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Photocatalytic performance of TiO_2-zeolite templated carbon composite in organic contamination degradation †

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TiO_2 composites with zeolite templated carbon (TiO_2-ZTC) and activated carbon (TiO_2-AC) were prepared and used as the photocatalysts for comparative studies with pure TiO_2. TiO_2-ZTC exhibited the highest rate of methylene blue degradation with a rate approximately 4 and 400 times higher than those of TiO_2-AC and pure TiO_2, respectively. Moreover, the highest catalytic performance of TiO_2-ZTC in gas-phase degradation of acetone was approximately 1.1 and 12.9 times higher than TiO_2-AC and pure TiO_2, respectively. These outstanding performances could be attributed to high surface area, pore volume, and hydrophobic surface property, leading to improving the adsorption properties of organic molecules.

Introduction

TiO_2 nanoparticle is a well-known semiconductor material normally applied as the catalyst in photocatalytic reaction due to advantageous properties such as suitable band gap energy, high thermal stability, nontoxicity, and availability.[1-5] However, the adsorption limitation of organic compounds and the recombination of electron-hole pairs are the drawback factors of TiO_2-based photocatalysts.[6,7] Composite materials are widely designed by uses of various types of porous materials with specific functions.[8-13] To overcome these problems, carbon-based materials are also considered as a potential candidate for the enhancement of photocatalytic efficiency due to their multifunctional properties such as high surface area, electron transfer property on the carbon surface, and surface hydrophobicity.[14-17] Carbon materials such as activated carbon (AC),[15] carbon nanotubes (CNTs)[6,14] and graphene[7,16,17] composite with TiO_2 nanoparticles have been widely used in photocatalytic degradation of organic compounds. Among them, graphene-TiO_2 composite catalyst has attracted much interest because of high surface area (~2,600 m^2/g) and electron mobility properties.[16,17] The outstanding properties and structures of carbon allotropes are therefore remarkable factors for improving the photocatalytic performance of the carbon-TiO_2 composite catalysts.

Zeolite templated carbon (ZTC) is a new-structure carbon material prepared by using zeolite Y as the template for the tailored-micropore structure preparation, resulting in ordered microporous carbon with sp^2-carbon hybridization and a very high surface area (~4,000 m^2/g). This structure composes of buckybowl-like nanographenes of three dimensional carbon network and oxygen-containing functional groups.[18-23] ZTC has been used in many applications such as hydrogen storage,[21,23] organic compound adsorption,[24] and as electrode material for electric double layer capacitors.[22,23] According to these unique properties, ZTC is therefore a potential candidate for use as photocatalyst supports.

In this work, the composite of TiO_2 nanoparticles with AC and ZTC supports were prepared and investigated in the liquid-phase methylene blue degradation and gas-phase acetone degradation. Characterizations using nitrogen adsorption-desorption technique, transmission electron microscopy, and X-ray diffraction as well as the evaluation of adsorption properties have been performed. The outstanding photocatalytic performance of TiO_2-ZTC with specific functions compared to TiO_2-AC and pure TiO_2 has been reported and discussed.

Experimental

Preparation of TiO_2-carbon composite catalyst.

TiO_2 composites with zeolite templated carbon (ZTC) and commercial activated carbon (AC, Shirasagi) were prepared by using incipient wetness impregnation method. The details of ZTC synthesis are reported elsewhere.[20] First, TiO_2 slurry (5 wt% TiO_2; Tayca Corporation, Japan) was mixed with 2-propanol solution and then added onto the carbon support. The obtained mixture was stirred at room temperature for 30 min at a stirring speed of 300 rpm. In order to evaporate 2-propanol, the obtained mixture was heated to 343 K under vacuum until 2-propanol was completely removed, and then dried at 373 K under atmosphere pressure for 12 h.

Characterization techniques.

Nitrogen adsorption-desorption isotherms at 77 K as well as water adsorption isotherms at 298 K were measured by using BELSORP-max (BEL Japan, Inc.). Prior to the measurements, each sample was degassed under vacuum at 473 K for 2 h. X-ray diffraction (XRD) patterns were recorded using Cu Kα radiation (λ = 1.5406 Å) on an X-ray diffractometer (Rigaku Ultima IV). Transmission electron microscopy (TEM) with an acceleration voltage of 200 kV (JEM-2010, JEOL) was used to observe the textural structure of composite catalysts.

Methylene blue adsorption measurement.

The adsorption capacities of TiO_2-ZTC, TiO_2-AC, and pure TiO_2 catalysts in methylene blue (MB) solution were investigated under dark condition at room temperature. Each catalyst (10 mg) was added into the MB solution (30 ml, concentrations: 0.3, 0.5, 0.7, and 1 mM) under stirring for 30 min. After reaching equilibrium, the absorption of the remaining MB at the wavelength around 664 nm was monitored by using UV-vis spectrometer (Shimadzu, UV-2450A). The adsorption isotherms of composite catalysts were evaluated by using following equation (1):

$$Q_m = (C_0 - C_e) \bullet V \bullet M_w / m \qquad \text{Eq. (1)}$$

where Q_m is molar adsorption capacity of MB per gram of catalyst (mg_{MB}/g_{catal}), C_0 is initial concentration of MB (mM), C_e is equilibrium concentration of MB (mM), V is volume of MB solution (L), M_w is molecular weight of MB (g/mol) and m is weight of catalyst (g_{catal}).

Liquid-phase degradation of methylene blue.

The performances of TiO_2-carbon composite catalysts in the degradation of MB were evaluated under light condition. In this series of experiments, the catalyst (10 mg) was suspended in 1 mmol/l of 30 ml MB solution, and then oxygen gas was introduced into the solution under dark condition for 30 min to obtain the adsorption–desorption equilibrium in order to eliminate the adsorption effect of catalyst. During the degradation reaction, the mixture was irradiated under UV light using a high-pressure mercury lamp with the intensity of 5 mW/cm^2 for 24 h under stirring. The changes of solution color were monitored by UV-vis spectrometer (Shimadzu, UV-2450A) at certain time intervals. The photocatalytic activity of TiO_2 powder (AMT-100; Tayca corp., Japan) was also tested as a reference.

Gas-phase degradation of acetone.

The gas-phase degradation of acetone was also tested in a specially constructed reaction cell equipped with the flat pyrex glass window. The fixed amount of each catalyst mixed with an inert silica (0.01 : 0.49 g) was placed in the reaction cell. Oxygen gas was fed into the reactor for 30 min, and then liquid acetone (0.3 mmol) was introduced into the reaction cell (volume: ca. 160 ml) and evaporated into the gas phase. The adsorption process was operated at room temperature under dark condition for 30 min to reach the adsorption-desorption equilibrium. The degradation of acetone was carried out under UV light irradiation using a high-pressure mercury lamp (light intensity: 5 mW/cm^2 at around 360 nm). The progress of the reaction was monitored by gas chromatography (Shimadzu GC-14B with TCD detector) through CO_2 detection.

Results and discussion

Textural properties of TiO_2-carbon composites and pure TiO_2 powder were examined using nitrogen adsorption technique. As shown in Table 1, the highest specific surface area and pore volume were observed in the case of TiO_2-ZTC composite with results approximately 2.5 times higher than those of TiO_2-AC. Both TiO_2-ZTC and TiO_2-AC composite catalysts show the type I isotherm, indicating the existence of microporous structure (Fig. S1(A)). As shown in Fig. S1(B), the pore-size distribution calculated by using the Saito and Foley (SF) method revealed that the TiO_2-ZTC composite catalyst had a larger pore size and broader micropore size in a range of 0.65-1.15 nm compared to TiO_2-AC composite catalyst (narrower pore size of 0.75 nm).

Table 1. Physical properties of pure TiO_2 and composite catalysts with different carbon supports.

Sample name	BET surface area (m^2/g)	Pore volume (cm^3/g)	Adsorption capacity of water[a] (cm^3/m^2)
TiO_2	280	0.45	0.43
TiO_2-ZTC	2167	1.56	0.01
TiO_2-AC	846	0.62	0.06

[a] Calculated from water adsorption at P/P_0 of 0.3and 298 K

Water adsorption measurement was used to evaluate the surface hydrophobicity of the composite catalysts. The amount of water adsorbed per unit surface area was determined at the relative pressure (P/P_0) of 0.3 and the temperature of 298 K, as shown in Table 1. The amounts of water adsorbed on TiO_2-ZTC surface were 6 times and 43 times lower than on TiO_2-AC and pure TiO_2 surfaces, respectively, indicating the highest hydrophobic surface property as compared to the other catalysts.

The significant differences of TiO_2 dispersion over ZTC and AC supports were observed by TEM technique, as shown in Fig. 1. With ZTC support, a relatively high dispersion of segregated TiO_2 nanoparticle clusters was observed, while AC support led to the formation of aggregate clusters of TiO_2 nanoparticles.

The adsorption performances of TiO_2-carbon composites were investigated under dark condition using an aqueous solution of

MB as the adsorbate. The differences of adsorption capacity were clearly observed as the color changes of MB solution.

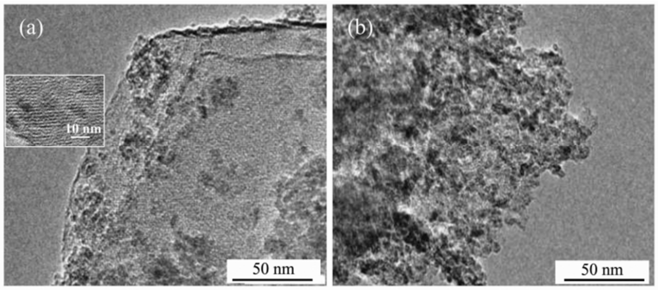

Fig. 1 TEM images of fresh catalysts: (a) TiO_2-ZTC and (b) TiO_2-AC.

As shown in Fig. S2, UV-vis absorption spectrum of MB solution (concentration: 0.3 mM) shows an intense peak at around 664 nm. The color change of MB solution in each sample after the adsorption process was observed in the photographic images (inset of Fig. S2). TiO_2-ZTC composite catalyst could completely adsorb MB, while TiO_2-AC composite catalyst shows moderate adsorption capacity. The lowest adsorption of MB was observed with pure TiO_2. As shown in Fig. 2, with increasing the concentration of MB (0.3, 0.5, 0.7, and 1 mM), the adsorption capacity (Q_m) of TiO_2-ZTC composite catalyst was increased (Fig. 2a), whereas those of TiO_2-AC composite catalyst (Fig. 2b) and pure TiO_2 (Fig. 2c) were nearly constant at 160 and 18 mg_{MB}/g_{catal}, respectively. This result clearly confirmed that ZTC support exhibited the superior adsorption capacity of MB in this concentration range due to its excellent physical properties including exceptionally high surface area, large pore volume, and high hydrophobic surface property. The superior adsorption capacity is also estimated to be governed by small particle size of ZTC and pi-interaction of ZTC surface and aromatic rings of MB.[25,26]

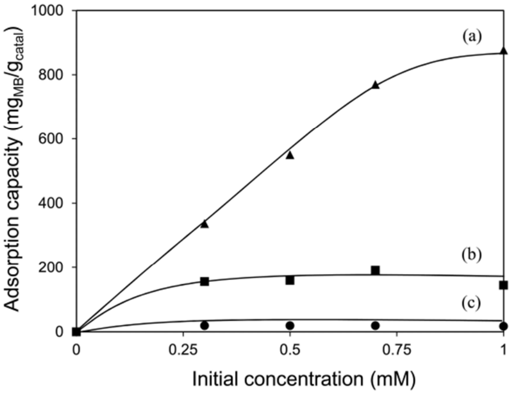

Fig. 2 Adsorption isotherm of MB with different catalysts: (a) TiO_2-ZTC, (b) TiO_2-AC, and (c) pure TiO_2.

The result of MB degradation on each catalyst under UV light irradiation is shown Fig. 3. The rate of MB degradation was calculated by using equation 2:

$$\ln (C_0/C) = kt \qquad \text{Eq. (2)}$$

where C is concentration (mM) at a given UV irradiation time, C_0 is concentration (mM) after adsorption under dark condition for 30 min, k is the apparent rate constant (h^{-1}) in degradation, and t is time (h).

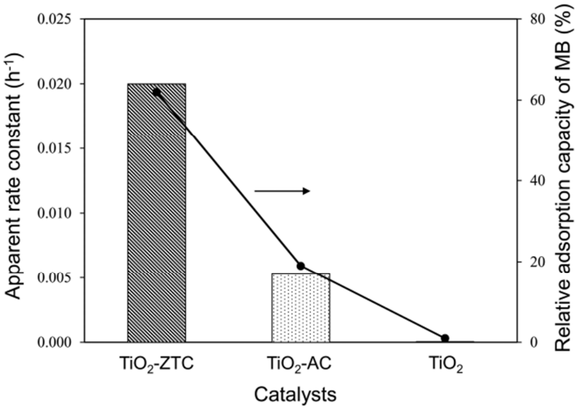

Fig. 3 Relationships between the photocatalytic degradation rate and adsorption capacity of methylene blue (MB) in water.

The TiO_2-carbon composite catalysts show better catalytic performance in the degradation of MB molecules than pure TiO_2. Among these, the highest rate of MB degradation was observed in the case of TiO_2-ZTC composite with a rate approximately 4 and 400 times higher than those of TiO_2-AC composite and pure TiO_2, respectively. This result confirmed that TiO_2 composite with ZTC support could enhance the liquid-phase MB degradation.

In addition, TiO_2-carbon composite catalysts were tested for the gas-phase degradation of acetone under UV light irradiation. As shown in Fig. 4, TiO_2-ZTC composite catalyst exhibited better acetone adsorption, approximately 1.59 times higher than TiO_2-AC catalyst. Based on the same amount of TiO_2, the highest yield of CO_2 product was observed in the case of TiO_2-ZTC composite catalyst, while the lowest was observed with pure TiO_2.

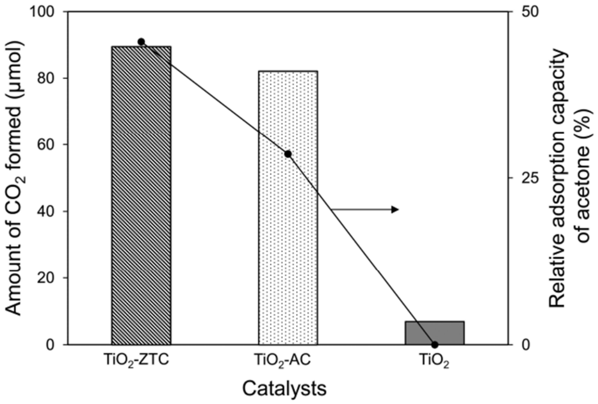

Fig. 4 Relationships between the amounts of CO_2 formed in the photocatalytic degradation of acetone and adsorption capacity of acetone.

The amount of CO_2 product obtained from TiO_2-ZTC composite catalyst was approximately 1.1 and 12.9 times higher than that obtained from TiO_2-AC and pure TiO_2, respectively. This indicated that the performance of TiO_2 on the ZTC support could be promoted not only in liquid-phase methylene blue degradation but also in gas-phase acetone degradation.

In order to confirm the crystalline phase of TiO_2 in all catalysts, XRD spectroscopy was applied (Fig. S3). The diffraction peaks at 2θ of 25°, 37°, 47°, 53°, 55°, and 63°, corresponding to (101), (004), (200), (105), (211), and (204) planes of TiO_2 anatase phase [20,21] were observed in all catalysts. It should be noted that the same TiO_2 anatase phase was obtained in all catalysts; this result implied that carbon allotropes therefore play a principal and important role for improving the catalytic performance in methylene blue and acetone degradation reactions.

According to the above results, ZTC exhibited excellent photocatalyst properties in the degradation of organic contaminants due to its unique physical and surface properties. The extremely large surface area and pore volume of ZTC help increase the dispersion of TiO_2 nanoparticles on the support, while the surface hydrophobicity of ZTC enhances the adsorption capacity of organic molecules. Furthermore, it should be noted that the electronic property of ZTC [27,28] could also induce the electron transfer from TiO_2 to ZTC surface and simultaneously reduce electron-hole pairs recombination on TiO_2 nanoparticle. These properties are the key factors, affecting higher photocatalytic performance in the degradation of organic compounds.

Conclusions

TiO_2-ZTC and TiO_2-AC composite catalysts were successfully synthesized by an impregnation method and used as catalysts in the degradation of methylene blue in water and acetone in the air. It was found that the rate of methylene blue degradation of TiO_2-ZTC composite catalyst was approximately 4 and 400 times higher than those of TiO_2-AC and pure TiO_2, respectively. Moreover, TiO_2-ZTC composite catalyst also performed the highest degradation of acetone to CO_2 product compared to other catalysts. These results could be attributed to unique characteristics of TiO_2-ZTC composite catalyst, such as exceptionally high surface area, pore volume, and hydrophobic surface property, resulting in the enhancement of adsorption capacity of organic molecules.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Nitrogen adsorption-desorption isotherms, pore size distribution curve data, UV-vis absorption spectra, photographic images of solutions, XRD patterns. See DOI: 10.1039/b000000x/

1 P. V. Kamat, *Chem. Rev.* 1993, **93 (1)**, 267.
2 M. A. Fox, M. T. Dulay, *Chem. Rev.*, 1993, **93,** 341-357.
3 M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
4 A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2000, **1**, 1.
5 T. Kamegawa, D. Yamahana, H. Yamashita, *J. Phys. Chem. C*, 2010, **114**, 15049.
6 J. Chen, G. Li, Y. Huang, H. Zhang, H. Zhao, T. An, *Appl. Catal. B: Environ.*, 2012, **123-124**, 69.
7 W. Wang, J. Yu, Q. Xiang, B. Cheng, *Appl. Catal. B: Environ.*, 2012, **119-120**, 109.
8 X. Qian, K. Fuku, K. Kuwahara, T. Kamegawa, K. Mori, H. Yamashita, *ChemSusChem*, 2014, **7**, 1528.
9 Y. Kuwahara, K. Maki, Y. Matsumura, T. Kamegawa, K. Mori, H. Yamashita, *J. Phys. Chem. C*, 2009, **113**, 1552.
10 K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji, J. P. Hill, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 1.
11 K. Ariga, Y. Yamauchi, G. Rydzek, Q. Ji, Y. Yonamine, K.C.-W. Wu, J. P. Hill, *Chem. Lett.*, 2014, **1**, 36.
12 F.-K. Shieh, C.-T. Hsiao, H.-M. Kao, Y.-C. Sue, K.-W. Lin, C.-C. Wu, X.-H. Chen, L. Wan, M.-H. Hsu, J. R. Hwu, C.-K. Tsung, K. C.-W. Wu, *RSC Adv.*, 2013, **3**, 25686.
13 H.-Y. Wu, F.-K. Shieh, H.-M. Kao, Y.-W. Chen, J. R. Deka, S.-H. Liao, K. C.-W. Wu, *Chem. -A Euro. J.*, 2013, **19**, 6358.
14 Y. -J. Xu, Y. Zhuang, X. Fu, *J. Phys. Chem. C*, 2010, **114**, 2669.
15 T. Torimoto, Y. Okawa, N. Takeda, H. Yoneyama, *J. Photochem. Photobiol. A: Chem.*, 1997, **103**, 153.
16 Y. Zhang, Z. -R. Tang, X. Fu, Y. -J. Xu, *ACS Nano*, 2010, **4**, 7303.
17 Q. Xiang, J. Yu, M. Jaroniec, *Chem. Soc. Rev.*, 2012, **41**, 782.
18 Z. Ma, T. Kyotani, Z. Liu, O. Terasaki, A. Tomita, *Chem. Mater.*, 2001, **13**, 4413.
19 Z. Ma, T. Kyotani, A. Tomita, *Chem. Commun.*, 2000, 2365.
20 H. Nishihara, Q. -H.Yang, P. -X. Hou, M. Unno, S. Yamauchi, R. Saito, J. I. Paredes, A. Martínez-Alonso, J. M. D. Tascón, Y. Sato, M. Terauchi, T. Kyotani, *Carbon*, 2009, **47**, 1220.
21 H. Nishihara, P.-X. Hou, L.-X. Li, M. Ito, M. Uchiyama, T. Kaburagi, A. Ikura, J. Katamura, T. Kawarada, K. Mizuuchi, T. Kyotani, *J. Phys. Chem. C*, 2009, **113**, 3189.
22 H. Itoi, H. Nishihara, T. Kogure, T. Kyotani, *J. Am. Chem. Soc.*, 2011, **133**, 1165.
23 H. Nishihara, T. Kyotani, *In Novel Carbon Adsorbents*, 2012, 295.

24 L. Ji, F. Liu, Z. Xu, S. Zheng, D. Zhu, *Environ. Sci. Technol.*, 2009, **43**, 7870.

25 N. L. Torad, M. Hu, S. Ishihara, H. Sukegawa, A. A. Belik, M. Imura, K. Ariga, Y. Sakka, Y. Yamauchi, *Small*, 2014, **10**, 2096.

26 N. L. Torad, M. Hu, Y. Kamachi, K. Takai, M. Imura, M. Naito, Y. Yamauchi, *Chem. Commun.*, 2013, **49**, 2521.

27 P. K. Khanna, N. Singh, S. Charan, *Mater. Lett.*, 2007, **61**, 4725.

28 J. Wang, J. Polleux, J. Lim, B. Dunn, *J. Phys. Chem. C*, 2007, **111**, 14925.