Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Catalysis Today 120 (2007) 163–167
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Design of TiO_2-SiC photocatalyst using TiC-SiC nano-particles for degradation of 2-propanol diluted in water

Hiromi Yamashita [a,*], Yoshikatsu Nishida [a], Shuai Yuan [a], Kohsuke Mori [a],
Masaaki Narisawa [b], Yasuyuki Matsumura [c], Tetsutaro Ohmichi [a], Iwao Katayama [a]

[a] Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565-0871, Japan
[b] Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Gakuencho 1-1, Sakai, Osaka 599-8531, Japan
[c] National Institute of Advanced Industrial Science and Technology (AIST), Kansai Center 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Abstract

TiO_2 photocatalyst deposited on SiC (TiO_2-SiC) was prepared by a calcination of nano-particles of TiC-SiC precursor obtained by a carbothermic reduction of SiO_2-TiO_2. The formation of the mixture of well-crystallized anatase and rutile phases of TiO_2 was observed on the calcined TiO_2-SiC photocatalyst, while amorphous TiO_2 species was main component on the TiO_2-SiO_2 photocatalyst prepared by a conventional sol–gel method. From the measurement on the water adsorption ability of photocatalysts, the TiO_2-SiC photocatalyst exhibited the hydrophobic surface property in comparison with TiO_2-SiO_2 and commercial TiO_2 powder (P-25) photocatalysts. Under UV-light irradiation, the TiO_2-SiC photocatalyst decomposed 2-propanol diluted in water into acetone, CO_2, and H_2O, and finally acetone was also decomposed into CO_2 and H_2O. The TiO_2-SiC photocatalyst exhibited the higher photocatalytic reactivity than TiO_2-SiO_2 photocatalyst prepared by the sol–gel method. Well-crystallized TiO_2 phase deposited on SiC and the hydrophobic surface of SiC support are important factors for the enhancement of photocatalytic reactivity for degradation of organic compounds in the liquid phase reaction.

Keywords: Photocatalyst; TiO_2; SiC; Photocatalytic degradation

1. Introduction

The design of highly efficient photocatalytic systems which work for the reduction of global atmospheric pollution and the purification of polluted water is of vital interest. TiO_2 semiconductor is known as one of the most stable and highly reactive photocatalysts [1–7]. The utilization of extremely small TiO_2 particles as photocatalysts has attracted a great deal of attention, especially for environmental applications. Because TiO_2 photocatalyst can completely mineralize toxic and nonbiodegradable organics to CO_2, H_2O, and inorganic constituents, many researches have been undertaken to purify polluted water by using TiO_2 photocatalyst.

For practical utilization of photocatalyst TiO_2 having higher photocatalytic reactivity is desirable. During the process of purification of polluted water, photocatalyst has to be separated from treated water. To separate the photocatalyst from water, photocatalyst has to be supported on bulk materials. It has been found that the highly dispersed titanium oxide photocatalysts anchored on the porous silica-based materials exhibit high and characteristic photocatalytic reactivity compared to bulk TiO_2 powder [1,6,7]. Especially the titanium oxide species prepared within the pores and frameworks of zeolite and mesoporous silica have been revealed to have unique local structures as well as high reactivity in the various photocatalytic reactions [8,9]. Furthermore, TiO_2 photocatalyst loaded on Si_3N_4 has also been successfully utilized as the catalyst for the photocatalytic degradation of pollutants diluted in water [10].

On the other hand, silicon carbide (SiC) has various attractive properties such as high thermostabilty, high mechanical strength, and high electrical conductivity. In addition, SiC is easy to be molded into a filter and has been used as catalyst support [11–17]. Although it may be a useful support for photocatalysts used in liquid phase, there have been no reports on the properties of TiO_2 photocatalysts loaded on SiC. Only the study on the photocatalysis of TiO_2 deposited on

---

* Corresponding author. Tel.: +81 6 6879 7457; fax: +81 6 6879 7457.
E-mail address: yamashita@mat.eng.osaka-u.ac.jp (H. Yamashita).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.07.038

the fiber of precursor SiC material has been reported in the similar system [18].

Recently, it has been found that nano-size TiC-SiC particles can be synthesized by a carbothermic reduction of SiO_2-TiO_2 [13]. In the present study, we deal with the preparation and characterization of TiO_2 photocatalysts loaded on SiC using the TiC-SiC precursor obtained by the carbothermic reduction of SiO_2-TiO_2 and carried out its successful utilization for the photocatalytic degradation of 2-propanol diluted in water.

2. Experimental

2.1. Preparation of catalysts

By the process for preparation of nano-size TiC-SiC particles reported in the previous study [13], the liquid mixtures of titanium tetraisopropoxide (TPOT), tetraethyl orthosilicate (TEOS), and phenolic resin were prepared. After the continuous stirring of the mixtures to the gelation, the obtained gels were dried in vacuum, and pyrolyzed at 1273 K in a nitrogen atmosphere. The material pyrolyzed at 1273 K was preheated at 1873 K under Ar flow to yield the TiC-SiC precursor by the carbothermic reduction. The obtained TiC-SiC powders were then calcined in air at 773 K and 1073 K to synthesize TiO_2 deposited on SiC powder (TiO_2-SiC). In order to compare photocatalytic reactivity with TiO_2-SiC, TiO_2-SiO_2 samples were prepared by the conventional sol–gel method using TEOS, TPOT, and ethanol [6].

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns of the samples were measured by Rigaku RINT2500 diffractometer with Cu Kα1 radiation. X-ray photoelectron spectroscopy (XPS) was recorded with JEOL microprobe system using the Mg Kα line. The XAFS spectra (XANES and EXAFS) were measured at the BL-9A facility [19] of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. A Si(1 1 1) double crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The normalized spectra were obtained by a procedure described in previous literature [20]. Water adsorption isotherms of the catalysts were recorded at 293 K using vacuum line system.

2.3. Photocatalytic degradation

The photocatalyst (50 mg) was transferred to a quartz cell with an aqueous solution of 2-propanol (2.6×10^{-3} mol dm^{-3}, 25 ml). Prior to UV-light irradiation, the suspension was stirred in a flow of O_2 for 1 h under dark conditions. The sample was then irradiated (1300 μW cm^{-2} at 340–370 nm) at 295 K using UV light ($\lambda > 250$ nm) from a 100 W high-pressure Hg lamp with continuous stirring under O_2 atmosphere in the system [7]. The products were analyzed by gas chromatography. The photocatalytic reactivity was estimated from the initial decrease in the concentration of 2-propanol after preadsorption of 2-propanol on the catalyst under dark condition.

3. Results and discussion

Fig. 1 shows the XRD patterns of untreated TiC-SiC precursor and TiO_2-SiC photocatalysts oxidized at 773 K and 1073 K, respectively. In the TiC-SiC precusor, very sharp peak corresponding to TiC and SiC were observed indicating that well-crystallized TiC-SiC material was obtained. After calcination, the formation of the mixture of anatase and rutile phases of TiO_2 crystalline was observed on TiO_2-SiC samples. At higher calcination temperature crystal size of TiO_2 grew up. The size of crystalline of sample calcined at 1073 K can be estimated from XRD line width as 18 nm (anatase), 17 nm (rutile), and 22 nm (SiC), respectively. On the other hand, TiO_2-SiO_2 photocatalysts prepared by the sol–gel method and calcined at 773 K exhibited no XRD peak due to the crystallized phases, indicating that the TiO_2 species exist in an amorphous phase.

Fig. 2 shows XANES spectra at Ti K-edge of untreated TiC-SiC precursor and TiO_2-SiC photocatalysts oxidized at 773 K and 1073 K, repsectively. The XANES spectra at the Ti K-edge showed several well-defined preedge peaks which are related to the local structure surrounding the Ti atom. The relative intensities of these preedge peaks provide useful information on the coordination number of the Ti atom [21]. TiO_2-SiC prepared by the oxidation at 1073 K exhibit three small well-defined preedge peaks which can be assigned to the presence of anatase phase with high crystallinity as a main species. These results obtained from XRD and XAFS measurements indicate that the TiC species of TiC-SiC precusor can be oxidized easily to form the mixture of anatase and rutile TiO_2 crystalline at 773 K and crystallized mainly into anatase TiO_2 at 1073 K on the SiC support.

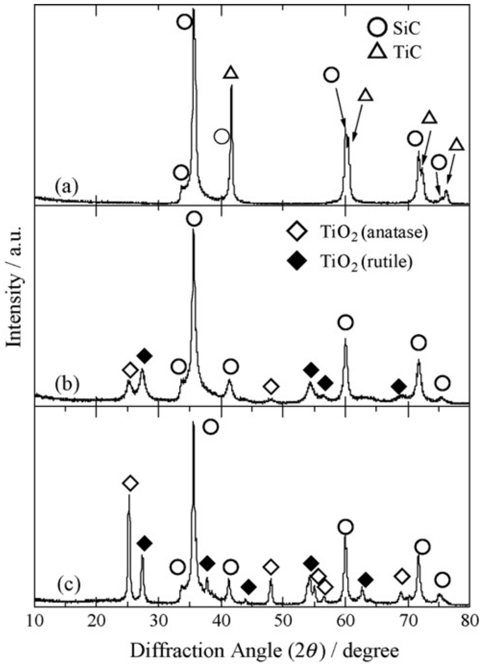


Fig. 1. XRD patterns of untreated TiC-SiC (a) and TiO_2-SiC photocatalysts prepared by calcination at 773 K (b) and 1073 K (c), respectively.

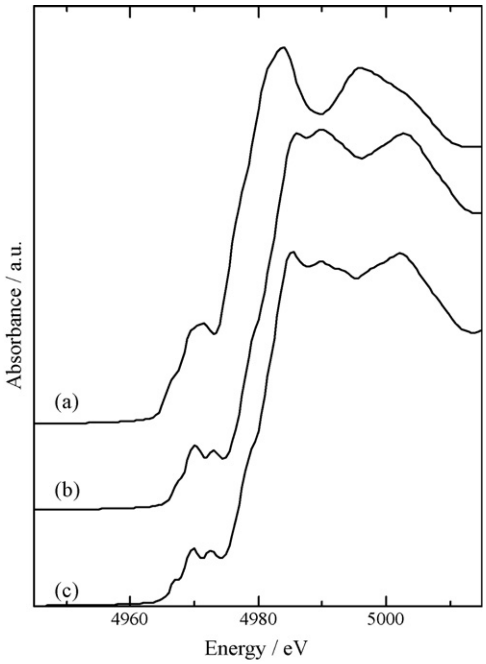


Fig. 2. Ti K-edge XANES spectra of untreated TiC-SiC (a) and TiO_2-SiC photocatalysts prepared by calcination at 773 K (b) and 1073 K (c), respectively.

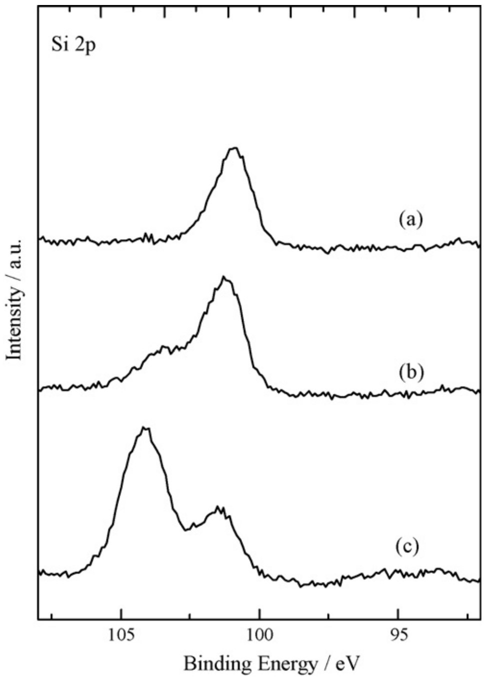


Fig. 4. Si 2p XPS spectra of untreated TiC-SiC (a) and TiO_2-SiC photocatalysts prepared by calcination at 773 K (b) and 1073 K (c), respectively.

Figs. 3 and 4 shows the Ti 2p and Si 2p XPS spectra measured with TiC-SiC precursor and TiO_2-SiC photocatalysts calcined at 773 K and 1073 K, respectively. The changes in the XPS bands after the calcination indicated that TiO_2 exists on the surface by calcination of TiC-SiC precursor at 773 K, while SiC is not oxidized. At higher calcination temperature (1073 K) not only TiC is oxidized into TiO_2 but also SiC is partially oxidized into SiO_2 and form the mixture of SiC and SiO_2 on the surface of catalyst.

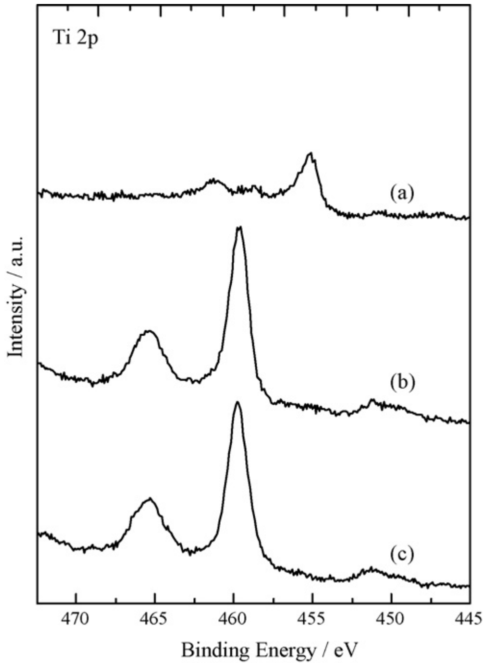


Fig. 3. Ti 2p XPS spectra of untreated TiC-SiC (a) and TiO_2-SiC photocatalysts prepared by calcination at 773 K (b) and 1073 K (c), respectively.

Scheme 1 shows the systematic diagrams for the formation of TiO_2-SiC photocatalyst prepared by the calcination of nano-size TiC-SiC precursor particles. During the calcination, TiC is oxidized more easily than SiC and deposited on the surface of SiC, while the surface SiC was oxidized partially at the higher calcination temperatures.

Fig. 5 shows the reaction time profiles of the liquid phase photocatalytic degradation of 2-propanol diluted in water on the TiO_2-SiC photocatalysts calcined at 773 K and 1073 K, TiO_2-SiO_2 photocatalyst prepared by the sol–gel method, and commercial TiO_2 powder (P-25). Under UV-light irradiation of photocatalysts 2-propanol is decomposed into acetone, CO_2,

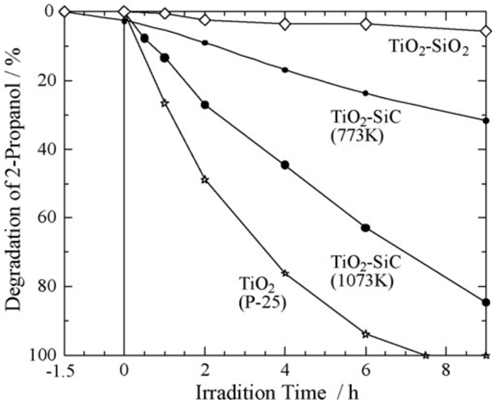
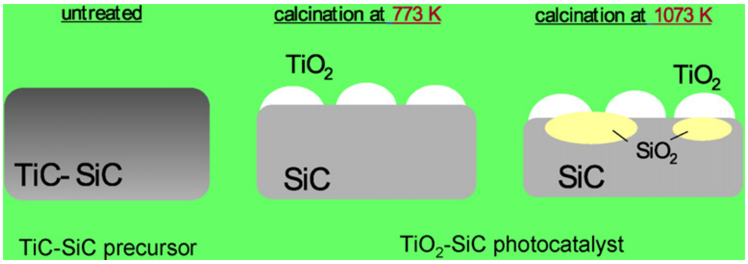


Fig. 5. Time profile for photocatalytic degradation of 2-propanol diluted in water on TiO_2-SiC photocatalyst calcined at 773 K and 1073 K, TiO_2-SiO_2 photocatalyst prepared by the sol–gel method followed by calcination at 1073 K, and commercial TiO_2 powder (P-25).



Scheme 1. Scheme for the formation of TiO_2-SiC photocatalyst from the precursor of nano-particles of TiC-SiC.

and H_2O, and finally, acetone is also decomposed into CO_2 and H_2O, as similar to the reaction scheme observed on TiO_2/HMS mesoporous silica [22]. The TiO_2-SiC photocatalysts decomposed 2-propanol faster than TiO_2-SiO_2 photocatalyst prepared by the sol–gel method. This result indicates that SiC is useful support for TiO_2 photocatalyst for degradation of organic compounds in water. Among the TiO_2-SiC catalysts, the photocatalyst calcined at 1073 K shows the higher reactivity than the photocatalyst calcined at 773 K.

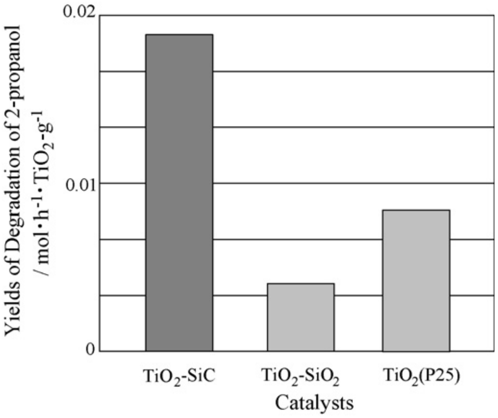


Fig. 6. Photocatalytic reactivity normalized per weight of TiO_2 for 2-propanol diluted in water on TiO_2-SiC photocatalysts calcined at 773 K and 1073 K, TiO_2-SiO_2 photocatalyst prepared by the sol–gel method followed by calcination at 1073 K, and commercial TiO_2 powder (P-25).

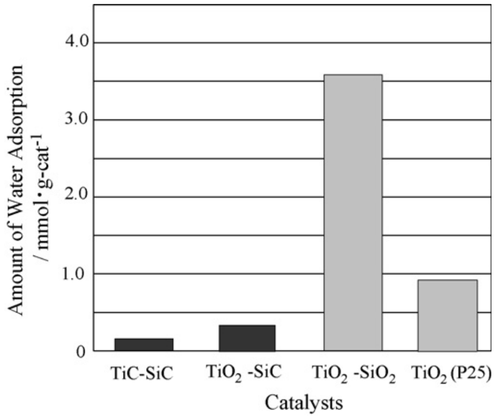


Fig. 7. Amount of water adsorption on untreated TiC-SiC, TiO_2-SiC photocatalysts calcined at 1073 K, TiO_2-SiO_2 photocatalyst prepared by the sol–gel method followed by calcination at 1073 K, and commercial TiO_2 powder (P-25).

Fig. 6 shows the photocatalytic reaction rate normalized per weight of TiO_2 of various catalysts estimated from the initial decrease in the concentration of 2-propanol. TiO_2-SiC photocatalyst prepared by the calcination of TiC-SiC at 1073 K exhibited the higher photocatalytic reactivity than TiO_2-SiO_2 photocatalyst prepared by the conventional sol–gel method and commercial TiO_2 powder P-25. This result indicates that well-crystallized TiO_2 deposited on SiC can demonstrate efficient photocatalytic reactivity.

Fig. 7 shows the amount of water adsorption on various catalysts. Amount of water adsorption on TiO_2-SiC photocatalyst prepared at 1073 K is much smaller than TiO_2-SiO_2 and TiO_2 powder (P-25). This result suggests that SiC support has the hydrophobic surface property. As reported previously [22], the photocatalytic reactivity of TiO_2 loaded on supports depend significantly on the hydrophilic–hydrophobic surface property of supports and the hydrophobic surface property is suitable for the photocatalytic degradation of organics diluted in water. In the present reaction system, the hydrophobic surface property of SiC support is also very important factor for the efficient photocatalytic reactivity of TiO_2-SiC photocatalyst for the liquid phase reaction.

4. Conclusions

TiO_2 photocatalysts deposited on SiC (TiO_2-SiC) which was prepared by the calcination of the TiC-SiC precursor showed high photocatalytic reactivity for the degradation of 2-propanol diluted in water. Comparing the reactivity per weight of TiO_2, TiO_2-SiC photocatalyst showed the higher photocatalytic reactivity than TiO_2-SiO_2 photocatalyst prepared by the conventional sol–gel method and commercial TiO_2 powder. The formation of well-crystallized TiO_2 on SiC and the hydrophobic surface of SiC were found to be related to the efficient photocatalytic reactivity of TiO_2-SiC photocatalyst. Since SiC is mechanically strong enough to be used as a filter for water purification, SiC is a good support for TiO_2 photocatalysts used in liquid phase reactions.

Acknowledgements

The present work is supported by the Grant-in-Aid for Scientific Research (KAKENHI) in Priority Area “Molecular Nano-Dynamics” from Ministry of Education, Culture, Sports, Science and Technology (Nos. 17034036 and 17360388). This work is partly performed under the project of collaborative research at the Joining and Welding Research Institute (JWRI) of Osaka University. The X-ray adsorption experiments were performed at the Photon Factory of KEK (2004G295).

References

[1] H. Yamashita, M. Anpo, Curr. Opin. Solid State Mater. Sci. 7 (2004) 471.

[2] S. Horikoshi, H. Hidaka, N. Serpone, Environ. Sci. Technol. 36 (2002) 1357.

[3] C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, Langmuir 16 (2000) 8964.

[4] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata, H. Yoneyama, J. Phys. Chem. 99 (1995) 9986.

[5] H. Yamashita, Y. Ichihashi, M. Harada, G. Stewart, M.A. Fox, M. Anpo, J. Catal. 158 (1996) 97.

[6] H. Yamashita, S. Kawasaki, Y. Ichihashi, M. Harada, M. Anpo, G. Stewart, M.A. Fox, C. Louis, M. Che, J. Phys. Chem. B 102 (1998) 5870.

[7] H. Yamashita, M. Honda, M. Harada, Y. Ichihashi, M. Anpo, Y. Hatano, J. Phys. Chem. B 102 (1998) 10707.

[8] H. Yamashita, Y. Ichihashi, M. Anpo, C. Louis, M. Che, J. Phys. Chem. 100 (1996) 16041.

[9] K. Ikeue, H. Yamashita, T. Takewaki, M. Anpo, J. Phys. Chem. B 105 (2001) 8350.

[10] H. Yamashita, K. Maekawa, Y. Nakatani, J.-J. Park, M. Anpo, Chem. Lett. (2003) 910.

[11] Z. Liu, W. Shen, W. Bu, H. Chen, Z. Hua, L. Zhang, L. Li, J. Shi, S. Tan, Microporous Mesoporous Mater. 82 (2005) 137.

[12] K. Guerfi, S. Lagerge, M.J. Meriziani, Y. Nedellec, G. Chauveteau, Thermochim. Acta 434 (2005) 140.

[13] M. Narisawa, H. Ukon, K. Okamura, S. Shimada, T. Katayama, J. Ceram. Soc. Jpn. 110 (2002) 518.

[14] N. Keller, C. Pham-Huu, M.J. Leduox, C. Estournes, G. Ehret, Appl. Catal. A—Gen. 187 (1999) 255.

[15] N. Keller, O. Reiff, V. Keller, M. Ledoux, Diamond Relat. Mater. 14 (2005) 1353.

[16] M.J. Ledoux, C. Pham-Huu, R.R. Chianelli, Curr. Opin. Solid. State Mater. 1 (1996) 96.

[17] L. Presant, J. Matta, F. Garin, M. Ledoux, P. Bernhardt, C. Pham, C. Pham-Huu, Appl. Catal. A—Gen. 266 (2004) 21.

[18] T. Ishikawa, H. Yamaoka, Y. Harada, T. Fujii, T. Nagasawa, Nature 416 (2002) 64.

[19] M. Nomura, A. Koyama, J. Synchrotron Radiat. 6 (1999) 182.

[20] H. Yamashita, M. Matsuoka, K. Tsuji, Y. Shioya, M. Anpo, J. Phys. Chem. 100 (1996) 397.

[21] J.M. Thomas, G. Sankar, J. Synchrotron Radiat. 8 (2001) 55.

[22] H. Yamashita, K. Maekawa, H. Nakao, M. Anpo, Appl. Surf. Sci. 237 (2004) 393.