposition of 4-NP over TS-1 can be enhanced due to the
Conclusions

In this study, TS-1 (Si/Ti=26.3) was synthesized and used as a catalyst for photocatalytic decomposition of 4-NP in aqueous solution. A large amount of titanium atoms are incorporated into framework of TS-1 and the amount of the extra framework titanium is very small. In the dark, the adsorption of 4-NP on TS-1 changes greatly with pH. In the absence of H$_2$O$_2$, TS-1 reveals only small photocatalytic activity. In the presence of H$_2$O$_2$, however, TS-1 shows a marked increase in photocatalytic activity. Especially, in acid conditions, the addition of H$_2$O$_2$ in reaction solution results in a remarkable enhancement of photocatalytic activity. Under UV illumination, ·OH radicals can be formed easily from titanium-hydroperoxide species which are formed by the interaction of framework titanium in TS-1 with H$_2$O$_2$. The enhancement of photocatalytic activity of TS-1 for decomposition of 4-NP by the addition of H$_2$O$_2$ can be attributed to the efficient formation of ·OH radicals and the close proximity of ·OH radicals to the reactant molecules.

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