Kinetic analysis on photocatalytic degradation of gaseous acetaldehyde, ammonia and hydrogen sulfide on nanosized porous TiO₂ films

Iis Sopyan*

Department of Manufacturing and Materials Engineering, Faculty of Engineering, International Islamic University Malaysia, PO Box 10, 50728 Kuala Lumpur, Malaysia

Received 27 July 2006; accepted 11 October 2006
Available online 28 November 2006

Abstract

The characteristics of the UV illumination-assisted degradation of gaseous acetaldehyde, hydrogen sulfide, and ammonia on highly active nanostructured-anatase and rutile films were investigated. It was found that the anatase film showed a higher photocatalytic activity than the counterpart did, however, the magnitude of difference in the photocatalytic activity of both films decreased in the order ammonia > acetaldehyde > hydrogen sulfide. To elucidate the reasons for the observation, the adsorption characteristics and the kinetics of photocatalytic degradation of the three reactants on both films were analyzed. The adsorption analysis examined using a simple Langmuir isotherm, showed that adsorbability on both films decreased in the order ammonia > acetaldehyde > hydrogen sulfide, which can be explained in terms of the decreasing electron-donor capacity. Acetaldehyde and ammonia adsorbed more strongly and with higher coverage on anatase film (1.2 and 5.6 molecules/nm², respectively) than on rutile (0.6 and 4.7 molecules/nm², respectively). Conversely, hydrogen sulfide molecules adsorbed more strongly on rutile film (0.7 molecules/nm²) than on anatase (0.4 molecules/nm²). Exposure to UV light illumination brought about the photocatalytic oxidation of the three gases in contact with both TiO₂ films, and the decrease in concentration were measured, and their kinetics are analyzed in terms of the Langmuir–Hinshelwood kinetic model. From the kinetic analysis, it was found that the anatase film showed the photocatalytic activities that were factors of 2.4 and 2.5 higher than the rutile film for the degradation of gaseous ammonia and acetaldehyde, respectively. However, the activity was only a factor of 1.5 higher for the photodegradation of hydrogen sulfide. These observations are systematically explained by the charge separation efficiency and the adsorption characteristics of each catalyst as well as by the physical and electrochemical properties of each reactant.

1. Introduction

Work on the gas–solid heterogeneous photocatalytic reactions has received much attention from view of the assessment of the reaction mechanism [1,2]. This gas-phase photocatalysis was initiated in pioneering work on the photodecomposition of nitric oxide by McLintock and Ritchie [3]. Recently, a large potential impact of the solid–gas photocatalysis on environmental applications has been suggested since a wide range of air contaminants, including alkanes, alkenes [4–6], halocarbons [7], alcohols [8], aldehydes [9], nitrogen-containing compounds [10], and ketones [11–13] can be partially or completely degraded with the TiO₂-assisted UV irradiation.

Kinetics of a heterogeneous photocatalytic reaction is greatly influenced by two major factors: the concentration of the substrate of the interest and the efficiency of charge separation in the bulk of photocatalyst. Several groups have reported on kinetic studies of the gas-phase heterogeneous photocatalytic reactions [12–14]. In this work, the effects of the adsorption affinity of substrates and the efficiency of charge separation in photocatalyst bulk on the kinetics of the photocatalytic reactions were investigated. In this regard, three gaseous compounds: acetaldehyde, hydrogen sulfide, and ammonia were picked up as model compounds. They were chosen because of its malodorous properties, and they can be considered as representatives...
for neutral, acidic, and basic compounds, respectively. A kinetic study was performed to elucidate the observed characteristics of the photocatalytic degradation of the three compounds. The adsorption of the three reactants in the dark was examined in terms of the Langmuir isotherm, and the kinetics of the photolytic reactions was examined in terms of the Langmuir–Hinshelwood (LH) kinetic model. The kinetic results will be discussed in relation to the adsorption properties of the films as well as to physical and electrochemical properties of the three compounds.

2. Methods and materials

2.1. Materials

The light source used was 10 W-black light bulbs (National Electric Co., Ltd.). A sealed, air-filled photoreactor vessel made of polypropylene resin, with a volume of 4000 cm$^3$ was used. On the side exposed to the UV light, a transparent silica glass plate window was used. Both films were used in photocatalytic studies.

2.2. Preparation of TiO$_2$ thin films

The first film is anatase-type and its preparation procedure has been published elsewhere [14]. Briefly, a titanic acid sol was prepared via the thermal hydrolysis of an aqueous titanyl sulfate solution followed by dispersion with nitric acid to form the titanic acid sol. The sol was then autoclaved for 15 min at 180 $^\circ$C. The BET surface area of the TiO$_2$ powder by drying the sol was 64 m$^2$/g. In order to enhance the viscosity of the sol, polyethylene glycol (PEG) was then added to the sol that its concentration was 40 wt%. A coating of the TiO$_2$ sol was applied to a fused silica plate substrate (6 cm $\times$ 8 cm) followed by sintering at 450 $^\circ$C in air for 30 min.

The rutile film was prepared by the following method [15]. Titanium tetrachloride was hydrolyzed in an aqueous sodium carbonate solution to give a titanium hydroxide solution. After being filtered and washed, the resultant was dispersed by adding nitric acid to yield a rutile sol. In order to enlarge rutile crystal, the sol was also autoclaved for 15 min at 180 $^\circ$C. The BET surface area of the TiO$_2$ powder by drying the sol was 45 m$^2$/g. After the addition of PEG, the TiO$_2$ sol was smeared on a glass plate substrate (5 cm $\times$ 10 cm) followed by sintering at 450 $^\circ$C in air for 30 min. The Raman spectrum was recorded on a Renishaw Ramascope using argon ion laser (514.5 nm) as the light source, with an exposure time of 10 s. Scanning electron microscopic (SEM) examination of the film was carried out on a Hitachi Co. Ltd. Model S-530.

2.3. Adsorption isotherm analysis

The decrease in concentrations of acetaldehyde was measured on a gas chromatograph, Ohkura Model C-103 equipped with 2-m Porapak-Q Columns and in both hydrogen sulfide and ammonia by Komyo Kitagawa Sampling Pump Model AP-1. Equilibrium was achieved about 40–60 min after sample injection. The “adsorbed concentration” $C_{ads}$ was calculated by subtracting the equilibrium concentration $C_{eq}$ from the initial concentration $C_{0}$. From an adsorption isotherm-type plot ($1/C_{ads}$ vs. $1/C_{eq}$), the Langmuir adsorption parameters, $C_{max}$ and $K_{ads}$, were determined. From the values of $C_{max}$ obtained, $n_{max}$, the number of moles of reactants adsorbed per gram of photocatalyst, and the surface density were determined.

2.4. Assessment of photocatalytic activity

The photocatalytic activities of both the films were evaluated by measuring the change in concentration of gas-phase acetaldehyde, hydrogen sulfide, and ammonia as a function of irradiation time. The photocatalytic system used in the present work consists of the Pyrex glass-made vessel, the fluorescent lights settled over the vessel so that the distance of each light to the film in the vessel is the same (about 17 cm), and a wooden case, to which the lights are attached. At this setting, the incident UV light intensity at the film surface was 2.1 mW cm$^{-2}$. A 20 cm$^{-2}$ area of the films was used for these photocatalytic activity measurements. Saturated gases of acetaldehyde, hydrogen sulfide, and ammonia were injected into the vessel using a syringe so that the concentration was 50–3000 ppmv. The irradiation was started after equilibrium between gaseous and adsorbed phases was reached, followed by the measurement of the decrease in concentration of the three gases. From a LH kinetic-type plot ($1/R$ vs. $1/C_{eq}$), LH kinetic parameters, $k$ (the apparent first-order degradation rate constant) and $K$ (the photoadsorption constant) were determined.

3. Results and discussion

3.1. Physical properties of anatase and rutile thin films

Fig. 1 shows a TEM picture of the anatase sol and a SEM micrograph of the anatase film. It is shown that particles in the sol are mainly 20 nm in diameter. These particles enlarged to small crystalline with average diameters of ca. 40–50 nm which constitute the polycrystalline films apparently rather porous. The crystallographic characteristic of the films was examined using X-ray diffraction and Raman, shown in Figs. 2 and 3, respectively. In the 2$\theta$ range from 20$^\circ$ to 60$^\circ$, five peaks were observed: 25.2, 38.5, 48.0, 53.9 and 55.2 for the anatase film and four peaks at 27.5, 36.1, 41.4, and 54.4 are observed for the rutile film. The Raman spectra in Fig. 3 also exhibited band that were attributable to the anatase film: 146, 397, 519 and 641 cm$^{-1}$ and to the rutile film at 131, 231, 443 and 613 cm$^{-1}$. These observations show that within the detection limits of the measurements, these films are purely anatase and rutile films, respectively.
3.2. Photocatalytic reaction of anatase and rutile films

Figs. 4a–c show plots of the decrease in the concentrations of ammonia, acetaldehyde, and hydrogen sulfide as a function of irradiation time. These are the results for the photodegradation of 50ppmv respective gas in contact with both the TiO₂ films under UV illumination of 1.7 mW cm⁻² intensity. About 60 min after the injection of the reactant gas into the vessel adsorption equilibrium was reached and then the irradiation was started. Just after being exposed to the UV illumination, the photocatalytic reactions obeyed apparent first-order kinetics. It is clear from the plots that the anatase film showed a higher photocatalytic activity than the counterpart did. However, the level of the difference in the activity depends on the kind of the reactant; it decreased in the order ammonia > acetaldehyde > hydrogen sulfide. To elucidate the factors governing the observation, the adsorption characteristics and the kinetics of photocatalytic degradation of the three reactants were analyzed using the Langmuir adsorption isotherm and the LH kinetic model. The results of these analyses will be then discussed with such physical properties as ionization potential and charge separation efficiency.

3.3. Adsorption analysis

Many researchers [16] reported that the adsorption of gas follows Langmuir isotherm, which can be expressed as follows:

\[ \Theta = \frac{n_{ads}}{n_{max}} = \frac{KC_{eq}}{1 + KC_{eq}}, \]

(1)

where \( \Theta \) is the surface coverage, \( n_{ads} \) is the number of adsorbed gaseous molecules, \( n_{max} \) is the number of the maximum adsorption sites available for the gas molecules, \( K \) is the adsorption equilibrium constant, and \( C_{eq} \) is the concentration of gas at equilibrium. Linearization of the above isotherm give rise to

\[ \frac{C_{eq}}{n_{ads}} = \frac{1}{K n_{max}} + \frac{C_{eq}}{n_{max}}. \]

(2)

Thus, according to Eq. (2) \( C_{eq}/n_{ads} \) vs. \( C_{eq} \) plots must be linear, and in fact they shown good linearity. Isotherm parameters obtained, \( n_{max} \) and \( K \), were determined using linear least-squares analysis. Assuming that a complete monolayer is formed at total adsorption, the following...
The equation is valid:

\[ \Gamma_{\text{max}} = \frac{N \cdot n_{\text{max}}}{10^{18}} \]  

where \( \Gamma_{\text{max}} \) is the maximum surface density of molecules on the film surface and \( N \) is Avogadro’s Number. Table 1 collects the Langmuir isotherm parameters \( n_{\text{max}} \) (the amount of moles adsorbed per cm\(^2\) catalyst) and \( K \) (the adsorption constant) for each reactant. A striking contrast in the adsorption characteristics between the three reactants are observed; the adsorption affinity increases with the increasing electron-donor ability in the order hydrogen sulfide < acetaldehyde < ammonia. The adsorption of organic compounds onto hydrous oxides and other surfaces has often been attributed to hydrogen-bond formation [17]. A hydrogen bond may form between two functional groups, one serving as a proton donor or Bronsted acidic group and another group serving as an electron donor or Lewis basic group. Ammonia, which is one of strong Lewis bases, showed high surface densities, i.e., 5.6 and 4.7 molecules nm\(^{-2}\) for anatase and rutile, respectively. This is mostly due to the interaction of ammonia molecules with hydroxyl groups of the TiO\(_2\) surface creating strong chemisorption of coordinative type [18,19]. Meanwhile, with a weaker basicity compared to ammonia molecules, acetaldehyde (considered as a “neutral” compound in this study) may adsorb on the oxide surface forming a weaker sorption. Smith [20] has shown that carboxylic acids are adsorbed either by hydrogen bonding of the carboxyl group or by proton transfer to the TiO\(_2\) surface. As it is reasonable to consider that the carboxyl group of the acetaldehyde also behaves as that in carboxylic acid, both compounds have comparable Lewis basicity. Lower surface densities of acetaldehyde molecules compared to ammonia, i.e., 1.2 molecules nm\(^{-2}\) for anatase and 0.6 molecules nm\(^{-2}\) for rutile, are apparently attributed to its relatively weaker adsorption affinity. This also can be due to larger size of acetaldehyde molecules compared to ammonia. On the other hand, hydrogen sulfide is too difficult to form hydrogen bonds with hydroxyl groups of the TiO\(_2\) surfaces. The S–H groups of H\(_2\)S has been reported to form hydrogen bonding only in strong basic environments [21]. Its weak adsorption affinity on the surfaces of both the TiO\(_2\) films was reflected by so low surface densities, i.e., 0.4 and 0.65 molecules nm\(^{-2}\) for anatase and rutile, respectively.

In addition, it can be seen that the adsorption affinities of acetaldehyde and ammonia are superior on the anatase than on the rutile, conversely, that of hydrogen sulfide are superior on the rutile film than on the counterpart. Apparently, the Lewis acidity of the surface of the catalyst holds a main role in the mechanism. Since hydroxyl groups of anatase is more acidic than those of rutile [19], for ammonia and acetaldehyde having stronger electron-donor capacities, their adsorption affinities on the anatase film are stronger than on the rutile film.

On the other hand, in the case of hydrogen sulfide, the reverse was true. Beck et al. [22] reported similar results on the adsorption of H\(_2\)S onto both anatase and rutile powders, that is, coverage of hydrogen sulfide on rutile is higher than on anatase. The surface concentration of hydrogen sulfide obtained in this work (0.4 molecules nm\(^{-2}\) for the anatase and 0.65 molecules nm\(^{-2}\) for the rutile) are in remarkably good agreement with those they estimated, i.e., 0.6 and 0.78 molecules nm\(^{-2}\) for anatase and rutile, respectively [22].
3.4. Kinetic analysis

Kinetics of photocatalytic reactions either in gas-phase or in liquid phase can be probed using a LH kinetic model [23, 24]. According to this model, the rate of reactant disappearance is only the product of an apparent rate constant and the Langmuir adsorption term, and hence mass transfer phenomena does not give any control to the overall kinetics of the photodegradation. Accordingly, the rate of a unimolecular surface reaction will obey the following equation:

$$ R = k \theta = \frac{k K_{eq} C_{eq}}{1 + K_{eq} C_{eq}}, $$

where $R$ and $k$ represent the degradation rate and the apparent first-order reaction rate constant, respectively.

Fig. 5 shows plots of the reciprocal of the initial degradation rate, $R^{-1}$, against the reciprocal of the equilibrium concentration, $C_{eq}^{-1}$, for the photocatalytic degradation of ammonia (a), acetaldehyde (b), and hydrogen sulfide (c) with both film photocatalysts. Good linearities were observed in the degradation of all the gases. Thus the treatment using the LH model is appropriate.

Analysis of the plots in the figure provided LH parameter values for the apparent degradation rate constant, $k$ which are listed in Table 2, along with the ionization potentials of the three compounds. It can be seen from the table that in the degradation of ammonia, the degradation rate with anatase film (hereafter referred to as $R_a$) is ca. eight times greater than the rate with the rutile film (hereafter referred to as $R_r$). In the case of the degradation of acetaldehyde, the $R_a$ to $R_r$ ratio is ca. 5, and in the case of the degradation of hydrogen sulfide, the ratio is only ca. 1.5.

It has been established that the photocatalytic activity of semiconductor photocatalysts is greatly determined by the number of the charge recombination centers and the surface area. The former give the effect to charge separation efficiency and the latter determine the surface concentration of the adsorbed reactants. When these factors could be well controlled a highly active photocatalyst can be realized [25]. Clearly, from the comparison of Tables 1 and 2, the adsorption characteristics of the reactants showed quite close correlation with the observed kinetics of the degradation of each reactant. Investigation of the dependence of the kind of the reactant for the same catalyst is accordingly discussed. In the case of the degradation by the rutile film, it is likely that the rate showed a reverse order compared to the ionization potentials. Higher the ionization potential, the slower is the degradation by the rutile. Additionally, remarkable differences in the degradation rate in comparison with the difference in the ionization potential were observed between ammonia and hydrogen sulfide as well as between hydrogen sulfide and acetaldehyde. The ionization potential of NH$_3$ (23.5 eV) is ca. twice larger than that of H$_2$S (10.46 eV), however, $R_r$ for both compounds was almost the same. Also, although the ionization potentials of hydrogen sulfide and acetaldehyde were comparable, $R_r$ for acetaldehyde was a factor of ca. four times larger than that for hydrogen sulfide. It is considered that the difference in the surface concentration was responsible for this observation. Similar tendency was also observed for the degradation by the anatase film. However, $R_a$ for ammonia becomes much higher than $R_r$ for hydrogen sulfide because of low adsorbability of hydrogen sulfide on anatase film.

Furthermore, a large difference between the degradation rate of ammonia and acetaldehyde was observed, in the cases with both the film photocatalysts, which can be attributed by the difference in the mechanism of the degradation of both reactants. It was reported elsewhere that the photocatalytic degradation of gaseous acetaldehyde by the anatase film is greatly mediated by several radical chain reaction mechanisms [14]. In photocatalytic degradation of ammonia, however, a mechanism involving a reversible reaction is reasonable to be taken into account. The irreversibility of the photoinduced surface reactions is of increasing importance when semiconductor powder is used as a photocatalyst. This is because, in the photocatalytic reaction systems employing TiO$_2$ photocatalysts of powder-type (including polycrystalline films as in this work), oxidation and reduction may occur simultaneously on the same particle surface [26]. In the photocatalytic degradation of ammonia, besides the mechanisms including the formation of oxidation products such as N$_2$O, NO, or NO$_2$ [27, 28] the following reversible reaction mechanism involving a direct reaction between hole and ammonia molecules is considered to give great share to the overall degradation mechanism since NH$_3^+$ is a good electron donor.

### Table 1

| Reactant            | $n_{max}$ ($\mu$mol m$^{-2}$) | $k$ (m$^{-2}$ $\mu$mol$^{-1}$) | $I_{max}$ (molecules nm$^{-2}$) |
|---------------------|-------------------------------|-------------------------------|-------------------------------|
|                     | Anatase | Rutile | Anatase | Rutile | Anatase | Rutile |
| Ammonia             | 9.0     | 7.9    | 0.39    | 0.31    | 5.6     | 4.7    |
| Acetaldehyde        | 2.0     | 0.9    | 0.83    | 0.30    | 1.2     | 0.6    |
| Hydrogen Sulfide    | 0.67    | 1.13   | 0.26    | 0.18    | 0.4     | 0.65   |

*The values of $n_{max}$ and $k$ have been normalized to the surface area of catalyst.
Thus, the two contrast mechanism is considered to be main factor leading to the observed striking difference in the degradation rate of acetaldehyde and ammonia.

On the other hand, the dependence of the kind of the catalyst for the same reactant is discussed as follows. In the degradation of ammonia and acetaldehyde, $R_a$ is much higher than $R_r$, by a factor of 8 and 5, respectively. This implies that when the amount of adsorption is very large, the photocatalytic efficiency of the degradation would be determined mostly by the charge separation efficiency in each catalyst. Especially in the case of ammonia, the difference is extremely large, implying that the mass transfer effect is almost completely neglectable.

In the case of the photocatalytic degradation of hydrogen sulfide, however, no so clear difference between $R_a$ and $R_r$ was observed. This was due to very weak adsorption affinity of the reactant onto the surface of both catalysts. As a consequence, the kinetics of the photoreaction is mostly governed by the adsorption characteristics of the catalyst.

4. Conclusions

The anatase film showed a higher photocatalytic activity than the rutile film; the magnitude of the difference decreased in the order ammonia > acetaldehyde > hydrogen sulfide. The determining factors were elucidated by analyzing the adsorption characteristics and the kinetics of photocatalytic degradation of the three reactants. The adsorability on both the films decreased in the order ammonia > acetaldehyde > hydrogen sulfide. Acetaldehyde and ammonia adsorbed more strongly and thus with higher coverage on the anatase film than on the rutile film. Conversely, hydrogen sulfide adsorbed more strongly on the rutile than on the anatase. The phoactivity for the anatase film was higher than for the rutile in all the photocatalytic degradation. Anatase showed activities that were factors of $\approx 8$ and $\approx 5$ higher than for the rutile for the degradation of ammonia and acetaldehyde; however, the activity was only a factor of $\approx 1.5$ higher for the photocatalytic degradation of hydrogen sulfide. Differences in the kinetics of the photodegradation of the three reactants in terms of the charge separation efficiency, the adsorption characteristics of each catalyst, the physical and electrochemical properties of each reactant were explained.
References

[1] R.M. Alberici, W.E. Jardim, Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide, Appl. Catal. B: Environ. 14 (1997) 55–68.

[2] C. Kornmann, D.W. Bahnemann, M.R. Hoffmann, Environmental photocatalysis: Is iron oxide (hematite) an active photocatalyst? A comparative study: α-Fe₂O₃, ZnO, TiO₂, J. Photochem. Photobiol. Part A: Chemistry 48 (1989) 161–169.

[3] I.S. McLintock, M. Ritchie, Reactions on titanium dioxide: photo-adsorption and oxidation of ethylene and propylene, Trans. Faraday Soc. 61 (1965) 1007–1016.

[4] M.E. Zorn, D.T. Tompkins, W.A. Zeltner, M.A. Anderson, Catalytic and photocatalytic oxidation of ethylene on titania-based thin films, Environ. Sci. Technol. 34 (2000) 5206–5210.

[5] S. Kataoka, D.T. Tompkins, M.A. Anderson, M.E. Zorn, W.A. Zeltner, Microwave-assisted heterogeneous photocatalytic oxidation, in: Proceedings of the Second World Congress on Microwave and Radio Frequency Processing, April 2-6, 2000, Orlando, FL, USA.

[6] M.E. Zorn, Photocatalytic oxidation of gas-phase compounds in confined areas: investigation of multiple component systems, in: Proceedings of the 13th Annual Wisconsin Space Conference, August 14–15, 2003, Wisconsin, USA.

[7] K. Urashima, J.S. Chang, Removal of volatile organic compounds from air streams and industrial flue gases by non-thermal plasma technology, IEEE Trans. Dielect. Electr. Insul. 7 (2000) 602–613.

[8] N.R. Blake, G.L. Griffin, Selectivity control during the photoassisted oxidation of 1-butanol on titanium dioxide, J. Phys. Chem. 92 (1988) 5697–5701.

[9] L. Stevens, J.A. Lanning, L.G. Anderson, W.A. Jacoby, N. Chornet, Investigation of the photocatalytic oxidation of low level carbonyl compounds, J. Air Waste Manage. Assoc. 48 (1998) 979–984.

[10] H.H. Kim, K. Tsunoda, S. Katsura, A. Mizuno, A Novel Plasma reactor for NOx control using photocatalyst and hydrogen peroxide injection, in: Proceedings of IEEE Industry Application Society Annual Meeting, New Orleans, USA, October 5–9, 1997, pp. 1937–1941.

[11] J. Peral, D.F. Ollis, Heterogeneous photocatalytic oxidation of gas phase organics for air purification—acetone, 1-butanol, butyraldehyde, formaldehyde, and metaxylene oxidation, J. Catal. 136 (1992) 554–565.

[12] J.M. Coronado, M.E. Zorn, I.T-. Tejedor, M.A. Anderson, Photocatalytic oxidation of ketones in the gas phase over TiO₂ thin films: a kinetic study on the influence of water vapor, Appl. Catal. B: Environ. 43 (2003) 329–344.

[13] M.E. Zorn, D.T. Tompkins, W.A. Zeltner, M.A. Anderson, Photocatalytic oxidation of acetonitrile vapor on TiO₂/ZrO₂ thin films, Appl. Catal. B: Environ. 23 (1999) 1–8.

[14] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, A. Fujishima, An efficient TiO₂ thin-film photocatalyst: photocatalytic properties in gas-phase acetaldehyde degradation, J. Photochem. Photobiol. Part A: Chemistry 98 (1996) 79–86.

[15] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, A. Fujishima, Efficient TiO₂ powder and film photocatalysts with rutile crystal structure, Chem. Lett. (1996) 69–70.

[16] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994.

[17] A.R. Brower, C.P. Huang, Adsorption characteristics of polyacrylate amino acids onto hydrous γ-Al₂O₃, J. Colloid Interface Sci. 105 (1985) 197–215.

[18] B. Ohtani, M. Kakimoto, S. Nishimoto, T. Kagiya, Photocatalytic adsorption and oxidation of ethylene and propylene, Trans. Faraday Soc. 61 (1965) 1007–1016.

[19] M. Primet, P. Pichat, M.V. Mathieu, Infrared study of the surface of titanium dioxides. I. Hydroxyl groups, J. Phys. Chem. 75 (1971) 1216–1220.

[20] L.T. Smith, Infra-red spectra of polar molecules adsorbed on titanium dioxide pigments, Nature (London) (1964) 67.

[21] G.C. Pimentel, A.L. McClellan, The Hydrogen Bond, Freeman, London, 1960.

[22] D.D. Beck, J.M. White, C.T. Ratcliffe, Catalytic reduction of CO with H₂S. II. Adsorption of H₂O and H₂S on anatase and rutile, J. Phys. Chem. 90 (1986) 3123–3131.

[23] K.E. O'Shea, G. Maziarz, Catalytic photooxidation of para-substituted phenols. A kinetic and mechanistic analysis, J. Org. Chem. 59 (1994) 5005.

[24] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata, H. Yoneyama, Effect of inert supports for titanium dioxide loading on enhancement of photodecomposition rate of gaseous propionaldehyde, J. Phys. Chem. 99 (1995) 9986–9991.

[25] B. Ohtani, M. Kakimoto, S. Nishimoto, T. Kagiya, Photocatalytic reaction of neat alcohols by metal-loaded titanium oxide (IV) particles, J. Photochem. Photobiol. Part A: Chemistry 70 (1993) 265–272.

[26] T. Sakata, T. Kawai, K. Hashimoto, Chem. Phys. Lett. 88 (1982) 50.

[27] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, A. Fujishima, Efficient TiO₂ powder and film photocatalysts with rutile crystal structure, Chem. Lett. (1996) 69–70.

[28] H. Mozzanega, J.-M. Herrmann, P. Pichat, NH₃ oxidation over UV-irradiated TiO₂ at room temperature, J. Phys. Chem. 83 (1979) 2251–2255.