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Photodecomposition of Kraft Lignin Catalyzed by Titanium Dioxide

Koichi KOBAYAKAWA,* Yuichi SATO, Shigeo NAKAMURA, and Akira FUJISHIMA†
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221
†Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113
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The photocatalytic reaction of kraft lignin at titanium dioxide photocatalyst was investigated. Kraft lignin was completely decomposed into carbon dioxide and water through dehydrodimers of phenol derivatives constituting kraft lignin, methanol and organic acids such as oxalic and formic acids. Aromatic compounds such as vanillin could not be recovered due to their tendency to dehydrodimerization and the strong oxidizing power of the photo-generated holes by the action of which the dehydrodimers were completely decomposed into carbon dioxide and water. The production of methane, ethane, and ethylene was much smaller than that in the decomposition with hydroxyl radicals in homogeneous solution.

The photo-generated holes at semiconductor powders suspended in solution generally have strong oxidizing power. For example, irradiated titanium dioxide can catalytically decompose substances, which cannot be completely decomposed by activated sludge processes, into inorganic substances like carbon dioxide and water entirely.[1–10)]

Lignin and its degradation products cannot be completely decomposed by such sludge processes[11,12)] and are the source of chemical oxygen demand (COD) of waste water from pulp and paper mills.[11)] Even though the COD value of the discharged water is less than the value regulated by Japanese law,[11)] the remaining lignin and its degradation products give an unfavorable impression of the discharged water owing to their brown color.[11)] In case the activated sludge process is repeated, the brown color will become lighter. However, this process is expensive so that an inexpensive alternative method is desirable.

Strong oxidants were required for the decomposition of lignin and its degradation products.[12–14)] It was reported that hydroxyl radicals produced by the reaction of hydrogen peroxide with UV light or ferric ions (Fenton's reagent) can decompose kraft lignin into carbon dioxide and hydrocarbon gases such as methane and ethane.[13)] The decomposition by semiconductor photocatalysts is another possibility due to their strong oxidizing power of the generated holes. This paper describes the catalytic photodecomposition of kraft lignin on TiO_2 photocatalyst.

While kraft lignin can be decomposed into inorganic substances, formation of many useful intermediates such as vanillin and vanillic acid can be expected as are recovered in the electrochemical oxidation of lignin.[15–17)] Therefore, in addition to the measurement of the COD value and the absorbance of the irradiated solution, we also identified and determined in detail possible intermediates.

Experimental

The aqueous test solution was 0.02 wt% in kraft lignin (alkali lignin derived from softwoods, Tokyo Kasei Kogyo). Rutile type TiO_2 powder (Furuuchi Chemical, 99.9%, 300 mesh) was used as photocatalyst. This powder showed comparatively high photocatalytic activity for the decomposition of kraft lignin among commercially available TiO_2 powders.[18)]

For the examination of the changes of COD, the color of solution and the products in the solution, irradiation was carried out in open system, that is, 0.500 g of TiO_2 powder and 20 cm^3 of air-saturated test solution were placed in a 50 cm^3 beaker and stirred magnetically under the irradiation of a 500 W high-pressure mercury lamp. The solutions were cooled with ice to prevent evaporation of the products. After irradiation for a predetermined time, the photocatalyst was centrifugated off and the filtrate was analyzed. Absorption spectra were measured using a spectrophotometer, and the COD values were calculated according to the JIS K0102 method. The degradation products were identified and determined by high-performance liquid chromatography (HPLC), gas chromatography (GC) and chemical analysis. The experimental conditions of HPLC and GC were as follows. For HPLC, packing material was ODS-silica (Hitachi Kasei, 3056); the column was 4 mm I.D.×150 mm long; the eluent, aqueous acetonitrile solution (15 v/v%) of 0.05% phosphoric acid; the flow rate of eluent, 1.0 $cm^3 min^{-1}$; the detector, UV (254 nm). For GC, the packing materials, PEG 20M (Shimarite F) and Unisole F-200; the column, 3.2 mm I.D.×2 m long (glass tube); the carrier gas, nitrogen; the detector, FID.

For the determination of the gaseous products irradiation was carried out in a closed system containing 70 cm^3 of the test solution and 1.5 g of TiO_2 powder under oxygen atmosphere. The gaseous products were identified and determined by a GC equipped with a column of active carbon packing and FID detector.

Results and Discussion

Changes of the Properties of the Test Solution with Reaction Time. The optical absorption spectrum of the test solution under nitrogen atmosphere did not change after irradiation for 8 h as shown by the curve b in Fig. 1. On the contrary, in the presence of dissolved oxygen, the brown color of the test solution became lighter with irradiation and disappeared after 8 h as shown by the curves c and d in Fig. 1. From this result, oxygen was necessary to scavenge the photo-generated electrons. The curve a in Fig. 2 shows the change of the absorbance at 280 nm as a function of irradiation time. This absorption originated predominantly from benzenoid compounds. Therefore, the curve a shows that they decreases almost linearly with irradiation time and disappears after 7 h.

The COD value, shown as the curve b in Fig. 2, also decreases with reaction time. After 7 h of irradiation, COD becomes almost zero suggesting that organic compounds are no more present in the solution. The irradiation time dependence of pH is also given in Fig. 2 (curve c). The pH of the test solution, initially slightly basic, is lowered with the decomposition of kraft lignin. It reaches the lowest value after 4 h and then increases again to neutral. Carbonic acid was identified by the production of CO_2 upon addition of hydrochloric acid to the white precipitate, obtained by adding barium chloride to the filtrate. Oxalic acids was also identified by chemical analysis. The accumulation of oxalic acids, which is stronger than carbonic, will make the solution acidic and its perfect decomposition to carbonic acid will increase the pH of the test solution.

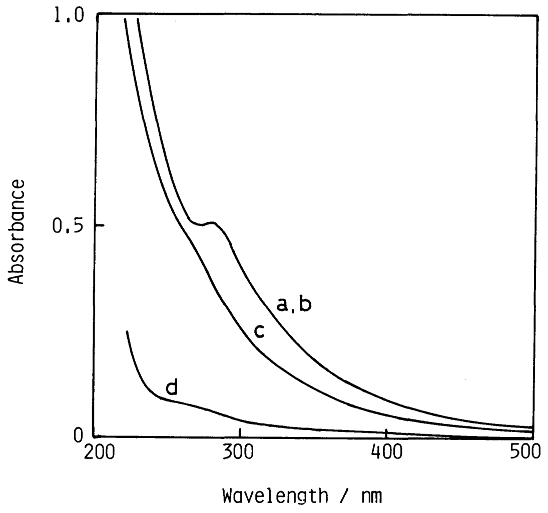

Fig. 1. Absorption spectra of the solution of kraft lignin. a: before irradiation (diluted 10 times, 20 ppm), b: after 8 h of irradiation under nitrogen atmosphere (diluted 10 times), c: after 6 h of irradiation, d: after 8 h of irradiation.

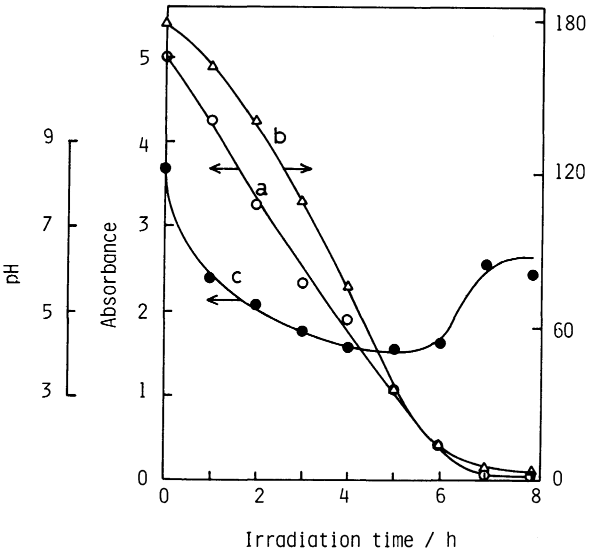

Fig. 2. Changes of the absorbance at 280 nm (a), COD (b), and pH (c) with irradiation time.

Products. Dehydrodimers: Prior to the determination of the degradation products, the separation performance of HPLC was confirmed. Under the conditions used, a number of phenol derivatives, which were expected as the degradation products from kraft lignin, were separated satisfactorily. Their retention times (t_R) were longer than two minutes. The larger the number of hydroxyl or carboxyl group in molecule, the shorter the retention time.

Figure 3 shows the HPLC chromatograms of the test solution before and after 3 h of photocatalytic reaction. Seven peaks are observed in the chromatogram of the starting solution (chromatogram a). Five peaks with retention times longer than 2 minutes were assigned to derivatives of phenol, such as catechol (t_R=4.0 min) and vanillin (t_R=6.7 min), by comparison with the retention time of the authentic compounds. As the degradation of kraft lignin proceeds, the heights of

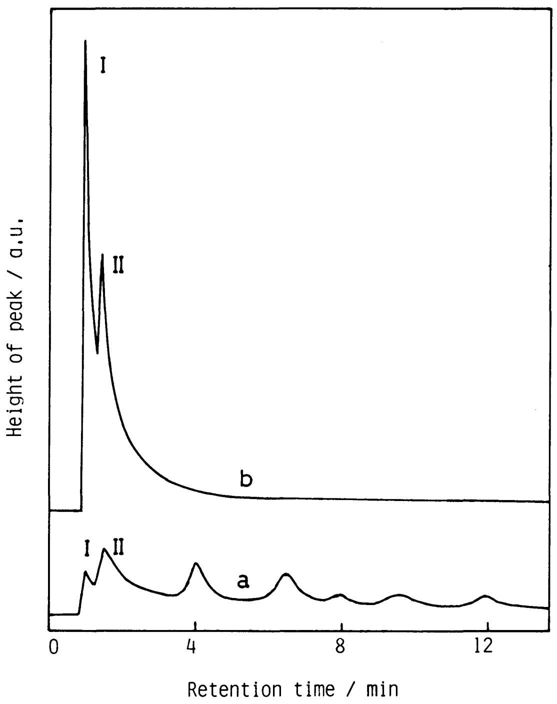

Fig. 3. HPLC chromatograms of the solution of kraft lignin. a: before irradiation, b: after 3 h of irradiation.

peaks longer than 2 minutes decrease, and after 3 h of irradiation they disappear as shown by the chromatogram b in Fig. 3. However, up to 4 h of irradiation two peaks denoted by I (t_R=1.0 min) and II (t_R=1.5 min) increased and then decreased with irradiation time as shown in Fig. 4. The substances corresponding to peaks I and II were thought to be dehydrodimers of the phenol derivatives constituting kraft lignin from following experimental results.

(i) Kraft lignin may be degraded by successive breaking from the terminal of the polymer, almost all of which are phenolic compounds. They are known to be dehydro-dimerized by electrochemical oxidation.19–21) Therefore, the phenol derivatives liberated from lignin polymer may be also dimerized by the TiO_2 photocatalyzed oxidation.

For the lack of authentic smaples, dehydrodimers of some phenol derivatives were prepared by electrochemical oxidation and their retention times were measured. Protocatechuic acid (3,4-dihydroxybenzoic acid) gave two oxidation products, possibly dehydrodimers, which had the same retention times as peaks I and II. Vanillic acid (4-hydroxy-3-methoxybenzoic acid) gave one prodcut which had the same retention time as peak I and demethoxylated, hydroxylated vanillic acid, that is, protocatechuic acid. The difference in the number of the dehydrodimers produced from above two compounds is attributed the different structure of these compounds. That is, the dimerization of phenol derivatives takes place at the *o*- and *p*-positions to hydroxyl group,19) so the formation of two types and one type of dimer was expected from protocatechuic and vanillic acid, respectively.

(ii) The t_R (1.5 min) of oxalic acid is identical with that of peak II. However, its peak height was only one half of that of peak II on the chromatogram a in Fig. 3, so that, oxalic acid was not the main product corresponding to peak II.

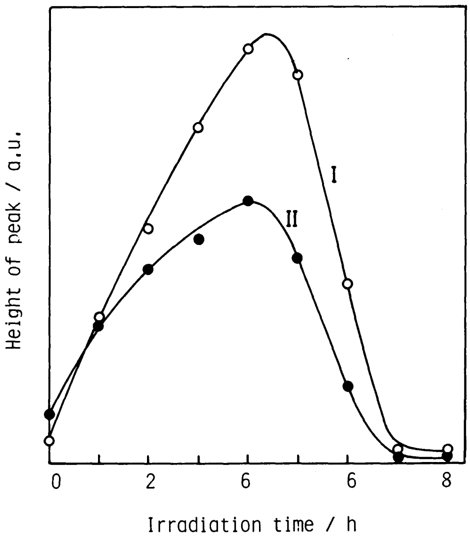

Fig. 4. Changes of the peak heights I and II of HPLC chromatograms as a function of irradiation time.

There is no peak which originates from kraft lignin itself in the chromatogram a in Fig. 3. Alkali lignin becomes insoluble in the acidic eluent, and the insoluble polymers cannot pass through the layer of packing material in the column. This is supported by the observation that a brown substance remained on the top of packing material.

In addition to the dehydrodimers of phenol derivatives, methanol, ethanol, formaldehyde, and oxalic acid were detected as intermediates in solution.

Methanol and Ethanol: The curve a in Fig. 5 shows the relation between the concentration of methanol and the irradiation time. Methanol is produced immediately after irradiation. Its concentration reaches a maximum value after one hour, remains at this value for 2 h and then decreases. Methanol may be formed from methoxy groups. This is confirmed by a catalytic photo-oxidation of vanillic acid and the identification of methanol in the reaction products.

The formation of ethanol was observed after 4 to 4.5 h of irradiation, as shown by the curve b in Fig. 5. This period was thought to be corresponding to the stage of the rapid decomposition of accumulated dimers as shown in Fig. 4.

Formaldehyde: Formaldehyde cannot be distinguished by the colorimetric method from acetaldehyde.22) However, the production of methanol is larger than that of ethanol as shown in Fig. 5, so that the aldehyde formed is considered mostly to be formaldehyde. The concentration of formaldehyde changes with irradiation time as shown in the curve c of Fig. 5. Formaldehyde is started to be produced immediately after methanol formation. The maximum concentration of formaldehyde is observed when the concentration of methanol has considerably decreased.

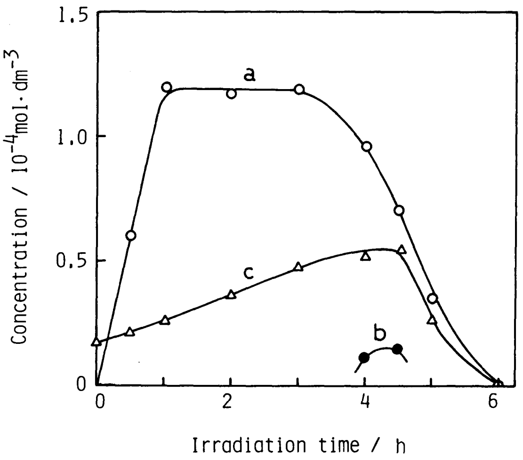

Fig. 5. Changes of the concentration of intermediates with irradiation time. a: methanol, b: ethanol, c: formaldehyde.

Formic Acid: Formic acid was not detected by GC. However, the production of methanol, formaldehyde, and CO_2 suggests the formation of formic acid.

Oxalic Acid: Oxalic acid was detected by glycolic acid formation method[23] and indole method.[24] It might be produced by the decomposition of benzene ring since it was produced by the photocatalytic decomposition of muconic acid (2,4-hexadiendioic acid),[18] the intermediate of benzene ring decomposition.

Gaseous Products: Trace amounts of methane and ethylene were detected. Both yields are about one molecule per twenty thousands of constituents of kraft lignin and are very small compared to those in the decomposition of kraft lignin by hydroxyl radicals.[13]

Decomposition of Kraft Lignin on the TiO_2 Photocatalyst. It was reported that hydroxyl radical, produced by the reaction of hydroxyl group on the photocatalyst surface or water molecule with photo-generated hole, take part in the photocatalytic reactions.[25] However, in the reaction under investigation, the participation of hydroxyl radical is thought to be small for the following reasons.

(i) The photocatalytic oxidation of benzene, phenol, and catechol proceeds by photo-generated holes.[10]

(ii) Large amount of methane, ethane, and ethylene are produced from the decomposition of lignin by Fenton's reagent which produces hydroxyl radicals,[13] whereas very small amounts of these compounds are formed by the TiO_2 catalyzed photoreaction.

(iii) Aromatic phenol compounds are not dimerized by hydroxyl radicals[26,27] whereas they are dimerized by TiO_2 photocatalyst.

So, the photocatalytic decomposition of kraft lignin on TiO_2 proceeds most likely via photo-generated holes.

Conclusion

Following conclusions were obtained.

(1) Kraft lignin is decomposed into inorganic compounds such as carbon dioxide and water by the action of the photo-generated holes.

(2) Aromatic compounds such as vanillin can not be recovered because they are predominantly dehydrodimerized and then decomposed by TiO_2 photocatalyst.

(3) The production of gaseous hydrocarbon products such as methane and ethane is less than that obtained in the decomposition by hydroxyl radicals in homogeneous solution.

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References

1) A. L. Prunden and D. F. Ollis, *J. Catal.*, **82**, 404 (1983).

2) C. Y. Hsiao, C. L. Lee, and D. F. Ollis, *J. Catal.*, **82**, 418 (1983).

3) M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgallero, M. Gratzel, and E. Serpone, *Nouv. J. Chim.*, **8**, 547 (1984).

4) H. Kawaguchi, *Environ. Technol. Lett.*, **5**, 471 (1984).

5) K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, and A. Itaya, *Bull. Chem. Soc. Jpn.*, **58**, 2015 (1985).

6) K. Okamoto, Y. Yamamoto, H. Tanaka, and A. Itaya, *Bull. Chem. Soc. Jpn.*, **58**, 2023 (1985).

7) I. Izumi, *Denki Kagaku*, **53**, 178 (1985).

8) H. Hidaka, H. Kubota, M. Grätzel, N. Serpone, and E. Pelizzetti, *Nouv. J. Chim.*, **9**, 67 (1985).

9) H. Hidaka, H. Kubota, M. Grätzel, E. Pelizzetti, and N. Serpone, *J. Photochem.*, **35**, 219 (1986).

10) K. Hashimoto, T. Kawai, and T. Sakata, *J. Phys. Chem.*, **88**, 4083 (1984).

11) M. Suzuki, *Sangyo Kogai*, **14**, 562 (1978).

12) K. Tatsumi, N. Takahashi, and K. Murayama, *Kogai*, **22**, 189 (1987).

13) K. Tatsumi, H. Araki, and M. Terashima, *Mokuzai Gakkaishi*, **26**, 327 (1980).

14) K. Tatsumi and M. Terashima, *Mokuzai Gakkaishi*, **27**, 210 (1981).

15) H. L. Chun and M. M. Baizer, "The Electrochemistry of Biomass and derived Materials," American Chemical Society (1985), p. 243.

16) A. Yoshiyama, T. Nonaka, T. C. Chou, and H. J. Tien, *Mokuzai Gakkaishi*, **34**, 155 (1988).

17) A. Yoshiyama, T. Nonaka, H. Kawakami, T. C. Chou, and H. J. Tien, *Mokuzai Gakkaishi*, **34**, 275 (1988).

18) K. Kobayakawa, T. Katsumata, H. Nagashima, Y. Sato, S. Nakamura, and A. Fujishima, *Nippon Kagaku Kaishi*, **1988**, 1175.

19) S. Torii, "Yuki Denkai Gosei," Kodansha (1981), p. 123.

20) F. Fichter, *Trans. Electrochem. Soc.*, **45**, 75 (1924).

21) F. J. Vermillion, Jr. and I. A. Pearl, *J. Electrochem. Soc.*, **111**, 1392 (1964).

22) T. Nash, *Biochem. J.*, **55**, 416 (1953).

23) F. D. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand (1953), Vol. 3, p. 379.

24) J. Bergerman and J. S. Elliot, *Anal. Chem.*, **27**, 1014 (1955).

25) C. D. Jaeger and A. J. Bard, *J. Phys. Chem.*, **83**, 314 (1979).

26) K. Tatsumi and N. Terashima, *Mokuzai Gakkaishi*, **29**, 530 (1983).

27) K. Tatsumi and N. Terashima, *Mokuzai Gakkaishi*, **30**, 580 (1984).