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The effect of the framework structure on the chemical properties of the vanadium oxide species incorporated within zeolites

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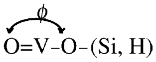
Abstract

V-silicalite catalysts (VS-1 and VS-2) prepared by hydrothermal synthesis have been studied by ESR, XAFS (XANES and EXAFS) and photoluminescence spectroscopy. The in situ characterization of these V-silicalites shows that vanadium is present within the zeolitic framework as a highly dispersed tetrahedrally coordinated V-oxides, VO_4 unit, having a short V=O bond length. Photoluminescence spectroscopy in static and dynamic mode, as well as XAFS studies allow to detect in the V-silicalites different V species than that present in V-HMS or V/SiO_2, in terms of V=O bond length, vibrational energy,  $\overset{\phi}{\overbrace{O{=}V{-}O}}{-}(Si, H)$ bond angle and lifetime of the excited triplet state. It is suggested that the combined contribution of the neighboring Si–OH group attached to the VO_4 unit and the zeolitic rigid framework structure of V-silicalites cause a more significant and pronounced effect on the chemical properties of the VO_4 unit than the flexible structure of V-HMS or V/SiO_2. Moreover, the dynamic quenching of the phosphorescence by the addition of reactant molecules such as NO or propane indicates that the V species in the excited triplet state can be expected to be the active sites for the photocatalytic reactions.

Keywords: Vanadium silicalites; ESR; XAFS; Photoluminescence

1. Introduction

In recent years, increasing attention has been paid to the study of new zeolitic materials, microporous metallosilicates as well as transition metal containing mesoporous molecular sieves, due to their unique and fascinating catalytic properties [1–10]. These characteristic properties enable their wide applications in well-defined and restricted reaction fields, not only in the photochemistry of adsorbed guest molecules included within the inter-surfaces of the host zeolites [11–13] but also in photocatalytic reactions such as the decomposition of NO [14–20], reduction of CO_2 with H_2O [21–24] and the isomerization of 2-butene [25,26].

V-silicalites have been shown to have different and/or, in some cases, improved photocatalytic performance as compared with supported vanadium oxide catalysts [27]. It is thus very important to obtain detailed information on the effect of the zeolitic framework structure on the function of the metal-oxide species prepared within the zeolite for the design and

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development of highly active and selective photocatalytic reaction systems. However, an identification of the chemical nature and localization of the active V-oxide species within the zeolitic framework as well as a distinction of their features with those of the V-oxide species present within mesoporous V-HMS or supported V-oxide catalysts are yet little known.

In this paper, the in situ characterization of the local structures of various types of V-oxide catalysts by photoluminescence, XAFS (XANES and EXAFS), ESR, FT-IR, UV-Vis and XRD is presented. Special attention has been focused on a clarification of the local structure of the V-oxide species incorporated within the zeolitic framework and a comparison of their features with those of the V-oxide species present within the mesoporous V-HMS molecular sieves or on the supported V-oxide catalyst.

2. Experimental

Two types of vanadium silicalites (VS-1 and VS-2, both with 0.2 wt.% V) were prepared by hydrothermal synthesis using tetraethylorthosilicate (TEOS), $VOSO_4$ and VCl_3 as the starting materials, and tetrapropylammonium hydroxide (TPAOH) and tetrabutylammonium hydroxide (TBAOH) as a structure directing agent, respectively, upon conditions reported in previous literature [28,29]. The V-HMS mesoporous molecular sieve (with 0.2 wt.% V) was synthesized using tetraethylorthosilicate (TEOS), $VOSO_4$ and dodecylamine (DDA) as the structure directing agent, upon conditions reported in previous literature [30]. The V/SiO_2 catalyst (with 0.2 wt.% V) was prepared by an impregnation of aqueous solution of NH_4VO_3 on the surface of SiO_2. Calcination of the samples was carried out in dry air at 773 K for 8 h. Prior to spectroscopic measurements, the catalyst was degassed at 723 K, heated in O_2 at the same temperature and then finally evacuated at 473 K. The photoluminescence and lifetimes measurements were performed at 77 K with a Shimadzu RF-501 spectrofluorophotometer and an apparatus for lifetime measurements, respectively. The XAFS (XANES and EXAFS) spectra were obtained at the BL-7C facility of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba. The V K-edge absorption spectra were recorded in the fluorescence mode at 295 K with a ring energy of 2.5 GeV. Data reduction was performed using a FACOM M1800 computer at the Kyoto University Data Processing Center [31]. XRD patterns were obtained with a Shimadzu XD-D1 using Cu Kα radiation. FT-IR and UV-Vis spectra were recorded at 295 K with a Shimadzu FT-IR-8500 and a Shimadzu UV-2200A spectrophotometers, respectively. The ESR spectra were recorded with a JEOL-2X spectrometer (X-band) at 77 K.

3. Results and discussion

The XRD and UV-Vis studies indicated (results not shown) that the VS-1 and VS-2 zeolites have silicalite-1 (MFI) and silicalite-2 (MEL) structures, respectively, and no aggregated V-oxide species are formed. A main diffraction line at $2\theta = 22.5$ was present for VS-1 zeolite in lower 2θ value than that of silicalite-1. It indicates the expansion of the VS-1 zeolite lattice due to the incorporation of V atoms in the framework sites. Moreover, FT-IR spectral investigations which showed significant bands at around 960–970 cm^{-1} on V-silicalites due to the stretching mode of a SiO_4 unit bonded to a metal ion also indicate the successful incorporation of vanadium ions into the zeolite framework, in agreement with previously reported data [28,29,32].

Moreover, the XRD and UV-Vis studies of V-HMS molecular sieve showed that this catalyst has the same structure as V-free HMS and no aggregated V-oxides are present [27].

The ESR technique was applied to investigate the nature and coordination of the V-oxide species present within the zeolite framework by monitoring the V^{4+} ions which were produced by the photoreduction of the catalyst with H_2 at 77 K. Photoreduction of the catalysts is so mild that no local structural rearrangement around the surface vanadium ions occurred. As shown in Fig. 1(a), the photoreduced VS-1 shows an ESR signal of eight equally spaced lines due to the $I = 7/2$ spin of the V atom.

The ESR parameters of this signal is in good agreement with those of the V^{4+} ions located in tetrahedral coordination [33]. It indicates that the V ions were incorporated upon synthesis in the zeolitic framework as tetrahedral V^{5+} species. The addition of a small

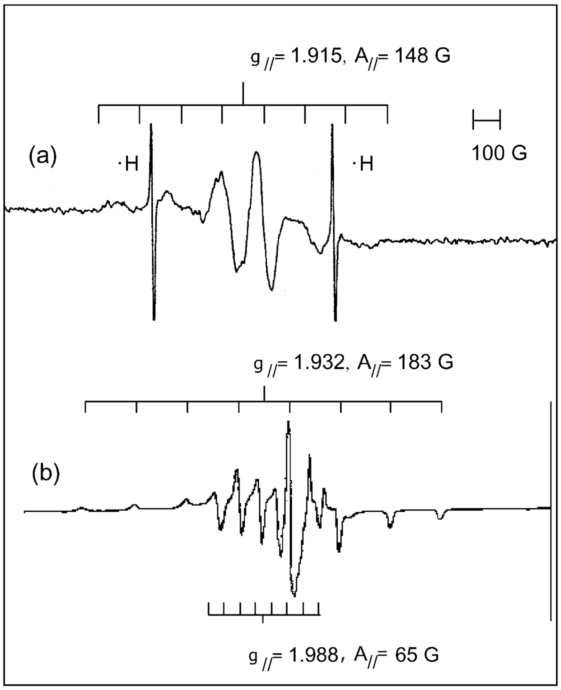


Fig. 1. ESR spectra of: (a) the photo-formed V^{4+} ions of the dehydrated VS-1 catalyst and (b) the hydrated VS-1 formed by adding a small amount of water into (a). V^{4+} ions were formed by UV irradiation of the VS-1 catalyst carried out at 77 K with a high pressure mercury lamp ($\lambda > 280$ nm) in the presence of 20 Torr of H_2.

amount of water into the catalyst led to formation of new ESR signal (Fig. 1(b)). This new signal can be attributed to distorted octahedral VO^{2+} ions, in agreement with previously reported data [33]. The change in the coordination state upon exposure of VS-1 to water molecules suggests that most of the V-oxide species exist on the surface of the zeolite where H_2O molecules are easily accessible. The ESR spectral parameters ($g_{//}$-tensors and $A_{//}$ values) of various types of V-oxide catalysts are given in Table 1.

Table 1
ESR parameters ($g_{//}$-tensors and $A_{//}$ values) and type of V-oxide species of V-oxide catalysts after photoreduction with H_2 at 77 K

Catalyst	Coordination	T (K)	$g_{//}$	$A_{//}$ (G)
VS-1	(V^{4+}) trigonal pyramid	77	1.92	148
VS-2	(V^{4+}) trigonal pyramid	77	1.88	142
V-HMS	(V^{4+}) trigonal pyramid	77	1.90	148
V/SiO_2	(V^{4+}) trigonal pyramid	77	1.91	144

They indicate that all types of V-oxide catalysts include highly dispersed tetrahedrally coordinated V-oxide species. The ESR data do not allow to distinguish the differences between the local structures of the V-oxide species present in different V-loaded materials. Moreover, the calcined VS-1 did not exhibit any ESR signal at 77 K, indicating the complete oxidation of V^{4+} to V^{5+} while no aggregated V-oxides could be observed.

In order to better describe the local structure of the V-oxide species present in the V-loaded materials, XAFS was used (both XANES and EXAFS). Fig. 2 shows the V K-edge XANES spectra of the dehydrated VS-1 (spectrum A), VS-2 (spectrum B), V/SiO_2 (spectrum C) catalysts and the reference $VO(O–i–C_3H_7)_3$ compound (spectrum D).

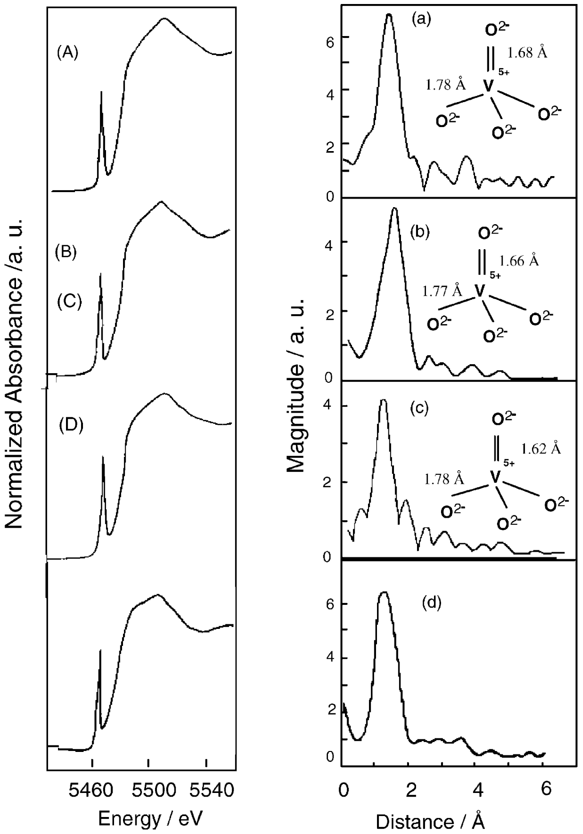


Fig. 2. XANES (left) and Fourier transforms of normalized k^3 weighted EXAFS (right) spectra of the VS-1 (A, a), VS-2 (B, b), V/SiO_2 (C, c) catalysts and the $VO(O–i–C_3H_7)_3$ compound (D, d) used as the reference sample.

The shape of the XANES spectra provides useful and detailed information on the local structure and coordination geometry of the central vanadium atoms [31]. A characteristic feature of both XANES spectra is the appearance of a pre-edge peak due to the so-called 1s–3d transition which is mainly caused by a mixing of the 2p orbitals of the oxygen atoms with the 3d orbitals of the vanadium atoms. This p–d mixing suggests the presence of a terminal monoxo-vanadyl group (V=O) [31]. The high intensity of the pre-edge peak and a quite similar XANES spectra of VS-1, VS-2 and V/SiO_2 (Fig. 2(A–C)) to that of the VO(O–i–C_3H_7)$_3$ compound (Fig. 2(D)), with four-fold coordinated vanadium atoms, indicate that VS-1, VS-2 and V/SiO_2 catalysts consists a V atoms in the tetrahedral coordination.

Furthermore, in the Fourier transforms of a normalized k^3 weighted EXAFS (FT-EXAFS) spectra of the dehydrated VS-1, VS-2 and V/SiO_2 only a single peak at about 1.6 Å (without phase-shift correction) is observed due to the presence of neighboring oxygen atoms (V–O), suggesting that vanadium ions are highly dispersed in these catalysts. In the curve fitting analysis of the FT-EXAFS spectra at 295 K, the best fitting were obtained with one oxygen in the shorter V–O distance of 1.68 Å for VS-1, of 1.66 Å for VS-2 and of 1.62 Å for V/SiO_2 and three oxygen atoms in the long V–O distance of 1.78 Å for VS-1 and V/SiO_2 and of 1.77 Å for VS-2.

Thus, the XAFS (XANES and EXAFS) spectra of the dehydrated VS-1, VS-2, V-HMS and V/SiO_2 show that vanadium ions are highly dispersed within the zeolite framework and on the SiO_2 surface having one oxygen in the shorter V–O distance and three oxygen atoms in the long V–O distance. The results obtained by curve fitting analysis of the various types of V-oxide catalysts are shown in Table 2. These results clearly suggest that the tetrahedrally coordinated V-oxide species are highly dispersed on these catalysts and the V=O bond distance of the V-silicalites are slightly elongated as compared with that of V-HMS or V/SiO_2.

Fig. 3 compares the phosphorescence spectra of VS-1 and V/SiO_2 catalysts. Both catalysts exhibit the phosphorescence spectra with maxima at around 450–550 nm with a well-resolved vibrational fine structure. These phosphorescence spectra are in good agreement with those previously reported for

Table 2
Results of curve fitting of V K-edge FT-EXAFS data with various types of V-oxide catalysts

Catalyst	Shell	*R* (Å)	CN
VS-1	V–O	1.68	1.0
		1.78	3.0
VS-2	V–O	1.66	1.0
		1.77	3.0
V-HMS	V–O	1.63	0.96
		1.77	3.1
V/SiO_2	V–O	1.62	0.95
		1.78	3.0
V_2O_5	V–O	1.59	1.0
		1.78	1.0
		1.88	2.0
		2.02	1.0

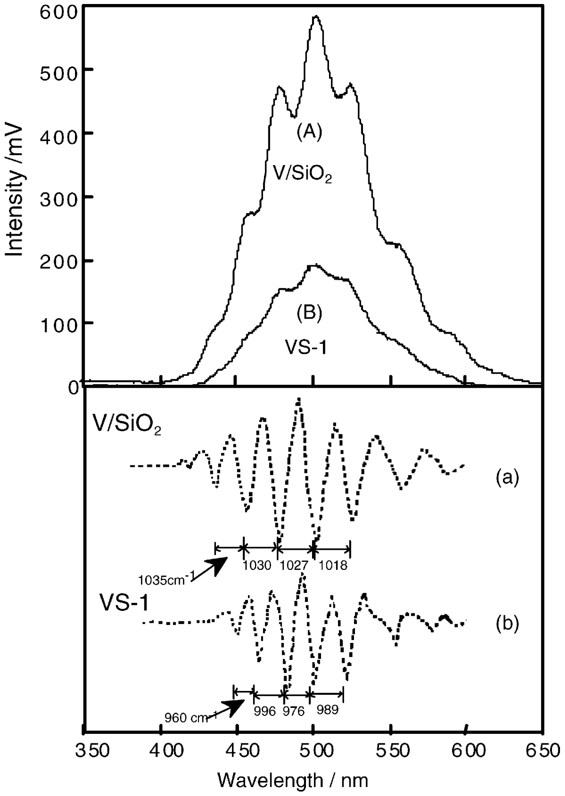


Fig. 3. Phosphorescence spectra of V/SiO_2 (A) and VS-1 (B) dehydrated at 473 K and their second-derivative spectra (a) and (b), respectively.

well-defined highly dispersed V-oxides anchored on Vycor glass or silica [34–38]. The fine structure of phosphorescence spectra corresponds to the transitions from the lowest vibrational level of the excited triplet state T_1 (V^{4+}–O^-) to the various vibrational levels of the ground state S_0 ($V^{5+}{=}O^{2-}$) [2].

The phosphorescence spectra scarcely changed when the excitation wavelengths were changed and decayed as a single exponential, suggesting that only one kind of V-oxide species is present in each catalyst. The phosphorescence and absorption (not shown) spectra can be attributed to the following charge transfer processes (Eq. (1)) on the surface vanadyl groups of the tetrahedrally coordinated V species involving an electron transfer from O^{2-} to V^{5+} and a reverse radiative decay process, i.e. the charge transfer from the excited triplet state to the singlet ground state [2].

$$(V^{5+}{=}O^{2-}) \underset{\text{phosphorescence}}{\overset{\text{absorption}}{\rightleftarrows}} (V^{4+}{-}O^{-})^{*} \tag{1}$$

The appearance of a strong phosphorescence for VS-1 catalyst enables us to probe the accessibility of the V-oxides present in this catalyst towards various molecules [18]. The addition of NO or propane into VS-1 leads to an efficient quenching of the phosphorescence as well as a shortening of the phosphorescence lifetimes (results not shown). It can be expected that the excited triplet state of the tetrahedrally coordinated V-oxide species located at the positions accessible to the added NO or propane are active species.

The second-derivative phosphorescence spectra of the V-oxide species of VS-1 and V/SiO$_2$ (Fig. 3) allow to determine the energy separation between the (0 → 0) and (0 → 1) vibrational transitions, in good agreement with the vibrational energy of the surface V=O bond obtained by IR or Raman measurements for various vanadia supported catalysts [2]. As shown in Table 3, VS-1 and VS-2 exhibit very similar energy separation of 960 and 980 cm^{-1}, respectively, which are slightly different from that observed for V-HMS (1010 cm^{-1}) and V/SiO$_2$ (1035 cm^{-1}). The vibrational energy determined for the V-oxide species present in these V-loaded materials decreases with an increasing in the V=O bond length from 1.62 to 1.68 Å in the following order: $V/SiO_2 <$ V-HMS $<$ VS-2 $<$ VS-1.

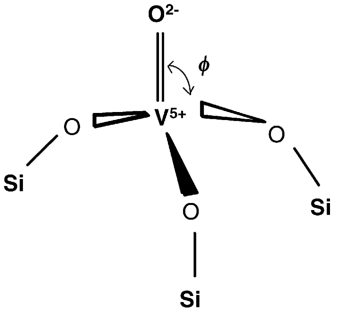
Moreover, the lifetimes of the excited triplet state determined at 77 K from the decay curves of the phosphorescence of the VS-1, VS-2, V-HMS and V/SiO$_2$ catalysts are equal 5.8, 6.9, 7.6 and 8.4 ms, respectively. The increase in the lifetime from 5.8 to 8.4 ms in the sequence, VS-1 $<$ VS-2 $\ll$ V-HMS $<$ V/SiO_2, can be interpreted in terms of an increase in the distortion of the VO_4 unit and a decrease in the V=O bond length [41,42].

The VO_4 units incorporated within the V-silicalites have a T_d-like symmetrical structure and exhibit a smaller $\overset{\phi}{\overparen{\mathrm{O{=}V{-}O}}}\mathrm{{-}(Si,\,H)}$ bond angle (ϕ) than that of V-HMS or V/SiO$_2$, on the basis of the valence shell electron pair repulsion (VSEPR) arguments [39,40] (see Scheme 1).

It is known that V-silicalites have a restraint and rather rigid framework structure, while V-HMS has the greatly flexible structure. Moreover, the VO_4 units of V-silicalites are in a weak interaction with the neighboring OH groups [27,41,42]. Our studies indicate that the rigid framework structure of V-silicalites causes

Table 3
Comparison of various physical and chemical parameters of the V-oxide species formed within the zeolite framework and SiO$_2$ surface

	VS-1	VS-2	V-HMS	V/SiO$_2$
Pore size (Å)	5.5	5.6	20–40	–
XAFS				
V=O bond (Å)	1.68	1.66	1.63	1.62
V–O bond (Å)	1.78	1.77	1.77	1.78
Coordination	Trigonal pyramid	Trigonal pyramid	Trigonal pyramid	Trigonal pyramid
V=O vibrational energy (cm^{-1})	960	980	1010	1035
Lifetime of the excited state (ms)	5.8	6.9	7.6	8.4
$\overset{\phi}{\overparen{\mathrm{O{=}V{-}O}}}\mathrm{{-}(Si,\,H)}$ bond angle (ϕ)	1	≤2	<3	≤4



Scheme 1.

a much stronger effect on the electronic properties of the VO_4 unit than the flexible structure of V-HMS or V/SiO_2.

4. Conclusions

The investigations of V-silicalites (VS-1 and VS-2) by means of various spectroscopies clearly showed that they include the isolated V-oxides with the trigonal pyramid within their zeolitic framework structure. Photoluminescence spectroscopy in static and dynamic mode, as well as XAFS studies allow to detect different V species in the V-silicalites than that present in V-HMS or V/SiO_2, in terms of V=O bond length, vibrational energy, $\overset{\phi}{\widehat{O{=}V{-}O}}{-}(\mathrm{Si,\ H})$ bond angle and lifetime of the excited triplet states. The interaction of neighboring Si–OH group to the VO_4 unit and the zeolitic rigid framework structure of V-silicalites cause a more significant and pronounced effect on the chemical properties of the VO_4 unit than the flexible structure of V-HMS or V/SiO_2. Moreover, the dynamic quenching of the phosphorescence by the addition of reactant molecules such as NO or propane indicates that the V species in its excited triplet state can be expected to be the active sites for the photocatalytic reactions.

References

[1] M. Anpo, Photofunctional Zeolites, NOVA Science Publishers Inc., Huntington, New York, 2000, p. 148.
[2] M. Anpo, M. Che, Adv. Catal. 44 (1999) 119, and references therein.
[3] B. Notari, Adv. Catal. 41 (1996) 253, and references therein.
[4] A. Corma, Chem. Rev. 97 (1997) 2373.
[5] K.I. Zamaraev, J.M. Thomas, Adv. Catal. 41 (1996) 335.
[6] P.B. Simon, R.A. van Santen, Adv. Catal. 42 (1998) 1.
[7] P.B. Venuto, Microp. Mesop. Mater. 2 (1994) 297.
[8] T. Tatsumi, M. Nakamura, S. Negishi, H. Tominaga, J. Chem. Soc., Chem. Commun. (1990) 476.
[9] T. Maschmeyer, F. Rey, G. Sankar, J.M. Thomas, Nature 378 (1995) 159.
[10] S. Bordiga, S. Coluccia, C. Lamberti, L. Marchese, A. Zecchina, F. Boscherini, F. Buffa, F. Genoni, G. Leofanti, G. Petrini, G. Vlaic, J. Phys. Chem. 98 (1994) 4125.
[11] J.M. Thomas, Chem. Rev. 93 (1993) 301.
[12] N.J. Turro, Z. Zhang, in: M. Anpo, T. Matsuura (Eds.), Photochemistry on Solid Surfaces, vol. 47, Elsevier, Amsterdam, 1989, p. 197.
[13] V. Ramamurthy, in: M. Anpo (Ed.), Surface Photochemistry, Wiley, Chichester, 1996, p. 65.
[14] M. Anpo, Catal. Surv. Jpn. 1 (1997) 169.
[15] M. Anpo, S.G. Zhang, H. Mishima, M. Matsuoka, H. Yamashita, Catal. Today 39 (1997) 159.
[16] H. Yamashita, Y. Ichihashi, M. Anpo, M. Hashimoto, C. Louis, M. Che, J. Phys. Chem. 100 (1996) 16041.
[17] S.G. Zhang, Y. Ichihashi, H. Yamashita, T. Tatsumi, M. Anpo, Chem. Lett. (1996) 895.
[18] M. Anpo, S.G. Zhang, S. Higashimoto, M. Matsuoka, H. Yamashita, Y. Ichihashi, Y. Matsumura, Y. Souma, J. Phys. Chem. B 103 (1999) 9295.
[19] S. Higashimoto, S.G. Zhang, H. Yamashita, M. Anpo, Chem. Lett. (1997) 1127.
[20] S. Higashimoto, R. Tsumura, S.G. Zhang, H. Yamashita, C. Louis, M. Che, M. Anpo, Chem. Lett. (2000) 408.
[21] H. Yamashita, Y. Fujii, Y. Ichihashi, S.G. Zhang, K. Ikeue, D.R. Park, K. Koyano, T. Tatsumi, M. Anpo, Catal. Today 45 (1998) 221.
[22] M. Anpo, H. Yamashita, K. Ikeue, Y. Fujii, S.G. Zhang, Y. Ichihashi, D.R. Park, Y. Suzuki, K. Koyano, T. Tatsumi, Catal. Today 44 (1998) 327.
[23] M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, M. Honda, J. Phys. Chem. 101 (1997) 2632.
[24] M. Anpo, K. Chiba, J. Mol. Catal. 74 (1992) 207.
[25] S.G. Zhang, S. Higashimoto, H. Yamashita, M. Anpo, J. Phys. Chem. B 102 (1998) 5590.
[26] S.G. Zhang, M. Ariyuki, H. Mishima, S. Higashimoto, H. Yamashita, M. Anpo, Microp. Mesop. Mater. 21 (1998) 621.
[27] S. Higashimoto, M. Matsuoka, S.G. Zhang, H. Yamashita, O. Kitao, H. Hidaka, M. Anpo, Microp. Mesop. Mater. 48 (2001) 329.
[28] P.R. Hari Prasad Rao, A. Ramaswamy, V.P. Ratnasamy, J. Catal. 137 (1992) 225.
[29] M.S. Rigutto, H. van Bekkum, Appl. Catal. 68 (1991) 297.
[30] W. Zhang, P.T. Tanev, T.J. Pinnavaia, J. Chem. Soc., Chem. Commun. (1996) 979.
[31] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 1 (1988) 2987.

[32] M.A. Camblor, A. Corma, J. Perez-Pariente, J. Chem. Soc., Chem. Commun. (1993) 557.
[33] G. Centi, S. Perathoner, F. Trifiro, A. Aboukais, C.F. Aïssi, M. Guelton, J. Phys. Chem. 96 (1992) 2617.
[34] A.M. Gritscov, V.A. Shvets, V.B. Kazansky, Chem. Phys. Lett. 35 (1975) 511.
[35] M. Anpo, I. Tanahashi, Y. Kubokawa, J. Phys. Chem. 84 (1980) 3340.
[36] M. Anpo, M. Sunamoto, T. Fujii, H. Patterson, M. Che, Res. Chem. Intermed. 11 (1989) 245.
[37] M. Anpo, M. Sunamoto, M. Che, J. Phys. Chem. 93 (1989) 1187.
[38] M. Anpo, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 2, Wiley, Weinheim, 1997, p. 664, and references therein.
[39] S. Dzwigaj, M. Matsuoka, R. Franck, M. Anpo, M. Che, J. Phys. Chem. B 102 (1998) 6309.
[40] S. Dzwigaj, M. Matsuoka, M. Anpo, M. Che, J. Phys. Chem. B 104 (2000) 6012.
[41] I.L. Moudrakovski, A. Sayari, C.I. Ratcliffe, J.A. Ripmeester, K.F. Preston, J. Phys. Chem. 98 (1994) 10895.
[42] T. Sen, A.V. Ramaswamy, P.R. Rajamohanan, S.J. Sivasanker, J. Phys. Chem. 100 (1996) 3809.