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Degradation of Chlorophenol by Photocatalysts with Various Transition Metals

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Abstract−In this research, the photocatalytic degradation of 4-chlorophenol (4-CP) in TiO_2 aqueous suspension was studied. TiO_2 photocatalysts were prepared by sol-gel method. The dominant anatase-structure on TiO_2 particles was observed after calcining the TiO_2 gel at 500 °C for 1 hr. Photocatalysts with various transition metals (Fe, Cu, Nd, Pd and Pt) loading were tested to evaluate the effect of transition metal impurities on photodegradation. The photocatalytic degradation in most cases follows first-order kinetics. The maximum photodegradation efficiency was obtained with TiO_2 dosage of 0.4 g/L, retention time of 1 min and air flow rate of 2,500 cc/min. The photodegradation efficiency with Pt-TiO_2 or Pd-TiO_2 is higher than pure TiO_2 powder. The optimal content value of Pt and Pd is 2 wt%. However, the photodegradation efficiency with Fe(1.0 wt%)-TiO_2 and Cu(1.0 wt%)-TiO_2 is lower than pure TiO_2 powder.

Key words: Photocatalytic Decomposition, 4-Chlorophenol, Titania Oxide, Transition Metal

INTRODUCTION

4-Chlorophenol (4-CP), a toxic organic compound, is widely used for production of dyes, drugs, and fungicide [Theurich et al., 1996; Moonsiri et al., 2004]. The presence of 4-CP has caused severe environmental pollution problems. In most of the treatment methods, such as adsorption on activated carbon and air bubbling, the pollutants are just removed from one phase to another phase and create secondary environmental problems. For example, activated carbon adsorption produces spent carbon as a waste by-product, and air bubbling creates an air pollution problem.

TiO_2 powder suspension system has been employed to degrade diverse organic pollutants [Lee et al., 2003]. In such a system, the TiO_2 photocatalysts are excited by ultraviolet (UV) or visible light to induce charge separation. The photo-generated holes would then oxidize the organic pollutants. Upon irradiation, the TiO_2 particle generates electron/hole pairs, that is, positive holes (h^+) in the valance band (VB) and free electron (e^-) in the conduction band (CB). The holes migrate to the TiO_2 particle surface and react with the absorbed water molecules, thus generating hydroxyl radicals which can oxidize a host of organic pollutants.

Many researchers have studied the photocatalytic degradation of organic compounds in diverse systems. In a slurry-based photocatalytic reactor system, the rate-determining step in the degradation process is considered to be the reduction of oxygen. The electrons on the TiO_2 surface generate reduced oxygen species such as the superoxide radical ions. The photo-generated electron-hole pairs can also recombine. Therefore, suppressing the recombination of hole-electron pairs and prolonging the lifetime of carriers are essential for improving the efficiency of net charge transfer at the TiO_2 surface/electrolyte interface. Therefore, TiO_2 photocatalysts with transition metal loading are focused on.

In this research, the photocatalytic degradation of 4-chlorophenol (4-CP) in TiO_2 aqueous suspension was studied. The effect of parameters such as calcination temperature of TiO_2 photocatalysts, dosage of TiO_2 photocatalysts, retention time, air flow rate and type of photocatalysts on photo-degradation were investigated.

EXPERIMENTAL

For a series of experiments, TiO_2 photocatalysts were prepared by sol-gel method. Titanium tetraisopropoxide (TTIP) was used as TiO_2 precursor. The TiO_2 solution was prepared by dissolving TTIP in isopropyl alcohol. The solution was acidified with HCl and mixed at 300 rpm for 3 hrs. The stabilized TiO_2 suspension was dried in a dry oven at 105 °C for 24 hrs and then calcined at the pre-selected temperature. TiO_2 photocatalysts with transition metal loading are manufactured with similar method except with transition metal precursors added. For the photocatalysts such as Fe-TiO_2, Cu-TiO_2, Nd-TiO_2, Pd-TiO_2 and Pt-TiO_2, $Fe(NO_3)_3\cdot 9H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, $Nd(NO_3)_3\cdot xH_2O$, $Pd(NO_3)_2\cdot xH_2O$ and $H_2PtCl_6\cdot 6H_2O$ were dissolved in the solution.

The degradation experiment was conducted in a semi-batch photocatalytic reactor with initial 4-CP concentration of 10 mg/L. The photocatalytic reactor is made of pyrex glass equipped with a magnetic stirring bar and a water circulating jacket. The UV lamp (15 W, Sankyo Denki Com. Blacklight Blue lamp, F15T8BLB, wave length: 315-400 nm) is placed at the center of the annulus photo-reactor. The TiO_2 aqueous solution is circulated by a peristaltic pump. The dissolved oxygen level of the solution is maintained with air bubbling.

Aqueous solution of the sample was placed in a glass reservoir. Prior to UV irradiation, TiO_2 aqueous solution was magnetically stirred for 1 hr to establish an adsorption and desorption equilibrium between 4-CP and the TiO_2 particles. At pre-selected intervals, samples were collected. Then the solutions were centrifuged, extracted with hexane, and analyzed with a gas chromatograph (Model 4890, Hewlett-Packard) equipped with an electron capture detector. The

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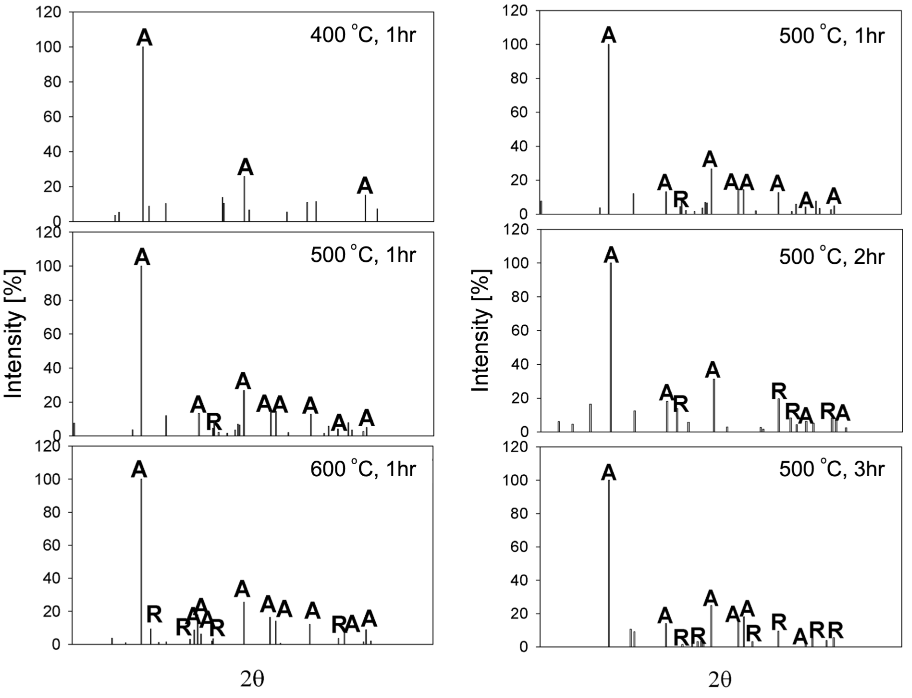

(A) (B)

Fig. 1. Calcination temperature (A) and calcinating duration (B) dependent XRD patterns of TiO_2 powders: A, Anatase; R, Rutile.

oven temperature was maintained at 140 °C. The injection port and detector temperatures were maintained at 230 °C and 250 °C, respectively.

RESULTS AND DISCUSSION

Structural characterization by XRD was carried out to verify the effect of hydrothermal treatments on the crystallographic structure and crystallite size of TiO_2. Two sets of TiO_2 samples were selected. One set(A) was made by sol-gel method and calcined at 400, 500 and 600 °C to evaluate the effect of calcination temperature. The other set(B) was calcined for 1, 2, and 3 hrs at 500 °C to evaluate the effect of calcining duration. The XRD patterns for each set are shown in Fig. 1. The broad diffraction lines of anatase are located in 25.5°, 38.1°, 48.2°, 53.9°, 55.4° and 62.8°(2θ) while those of rutile are located in 27.4°, 36.1°, 41.2° and 54.3°(2θ) [Wu et al., 2004]. The dominant anatase-structures on TiO_2 particles are observed after calcining the TiO_2 gel at 400 °C and 500 °C for 1 hr. But both of anatase and rutile were observed after calcining at 600 °C. Fig. 1 shows the presence of anatase and rutile structures depends on the calcination temperature. In several articles [Sclafani and Herrmann, 1996], anatase has shown much better a photocatalytic activity than that of rutile.

The different characteristics between rutile and anatase are attributed to the different position of the conduction band (more positive for rutile) and to the higher recombination rate of electron-hole pairs in rutile.

To evaluate the photocatalytic activity, degradation experiments were conducted with various calcination temperatures and calcining durations. Fig. 2 shows the effects of calcining temperature and duration on the photocatalytic degradation efficiency. The best degradation efficiency was obtained from the experiment with the photocatalyst manufactured at 500 °C for 1 hr. Therefore, TiO_2 photocatalysts calcinated at 500 °C for 1 hr were used for the following photocatalytic degradation experiments.

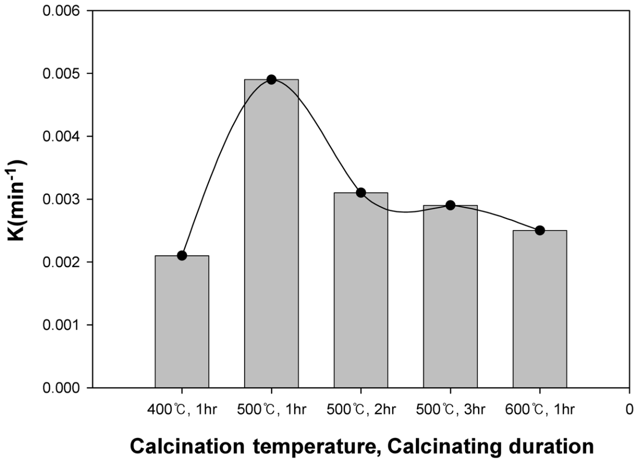

Fig. 2. Rate constants of 4-CP degradation with different calcination temperatures and calcinating duration.

Fig. 3 shows the effect of TiO_2 dosage on photocatalytic degradation of 4-CP in aqueous solution. The degradation rate constant increases with increasing of the TiO_2 dosage, but decreases with further increasing the TiO_2 dosage over 0.4 g/L. The limiting value (0.4 g/L) mainly results from following two factors: (a) aggregation of TiO_2 particles at high dosage, causing a decrease in the number of surface active sites, and (b) increase in opacity, which means that TiO_2 particles at high dosage lead to a decrease in the passage of ir-

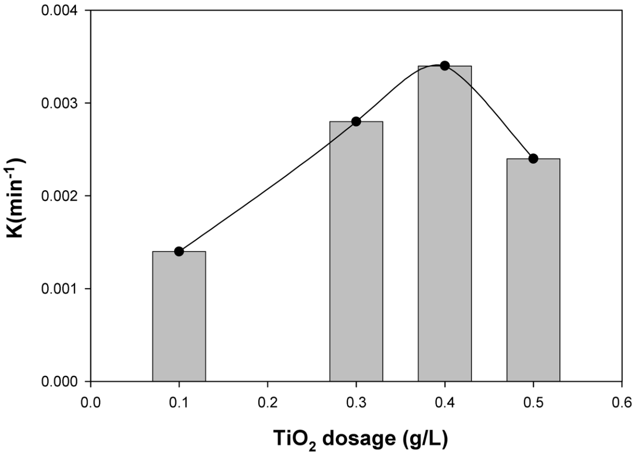

Fig. 3. Rate constants of 4-CP degradation with different TiO$_2$ dosages.

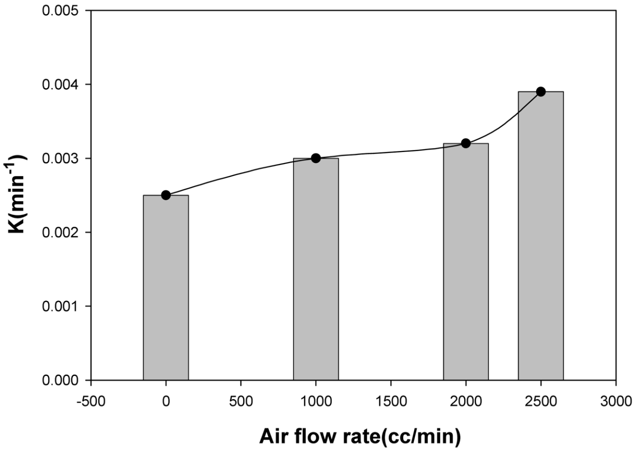

Fig. 5. Rate constants of 4-CP degradation with different air flow rate.

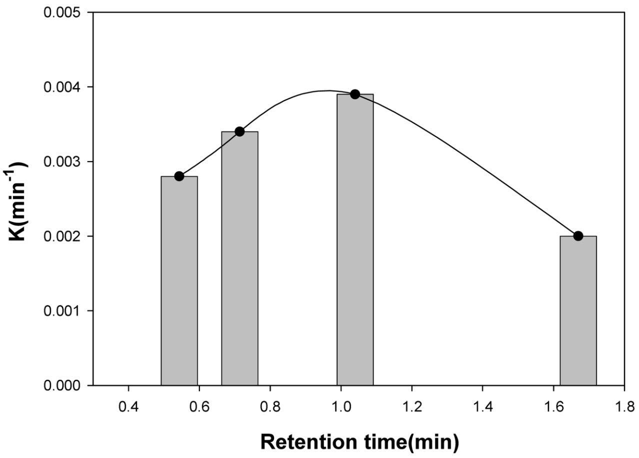

Fig. 4. Rate constants of 4-CP degradation with different retention time.

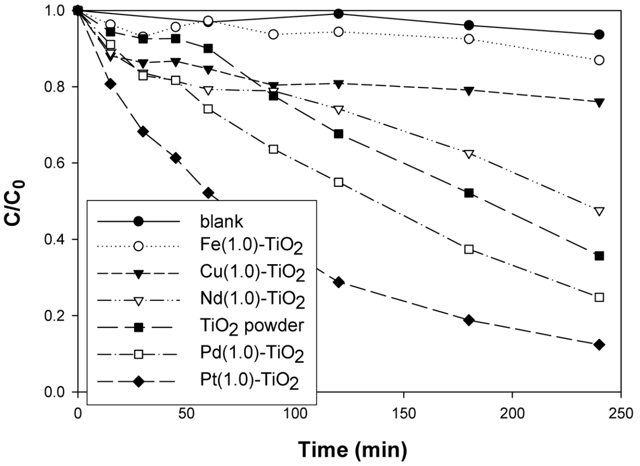

Fig. 6. Normalized concentration of 4-CP with various photocatalysts.

radiation through the sample [Chen and Ray, 1998; Ku et al., 1996].

Fig. 4 shows the effect of retention time on the photo-degradation rate constant of 4-CP. It is assumed that the proportion of solute adsorbed on the photo-catalyst to that remaining in the aqueous stream is independent of the retention time, that is, the rate constant should be constant even though the flow rate may change. But, it was observed that an increase of retention time through the illuminated photo-reactor caused better photo-degradation efficiency in other studies [Matthews, 1987]. The results also show that the photo-degradation rate constant increases with increasing of retention time. However, at retention time above 1.0 min the rate constant decreases. Increasing the retention time causes a reduction of mass transfer, which greatly minimizes the reaction rates [Ekabi and Serpone, 1988]. That is, the sample in the photo-reactor does not seem to be mixed well at the low flow rate. In fact, mixing of TiO$_2$ particles is influenced by the flow of the aqueous mixture. The lower flow rate leads to incomplete mixing in the photocatalytic reactor, resulting in decreasing of degradation rates.

The dissolved oxygen level of the solution is maintained with air bubbling. The effect of air flow rate on the photo-degradation rate constant is shown in Fig. 5. As it is shown in Fig. 5, the rate constant slightly increases with air flow rate. The dissolved oxygen seems to enhance the separation of photo-generated electrons and holes, and then facilitates the production of OH radicals. It is noteworthy that the photocatalytic experiment without air supply shows still quite high degradation efficiency. Since the glass reservoir used in this study is an open system, oxygen is continually supplied to the aqueous solution through contact with the atmosphere. Herein it appears that the level of dissolved oxygen under air equilibration conditions is sufficient to meet the requirements of the photocatalytic process [Zhang et al., 2002]. This implies that in commercial applications it is possible to replace pure oxygen with air.

The photo-degradation experiments were carried out using photocatalysts doped with transition metals such as Fe, Cu, Nd, Pd and Pt. The doping level in all cases was kept constant at about 1.0 wt%. Fig. 6 shows the effect of various photocatalysts on photocatalytic degradation. The Pt(1.0 wt%)-TiO$_2$ achieves about 90% of degradation efficiency at 240 min of operation time and the Pd(1.0 wt%)-TiO$_2$ about 75%, while pure TiO$_2$ powder has achieved about 65%. When material such as nickel and palladium was added on the surface of the other metal oxide powder, enhancement was also observed [Kim, 2004]. In photocatalysis the addition of transition metals to a semiconductor can enhance its photocatalytic activity by changing the semiconductor surface properties. The metals actually cover a small area of the semiconductor surface; thereafter, metal particles form clusters on the surface. After excitation the electron migrates to the metal where it becomes trapped; thus electron/hole recombination can be suppressed. The hole is then free to diffuse to the semiconductor surface where oxidation of organic species can occur [Linsebigler, 1995].

However, the Fe(1.0 wt%)-TiO_2 and the Cu(1.0 wt%)-TiO_2 show lower photo-degradation efficiencies than that of the pure TiO_2 powder. For the photo-degradation of 4-CP, Fe-TiO_2 particles show a detrimental effect or no effect on the reactivity of TiO_2. Brezova et al. [2002] proposed that copper exists on the TiO_2 surface as a mixture of Cu^0 and Cu_2O. The reduction of Cu^{2+} by photo-generated electrons may compete with the formation of superoxide anion-radicals, and consequently may reduce the formation of peroxidic species, destroying phenol molecules, in photocatalytic systems. In other literature there are also reports of the formation of surface complex structures of Cu^{2+} ions with organic compounds present in the suspensions, which can act as surface poison [Bideau et al., 1992].

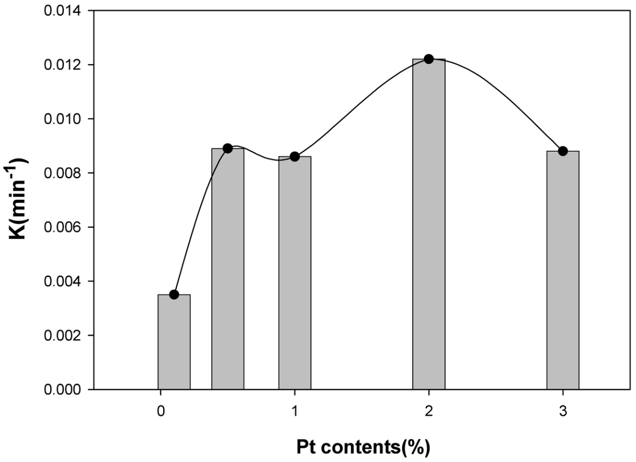

Fig. 7. Rate constants of 4-CP degradation with various Pt contents.

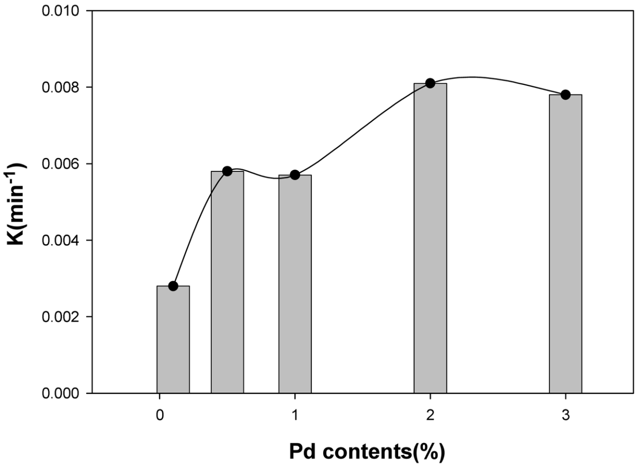

Fig. 8. Rate constants of 4-CP degradation with various Pd contents.

The various photocatalysts were tested to evaluate the effect of transition metal contents on photo-degradation. The results with Pt-TiO_2 and Pd-TiO_2 are shown in Fig. 7 and Fig. 8, respectively. The photo-degradation efficiency increases with the increase of Pt or Pd content on photocatalysts in the content range of 0 to 2 wt%, and decreases with further increase of metal contents. Transition metals at a lower concentration can act as an electron trap. Therefore, the photo-generated electrons appear to be trapped effectively by Pt or Pd. Thus, the recombination rate between photo-generated electrons and holes can be decreased. At a result, more holes can reach the surface of a photocatalyst and degrade more contaminants. However, at a higher concentration the transition metals act as a recombination site; then the recombination rate between electrons and holes increases exponentially with the increase of transition metal concentration. This is because the average distance between trap sites decreases by increasing the number of transition metal sites within a particle [Li and Li, 2002].

CONCLUSIONS

The 4-chlorophenol in aqueous solution was successfully degraded by photocatalytic reaction in a semi-batch system. The photocatalytic degradation in most cases follows first-order kinetics. The maximum photo-degradation efficiency is obtained with TiO_2 dosage of 0.4 g/L, retention time of 1 min and air flow rate of 2,500 cc/min. Various photocatalysts were tested to evaluate the effect of transition metal impurities on photo-degradation. The photo-degradation efficiency with Pt-TiO_2 or Pd-TiO_2 is higher than pure TiO_2 powder. The optimal content value of Pt and Pd is 2 wt%. Transition metal loading influences the photo-degradation efficiency by acting as electron traps, consequently reducing the e^-/h^+ pair recombination rate.

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