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# Preparation of hydrophobically modified single-site Ti-containing mesoporous silica (TiSBA-15) and their enhanced catalytic performances

Takashi Kamegawa, Norihiko Suzuki, Keita Tsuji, Joji Sonoda, Yasutaka Kuwahara, Kohsuke Mori, Hiromi Yamashita*

*Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

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## ABSTRACT

Hydrophobic modification of single-site Ti-oxide moieties containing mesoporous silica (TiSBA-15) surfaces was performed by using triethoxyfluorosilane (TEFS) as a silylation reagent. The pore structure as well as the high surface area of TiSBA-15 was retained even after modification of these surfaces. TiSBA-15 modified with suitable amount of TEFS exhibited higher catalytic performance for the selective oxidation of cyclooctene to 1,2-epoxy cyclooctane using aqueous $H_2O_2$ as an oxidant than the unmodified TiSBA-15. The improvement of surface hydrophilic–hydrophobic properties of TiSBA-15 is quite effective for the enhancement of catalytic activity.

## 1. Introduction

Recently, the modification of the physical and chemical properties of porous siliceous materials has often been performed by incorporation of desired functional moieties within their frameworks or anchoring on their surfaces as part of the walls [1,2]. In the case of post functionalization of porous siliceous materials, the grafting of silylation reagents on their surface are often adopted to improve the characteristics such as thermal stability, adsorption properties of substances as well as tailor the sizes of pores [3,4]. In our previous works, surface modification of porous siliceous materials such as zeolite and mesoporous silica as a support of catalytically active species was investigated by using fluorine group containing silylation reagent, i.e. triethoxyfluorosilane (TEFS; $(C_2H_5O)_3SiF$), leading to the formation of quite hydrophobic surfaces and the enhancement of reaction rates [5,6]. The inorganic functional moieties (≡Si–F) anchored on the surface also showed the high thermal stability as compared to other organic groups such as long alkyl chain moieties.

On the other hand, it is well known that the isolated tetrahedrally coordinated transition metal oxides containing porous siliceous materials exhibited the unique catalytic and photocatalytic activities, which were remarkable different catalytic performances compared to those on corresponding bulk oxides [7–18]. The transition metal oxides are considered to be highly dispersed within the frameworks of them and work as well-defined catalytically active sites. For example, isolated tetrahedral Ti-oxide moieties within the frameworks of zeolite and mesoporous silica, i.e. single-site Ti-oxide moieties, showed excellent catalytic performances with high selectivity of desired product in oxidation reaction processes by using hydrogen peroxide ($H_2O_2$) or alkyl hydroperoxide as an oxidant [11–17]. These environmentally friendly systems are promising in reducing the undesired byproducts. The characteristics of porous materials also affect the reaction rates and adsorption properties of substances in these reaction systems. The simple method for improving the characteristics of these porous materials is post functionalization of their surfaces using silylation reagent. Definitely, hydrophobically modified porous siliceous materials were prepared by using HF as well as fluorine containing template for construction of porous structure [16–19]. In the present work, we dealt with the post functionalization of single-site Ti-oxide moieties containing mesoporous silica (TiSBA-15) by grafting of TEFS as a silylation reagent and their characterizations. The effect of the surface modification on the catalytic performances was investigated through the oxidation reaction of cyclooctene using aqueous $H_2O_2$ as a model reaction.

## 2. Experimental

### 2.1. Synthesis of TiSBA-15

Ti-containing mesoporous silica (TiSBA-15) was synthesized in accordance with previous literature [20,21], using titanium isopropoxide (TIP), trimethoxysilane (TMOS), ammonium fluoride

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

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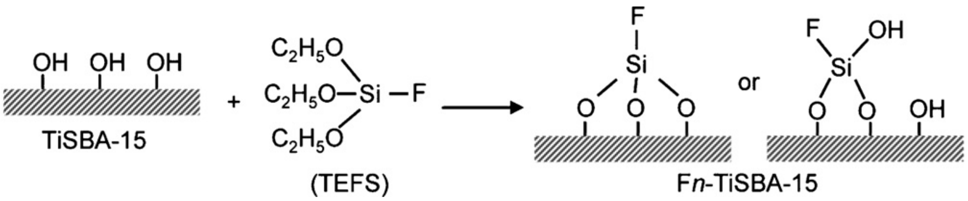

**Scheme 1.** Reaction scheme for surface hydrophobic modification of TiSBA-15 by TEFS.

($NH_4F$) and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as a template. 4.0 g of Pluronic P123 and small amount of $NH_4F$ (molar ratio of F/Si = 0.03) was dissolved in 100 g of HCl aqueous solution (pH 1.0) with stirring at 313 K. Then, 4.7 g of TMOS mixed with TIP (Ti/Si = 0.005) was added into the above solution with vigorous stirring at same temperature. After continuous stirring for 20 h, mixture was aged under static conditions at 333 K for 48 h. The product was washed with deionized water, dried at 333 K for 12 h and then calcined at 823 K for 10 h in air. The amount of Ti-oxide moieties within prepared TiSBA-15 was determined to be 0.1 wt% as Ti metal by inductively coupled plasma (ICP) analysis.

### 2.2. Surface modification of TiSBA-15 by TEFS

The surface modification of obtained TiSBA-15 was performed by grafting of triethoxyfluorosilane (TEFS). The mixture of dry toluene and desired amounts of TEFS was added to TiSBA-15 pre-evacuated at 423 K for 2 h, and then mixture was stirred at 298 K for 5 h. After evaporation of dry toluene, recovered powder was dried at 373 K for 12 h and then calcined at 773 K for 5 h in air. The surface modification of TiSBA-15 is thought to proceed according to Scheme 1 by reaction of surface hydroxyl groups and TEFS [5,6]. After surface modification by TEFS, samples were denoted as F*n*-TiSBA-15, where *n* described the loaded amount of TEFS (*n* = 2, 5, 10 and 20 wt%).

### 2.3. Characterization procedure of catalyst

The powder XRD measurements were performed using a Rigaku Ultima IV X-ray diffractometer with Cu K$\alpha$ radiation. X-ray photoelectron spectroscopy was performed with a JEOL microprobe system using the Mg K$\alpha$ radiation. Binding energy was calibrated using the $C_{1s}$ photoelectronic peak at 285.0 eV. Diffuse reflectance UV–vis spectra were recorded at 298 K with a Shimadzu UV-2450A double-beam digital spectrophotometer. Photoluminescence spectra were also measured at 298 K using a Spex Fluorog-3 spectrophotometer. Prior to the measurements of UV–vis and photoluminescence spectra, samples were calcined in $O_2$ (>2.66 kPa) at 723 K for 1 h and then degassed at 473 K for 1 h. Nitrogen adsorption–desorption isotherms at 77 K and water adsorption–desorption isotherms at 298 K were recorded by using a BEL-SORP max (BEL Japan, Inc.) after degassing of samples under vacuum at 473 K for 2 h.

### 2.4. Catalytic reaction

The epoxidation of cyclooctene to 1,2-epoxy cyclooctane was used as a model reaction. Catalyst (TiSBA-15 or F*n*-TiSBA-15; 50 mg), cyclooctene (1 mmol), acetonitrile (10 ml) and 30% $H_2O_2$ (1.0 ml) were charged into the reaction vessel equipped with a reflux condenser and then heated at 343 K with magnetic stirring under an argon atmosphere. After the reaction, the resulting solution was recovered by filtration and analysed by an internal standard technique using a gas chromatograph (Shimadzu GC-14B with FID detector) equipped with TC-1 capillary column. Biphenyl was used as an internal standard. The turnover number (TON) was defined as the ratio of the amounts of produced 1,2-epoxy cyclooctane to those of Ti-oxide moieties included in each catalyst.

## 3. Results and discussion

### 3.1. Characterization of the local structure of Ti-oxide moieties

The local structure of Ti-oxide moieties incorporated within mesoporous silica (SBA-15) frameworks was investigated by UV–vis measurement. TiSBA-15 exhibited the typical absorption peak at around 210 nm (Fig. 1(A,a)), which can be assigned to the ligand to metal charge transfer (LMCT) transition of tetrahedrally coordinated Ti-oxide moieties [18,22–25]. The absorption band at 200–240 nm and 240–280 nm are attributed to the isolated tetrahedral Ti-oxide monomers and dimers or small oligomers, respectively [18,22–25]. Considering the small absorption at around 250 nm, isolated tetrahedral Ti-oxide monomers, i.e. single-site Ti-oxide moieties, dominantly exist in the frameworks of prepared TiSBA-15. As shown in Fig. 1(A,a–c), the shape and position of absorption spectra was hardly changed after surface modification of TiSBA-15 by TEFS. The photoluminescence (PL) spectra of TiSBA-15 before and after surface modification were shown in Fig. 1(B,a–c). PL spectroscopy provides insight to the local structure of transition metal oxides highly dispersed on various supports or incorporated within the frameworks of porous materials [26]. Each sample exhibited the typical PL spectrum in the wavelength region from 350 to 650 nm upon excitation of its LMCT band of tetrahedrally coordinated Ti-oxide moieties at around 210 nm at 298 K. The formation of charge transfer excited state $[(Ti^{3+}–O^{-})^{*}]$ is brought to the electron transfer from neighbor-

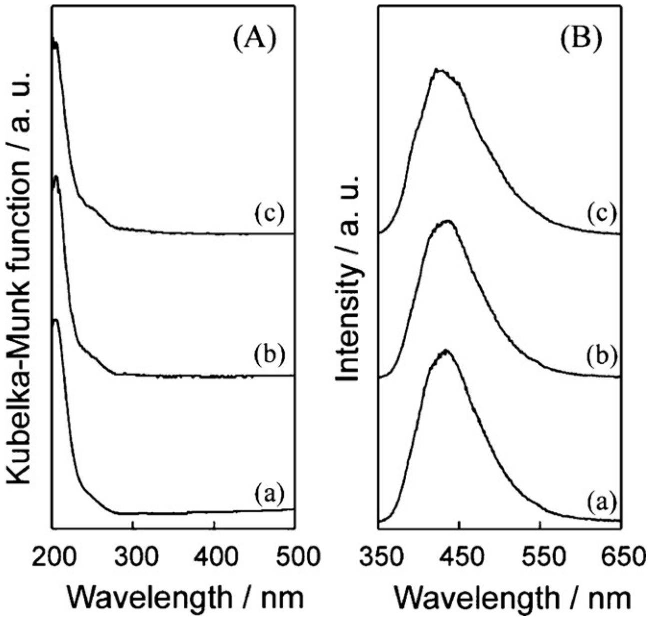

**Fig. 1.** (A) Diffuse reflectance UV–vis spectra and (B) photoluminescence spectra of (a) TiSBA-15, (b) F5-TiSBA-15 and (c) F20-TiSBA-15 measured at 298 K.

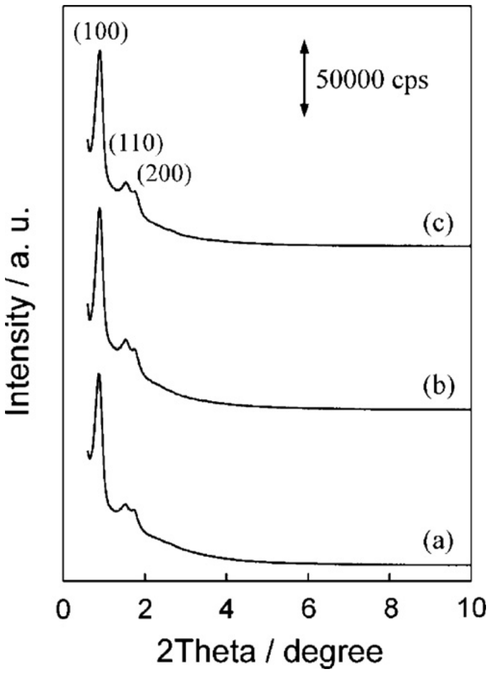

**Fig. 2.** XRD patterns of (a) TiSBA-15, (b) F5-TiSBA-15 and (c) F20-TiSBA-15.

ing oxygen [($O^{2-}$)] to titanium [($Ti^{4+}$)]. This PL can be assigned to the reverse radiative decay process from the thus formed charge transfer excited triplet state [$(Ti^{3+}–O^-)^*$] to the ground state of Ti-oxide moieties having a tetrahedral coordination (Eq. (1)) [18,22–25].

$$Ti^{4+} - O^{2-} \underset{h\nu'}{\overset{h\nu}{\rightleftarrows}} (Ti^{3+} - O^-)^* \quad (1)$$

The PL peak position and intensity of F*n*-TiSBA-15 ($n$ = 5, 20) were scarcely changed as compared to those of original TiSBA-15 (Fig. 1(B,a–c)). These results indicated that the local structure of Ti-oxide moieties was hardly affected by grafting of TEFS on their surfaces.

### *3.2. Investigations on the characteristics of TiSBA-15 and Fn-TiSBA-15*

The presence of mesoporous structure was confirmed by XRD measurements. As shown in Fig. 2, the three typical peaks, which can be indexed as the (1 0 0), (1 1 0) and (2 0 0) reflections, were clearly observed in the region of $2\theta < 5°$. These results suggested the formation of single-site Ti-moieties containing hexagonal mesoporous silica (TiSBA-15) with highly ordered structures [20,21]. The XRD peak intensity of F*n*-TiSBA-15 ($n$ = 5, 20) was slightly decreased as compared to that of original TiSBA-15, while the clear diffraction peaks were observed even after modification by TEFS (Fig. 2(b,c)). The nitrogen adsorption–desorption measurement was also performed to elucidate characteristics of TiSBA-15 such as pore size distribution, pore volume and specific surface area before and after surface modification. Fig. 3 shows the nitrogen adsorption–desorption isotherm of each sample at 77 K. The typical type IV isotherm was observed with steep hysteresis at high relative pressure ($P/P_0 = 0.7$). The obtained results from the analyses of these isotherms were summarized in Table 1. The small loss of large surface area of TiSBA-15 was observed after surface modification. The pore size distribution curve of each sample was also shown in inset of Fig. 3. The average pore diameter was estimated to be ca. 8.0 nm. The distribution peak became slightly lower with increasing the loading amount of TEFS due to the decreases of pore volumes. These results indicated that the mesoporous structure of prepared samples was maintained after surface modification by TEFS, which is in accordance with the results of XRD investigations.

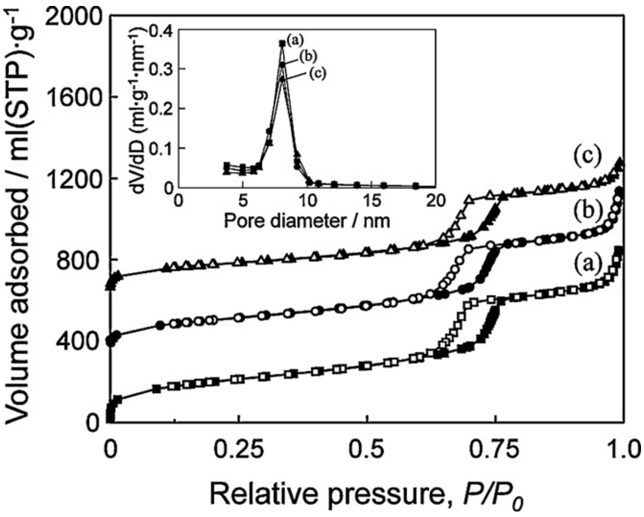

**Fig. 3.** Nitrogen adsorption–desorption isotherms and pore size distribution curve (inset) of (a) TiSBA-15, (b) F5-TiSBA-15 and (c) F20-TiSBA-15.

The presence of fluorine moieties (≡Si–F) on the surface of F*n*-TiSBA-15 were confirmed by XPS analysis (data not shown). F*n*-TiSBA-15 exhibited the $F_{1s}$ XPS peak at around 689 eV, which was assigned to the covalent F atoms [6,27]. In the case of original TiSBA-15, the $F_{1s}$ XPS peak was hardly observed in the region from 680 to 700 eV. These results indicated that the fluorine moieties (≡Si–F) were anchored on TiSBA-15 surface through the surface modification process as shown in Scheme 1.

The variation of the surface hydrophilic–hydrophobic properties of TiSBA-15 before and after surface modification by TEFS was investigated by measurements of water adsorption–desorption isotherms. As shown in Fig. 4, the water adsorption capacity of samples was decreased in response to an increase of grafted amount of TEFS on TiSBA-15. As shown in Table 1, relative water adsorption capacity of F*n*-TiSBA-15 at $P/P_0 = 0.6$ was clearly decreased with increasing the grafted amount of TEFS. The interaction between the

**Table 1**
Characteristics of TiSBA-15 and hydrophobically modified TiSBA-15.

| Sample | TEFS loading, wt% | $S_{BET}$, $m^2\ g^{-1}$ | Relative percentage of $S_{BET}$[a], % | Pore volume[b], $cm^3\ g^{-1}$ | Relative water adsorption capacity[c], % |
|---|---|---|---|---|---|
| TiSBA-15 | 0 | 730 | 100 | 1.12 | 100 |
| F2-TiSBA-15 | 2 | 609 | 83.4 | 1.01 | 62 |
| F5-TiSBA-15 | 5 | 582 | 79.7 | 0.98 | 51 |
| F10-TiSBA-15 | 10 | 541 | 74.1 | 0.95 | 41 |
| F20-TiSBA-15 | 20 | 468 | 64.1 | 0.88 | 15 |

[a] Relative percentages to BET surface area of TiSBA-15.
[b] Determined from BJH method.
[c] Relative percentages to water adsorption capacity of TiSBA-15 at $P/P_o = 0.6$.

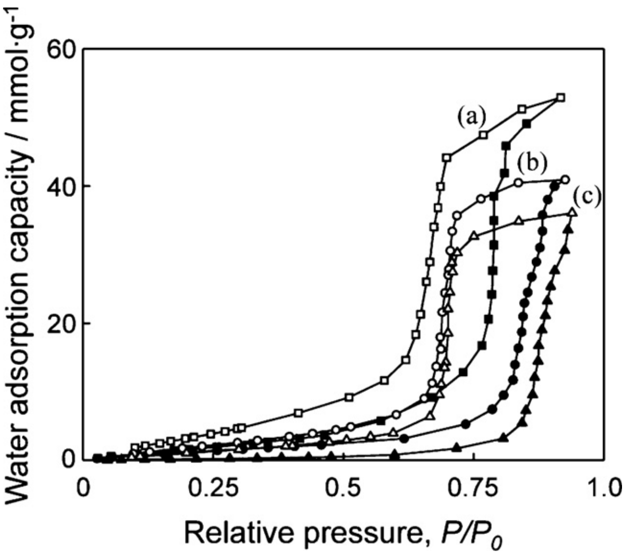

**Fig. 4.** Water adsorption–desorption isotherms of (a) TiSBA-15, (b) F5-TiSBA-15 and (c) F20-TiSBA-15 measured at 298 K.

surface of samples and water molecules become weak after surface modification by TEFS, leading to the decreases of adsorbed amount of water at lower relative pressure ($P/P_0$). The sharp increases of water adsorption capacity at high relative pressure were attributed to the capillary condensation of water into the mesopores. The hydroxyl groups on the surface of TiSBA-15 were substituted by fluorine moieties, which can anchor the hydrophobic fluorine moieties as well as reduce the number of hydroxyl groups on the surface of TiSBA-15. Therefore, the differences in the amount of adsorbed water can be ascribable to the different concentrations of surface hydroxyl groups and the effect of the hydrophobic fluorine moieties in each sample.

### *3.3. Catalytic reaction on TiSBA-15 and Fn-TiSBA-15*

Among a large variety of heterogeneous catalysts, Ti-containing porous siliceous materials are focused as suitable catalysts for oxidation reaction using $H_2O_2$ or alkyl hydroperoxide as an oxidant [11–14]. The oxidation reaction with high selectivity of desired compounds is of importance in the production of fine chemicals. In order to clarify the effect of the surface hydrophobic modification of TiSBA-15 on their potential catalytic performances, the liquid-phase oxidation of cyclooctene using aqueous $H_2O_2$ was performed as a model reaction. Fig. 5 shows the turnover number (TON) in the oxidation of cyclooctene to 1,2-epoxy cyclooctane on TiSBA-15 before and after surface modification. The corresponding 1,2-epoxy cyclooctane was produced with high selectivity as high as 97% on each catalyst. The higher catalytic performance was observed for F2-TiSBA-15 and F5-TiSBA-15, which exhibited the less hydrophilicity compared to original TiSBA-15. Meanwhile, the catalytic performance was decreased with increasing the grafted amount of TEFS. The improvement of catalytic performance was hardly observed in the case of F10-TiSBA-15 and F20-TiSBA-15, although these catalysts showed the good hydrophobicity compared to F2-TiSBA-15 and F5-TiSBA-15. These results suggest that the catalytically active single-site Ti-oxide moieties within the frameworks of TiSBA-15 are gradually covered by surface modification with increasing the grafted amount of TEFS. In fact, the catalytic performance of TiSBA-15 and F10-TiSBA-15 was comparable, while these catalysts showed different surface hydrophilic–hydrophobic properties as a result of surface modification by TEFS. Therefore, the surface modification with suitable amount of TEFS without covering largely of the underlying catalytically active Ti-oxide moieties was effective for enhancement of catalytic performances.

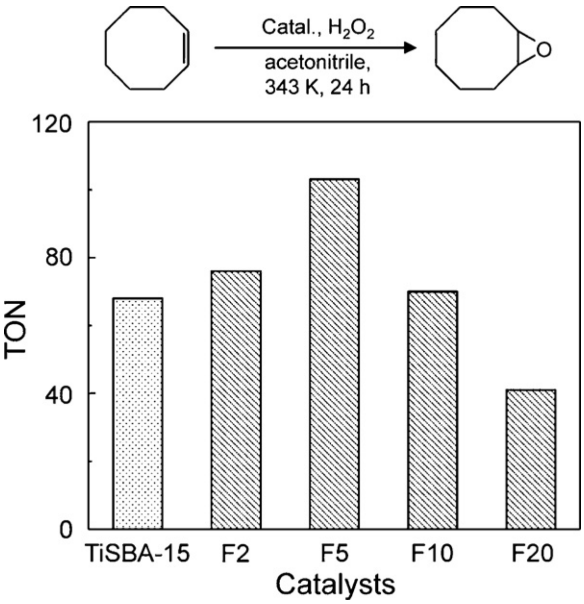

**Fig. 5.** The turnover number (TON) for selective oxidation of cyclooctene to 1,2-epoxy cyclooctane using aqueous $H_2O_2$ at 343 K on TiSBA-15 and F*n*-TiSBA-15 ($n = 2$, 5,10 and 20. These catalysts were denoted as F2, F5, F10 and F20, respectively). Reaction time: 24 h.

## 4. Conclusions

Through the post functionalization of TiSBA-15 by using TEFS as a silylation reagent, the hydrophobic modification of TiSBA-15 surface was successfully achieved without the loss of large surface area and mesoporous structure. The comparative studies on the oxidation reaction of cyclooctene to 1,2-epoxy cyclooctane using aqueous $H_2O_2$ as an oxidant revealed that the catalytic performance of TiSBA-15 was enhanced by the modification of them by suitable amount of TEFS. The enhancement of catalytic performance by this simple post modification was attributed to improving the hydrophobicity of TiSBA-15 surface.

## Acknowledgement

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## References

[1] A. Stein, B.J. Melde, R.C. Schroden, Adv. Mater. 12 (2000) 1403.
[2] A.P. Wight, M.E. Davis, Chem. Rev. 102 (2002) 3589.
[3] K. Moller, T. Bein, Chem. Mater. 10 (1998) 2950.
[4] T. Kimura, M. Suzuki, M. Maeda, S. Tomura, Microporous Mesoporous Mater. 95 (2006) 213.
[5] Y. Kuwahara, T. Kamegawa, K. Mori, H. Yamashita, Chem. Commun. (2008) 4783.
[6] Y. Kuwahara, K. Maki, Y. Matsumura, T. Kamegawa, K. Mori, H. Yamashita, J. Phys. Chem. C 113 (2009) 1552.
[7] H. Yamashita, K. Mori, Chem. Lett. 36 (2007) 348.
[8] T. Kamegawa, R. Takeuchi, M. Matusoka, M. Anpo, Catal. Today 111 (2006) 248.
[9] H. Yamashita, K. Yoshizawa, M. Ariyuki, S. Higashimoto, M. Che, M. Anpo, Chem. Commun. (2001) 435.
[10] T. Kamegawa, J. Morishima, M. Matsuoka, J.M. Thomas, M. Anpo, J. Phys. Chem. C 111 (2007) 1076.
[11] B. Notari, Catal. Today 18 (1993) 163.
[12] J.M. Thomas, R. Raja, D.W. Lewis, Angew. Chem. Int. Ed. 44 (2008) 6456.

[13] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485.
[14] P. Wu, T. Tatsumi, Catal. Surv. Asia 8 (2004) 137.
[15] K. Mori, K. Sugihara, Y. Kondo, T. Takeuchi, S. Morimoto, H. Yamashita, J. Phys. Chem. C 112 (2008) 16478.
[16] Y. Goa, P. Wu, T. Tatsumi, J. Phys. Chem. B 108 (2004) 4242.
[17] J. Sonoda, T. Kamegawa, Y. Kuwahara, K. Mori, H. Yamashita, Bull. Chem. Soc. Jpn. 83 (2010) 592.
[18] K. Ikeue, H. Yamashita, M. Anpo, J. Phys. Chem. B 105 (2001) 8350.
[19] H. Yamashita, K. Maekawa, H. Nakao, M. Anpo, Appl. Surf. Sci. 237 (2004) 393.
[20] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
[21] W.H. Zhang, J. Lu, B. Han, M. Li, J. Xiu, P. Ying, C. Li, Chem. Mater. 14 (2002) 3413.
[22] H. Yamashita, S. Kawasaki, Y. Ichihashi, M. Harada, M. Takeuchi, M. Anpo, G. Stewart, M.A. Fox, C. Louis, M. Che, J. Phys. Chem. B 102 (1998) 5870.
[23] L. Marchese, T. Maschmeyer, E. Gianotti, S. Coluccia, J.M. Thomas, J. Phys. Chem. B 101 (1997) 8836.
[24] L. Marchese, E. Gianotti, V. Dellarocca, T. Maschmeyer, F. Rey, S. Coluccia, J.M. Thomas, Phys. Chem. Chem. Phys. 1 (1999) 585.
[25] M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, E. Giamello, J. Phys. Chem. 89 (1985) 5017.
[26] G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Wiley-VCH, 2008.
[27] Y.Q. Wang, P.M.A. Sherwood, Chem. Mater. 16 (2004) 5427.