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Development of the efficient TiO_2 photocatalyst in photoassisted selective catalytic reduction of NO with NH_3

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Abstract

Photoassisted selective catalytic reduction (photo-SCR) of NO with NH_3 in the presence of O_2 takes place at room temperature over TiO_2 photocatalyst. From the results of photo-SCR reaction over various TiO_2, we found that JRC-TIO-11 exhibited the best activity. The reaction activity correlated to the amount of acid sites of TiO_2, but did not depend on the specific surface area and crystal diameter. The mixture of rutile and anatase shows higher activity than any of the corresponding TiO_2 single phase catalyst.

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Keywords: TiO_2; Photocatalyst; SCR; NH_3; NO

1. Introduction

NO_x is an air pollutant and causes town smog and acid rain. Therefore, the development of the removal technology of NO_x, which is exhausted from the stationary emission source and the mobile emission source, is necessary. At present from the stationary emission sources such as a power plant, a waste incinerator and an industrial boiler, NO_x in the exhaust gas is removed by the selective catalytic reduction system with NH_3 (NH_3-SCR) in the presence of O_2 at 573–673 K over V_2O_5-WO_3/TiO_2 or MoO_3-WO_3/TiO_2 catalyst [1–4]. But these catalysts are deactivated by highly concentrated SO_x, halogen compounds and fly ash contained in the exhaust gas emitted from the waste incinerator. Therefore, the SCR process should be placed at downstream of the desulfurizer, dehalogenizer and electrostatic precipitators. However, the temperature of the gas, which is introduced in the SCR process, falls down below 453 K, resulting in necessary to reheat the catalyst bed and/or gas up to the operating temperature of the catalyst. Recently, some research groups have developed new catalysts capable to be activated at low temperatures [5–10].

We have reported that photoassisted selective catalytic reduction (photo-SCR) with NH_3 in the presence of O_2 proceeds at room temperature over Rb_2O-V_2O_5/SiO_2 [11], TiO_2/SiO_2 [12] and TiO_2 [13,14] under irradiation. Above all over TiO_2, NO conversion and N_2 selectivity attained to 83% and 96%, respectively, in the conventional fixed bed flow system [13]. We have already proposed the reasonable reaction mechanism of the photo-SCR with NH_3 over TiO_2 elucidated by various spectroscopies [14,15]. Moreover, the reaction kinetic orders of gases (NO, NH_3 and O_2) and light intensity were determined [16]. However, the clarification of the relationship between the physico-chemical property of TiO_2 and catalytic activity of photo-SCR remains still unclear. In this study, we carried out photo-SCR reaction over various TiO_2 catalysts, and investigated what kind of TiO_2 shows the most activity in this reaction.

2. Experimental

2.1. Preparation of catalysts

TiO_2 samples used in this study were supplied from the Japan Catalysis Society (JRC-TIO-1–13) and Ishihara Sangyo Kaisha Ltd. (ST-01). After these samples were hydrated in distilled water for 2 h at 353 K and filtered with suction, they were dried at 383 K overnight. The catalysts were calcined in

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dry air at 373–1173 K for 3 h. After calcinations, the catalysts were grinded into powder from 26 to 50 mesh. The rutile–anatase mixture TiO_2 was obtained by physical mixing with JRC-TIO-3 and JRC-TIO-8 (abbreviated to M-TiO), which were prepared and grinded into powder under 100 mesh.

2.2. Characterization of catalysts

Crystal phase of each catalyst was determined by X-ray diffraction technique (XRD). SHIMADZU XD-D1 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) was used. The ratio of anatase phase to rutile phase was determined by the intensity of XRD peak of rutile (1 1 0) face and anatase (1 0 1) face. The crystallite size was estimated by the use of Sherrer equation. The specific surface areas of catalysts were determined using N_2 adsorption isotherm at 77 K.

2.3. The measurements of NH_3 chemisorption amount on TiO_2

NH_3 chemisorption amount on TiO_2 was evaluated using adsorption isotherms. Before measurement, TiO_2 sample was evacuated at 673 K for 30 min and was treated by 80 Torr O_2 at 673 K for 1 h, followed by evacuation at 673 K for 30 min. NH_3 was introduced to TiO_2 and an adsorption (chemisorption and physisorption) isotherm was recorded at room temperature. After that, NH_3 was evacuated at room temperature for 30 min. Then NH_3 was introduced to TiO_2 again to record adsorption (physisorption) isotherm. NH_3 chemisorption amount was determined by subtraction of the second adsorption isotherm from the first one.

2.4. Catalytic reaction

The catalytic test, photoassisted selective catalytic reduction with NH_3, was carried out in a conventional fixed bed flow system at an atmospheric pressure. Catalysts were filled up in a quartz reactor, which has flat facets (50 mm × 15 mm × 1 mm), and were fixed with quartz wool. Before the photocatalytic reaction, catalysts were pretreated at 373–673 K by flowing 10% O_2 diluted with Ar at flow rate of 50 ml/min. The composition of the reaction gas was NO: 1000 ppm, NH_3: 1000 ppm and O_2: 2% (Ar balance) and the flow rate was 100–400 ml/min. As a light source, Perkin-Elmer PE300BF 300 W Xe lamp was used, and samples were illuminated from the one side of the flat facet of the reactor. The concentrations of produced N_2 and N_2O in the photo-SCR reaction were determined by SHIMADZU GC-8ATCD gas chromatograph equipped with columns packed with MS-5A and Porapak Q using Ar as a carrier gas.

3. Result and discussion

3.1. Reaction and characterization of TiO_2 calcined at various temperatures

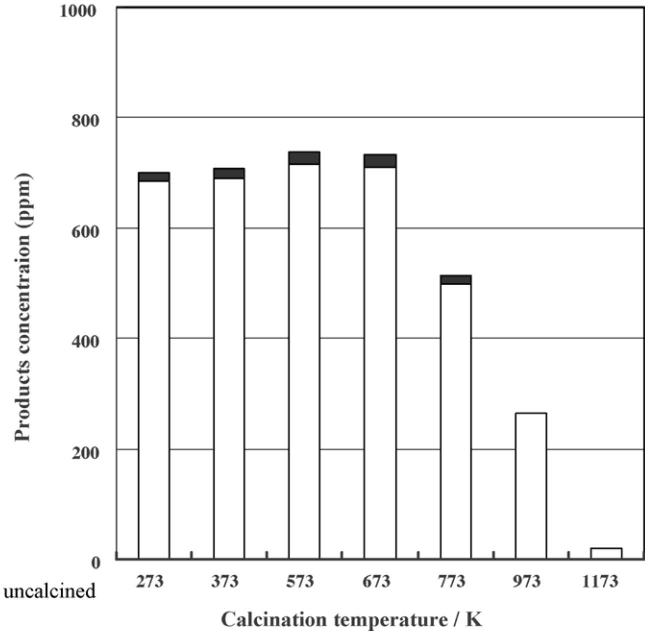

Fig. 1. Activity in photo-SCR with NH_3 over ST-01 calcined various temperatures (GHSV = 16,000 h^{-1}): (□) N_2 and (■) N_2O.

Fig. 1 shows outlet concentrations of products (N_2 and N_2O) in photo-SCR with NH_3 over ST-01 uncalcined and calcined at 373–1173 K (GHSV = 16,000 h^{-1}). The TiO_2 samples calcined at the temperatures higher than 673 K were pretreated at 673 K and the others were pretreated at the same temperature as calcination. N_2 production was increased gradually with the calcination temperature. At 673 K, NO conversion and N_2 selectivity were found to be 75% and 96%, respectively. Over 673 K, NO conversion was decreased dramatically, and NO conversion was 2% at 1173 K. TiO_2 calcined at 673 K showed the good activity in the photo-SCR reaction.

Fig. 2 shows the XRD patterns of ST-01 samples calcined at various temperatures. The uncalcined sample shows principally

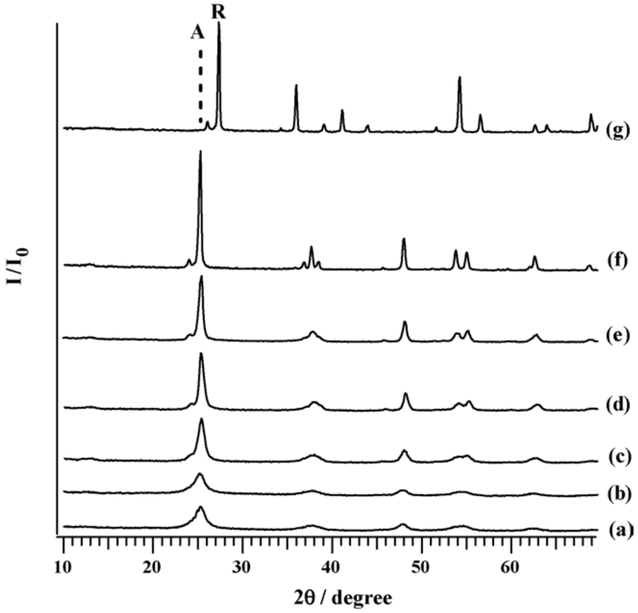

Fig. 2. XRD patterns of ST-01 calcined at: (a) room temperature, (b) 373 K, (c) 573 K, (d) 673 K, (e) 773 K, (f) 973 K and (g) 1173 K. (A) Anatase and (R) rutile.

Table 1
Specific surface areas of ST-01 calcined at various temperatures

Calcinations *T* (K)	*Sa* (m^2/g)
No calcined	237
373	273
573	129
673	93.2
773	79.8
973	10
1173	1–2

anatase. By calcination up to 973 K, all samples exhibited anatase phase and crystal growth can be seen with an increase in calcination temperature. The phase transformation from anatase to rutile took place between calcination temperatures of 973 K and 1173 K and the sample calcined at 1173 K exhibited rutile phase only. This is consistent with the report by Djerad et al. that phase transformation from anatase to rutile is starting from 873 K and was complete at 1073 K [17]. As shown in Fig. 1, NO conversion was decreased on the catalyst sample calcined at the temperatures higher than 673 K. On the other hand, the crystal phase of TiO_2 keeps anatase single phase till 973 K. It is likely that the phase of the surface layer changed from anatase to rutile at lower temperatures than 973 K during the bulk phase keeps anatase.

Table 1 shows the specific surface area of ST-01 samples calcined at various temperatures. The specific surface area of the sample calcined at 373 K was larger than that of uncalcined TiO_2. However, it is decreased with an increase in the calcination temperature. In particular, the specific surface area decreased between 373 K and 573 K, and between 773 K and 973 K drastically. Although the specific surface areas of the samples calcined at 573 K and 673 K were about half of those of uncalcined and calcined at 373 K, the conversion of NO hardly changed. The conversion of NO decreases dramatically by calcination in the temperature range from 673 K to 773 K, but it is noted that the specific surface areas of the samples calcined at 673 K and 773 K were almost the same. This suggests that the activity of photo-SCR with NH_3 does not depend on the specific surface area.

It is known that the acidity of oxides varies with the calcination temperatures. Generally, the amount of Lewis acid sites is increased with an increase in a calcination temperature in the case of metal oxides. Since in the photo-SCR, NH_3 is adsorbed on Lewis acid sites of TiO_2 [14], it is natural to guess that the acidity of TiO_2 is an important key to the activity. Increase in the calcination temperature enhances the acidity of TiO_2, and therefore, TiO_2 calcined at 673 K has the highest activity in TiO_2 samples calcined up to 673 K. On the contrary, the activities of TiO_2 calcined at over 673 K decreased gradually as the increase in calcination temperature. This would be due to the decrease in the amount of acid sites and the sintering of TiO_2.

3.2. Reaction and characterization of various TiO_2

Table 2 shows the specific surface area, crystal phase and the crystallite size of various TiO_2 calcined at 673 K, and Table 3 shows the results of photo-SCR reaction with NH_3 over these TiO_2 under several gas hourly space velocity (GHSV). JRC-TIO-11, the mixture of rutile and anatase phases, exhibited the highest activity of all TiO_2 samples. JRC-TIO-8 and JRC-TIO-3 were the most active catalysts consisting of anatase and rutile single phases, respectively. Combining the catalyst activities (Table 3) with the results of characterization (Table 2), it is suggested that activity does not correlate with the crystal phase, the crystallite size or the specific surface area. In spite of the same specific surface areas, the activity of JRC-TIO-1 is entirely lower than that of JRC-TIO-11. This may be owing to the different phase. NO conversion of the reaction over JRC-TIO-12 is lower than JRC-TIO-8 although they exhibit the same anatase, almost the same crystallite size and specific surface area. Therefore, either of the specific surface area, the crystal phase or the crystallite size, is not the factor to determine the activity of the photo-SCR.

Table 2
Properties of various catalysts

Catalysts	*Sa* (m^2/g)	Phase	D_c (Å)
JRC-TIO-1	71.1	A	187
JRC-TIO-2	15.6	A	535
JRC-TIO-3	45.6	R	219
JRC-TIO-4	47.8	R, 29.4%	382
		A, 70.6%	259
JRC-TIO-5	3–4	R, 92.4%	2200
		A, 7.6%	1000
JRC-TIO-6	58.0	R	240
JRC-TIO-7	108	A	197
JRC-TIO-8	93.2	A	155
JRC-TIO-9	95.2	A	197
JRC-TIO-10	100	A	169
JRC-TIO-11	76.6	R, 8.7%	200
		A, 91.3%	153
JRC-TIO-12	98.7	A	159
JRC-TIO-13	71.1	A	237

A: anatase, R: rutile.

Previously we have proposed the reasonable reaction mechanism of the photo-SCR with NH_3 over TiO_2 by various spectroscopies [14,15]. First, NH_3 is adsorbed on Lewis acid site of TiO_2. The adsorbed NH_3 molecule traps a positive hole generated by photoexcitation to form an amide radical. Ti^{4+} is reduced to Ti^{3+} by trapping an electron. The amide radical reacts with NO in the gas phase readily to form nitrosoamide species. The nitrosoamide species is spontaneously decomposed to N_2 and H_2O. Finally, reduced Ti^{3+} is re-oxidized to Ti^{4+} by O_2. The kinetic consideration showed that the rate-determining step is the step where nitorosamide species is decomposed [16]. From the mechanism we suppose that the increase in concentration of nitrosoamide enhances reaction activity. Therefore, the increase in the amount of acid sites is significantly important for the enhancement of photo-SCR activity.

We investigated the correlation between the photo-SCR activity and the NH_3 chemisorption amount. Fig. 3 shows the

Table 3
Results of photo-SCR reaction with NH_3 over various TiO_2 photocatalysts

Catalysts	GHSV = 32000 h^{-1}		GHSV = 16000 h^{-1}		GHSV = 8000 h^{-1}	
	NO conversion (%)	N_2 selectivity (%)	NO conversion (%)	N_2 selectivity (%)	NO conversion (%)	N_2 selectivity (%)
JRC-TIO-1	36	100	60	100	87	100
JRC-TIO-2	14.5	100	21	100	32.5	100
JRC-TIO-3	53	100	78	100	89	100
JRC-TIO-4	35.5	100	58	100	80	100
JRC-TIO-5	31	100	41	100	58	100
JRC-TIO-6	20	100	35	100	57	100
JRC-TIO-7	35	100	59	100	83.4	97.1
JRC-TIO-8	51.7	98.6	80.7	98.1	87.1	97.6
JRC-TIO-9	31	100	56.8	96.8	81.5	96.9
JRC-TIO-10	35.5	100	59	100	86	97.7
JRC-TIO-11	63	100	90	98.9	95	96.8
JRC-TIO-12	41	100	66.9	97.9	84.3	97.3
JRC-TIO-13	33	100	56	100	79	100

Reaction condition: NO 1000 ppm, NH_3 1000 ppm and O_2 2% (Ar balance).

photo-SCR activity at 32,000 h^{-1} plotted for the NH_3 chemisorption amount over various TiO_2. JRC-TIO-11, the most active catalyst, also exhibited the largest NH_3 chemisorption amount and JRC-TIO-2 and JRC-TIO-6, poorly active catalysts, showed low NH_3 chemisorption amount. As a whole, higher the photo-SCR activity is, larger the NH_3 chemisorption amount is. The larger NH_3 adsorption amount leads to the higher surface concentration of amide radical as well as nitrosoamide species. These results indicate that the photo-SCR activity depends on the NH_3 chemisorption amount and support that the amount of acid sites on TiO_2 is an important key to photo-SCR.

However, the activity over JRC-TIO-5 was more than twice as high as that over JRC-TIO-2 and JRC-TIO-6 although the NH_3 chemisorption amount of JRC-TIO-5 was less than half of JRC-TIO-2 and JRC-TIO-6. The JRC-TIO-5 is comprised of a mixture of rutile and anatase, while JRC-TIO-2 and JRC-TIO-6 consists of anatase and rutile single phases, respectively (Table 2). It is likely that the coexistence of rutile and anatase brings about the mutual interaction which improves the activity exhibited by original single phase metal oxides.

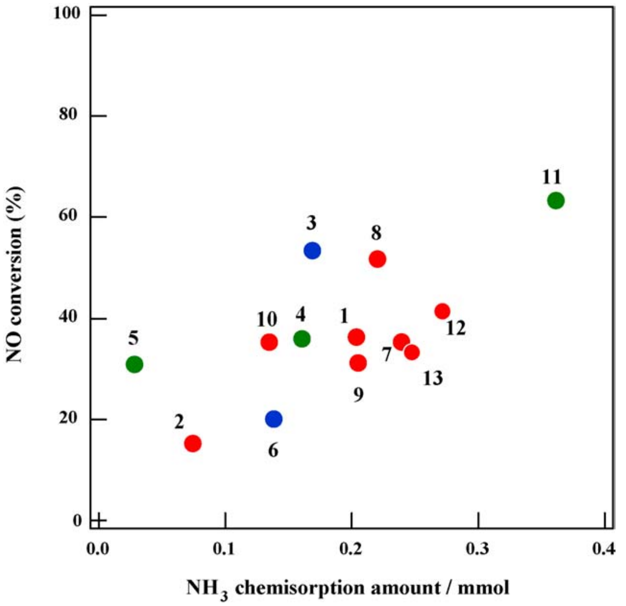

Fig. 3. The photo-SCR activity at 32,000 h^{-1} plotted against the NH_3 chemisorption amount over various TiO_2.

3.3. The photo-SCR reaction over rutile and anatase mixed TiO_2

JRC-TIO-11 consisting of a mixture of rutile and anatase was found to be the most active catalyst in photo-SCR as shown in Tables 2 and 3. JRC-TIO-5 showed higher activity than JRC-TIO-2 and JRC-TIO-6 as described above. There have been several reports that rutile and anatase phases showed the mutual interaction [18–20]. We suppose that the interaction between rutile and anatase phases enhances the photocatalytic activity. In order to examine the interaction and to develop the reaction activity, we prepared the sample of physical mixture of rutile and anatase. JRC-TIO-3, the most active catalyst of the rutiles, and JRC-TIO-8, the most active one of the anatases, were physically mixed (M-TiO), and photo-SCR was carried out over M-TiO.

Table 4 shows the results of the photo-SCR reaction over JRC-TIO-3, JRC-TIO-8 and M-TiO in 16,000 h^{-1}. M-TiO had 54% of rutile and 46% of anatase phases evaluated from XRD pattern. If there were no interaction between rutile and anatase phases, we would expect that NO conversion is about 80% because of 78% of NO conversion of JRC-TIO-3 and 80.7% of NO conversion of JRC-TIO-8. However, the photo-SCR activity of M-TiO was enhanced in comparison with the activities of JRC-TIO-3 and JRC-TIO-8, and 93.5% of NO conversion was achieved. This result suggests the synergetic effect on the mixture of rutile and anatase. Ohno et al. reported that physical mixture of large rutile particles and small anatase particles enhanced the photocatalytic activity of naphthalene [18]. They concluded that the presence of a small amount of anatase phase was important for achieving high photocatalytic activity. In our case, however, the crystallite size of rutile powder (JRC-TIO-3) is 219 nm and that of anatase powder

Table 4
Results of photo-SCR reaction with NH_3

Catalysts	N_2 production (ppm)	N_2O production (ppm)	NO conversion (%)	N_2 selectivity (%)
JRC-TIO-3	780	0	78	100
JRC-TIO-8	790	15	80.7	98.1
M-TiO	910	25	93.5	97.3

Reaction condition: NO 1000 ppm, NH_3 1000 ppm and O_2 2% (Ar balance); GHSV 16,000 h^{-1}.

(JRC-TIO-8) is 155 nm, there is no appreciable difference in the size. Therefore, it is thought that the synergistism between rutile and anatase powders does not depend on the particle sizes of anatase and rutile only, but also on the electronic interaction between rutile and anatase phases. There have been some reports that the stabilization of charge separation by electron transfer from anatase to rutile slows recombination of electrons and holes [21–24]. This interaction between rutile and anatase suppresses the recombination by rapid electron transfer from anatase to rutile at the anatase–rutile interface under irradiation. This interaction enhances the catalytic activity in the photo-SCR. However, the effect of interaction between rutile and anatase would be a minor factor for the photo-SCR activity in comparison with that of NH_3 chemisorption amount taking it into account that JRC-TIO-4 and JRC-TIO-5 exhibited the normal reactivity in spite of mixture of rutile and anatase (in Fig. 3).

4. Conclusion

In the photo-SCR reaction with NH_3, TiO_2 calcined at 673 K exhibits the high activity, in spite of decreasing the specific surface area by calcination at high temperature. NH_3 adsorption experiment showed that the NH_3 chemisorption amount was the important factor for the photo-SCR activity. The larger NH_3 chemisorption amount in TiO_2 means the higher surface concentration of intermediates (amide radical and nitrosoamide species) in the photo-SCR. Therefore, TiO_2 which has higher NH_3 adsorption capability showed higher activity. Additionally, we found that the photo-SCR activity is improved over the mixture sample of anatase and rutile rather than the original single phase TiO_2. We propose that the interaction between rutile and anatase in the physical mixture enhances the catalytic activity in the photo-SCR.

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References

[1] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
[2] S. Cho, Chem. Eng. Prog. 90 (1994) 39.
[3] V. Parvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
[4] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B: Environ. 18 (1998) 1.
[5] W. Kijlstra, D. Brands, H. Smit, E. Poels, A. Bliek, J. Catal. 171 (1997) 219.
[6] A. Kato, S. Matsuda, F. Nakajima, M. Imanri, I. Watanabe, J. Phys. Chem. 85 (1981) 1710.
[7] R. Long, R. Yang, R. Chang, Chem. Commun. 5 (2002) 452.
[8] G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur, R.J. Willey, J. Catal. 157 (1995) 523Y.
[9] D. Pena, B. Uphade, P. Smirniotis, J. Catal. 221 (2004) 421.
[10] G. Centi, S. Perathoner, D. Biglino, E. Giamello, J. Catal. 151 (1995) 75.
[11] T. Tanaka, K. Teramura, T. Funabiki, Phys. Chem. Chem. Phys. 2 (2000) 2681.
[12] T. Tanaka, K. Teramura, T. Yamamoto, S. Takenaka, S. Yoshida, T. Funabiki, J. Photochem. Photobiol. A 148 (2002) 277.
[13] T. Tanaka, K. Teramura, K. Arakaki, T. Funabiki, Chem. Commun. 22 (2002) 2742.
[14] K. Teramura, T. Tanaka, T. Funabiki, Langmuir 19 (2003) 1209.
[15] K. Teramura, T. Tanaka, T. Funabiki, Chem. Lett. 32 (2003) 1184.
[16] K. Teramura, T. Tanaka, S. Yamazoe, K. Arakaki, T. Funabiki, Appl. Catal. B: Environ. 53 (2004) 29.
[17] S. Djerad, L. Tifouti, M. Crocoll, W. Weisweiler, J. Mol. Catal. A: Chem. 208 (2004) 257.
[18] T. Ohno, K. Tokieda, S. Higashida, M. Matsumura, Appl. Catal. A: Gen. 244 (2003) 383.
[19] D. Hurum, A. Agrios, K. Gray, T. Rajh, M. Thurnauer, J. Phys. Chem. B 107 (2003) 4545.
[20] K. Raju, M. Yaseen, Langmuir 8 (1992) 43.
[21] G. Riegel, J.R. Bolton, J. Phys. Chem. 99 (1995) 4215.
[22] A. Datye, G. Riegel, J. Bolton, M. Huang, M. Prairie, J. Solid State Chem. 115 (1995) 236.
[23] W. Farneth, R. McLean, J. Bolt, E. Dokou, M. Barteau, Langmuir 15 (1999) 8569.
[24] M. Yan, F. Chen, J. Zhang, M. Anpo, J. Phys. Chem. B 109 (2005) 8673.