Journal of Catalysis **196,** 190–194 (2000)
doi:10.1006/jcat.2000.3027, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

High-Surface-Area SiO_2–ZrO_2 Prepared by Depositing Silica on Zirconia in Aqueous Ammonia Solution

Satoshi Sato,[1] Ryoji Takahashi,[1] Toshiaki Sodesawa, Shimei Tanaka, Koichi Oguma, and Katsuyuki Ogura

Department of Materials Technology, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan

Received March 23, 2000; revised August 4, 2000; accepted August 4, 2000

Preparation of high-surface-area SiO_2–ZrO_2 by deposition of silicate species on zirconia under hydrothermal conditions in an aqueous ammonia solution was investigated. A fresh precipitate of $ZrO(OH)_2$ was heated in a pressure vessel with several pieces of quartz glass tube at 100°C. In the measurement of ICP-AES and solid-state ^{29}Si NMR, it was elucidated that a silica component dissolved from the glass in the basic solution was deposited on the $ZrO(OH)_2$ precipitate and that the silica content increased with increasing hydrothermal period. The resulting SiO_2–ZrO_2 had a specific surface area higher than 240 m^2 g^{-1} even after calcination at 500°C. In contrast to the pure ZrO_2 particles readily aggregating, the silicate species deposited on the surface of ZrO_2 particles prevented the agglomeration of the primary particles during calcination, resulting in high-surface-area SiO_2–ZrO_2.

Key Words: **high-surface-area SiO_2–ZrO_2; deposition of silica on zirconia; hydrothermal conditions in basic solution; dissolution–deposition of silica.**

INTRODUCTION

It is known that SiO_2 dissolves in an alkaline solution (1–3). A rough surface of silica gel grows smooth in alkaline solution by dissolution–deposition to decrease surface energy. In the same way, fine silica particles suspended in the alkaline solution grow in size. The dissolution rate increases steeply with an increase in the pH of the solution at $pH > 8$ (2). For example, the concentration of Si is ca. 20–40 ppm when several hundred silica glass beads with total surface area 60 cm^2 are dissolved at pH of 10.8 for 100 h at 85°C (3). Both the dissolution rate and the solubility increase with increasing temperature. In the case of borosilicate glass such as Pyrex, silica species also dissolve in an alkaline solution, but the dissolution rate is slower than that of quartz glass (4).

On the other hand, we have reported that silica deposited on alumina in the vapor phase induces Brønsted acid sites on the surface (5–7). The other supported mixed oxides such as SiO_2–ZrO_2 and SiO_2–TiO_2 have been also prepared by depositing silicate species in the vapor phase (8, 9), while the ZrO_2 and TiO_2 supports have surface areas smaller than 70 m^2 g^{-1}. It has been reported that the surface area of ZrO_2 is enlarged by the presence of a small amount of silica in the sol–gel process (10, 11). In the bulk-substituted SiO_2–ZrO_2 prepared using a mixture of silicon and zirconium alkoxides in a sol–gel process, the surface area monotonically increases with SiO_2 content from 19 m^2 g^{-1} of pure zirconia to 558 m^2 g^{-1} of pure silica (10). Incidentally, Chuah *et al.* have recently reported that an as-dried precipitate of zirconium hydroxide such as $ZrO(OH)_2$ or $ZrO_2 \cdot H_2O$ has a surface area as high as 250 m^2 g^{-1} (12–14).

In this work, we apply the dissolution–deposition characteristics of silica to the preparation of supported composite metal oxides. Preliminarily, we have tested several hydroxides of metals such as aluminum, titanium, and zirconium as substrates on which silica dissolved in a basic solution at 100°C was deposited. We have observed that silica deposition occurs only on zirconia, neither on alumina nor on titania. We have also found that the resulting zirconia sample on which silica species have been deposited has specific surface areas higher than 200 m^2 g^{-1} even after calcination at 500°C.

In this paper, we prepare SiO_2–ZrO_2 with high surface area by depositing silica on zirconia in the liquid phase under hydrothermal (HT) conditions. In addition to the HT process, reflux procedures for preparing SiO_2–ZrO_2 are also examined.

EXPERIMENTAL

Sample Preparation

All reagents were supplied by Wako Chemical Ltd. (Japan). A $ZrO(OH)_2$ precipitate was obtained by adding

---

[1] To whom correspondence should be addressed. E-mail: satoshi@tc.chiba-u.ac.jp.

0021-9517/00 $35.00

10 wt% of zirconyl nitrate dihydrate solution into 5 mol dm^{-3} of ammonia solution (12). After the filtration, the precipitate (12.2 mmol of Zr) was placed in a polytetrafluoroethylene (PTFE) vessel together with 45 cm^3 of the mother solution at pH 9.8–9.9 and was heated at 100°C for 24–192 h in a pressure vessel with volume 50 cm^3. In the HT process of silica deposition, several pieces of quartz glass tube (ca. 9 g) that had total surface area of ca. 190 cm^2 were immersed in the solution. The precipitate filtered was dried at 110°C for 24 h and then calcined in air at 500°C for 3 h to obtain a SiO_2–ZrO_2 sample.

In a reflux procedure, the fresh precipitate (12.2 mmol of Zr) with 45 cm^3 of the mother solution was also aged under reflux conditions in a flask made of either polymethylpentene (PMP) or Pyrex glass with volume 100 cm^3 for 24–192 h.

Characterization

The specific surface area of the sample was determined by the BET method using the N_2 adsorption isotherm at −196°C in a conventional volumetric gas adsorption apparatus. Prior to the adsorption, the samples were heated to 110 and 300°C for 1 h in vacuum, for the dried and calcined samples, respectively.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine Si in the SiO_2–ZrO_2 sample with Shimadzu (Japan) ICPV-1000 equipment. Each sample (10.0 mg) was dissolved for 15 h in a mixture of 0.5 cm^3 of HF (46 wt%) and 1.0 cm^3 of HCl (36 wt%) aqueous solutions at 150°C in a pressure vessel with a PTFE flask. Samples were diluted to 100 cm^3 with a boric acid (6 wt%) aqueous solution for the ICP-AES measurement (15).

Solid-state ^{29}Si NMR spectra were recorded on a DPX-300 multinuclear spectrometer (Bruker, Germany) at 59.64 MHz with a single pulse of 30° tip, high-power ^1H decoupling, and magic angle spinning (MAS) speed of 4.00 kHz; 1024 FID signals were accumulated with repetition delay time 30 s. The ^{29}Si chemical shifts are referenced to tetramethylsilane (TMS) using sodium 4,4-dimethyl-4-silapentanesulfonate (DSS, 1.534 ppm) as an external standard.

RESULTS AND DISCUSSION

In the HT process of $ZrO(OH)_2$ precipitate in a basic solution with quartz glass chips, it was observed that the glass chips were reduced in weight. The reduced weight of glass, which is based on unit weight of SiO_2–ZrO_2 yielded, increased with increasing HT period (Table 1A). Without $ZrO(OH)_2$ precipitate, however, less dissolution of glass was observed in the HT process in the basic solution with glass chips: the glass chips were reduced in weight less than 1 mg. Thus, it can be said that SiO_2 species dissolved from the glass successively deposited on the $ZrO(OH)_2$ precipitate under HT conditions. The amount of SiO_2 species in the sample was quantified by ICP-AES. The SiO_2 content increased with increasing HT period, and it was comparable to the amount of glass dissolved. Since a SiO_2–ZrO_2 composite has high alkali resistance (16), it is reasonable that the reverse reaction, dissolution of SiO_2 from SiO_2–ZrO_2, hardly proceeds in the present ZrO_2 system.

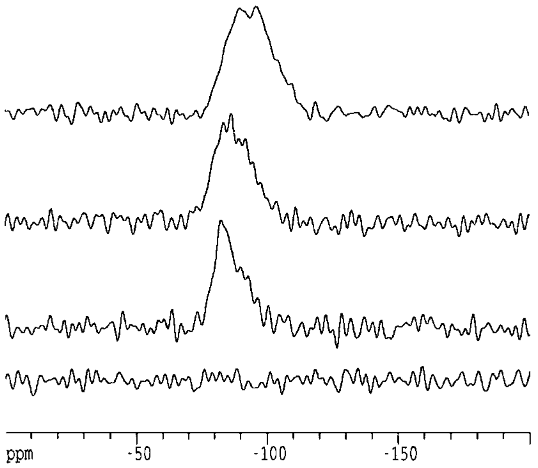

FIG. 1. ^{29}Si MAS NMR spectra of SiO_2–ZrO_2 with different hydrothermal periods: (a) ZrO_2 without HT process; (b) HT-treated for 48 h; (c) 96 h; (d) 192 h. Samples were calcined at 500°C for 3 h.

Figure 1 illustrates the ^{29}Si MAS NMR spectra of several SiO_2–ZrO_2 samples. Although no ^{29}Si resonance was observed in the original ZrO_2 sample (Fig. 1a), broad ^{29}Si resonances were observed at around −85 ppm in the SiO_2–ZrO_2 samples (Figs. 1b and 1c). Only the 4-coordinate Si species exists in the samples as shown by the absence of resonances in magnetic fields higher than −200 ppm (17). This indicates that all Si species are not incorporated into the ZrO_2 crystallites, because only 7- or 8-coordinate cations and vacant sites are accessible in the fluorite-type ZrO_2 crystal. The ^{29}Si chemical shift observed at around −85 ppm suggests that Q_1–Q_2 Si species were generated on the surface and that an Si–O–Zr bond forms on the surface of ZrO_2, comparable to the chemical shift of the Si–O–Al species in silica deposited on alumina using tetraethoxysilane in vapor phase (7). The ^{29}Si resonance was slightly shifted to higher magnetic field with increasing HT period (Figs. 1b, 1c, and 1d). This shift resembles the ^{29}Si resonance shift observed in silicate species deposited on alumina (7), suggesting that the silicate species with 4-coordinate Si accumulates on the ZrO_2 particle. In addition, a small resonance was observed at −110 ppm at SiO_2 content of 19.3 wt% (Fig. 1d). The resonance at −110 ppm, assigned to Q_4 Si, requires a third layer over the silica bilayer (7), suggesting an SiO_2 multilayer on the SiO_2–ZrO_2 sample. The sample has mainly a silica bilayer because the small resonance observed at −110 ppm shows that the third layer begins to form over the bilayer.

The highest silica loading of 19.3 wt% on ZrO_2 corresponds to a silica layer thickness of 0.47 nm, which is calculated using the SA of 233 $m^2\ g^{-1}$ and an amorphous silica density of 2.2 $g\ cm^{-3}$. In a silica–alumina with SA 203 $m^2\ g^{-1}$ prepared by depositing silica on alumina (7), the silica loading of 11.8 wt%, at which a small signal of the Q_4 Si species appears, corresponds to a silica layer thickness of 0.30 nm. The silica–alumina, however, has the island structure of silica with a bilayer. The height of the SiO_4 tetrahedron, i.e., the distance between the upper O–O bond and the lower O–O, is ca. 0.20 nm, which is calculated from the Si–O bond length of 0.1626–0.1646 nm and the O–Si–O angle of 103°–109.5° (18). Thus, the silica layer on ZrO_2 with thickness 0.47 nm probably consists of a silica bilayer, which is in good harmony with the NMR results. In other words, the present SiO_2–ZrO_2 particle has the structure of a zirconia egg and silica-layered eggshell, rather than of islands of silica.

Table 1 also summarizes surface-area data from several SiO_2–ZrO_2. In the samples dried at 110°C, specific surface areas were almost constant between 220 and 280 $m^2\ g^{-1}$ after the HT process with glass chips (Table 1A). In the samples calcined at 500°C, specific surface areas varied with the HT period. Compared with the samples before and after calcination, specific surface areas of the samples with an HT period longer than 96 h were unchanged as high as 230 $m^2\ g^{-1}$, while those with a shorter HT period decreased during calcination. The facts indicate that a high surface area of as-dried precipitate is maintained after calcination, and that it is probably caused by silica deposition. At an HT period of 96 h, the silica loading of 10.2 wt% is calculated to have a layer thickness of 0.23 nm, which corresponds to a silica monolayer. Above the monolayer thickness, it is probable that the silica layer stabilizes the ZrO_2 primary particles. In addition, even after 10 h calcination of the SiO_2–ZrO_2 with 120-h HT treatment, the surface area was the same as that calcined for 3 h.

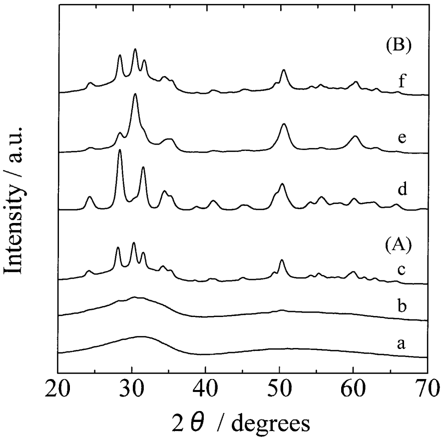

FIG. 2. XRD profiles of SiO_2–ZrO_2 treated with quartz glass with different hydrothermal periods: (A) dried at 110°C, (B) calcined at 500°C. (a) HT period of 0 h; (b) 2 h; (c) 5 h; (d) 0 h; (e) 2 h; (f) 5 h.

TABLE 1

Physical Properties of SiO_2–ZrO_2 Prepared under Hydrothermal Conditions

Hydrothermal treatment (h)	Quartz glass dissolved[a] ($mg\ g_{cat}^{-1}$)	SiO_2 content[b] ($mg\ g_{cat}^{-1}$)	SA[c] of sample dried at 110°C ($m^2\ g^{-1}$)	SA[c] of sample calcined at 500°C ($m^2\ g^{-1}$)
(A) With quartz glass chips				
0	—	0	222	44
24	—	—	287	76
48	53	45	293	169
96	122	102	—	221
120	153	—	233	237
144	171	127	250	243
192	214	193	233	233
(B) Without glass				
0	—	0	222	44
48	—	0	132	35
96	—	0	151	42
144	—	0	82	45
192	—	0	92	34

[a] Measured by the decrease in weight of quartz glass chips after hydrothermal treatment.

[b] Measured by ICP-AES.

[c] SA, specific surface area.

Pure ZrO_2 has different trends (Table 1B); the specific surface area of pure ZrO_2 dried at 110°C decreased from 220 to 90 $m^2\ g^{-1}$ when the HT period increased from 0 to 192 h. After the calcination, the specific surface areas of pure ZrO_2 were almost constant at ca. 40 $m^2\ g^{-1}$ regardless of the HT period.

In the XRD measurement of the as-dried samples (Figs. 2A and 3A), the original $ZrO(OH)_2$ precipitate was amorphous, while crystal phases appeared after the HT treatment of amorphous $ZrO(OH)_2$ precipitate. In

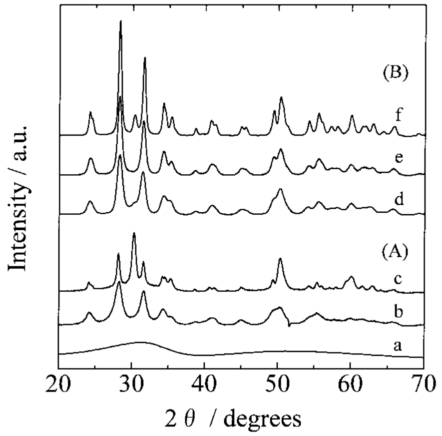

FIG. 3. XRD profiles of ZrO_2 treated without glass with different hydrothermal periods: (A) dried at 110°C, (B) calcined at 500°C. (a) HT period of 0 h; (b) 2 h; (c) 4 h; (d) 0 h; (e) 2 h; (f) 4 h.

the $ZrO(OH)_2$ treated without glass chips, crystal phases appeared even after the HT treatment of amorphous $ZrO(OH)_2$ precipitate for 48 h (Fig. 3b). The crystallization of $ZrO(OH)_2$ to ZrO_2 with a mixture of monoclinic and tetragonal phases, rather than calcination, was observed during the HT process (Figs. 2 and 3). Crystallization rates with glass chips are slower than those without glass. Decrease in the crystallization rate of ZrO_2 particle is probably caused by inhibition of aggregation of ZrO_2 particles due to silica coating in the HT process with glass. The XRD results are similar to those in a report about high-surface-area zirconia (12), in a section connected with the reflux procedure.

For silica–alumina prepared by depositing silica on alumina support in the vapor phase, the alumina particles exhibit heat resistance to sintering (19, 20). The silica layer on alumina particles acts as an obstacle to sintering because of the different crystal structure. In the same way, the silicate species deposited on the ZrO_2 precursors is speculated to prevent sintering and keep the original particle size, whereas the pure $ZrO(OH)_2$ precipitate readily sinters.

Pure zirconia is known to have only Lewis acid sites (21). For SiO_2–ZrO_2 derived from sol–gel process (22), it is reported that Lewis acid sites are predominant, together with weak Brønsted acid sites. Thus, a change in acidic nature by deposition of silica can be expected in the analog of silica–alumina (23); Lewis acid sites will be altered into Brønsted acid sites by silica deposition. Moreover, the number of acid sites can be expected to increase with increasing surface area (10); it will be proportional to the specific surface area if the acid site density is unchanged by silica deposition. Further work needs a study on the intrinsic acidic nature of SiO_2–ZrO_2.

High-surface-area SiO_2–ZrO_2 has already been reported (10, 11). Soled and McVicker reported that the surface area of bulk-substituted SiO_2–ZrO_2 at SiO_2 content of 25 mol% (14 wt%) is at most 150 m^2 g^{-1} after calcination for 3 h at 500°C (10). In a SiO_2–ZrO_2 system prepared by immersing zirconium hydroxide in tetraethoxysilane ethanol solution, a small amount of silica impregnated onto ZrO_2 also stabilizes the surface area of ZrO_2; the surface area is 166 m^2 g^{-1} at 14 wt% SiO_2 (10). Miller *et al.* reported the supercritical drying of sol–gel-derived SiO_2–ZrO_2 (11); pure ZrO_2 had surface area exceeding 110 m^2 g^{-1} after calcination for 2 h at 500°C, and the surface area increased to 150 m^2 g^{-1} at 5 mol% SiO_2. These results indicate that silicon alkoxide, as well as a glass chip, is accessible as a silica source for the stabilization of the surface area of zirconia by silica deposition.

Instead of the HT process, we also applied reflux conditions to prepare SiO_2–ZrO_2 by the liquid-phase deposition of silica. For the ZrO_2 samples heated in the mother solution under reflux conditions with quartz glass chips using a flask made of plastics (Table 2, A), specific surface areas increased up to 300 m^2 g^{-1} with increasing reflux period. In the case of reflux with glass chips, it was also observed that the glass chips were reduced in weight after the reflux and that the amount both of glass dissolved and silica deposited increased with increasing reflux period (Table 2A). The results show that the reflux conditions are also effective for the preparation of high-surface-area SiO_2–ZrO_2.

TABLE 2

Physical Properties of Samples Aging under Different Reflux Conditions

Reflux period (h)	Glass dissolved[a] (mg g_{cat}^{-1})	SiO_2 content[b] (mg g_{cat}^{-1})	SA[c] of sample dried at 110°C (m^2 g^{-1})	SA[c] of sample calcined at 500°C (m^2 g^{-1})
(A) Reflux with quartz glass chips in a flask made of PMP[d]				
0	—	0	222	44
24	35	19	359	183
48	65	46	302	234
96	103	106	321	258
192	188	130	316	304
(B) Reflux without glass in a flask made of PMP[d]				
48	—	—	304	76
96	—	—	253	78
(C) Reflux in a flask made of Pyrex glass				
48	78	67	384	222
96	138	113	347	283

[a] Measured by the decrease in weight of glass flask and quartz glass chips after reflux.

[b] Measured by ICP-AES.

[c] SA, specific surface area.

[d] PMP, polymethylpentene.

Also, Chuah *et al.* have reported that ZrO_2 with specific surface area as high as 250 m^2 g^{-1} was prepared by calcinating a $ZrO(OH)_2$ precipitate aged under reflux conditions in a basic solution, such as a NaOH, KOH, and NH_3 aqueous solution, using a Pyrex flask (12). The aging of wet $ZrO(OH)_2$ precipitate under reflux conditions increases the thermal stability of ZrO_2; the calcined ZrO_2 maintains the high specific surface area of the as-dried precipitate (12). The reason was explained as follows: the defects in the wet $ZrO(OH)_2$ precipitate were removed by the dissolution–deposition of ZrO_2 under the reflux conditions, and the thermal resistance of ZrO_2 increased. We suspect that the phenomenon under the reflux conditions in a basic solution with $ZrO(OH)_2$ precipitate is the same as what we present.

We have also reproduced the results reported by Chuah *et al.* (Fig. 8 in Ref. 12) using a Pyrex flask. In the samples calcined at 500°C, the specific surface area of ZrO_2 increased from 44 to 283 m^2 g^{-1} with increasing reflux time from 0 to 96 h (Table 2C). It was also observed that the glass components of Pyrex flask were reduced in weight after the reflux. However, no such high specific surface area was observed in a ZrO_2 sample aged in a plastic flask without glass chips (Table 2,B). Both the amount of glass dissolved and the SiO_2 content increased with increasing reflux period (Table 2C). These results clearly show that the reflux conditions in the basic solution contacted with a glass surface are attributable to the enlargement of the resulting specific surface area of ZrO_2. It is probable that the high specific surface-area ZrO_2 reported by Chuah *et al.* (12, 13) is caused not by the removal of defects in the wet ZrO_2 particles through the dissolution–deposition of ZrO_2, but by SiO_2 coating the wet $ZrO(OH)_2$ precipitates. In addition, much more silica species would be deposited on ZrO_2 particles under other reflux conditions with such a NaOH and KOH solution (12, 14) because the dissolution rate of silica is high in a higher-pH solution (2).

In the solid-state ^{29}Si and ^{11}B NMR of the samples prepared in the Pyrex glass vessel (spectra not shown), we observed not only silicate species but also borate species. This fact suggests that contamination from a glass vessel drastically affects the properties of resultant materials. One has to take account of the dissolution of glass by contact with a high-temperature basic solution during the preparation of catalyst.

In the ZrO_2 samples aged under the silicaless conditions, specific surface areas of the samples calcined at 500°C were at most 78 $m^2\,g^{-1}$, and they were ca. twice as large as that of ZrO_2 without reflux (Table 1B). In a plastic flask, it was also reported that a sulfated ZrO_2 with specific surface area 121 $m^2\,g^{-1}$ was prepared by refluxing at pH 5 for 63 days (24). Although the values are smaller than those for samples aged in a Pyrex glass flask, it can be shown that reflux under silicaless conditions can enlarge the surface area of pure ZrO_2.

CONCLUSION

Deposition of silica on ZrO_2 was investigated under hydrothermal conditions. When a fresh precipitate of $ZrO(OH)_2$ was heated in a pressure vessel with several pieces of quartz glass chip, the glass chips were dissolved in an ammonia basic solution. ICP-AES and solid-state ^{29}Si NMR revealed that the silica dissolved was deposited on the $ZrO(OH)_2$ precipitate and that the silica content in the sample increased with increasing hydrothermal period.

The resulting SiO_2–ZrO_2 had a specific surface area higher than 240 $m^2\,g^{-1}$ even after calcination at 500°C. The specific surface area of pure ZrO_2 obtained from the original precipitate was at most 45 $m^2\,g^{-1}$, while that of the original precipitate dried at 110°C was 222 $m^2\,g^{-1}$. In contrast to pure ZrO_2 readily aggregating during calcination, the silicate species deposited on the surface of ZrO_2 particles prevent the agglomeration of the primary particles during calcination, resulting in high-surface-area SiO_2–ZrO_2.

REFERENCES

1. Iler, R. K., “The Chemistry of Silica,” p. 30. Wiley, New York, 1979.
2. Wijnen, P. W. J., Beelen, T. P. M., de Haan, J. W., Rummens, C. P. J., van de Ven, L. J. M., and van Santen, R. A., *J. Non-Cryst. Solids* **109**, 85 (1989).
3. Mazer, J. J., and Walter, J. V., *J. Non-Cryst. Solids* **170**, 32 (1994).
4. Perera, G., and Doremus, R. H., *J. Am. Ceram. Soc.* **74**, 1554 (1991).
5. Sato, S., Toita, M., Yu, Y. Q., Sodesawa, T., and Nozaki, F., *Chem. Lett.* 1535 (1987).
6. Sato, S., Toita, M., Sodesawa, T., and Nozaki, F., *Appl. Catal.* **62**, 73 (1990).
7. Sato, S., Sodesawa, T., Nozaki, F., and Shoji, H., *J. Mol. Catal.* **66**, 343 (1991).
8. Jin, T., Okuhara, T., and White, J. M., *J. Chem. Soc. Chem. Commun.* 1248 (1987).
9. Niwa, M., Katada, N., and Murakami, Y., *J. Catal.* **134**, 340 (1992).
10. Soled, S., and McVicker, G. B., *Catal. Today* **14**, 189 (1992).
11. Miller, J. B., Rankin, S. E., and Ko, E. I., *J. Catal.* **148**, 673 (1994).
12. Chuah, G. K., Jaenicke, S., and Pong, B. K., *J. Catal.* **175**, 80 (1998).
13. Chuah, G. K., and Jaenicke, S., *Appl. Catal. A* **163**, 261 (1997).
14. Chuah, G. K., Jaenicke, S., Chong, S. A., and Cham, K. S., *Appl. Catal. A* **145**, 267 (1996).
15. Uchida, T., Iida, C., Yamasaki, K., Kanaoka, S., Ohmori, Y., and Masuda, T., *Bunseki Kagaku* **33**, 242 (1984). [In Japanese]
16. Larner, L. J., Speakman, K., and Majumdar, A., *J. Non-Cryst. Solids* **20**, 43 (1976).
17. Mudrakovskii, I. L., Mastikhin, V. M., Shmachkova, V. P., and Kotsarenko, N. S., *Chem. Phys. Lett.* **120**, 424 (1985).
18. Brinker, C. J., Brow, R. K., Tallant, D. R., and Kirkpatrick, R. J., *J. Non-Cryst. Solids* **120**, 26 (1990).
19. Katada, N., and Niwa, M., *Chem. Vap. Deposition* **2**, 125 (1996).
20. Katada, N., Ishiguro, H., Muto, K., and Niwa, M., *Chem. Vap. Deposition* **1**, 54 (1995).
21. Yamaguchi, T., *Catal. Today* **20**, 199 (1994).
22. Lopez, T., Tzompantzi, F., Navarrete, J., Gomez, R., Boldu, J. L., Munoz, E., and Novaro, O., *J. Catal.* **181**, 285 (1999).
23. Sato, S., Tokumitsu, M., Sodesawa, T., and Nozaki, F., *Bull. Chem. Soc. Jpn.* **64**, 1005 (1991).
24. Stichert, W., and Schüth, F., *J. Catal.* **174**, 242 (1998).