2. Mechanisms of photo-induced oxidative decomposition

(Abstract)

The history of science of photoinduced chemical reactions on the specific metal oxides, *i.e.*, photocatalysis, is already almost one hundred years starting from the photoeffect on TiO_2 and ZnO [1]. Nevertheless, it is actually only two decades ago that TiO_2 photocatalysts were practically utilized for the oxidation of organic pollutants [2, 3]. At a glance of a tremendous number of research papers on photocatalysis published so far, OH radical (•OH) has been often regarded to be involved in the actual oxidation mechanism of photocatalytic reactions. Recently, the detailed mechanisms of the photocatalytic reactions at a molecular level were reviewed by the authors [4]. Then, the present chapter is devoted to a systematic description of reaction mechanisms for photo-induced decomposition with TiO_2 photocatalysts. The following topics will be described in this chapter; (1) the structure of the TiO_2 surface involving the effect of hydration, (2) the photoinduced holes and electrons, and the formation of reactive oxygen species, (3) the detection methods of •OH, (4) the formation mechanism of •OH, and finally (5) the reaction mechanism of some representative organic substances.

(References)

[1] Renz, C., (1921) Photo-Reactions of the Oxides of Titanium, Cerium, and the Earth-Acids, *Helv. Chim. Acta*, 4, 961-968.

[2] Fujishima, A., Zhang, X., Tryk, D. A., (2008) TiO_2 Photocatalysis and Related Surface Phenomena, *Surface Science Reports,* 63, 515-582.

[3] Nosaka, Y., Nosaka, A., (2016) Introduction to Photocatalysis: From Basic Science to Applications, Royal Society of Chemistry. London, 272pp.

[4] Nosaka, Y., Nosaka, A. Y., (2017) Generation and Detection of Reactive Oxygen Species in Photocatalysis, *Chem. Rev.,* 117(17), 11302−11336.

[5] Nosaka, A. Y., Nosaka, Y., (2005) Characteristics of Water Adsorbed on TiO_2 Photocatalytic Surfaces as Studied by ^{1}HNMR Spectroscopy, *Bull. Chem. Soc. Jpn.,* 78(9), 1595-1607.

[6] Henderson, M. A., (1996) Structural Sensitivity in the Dissociation of Water on TiO_2 Single-Crystal Surfaces, *Langmuir*, 12 (21), 5093-5098.

[7] Parfitt, G. D., (1976) The surface of Titanium Oxide, *Prog. Surf. Membrane Sci.,* 11, 181-226.

[8] Hadjiivanov, K. I., Klissurski, D. G., (1996) Surface Chemistry of Titania (Anatase) and Titania-Supported Catalysts, *Chem. Soc. Rev.,* 25, 61-69.

[9] Nosaka, A. Y., Nishino, J., Fujiwara, T., Ikegami, T., Yagi, H., Akutsu, H., Nosaka, Y., (2006) Effects of Thermal Treatments on the Recovery of Adsorbed Water and Photocatalytic Activities of TiO_2 Photocatalytic Systems, *J. Phys. Chem.* B, 110 (16), 8380-8385.

[10] Bourikas, K., Kordulis, C., Lycourghiotis, A., (2014) Titanium Dioxide (Anatase and Rutile): Surface

Chemistry, Liquid–Solid Interface Chemistry, and Scientific Synthesis of Supported Catalysts, *Chem. Rev*., 114, 9754–9823.

[11] Nosaka, A. Y., Fujiwara, T., Yagi, H., Akutsu, H., Nosaka, Y., (2004) Characteristics of Water Adsorbed on TiO_2 Photocatalytic Systems on Temperature Increase as Studied by Solid-State ^{1}H-NMR Spectroscopy, *J. Phys. Chem.* B, 108 (26), 9121-9125.

[12] Uosaki, K., Yano, T., Nihonyanagi, S., (2004) Interfacial Water Structure at As-Prepared and UV-Induced Hydrophilic TiO_2 Surfaces. Studied by Sum Frequency Generation Spectroscopy and Quartz Crystal Microbalance, *J. Phys. Chem.* B, 108, 19086–19088.

[13] Carneiro, J. T., Savenije, T. J., Moulijn, J. A., Mul, G., (2010) Toward a Physically Sound Structure-Activity Relationship of TiO_2-Based Photocatalysts, *J. Phys. Chem.* C, 114, 327–332.

[14] Valentin, C. D., Selloni, A., (2011) Bulk and Surface Polarons in Photoexcited Anatase TiO_2, *J. Phys. Chem. Lett.*, 2, 2223–2228.

[15] Nakaoka, Y., Nosaka, Y., (1997) ESR Investigation into the Effects of Heat Treatment and Crystal Structure on Radicals Produced over Irradiated TiO_2 Powder, *J. Photochem. Photobiol*. A, 110, 299-307.

[16] Howe, R. F., Grätzel, M., (1987) EPR Study of Hydrated Anatase under UV Irradiation, *J. Phys. Chem.,* 91, 3906 -3909.

[17] Coronado, J. M., Maira, A. J., Conesa, J. C., Yeung, K. L., Augugliaro, V., Soria, J., (2001) EPR Study of the Surface Characteristics of Nanostructured TiO_2 under UV Irradiation, *Langmuir*, 17(17), 5368-5374.

[18] Yamakata, A., Vequizo, J. J. M., Matsunaga, H., (2015) Distinctive Behavior of Photogenerated Electrons and Holes in Anatase and Rutile TiO_2 Powders, *J. Phys. Chem. C*, 119, 24538–24545.

[19] Bahnemann, W., Hilgendorff, M., Memming, R., (1997) Charge Carrier Dynamics at TiO_2 Particles: Reactivity of Free and Trapped Holes, *J. Phys. Chem.* B, 101, 4265-4275.

[20] Kamat, P. V., Bedja, I., Hotchandani. S., (1994) Photoinduced Charge Transfer between Carbon and Semiconductor Clusters. One-Electron Reduction of C60 in Colloidal TiO_2 Semiconductor Suspensions, *J. Phys. Chem.,* 98(37), 9137 –9142.

[21] Yang, X., Tamai, N., (2001) How Fast is Interfacial Hole Transfer? *In situ* Monitoring of Carrier Dynamics in Anatase TiO_2 Nanoparticles by Femtosecond Laser Spectroscopy, *Phys. Chem. Chem. Phys.,* 3, 3393-3398.

[22] Szczepankiewicz, S. H., Moss, J. A., Hoffmann, M. R., (2002) Slow Surface Charge Trapping Kinetics on Irradiated TiO_2, *J. Phys. Chem.* B, 106(11), 2922-2927.

[23] Bielski, B. H. J., Cabelli, D. E., Arudi, R. L., (1985) Reactivity of HO_2/O_2^- Radicals in Aqueous Solution, *J. Phys. Chem. Ref. Data,* 14(4), 1041-1100.

[24] Daimon, T., Nosaka, Y., (2007) Formation and Behavior of Singlet Molecular Oxygen in TiO_2 Photocatalysis Studied by Detection of Near-Infrared Phosphorescence, *J. Phys. Chem.* C, 111(11),

4420-4424.

[25] Daimon, T., Hirakawa, T., Nosaka, Y., (2008) Monitoring the Formation and Decay of Singlet Molecular Oxygen in TiO_2 Photocatalytic Systems and the Reaction with Organic Molecules, *Electrochemistry,* 76(2), 136-139.

[26] Nosaka, Y., Yamashita, Y, Fukuyama, H., (1997) Application of Chemiluminescent Probe to Monitoring Superoxide Radicals and Hydrogen Peroxide in TiO_2 Photocatalysis, *J. Phys. Chem.* B, 101(30), 5822 -5827.

[27] Hirakawa, T., Nosaka, Y., (2002) Properties of $\bullet O_2^-$ and •OH Formed in TiO_2 Aqueous Suspensions by Photocatalytic Reaction and the Influence of H_2O_2 and Some Ions, *Langmuir,* 18 (8), 3247-3254.

[28] Ishibashi, K., Fujishima, A., Watanabe, T., Hashimoto, K., (2000) Generation and Deactivation Processes of Superoxide Formed on TiO_2 Film Illuminated by Very Weak UV Light in Air or Water, *J. Phys. Chem.* B, 104(20), 4934-4938.

[29] Buxton, G. V., Greenstock, C. L., Helman, W. P., Ross, A. B., (1988) Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxy Radicals ($\bullet OH/\bullet O^-$) in Aqueous Solution, *J. Phys. Chem. Ref. Data,* 17(2), 513-886.

[30] Filippone, F., Mattioli, G., Bonapasta, A. A., (2007) Reaction Intermediates and Pathways in the Photoreduction of Oxygen Molecules at the (101) TiO_2 (Anatase) Surface, *Catal. Today,* 129, 169–176.

[31] Nakamura, R., Nakato, Y., (2010) Molecular Mechanism of Water Oxidation Reaction at Photo-Irradiated TiO_2 and Related Metal Oxide Surfaces. Solid State Phenom., 162, 1–27.

[32] Nakamura, R., Nakato, Y., (2004) Primary Intermediates of Oxygen Photoevolution Reaction on TiO_2 (Rutile) Particles, Revealed by in Situ FTIR Absorption and Photoluminescence Measurements, *J. Am. Chem. Soc.*,126(4), 1290-1298.

[33] Muryn, C. A., Hardman, P. J., Crouch, J. J., Raiker, G. N., Thornton, G. D., Law, S. L., (1991) Step and point defect effects on TiO_2 (100) reactivity, *Surf. Sci.*, 251-252, 747-752.

[34] Du, Y., Rabani, J., (2003) The Measure of TiO_2 Photocatalytic Efficiency and the Comparison of Different Photocatalytic Titania, *J. Phys. Chem.* B, 107, 11970-11978.

[35] Zhang, J., Nosaka, Y., (2014) Photocatalytic Oxidation Mechanism of Methanol and the Other Reactants in Irradiated TiO_2 Aqueous Suspension Investigated by OH Radical Detection, *Appl. Catal. B*, 166-167, 32-36.

[36] Micic, O. I., Zhang, Y., Cromack, K. R., Trifunac, A. D., Thurnauer M. C., (1993) Trapped Holes on TiO_2 Colloids Studied by Electron Paramagnetic Resonance, *J. Phys. Chem.,* 97,7277-7283.

[37] Noda, H., Oikawa, K., Ohya-Nishiguchi, H., Kamada, H., (1994) Efficient Hydroxyl Radical Production and Their Reactivity with Ethanol in the Presence of Photoexcited Semiconductors, *Bull. Chem. Soc. Jpn.*, 67(8), 2031-2037.

[38] Grela, M. A., Coronel, M. E. J., Colussi, A. J., (1996) Quantitative Spin-Trapping Studies of Weakly Illuminated Titanium Dioxide Sols. Implications for the Mechanism of Photocatalysis, *J. Phys. Chem.*,

100(42), 16940-16946.

[39] Schwarz, P. F., Turro, N. J., Bossmann, S. H., Braun, A. M., Wahab, A.-M. A. A., Durr, H., (1997) A New Method to Determine the Generation of Hydroxyl Radicals in Illuminated TiO_2 Suspensions, *J. Phys. Chem.* B, 101(36), 7127-7134.

[40] Kishioka, S., Ohsaka, T., Tokuda, K., (2003) Electrochemical Studies of Acid-Promoted Disproportionation of Nitroxyl Radical, *Electrochem. Acta*, 48, 1589-1594.

[41] Nosaka, Y., Komori, S., Yawata, K., Hirakawa, T., Nosaka, A. Y., (2003) Photocatalytic OH Radical Formation in TiO_2 Aqueous Suspension Studied by Several Detection Methods, *Phys. Chem. Chem. Phys.,* 5, 4731–4735.

[42] Matthews, R. W., (1980) The Radiation Chemistry of the Terephthalic Dosimeter, *Radiat. Res*., 83(1), 27-41.

[43] Ishibashi, K., Fujishima, A., Watanabe, T., Hashimoto, K., (2000) Detection of Active Oxidative Species in TiO_2 Photocatalysis using the Fluorescence Technique, *Electrochem. Commun*., 2, 207-210.

[44] Ishibashi, K., Fujishima, A., Watanabe, T., Hashimoto, K., (2000) Quantum Yields of Active Oxidative Species Formed on TiO_2 Photocatalyst, *J. Photochem. Photobiol.* A, 134, 139–142.

[45] Zhang, J., Nosaka, Y., (2015) Mechanism of the OH Radical Generation in Photocatalysis with TiO_2 of Different Crystalline Types, *J. Phys. Chem. C,* 118(20), 10824-10832.

[46] Matsumi, Y., Kono, M., Ichikawa, T., Takahashi, K., Kondo, Y., (2002) Laser-Induced Fluorescence Instrument for the Detection of Tropospheric OH Radicals, *Bull. Chem. Soc. Jpn.*, 75(4), 711–717.

[47] Murakami, Y., Endo, K., Ohta, I., Nosaka, A. Y., Nosaka, Y., (2007) Can OH Radicals Diffuse from the UV-Irradiated Photocatalytic TiO_2 Surfaces? Laser-Induced-Fluorescence Study, *J. Phys. Chem.* C, 111(30), 11339-11346.

[48] Naito, K., Tachikawa, T., Fujitsuka, M., Majima, T., (2008) Real-Time Single-Molecule Imaging of the Spatial and Temporal Distribution of Reactive Oxygen Species with Fluorescent Probes: Applications to TiO_2 Photocatalysts, *J. Phys. Chem.* C, 112(4), 1048-1059.

[49] Kim, W., Tachikawa, T., Moon, G., Majima, T., Choi, W., (2014) Molecular-Level Understanding of the Photocatalytic Activity Difference Between Anatase and Rutile Nanoparticles, *Angew. Chem. Int. Ed.*, 53, 14036−14041.

[50] Lawless, D., Serpone, N., Meisel, D., (1991) Role of OH Radicals and Trapped Holes in Photocatalysis. A Pulse Radiolysis Study, *J. Phys. Chem.,* 95, 5166−5170.

[51] Salvador, P., (2007) On the Nature of Photogenerated Radical Species Active in the Oxidative Degradation of Dissolved Pollutants with TiO_2 Aqueous Suspensions: A Revision in the Light of the Electronic Structure of Adsorbed Water, *J. Phys. Chem.* C, 111(45)*,* 17038-17043.

[52] Imanishi, A., Okamura, T., Ohashi, N., Nakamura, R., Nakato, Y., (2007) Mechanism of Water Photooxidation Reaction at Atomically Flat TiO_2 (Rutile) (110) and (100) Surfaces: Dependence on Solution pH, *J. Am. Chem. Soc.*, 129(37), 11569-11578.

[53] Kakuma, Y., Nosaka, A. Y., Nosaka, Y., (2015) Difference in TiO_2 Photocatalytic Mechanism Between Rutile and Anatase Studied by the Detection of Active Oxygen and Surface Species in Water, *Phys. Chem. Chem. Phys.,* 17(28), 18691−18698.

[54] Nakabayashi, Y., Nosaka, Y., (2015) The pH Dependence of OH Radical Formation in Photo-Electrochemical Water Oxidation with Rutile TiO_2 Single Crystals, *Phys. Chem. Chem. Phys.*, 17(45), 30570-30576.

[55] Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., Bahnemann, D. W., (2014) Understanding TiO_2 Photocatalysis: Mechanisms and Materials, *Chem. Rev.,* 114, 9919−9986.

[56] Montoya, J. F., Atitar, M. F., Bahnemann, D. W., Peral, J., Salvador, P., (2014) Comprehensive Kinetic and Mechanistic Analysis of TiO_2 Photocatalytic Reactions According to the Direct−Indirect Model: (II) Experimental Validation, *J. Phys. Chem. C*, 118, 14276−14290.

[57] Maldotti, A., Molinari, A., Madelli, R. A., (2002) Photocatalysis with Organized Systems for the Oxofunctionalization of Hydrocarbons by O_2, *Chem. Rev*.,102(10), 3811-3836.

[58] Clinton, N. A., Kenley, R. A., Traylor, T. G., (1975) Autoxidation of Acetaldehyde. Ⅲ. Oxygen-Labeling Studies, *J. Am. Chem. Soc.,* 97(13), 3757-3762.

[59] Ikeda, K., Sakai, H., Ryo, R., Hashimoto, K., Fujishima, A., (1997) Photocatalytic Reactions Involving Radical Chain Reactions Using Microelectrodes, *J. Phys. Chem.* B,101, 2617-2620.

[60] Araña, J., Doña-Rodrıguez, J. M., Cabo, C. G., Diaz, O. G., Herrera-Melián, J. A., Pérez-Peña, J., (2004) FTIR Study of Gas-Phase Alcohols Photocatalytic Degradation with TiO_2 and AC-TiO_2, *Appl. Cat*. B, 53, 221–232.

[61] Micic, O. I., Zhang, Y., Cromack, K. R.. Trifunac, A. D., Thurnauer, M. C., (1993) Photoinduced Hole Transfer from TiO_2 to Methanol Molecules in Aqueous Solution Studied by Electron Paramagnetic Resonance, *J. Phys. Chem.*, 97(50), 13284-13288.

[62] Brownson, J. R. S., Tejedor-Tejedor, M. I., Anderson, M. A., (2006) FTIR Spectroscopy of Alcohol and Formate Interactions with Mesoporous TiO_2 Surfaces, *J. Phys. Chem*. B, 110(25), 12494-12499.

[63] Kaise, M., Nagai, H., Tokuhashi, K., Kondo, S., Nimura, S., Kikuchi, O., (1994) Electron Spin Resonance Studies of Photocatalytic Interface Reactions of Suspended M/TiO_2 (M = Pt, Pd, Ir, Rh, Os, or Ru) with Alcohol and Acetic Acid in Aqueous Media, *Langmuir*, 10(5), 1345-1347.

[64] Perissinotti, L. L., Brusa, M. A., Grela, M. A., (2001) Yield of Carboxyl Anion Radicals in the Photocatalytic Degradation of Formate over TiO_2 Particles, *Langmuir*, 17(26), 8422-8427.

[65] Yu, Z., Chuang, S. S. C., (2007) In situ IR study of adsorbed species and photogenerated electrons during photocatalytic oxidation of ethanol on TiO_2, *J. Catal.,* 246, 118–126

[66] Xu, W., Raftery, D., (2001) Photocatalytic Oxidation of 2-Propanol on TiO_2 Powder and TiO_2 Monolayer Catalysts Studied by Solid-State NMR, *J. Phys. Chem.* B, 105(19), 4343-4349.

[67] Brinkley, D., Engel, T., (2000) Evidence for Structure Sensitivity in the Thermally Activated and Photocatalytic Dehydrogenation of 2-Propanol on TiO_2, *J. Phys. Chem.* B, 104(42), 9836-9841.

[68] Attwood, A. L., Edwards, J. L., Rowlands, C. C., Murphy, D. M., (2003) Identification of a Surface Alkylperoxy Radical in the Photocatalytic Oxidation of Acetone/O_2 over TiO_2, *J. Phys. Chem.* A, 107(11), 1779-1782.

[69] Jenkins, C. A., Murphy, D. M., (1999) Thermal and Photoreactivity of TiO_2 at the Gas-Solid Interface with Aliphatic and Aromatic Aldehydes, *J. Phys. Chem.* B, 103(6), 1019-1026.

[70] Nosaka, Y., Kishimoto, M., Nishino, J., (1998) Factors Governing the Initial Process of TiO_2 Photocatalysis Studied by Means of in-Situ Electron Spin Resonance Measurements, *J. Phys. Chem. B*, 102(50), 10279-10283.

[71] Kim, S., Choi, W., (2002) Photocatalytic Degradation of $(CH_3)_nNH_{4-n}^+$ ($0 \leq n \leq 4$) in TiO_2 Suspension: The Role of OH Radicals, *Environ. Sci. Technol.*, 36(9), 2019-2025.

[72] Matsushita, M., Tran, T. H., Nosaka, A. Y., Nosaka, Y., (2007) Photo-Oxidation Mechanism of L-Alanine in TiO_2 Photocatalytic Systems as Studied by Proton NMR Spectroscopy, *Catal. Today,* 120, 240–244.

[73] Tran, T. H., Nosaka, A. Y., Nosaka, Y., (2006) Adsorption and Photocatalytic Decomposition of Amino Acids in TiO_2 Photocatalytic Systems, *J. Phys. Chem.* B, 110(50), 25525–25531.

[74] Nosaka, A. Y., Tanaka, G., Nosaka, Y., (2014) Study by Use of ^1H NMR Spectroscopy of the Adsorption and Decomposition of Glycine, Leucine, and Derivatives in TiO_2 Photocatalysis, *J. Phys. Chem.* B, 118(27), 7561–7567.

[75] Bui, T. D., Kimura, A., Ikeda, S., Matsumura, M., (2010) Determination of Oxygen Sources for Oxidation of Benzene on TiO_2 Photocatalysts in Aqueous Solutions Containing Molecular Oxygen, *J. Am. Chem. Soc.*, 132(24), 8453–8458.

[76] Palmisano, G., Addamo, M., Augugliaro, V., Caronna, T., Garcıa-Lopez, E., Loddo, V., Palmisano, L., (2006) Influence of the Substituent on Selective Photocatalytic Oxidation of Aromatic Compounds in Aqueous TiO_2 Suspensions, *Chem. Commun.,* 1012–1014.

[77] Blount, M. C., Falconer, J. L., (2002) Steady-State Surface Species During Toluene Photocatalysis, *Appl. Catal.* B, 39, 39–50.

[78] Choi, W., Hoffmann, M. R., (1996) Kinetics and Mechanism of CCl_4 Photoreductive Degradation on TiO_2: The Role of Trichloromethyl Radical and Dichlorocarbene, *J. Phys. Chem.*, 100(6), 2161-2169.

[S1] Nosaka, Y., Nosaka, A. Y. (2019) Comment on “Singlet Oxygen $^1O_2$ in Photocatalysis on TiO_2. Where Does It Come from?” *J. Phys. Chem. C* 123 (45), 27993-27995.

[S2] Nosaka, Y., Nosaka, A. Y. (2019) Comment on “Coumarin as a Quantitative Probe for Hydroxyl Radical Formation in Heterogeneous Photocatalysis”. *J. Phys. Chem. C* 123(33) 20682-20684.

[S3] Nosaka, Y., Nosaka, A. Y. (2017) Generation and Detection of Reactive Oxygen Species in Photocatalysis. *Chem. Rev.* 117(17), 11302−11336.

[S4] Zhang, J., Nosaka, Y. (2015) Photocatalytic oxidation mechanism of methanol and the other reactants in irradiated TiO_2 aqueous suspension investigated by OH radical detection. *Appl. Catal. B, Environ* . 166-167, 32-36.