ELSEVIER

Catalysis Today 45 (1998) 129–134

CATALYSIS TODAY

Catalytic decomposition of N_2O over supported Rh catalysts: effects of supports and Rh dispersion

Koichi Yuzaki, Takayoshi Yarimizu, Kenji Aoyagi, Shin-ichi Ito, Kimio Kunimori*

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Abstract

The study of catalytic decomposition of nitrous oxide to nitrogen and oxygen over Rh catalysts supported on various supports (USY, NaY, Al_2O_3, ZrO_2, FSM-16, CeO_2, La_2O_3) showed that the activities of Rh/Al_2O_3 and Rh/USY (ultrastable Y zeolite) catalysts were comparable to or higher than the other catalysts reported in the literatures. The catalytic activity of N_2O decomposition was sensitive not only to the Rh dispersion but also to the preparation variables such as the Rh precursors and the supports used. A pulsed N_2O experiment over a Rh/USY catalyst suggested that the catalytic N_2O decomposition occurs on oxygen-covered surface and that O_2 may be freed on collision of N_2O molecules with the adsorbed oxygen atoms.

Keywords: N_2O decomposition; Rh/USY; Rh/NaY; Effects of supports; Rh dispersion; TOF

1. Introduction

Nitrous oxide (N_2O), which has been considered as a greenhouse gas, also contributes to catalytic stratospheric ozone destruction. Most of the previous works place great emphasis on the kinetics of the decomposition of N_2O rather than the activities. Recently, Li and Armor [1] reported that a Rh/ZSM-5 catalyst was very active for catalytic decomposition of N_2O to N_2 and $\frac{1}{2}O_2$ at low temperature (e.g., 300°C). Since then, several works [2–7] have been reported for the catalytic decomposition of N_2O over metal (Rh, Ru, Fe, Co and Ni) catalysts. Oi et al. [5,6] have studied the activities of various Rh-loaded metal oxides, and concluded that Rh/ZnO was the most active catalyst. However, so far little have been known about the effects of Rh dispersion (the percentage exposed) and the preparation variables such as Rh precursors ($Rh(NO_3)_3$, $RhCl_3$). In this work, the catalytic decomposition of N_2O has been studied over Rh catalysts supported on various oxides such as Al_2O_3, CeO_2, La_2O_3, FSM-16, ZrO_2, NaY and USY (ultrastable Y zeolite), and the TOF values based on the Rh dispersion were compared with those in the literatures. In addition, a pulsed N_2O experiment was performed to get information on the mechanism of the decomposition of N_2O.

2. Experimental

The catalyst supports used are NaY (SK-40, GL Science), USY (TOSOH, Si/Al_2=14.6), FSM-16

*Corresponding author. Tel.: +81-298-53-5026; fax: +81-298-55-7440; e-mail: kunimori@ims.tsukuba.ac.jp

0920-5861/98/$ – see front matter
PII: S0920-5861(98)00259-4

Table 1
Comparison of the Rh dispersion and the TOF values of Rh catalysts (950 ppm N_2O) (the precursor used was aqueous solution of $Rh(NO_3)_3$ for all the catalysts)

Catalyst	BET area (m^2/g)	H/Rh	CO/Rh	TOF ($\times 10^{-3}$ s^{-1})[a]	TOF ($\times 10^{-3}$ s^{-1})[b]
Rh/USY (700)	695.1	0.62	0.47	8.83	11.7
Rh/Al_2O_3 (600)	168.2	0.83	0.75	2.91	3.48
Rh/ZrO_2 (600)	11.2	0.13	0.10	1.15	1.48
Rh/ZrO_2 (500)	24.7	0.38	0.21	2.11	3.85
Rh/FSM-16 (550)	1020	0.60	0.30	0.21	0.42
Rh/CeO_2 (600)	21.8	0.43	0.32	0.91	1.23
Rh/La_2O_3 (600)	9.1	0.37	0.11	0.04	0.13
Rh/ZSM-5[c]	–	–	–	2.66[d]	–
Rh/ZnO[e]	10.0	–	–	–	2.91[f]
Rh/ZnO[g]	10.0	–	0.25	–	18.5

[a]At 250°C, based on the H/Rh value.
[b]At 250°C, based on the CO/Rh value.
[c]From [1]. The Rh loading was 0.6 wt%.
[d]Calculated by assuming H/Rh=1.
[e]From [5]. The Rh loading was 1 wt% (after H_2 reduction at 500°C).
[f]Calculated by assuming CO/Rh=0.25.
[g]From [6]. The Rh loading was 0.5 wt% (after the calcination in air at 500°C).

(TOYOTA Centre R&D Labs) [8] and Al_2O_3 (JRC-ALO-4). We also prepared oxide supports (ZrO_2, CeO_2, La_2O_3) in our laboratory. Dropping aqueous ammonia to each nitrate solution of transition metal elements ($ZrO(NO_3)_2$, $Ce(NO_3)_3$, $La(NO_3)_3$) up to pH=9 produces the hydroxide precipitate. It was then filtered and dried at 110°C overnight followed by calcination in air for 3 h at 500°C or 600°C. The NaY and USY supports were precalcined in air for 3 h at 600°C and 700°C, respectively. The Al_2O_3 and La_2O_3 supports were precalcined in air for 3 h at 600°C, and the FSM-16 support was precalcined in air for 3 h at 550°C. The ZrO_2 support was precalcined in air for 3 h at temperatures 500°C and 600°C. Rh/zeolite (NaY, USY) catalysts were prepared by incipient wetness impregnation with aqueous solutions of $RhCl_3$ or $Rh(NO_3)_3$ followed by calcination in air for 3 h at 600°C. Rh/FSM-16 and Rh/oxide (Al_2O_3, ZrO_2, CeO_2, La_2O_3) catalysts were prepared by the same method for Rh/zeolite catalysts followed by calcination in air for 3 h at 500°C. A Rh/NaY catalyst was also prepared by an ion exchange (IE) with hexa-aquoion, $Rh(H_2O)_6^{3+}$, using $RhCl_3$ (aq) solution (pH 4–5) [9,10] followed by calcination in air for 3 h at 400°C. The Rh loading was 2 wt% for all the catalysts studied except for Rh/Al_2O_3 catalysts (0.1, 0.5, 1, 2 wt% Rh).

N_2O decomposition reactions were carried out on a 50 mg catalyst sample with a total flow rate of 50 cm^3/min using a micro-catalytic reactor [11]. N_2O concentration was 950 or 5000 ppm. Unless otherwise stated, the catalysts were pretreated in H_2 for 1 h at 500°C. The H_2 and CO chemisorption measurements were performed by a conventional volumetric adsorption apparatus [12,13]. The total adsorption of H_2 (H/Rh), as well as irreversible adsorption of CO (CO/Rh), was measured after H_2 reduction for 1 h at 500°C. The TOF values (molecules of N_2O converted per number of surface Rh per second) were calculated by assuming that the adsorption stoichiometry (H/surface Rh or CO/surface Rh) is unity, and the values shown in tables were obtained by extrapolation of the Arrhenius plots at low N_2O conversion (0.5–20%). The BET surface areas were measured by a gas sorption analyzer (Coulter Omunisorp Series) (see Table 1). As a help to elucidate the mechanism of N_2O decomposition, a pulsed N_2O experiment was performed in a micro-catalytic pulse reactor. A helium gas was used as a carrier gas (flow rate, 55 cm^3/min) and a pulse (1.26 cm^3) of 0.517% N_2O in helium was injected by a jacketed switching valve purged with helium. The catalyst used was Rh/USY (20 mg), and it was treated in O_2 for 1 h at 500°C followed by H_2 reduction for 1 h at 500°C before the measurement.

3. Results and discussion

3.1. The activity of Rh catalysts on various supports

The N_2O decomposition reaction was catalytic (i.e., no occurrence of non-catalytic N_2O reduction) because the product O_2:N_2 ratio was 1:2, and the catalytic activity did not decrease during the continuous reaction for more than 8 h. As shown in Fig. 1, the activity of N_2O decomposition varies with the supports used for preparing the Rh catalysts. The activities of Rh/USY and Rh/Al_2O_3 are clearly much higher than those of the other catalysts shown in Fig. 1. The N_2O decomposition activity of the Rh catalysts supported on various oxides decreases in the following order: Rh/USY>Rh/Al_2O_3>Rh/ZrO_2>Rh/CeO_2>Rh/FSM-16≫Rh/La_2O_3.

Table 1 compares the BET surface areas, Rh dispersions, and TOF values of the supported Rh catalysts. Here, the numerical value in parentheses indicates the precalcination temperature of the support. The Rh/Al_2O_3 showed a higher TOF value and the Rh/USY showed the highest TOF value, while the Rh/La_2O_3 exhibited the lowest TOF value. The order of the TOF value is similar to the result of the N_2O decomposition activity. The activities of the Rh/Al_2O_3 and Rh/USY catalysts were comparable to or higher than those of Rh/ZSM-5 [1] and Rh/ZnO [5,6]. For the Rh/FSM-16, in spite of the remarkable wide surface area of FSM-16, the Rh is not so highly dispersed judging from the H/Rh and the CO/Rh values, and the TOF value is extremely low. For the Rh/ZrO_2 (600), the Rh is not well dispersed judging from the Rh dispersion values, but the TOF value is higher than that of the Rh/La_2O_3 (600). So, a ZrO_2 support was precalcined in air for 3 h at 500°C for the purpose of obtaining a more highly dispersed Rh catalyst. It is clear that for the Rh/ZrO_2 (500) the H/Rh and the CO/Rh values increased according to the increase of the surface area of the ZrO_2 support. Furthermore the TOF value also increased, and it was comparable to that of Rh/Al_2O_3 (600). We go into details below about Rh/Al_2O_3 and Rh/zeolite (USY, NaY) catalysts.

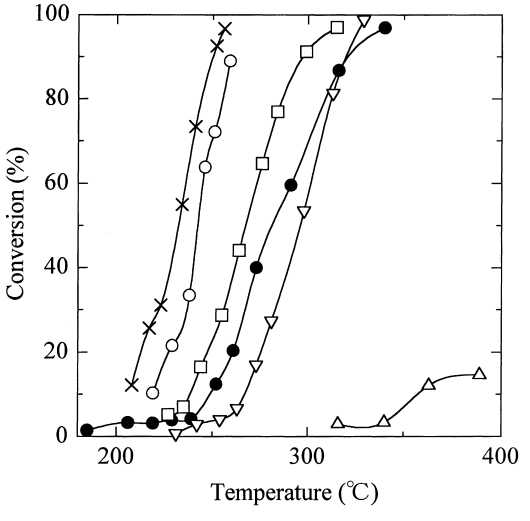

Fig. 1. N_2O conversion on Rh catalysts as a function of catalyst temperature: (×) USY (700); (○) Al_2O_3 (600); (●) CeO_2 (600); (▽) FSM-16 (550); (□) ZrO_2 (500); (△) La_2O_3 (600). The Rh precursor was $Rh(NO_3)_3$ for all the catalysts. N_2O concentration was 950 ppm in He.

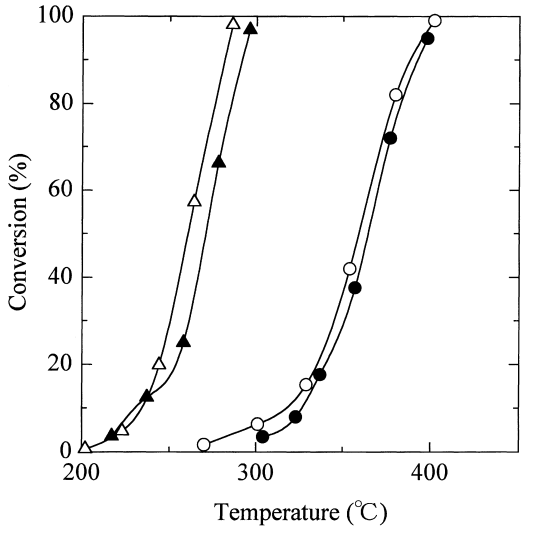

Fig. 2. N_2O conversion on Rh/Al_2O_3 catalysts as a function of catalyst temperature. The effect of Rh precursor: (●,○) using $RhCl_3$; (▲,△) using $Rh(NO_3)_3$. N_2O concentration was 0.5% in He. ((●,▲) after the reduction in H_2 at 200°C; (○,△) after the reduction in H_2 at 500°C.)

3.2. Rh/Al_2O_3 catalysts

Fig. 2 shows the effect of Rh precursor ($Rh(NO_3)_3$, $RhCl_3$) and the reduction temperature on N_2O decomposition. The Rh/Al_2O_3 (NO_3) prepared from $Rh(NO_3)_3$ showed high activities, while the Rh/Al_2O_3 (Cl) from $RhCl_3$ exhibited much lower activ-

Table 2
Comparison of the Rh dispersion and the TOF values of the Rh/Al_2O_3 catalysts (5000 ppm N_2O)

Catalyst	H/Rh	CO/Rh	TOF ($\times 10^{-3}$ s^{-1})[a]	TOF ($\times 10^{-3}$ s^{-1})[b]
2 wt% Rh/Al_2O_3 (Cl)[c]	1.16	1.10	0.94	0.99
0.5 wt% Rh/Al_2O_3 (Cl)	1.10	1.07	0.31	0.35
2 wt% Rh/Al_2O_3 (NO_3)[d]	0.83	0.75	195.9	218.7
1 wt% Rh/Al_2O_3 (NO_3)	1.09	1.08	110.8	111.9
0.5 wt% Rh/Al_2O_3 (NO_3)	1.11	1.18	130.0	122.5
0.1 wt% Rh/Al_2O_3 (NO_3)	–	–	26.8[e]	–

[a]At 300°C, based on the H/Rh value.
[b]At 300°C, based on the CO/Rh value.
[c]Cl:$RhCl_3$.
[d]NO_3:$Rh(NO_3)_3$.
[e]Calculated by assuming H/Rh=1.

ities. For the Rh/Al_2O_3 (Cl), in spite of its high Rh dispersion (see Table 2), the catalytic activity was severely suppressed probably due to the effect of residual Cl in the catalyst. Namely, the presence of Cl appears not to affect the H_2 and CO adsorption in the Rh/Al_2O_3 catalysts, but our present results show that the activity of N_2O decomposition is very sensitive to the presence of Cl. As shown in Fig. 2, after the H_2 reduction at 500°C the catalysts were a little more active than those after the H_2 reduction at 200°C.

Fig. 3 shows the effect of Rh loading on the catalytic activity of Rh/Al_2O_3 (NO_3) on N_2O decomposition. For the 0.1 wt% Rh/Al_2O_3 catalyst, since we could not calculate the H/Rh and CO/Rh values because of very small amount of H_2 and CO adsorption, the TOF value of this catalyst was calculated by assuming the H/Rh=1. In the Rh/Al_2O_3 (NO_3), the higher the Rh loading was, the better was the conversion of N_2O decomposition, and 2 wt% Rh/Al_2O_3 catalyst was the most active of all the Rh/Al_2O_3 catalysts (see Fig. 3).

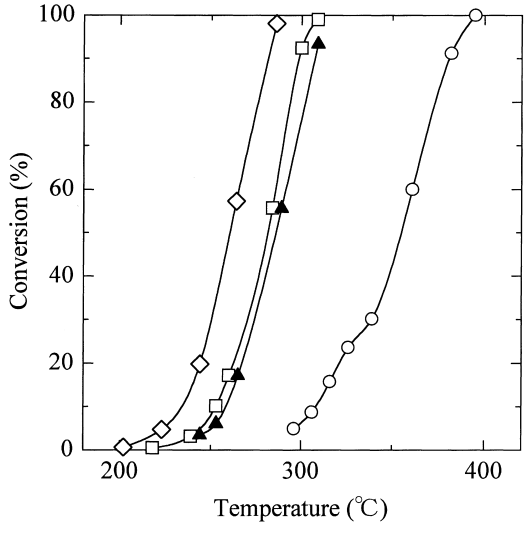

Fig. 3. N_2O conversion on Rh/Al_2O_3 (600) catalysts as a function of catalyst temperature. The effect of Rh loading: (○) 0.1 wt%; (▲) 0.5 wt%; (□) 1 wt%; (◇) 2 wt%. N_2O concentration was 0.5% in He.

3.3. *Rh/USY and Rh/NaY catalysts*

Fig. 4 shows the activities of Rh/zeolite (USY, NaY) catalysts for N_2O decomposition as a function of temperature. The Rh/USY (NO_3) prepared from $Rh(NO_3)_3$ and the Rh/NaY (IE) prepared by the ion exchange with $Rh(H_2O)_6^{3+}$ showed much higher than those of the other catalysts shown in Fig. 4, and the Rh/USY (NO_3) showed the highest activity of all the catalysts studied in our laboratory. The activity of the Rh/NaY (NO_3) prepared from $Rh(NO_3)_3$ was lower than that of the Rh/NaY (IE). Moreover, the activity of the Rh/NaY (Cl) prepared from $RhCl_3$ was much lower than that of the Rh/NaY (NO_3). This lower activity of the Rh/NaY (Cl) as well as the Rh/Al_2O_3 (Cl) may be caused by the residual Cl in the catalyst, because the activity of the Rh/NaY (Cl) was increased by washing the catalyst with hot water, but it was still lower than that of the Rh/NaY (NO_3).

Table 3 summarizes the H/Rh and CO/Rh values and the TOF values of the Rh/zeolite catalysts. The TOF values of Rh/USY (NO_3) (calcined in air for 1 h

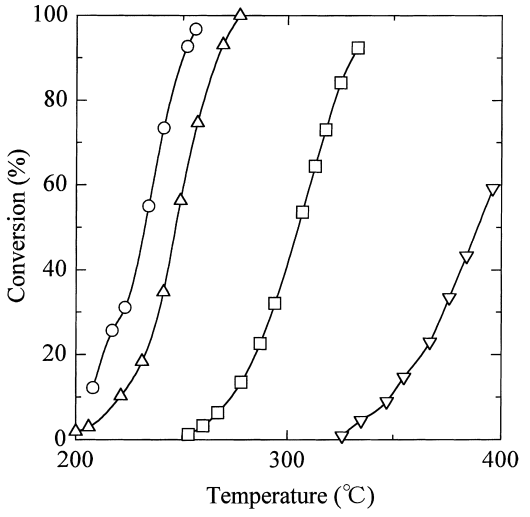

Fig. 4. N_2O conversion on Rh/zeolite catalysts as a function of catalyst temperature. (○) Rh/USY (NO_3); (△) Rh/NaY (IE); (□) Rh/NaY (NO_3); (▽) Rh/NaY (Cl). N_2O concentration was 950 ppm in He.

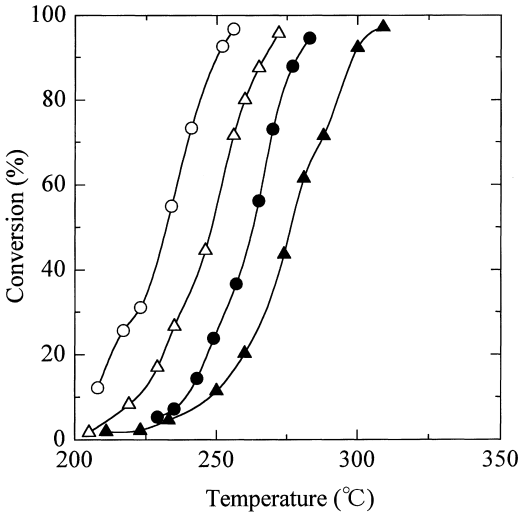

Fig. 5. N_2O conversion on Rh/USY (NO_3) catalysts as a function of catalyst temperature. Effect of the temperature at which the samples were calcined in air after the incipient wetness impregnation with $Rh(NO_3)_3$. (●,▲) after the air calcination at 500°C; (○,△) after the air calcination at 600°C. N_2O concentration were 950 ppm (●,○) or 5000 ppm (▲,△).

at 600°C after the impregnation of $Rh(NO_3)_3$) and Rh/NaY (IE) were higher than those of the other catalysts. There is a good correlation between the activities from the TOF values and the Rh dispersion when compared with the catalysts on the same support of NaY. However, this result cannot be applicable to the Rh/USY (NO_3) catalysts. Fig. 5 shows the effect of temperature at which the 2 wt% Rh/USY catalysts were calcined after the impregnation of $Rh(NO_3)_3$ on the conversion of N_2O decomposition. Here, we consider that the high H/Rh value (1.49) of the Rh/USY (NO_3) was obtained as a result of hydrogen spillover onto the USY support (see Table 3). The Rh dispersion of the catalyst calcined at 500°C was higher than that of the catalyst calcined at 600°C judging from the CO/Rh values, but for the conversion of N_2O decomposition and the TOF value, the latter was clearly higher than the former (see Fig. 5). Namely, for the Rh/USY (NO_3) catalysts, there is no correlation between the activities of N_2O decomposition and the Rh dispersion. The origin of the higher activity after the calcination at 600°C is not clear at the present stage.

The effects of N_2O pressure and O_2 pressure on the rate of N_2O decomposition were also studied for the Rh/USY (NO_3): the reaction order to N_2O was 0.25 ± 0.01, and the reaction order to O_2 was -0.08 ± 0.02. Namely, the activity was only slightly decreased by the addition of O_2.

Table 3
Comparison of the Rh dispersion and the TOF values of Rh/zeolite catalysts (950 ppm N_2O)

Catalyst	Pretreatment (°C)[a]	H/Rh	CO/Rh	TOF ($\times10^{-3}$ s^{-1})[b]	TOF ($\times10^{-3}$ s^{-1})[c]
Rh/USY (NO_3)	600	0.62	0.47	8.83	11.7
	500	1.49	0.62	0.62	1.50
Rh/NaY (IE)	400	0.95	1.00	2.73	2.61
Rh/NaY (NO_3)	600	0.27	0.19	0.23	0.33
	500	0.45	0.38	0.37	0.43

[a]The temperature at which the catalyst was calcined in air for 3 h after the Rh was loaded.
[b]At 250°C, based on the H/Rh value.

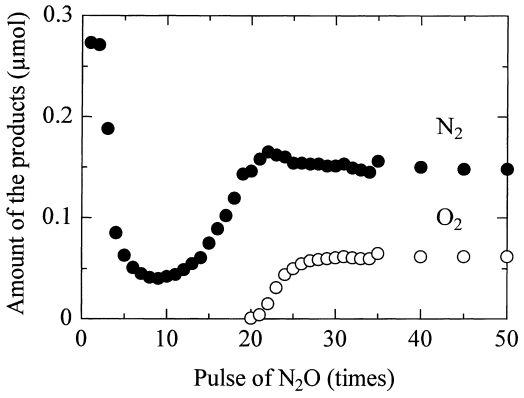

Fig. 6. The amount of the products from each pulse of N_2O over 2 wt% Rh/USY (NO_3) catalyst at 260°C.

3.4. Pulsed N_2O decomposition

Fig. 6 shows the amount of the products (nitrogen and oxygen) from N_2O decomposition over the Rh/USY (NO_3) at 260°C to each pulse (0.517% N_2O in helium). An interval of pulses was about 4 min. Until the 19th, the product was only nitrogen. The amount was 0.272 μmol (equivalent to 100% conversion of N_2O) for the first pulse, and it decreased until the 9th. After the 10th it increased slowly, and finally reached a stable state. On the other hand, oxygen was produced after the 19th, and the amount also increased slowly, finally reached a stable state. In previous works, Winter [14–16] and Hall et al. [17,18] proposed the following reaction scheme.

$$N_2O(g) + \square \rightarrow N_2(g) + O(ads) \quad (1)$$

$$2O(ads) \rightarrow O_2(g) + 2\square \quad (2)$$

$$N_2O(g) + O(ads) \rightarrow N_2(g) + O_2(g) + \square \quad (3)$$

$$O_2(g) + 2\square \rightarrow 2O(ads), \quad (4)$$

where □ and O(ads) are empty sites and sites adsorbed by oxygen atoms, respectively. It is clear that the recombination of oxygen on the catalyst surface to produce O_2 (reaction (2)) did not occur until the 19th. Furthermore an O_2 TPD measurement from completely oxygen covered surface showed that O_2 was not desorbed up to 600°C. So, one possibility may be that O_2 is freed not by the recombination of oxygen (reaction (2)) but on collision of N_2O molecules with the adsorbed oxygen atoms (reaction (3)). However, further experiments using tracer techniques will be necessary to elucidate the mechanism of N_2O decomposition.

References

[1] Y. Li, J.N. Armor, Appl. Catal. B 1 (1992) 21.
[2] Y.-F. Chang, J.G. McCarty, E.D. Wachsman, V.L. Wong, Appl. Catal. B 4 (1994) 283.
[3] Y.-F. Chang, J.G. McCarty, Y.L. Zhang, Catal. Lett. 34 (1995) 163.
[4] Y.-F. Chang, J.G. McCarty, E.D. Wachsman, Appl. Catal. B 6 (1995) 21.
[5] J. Oi, A. Obuchi, A. Ogata, H. Yagita, G.R. Bamwenda, K. Mizuno, Chem. Lett. (1995) 453.
[6] J. Oi, A. Obuchi, G.R. Bamwenda, A. Ogata, H. Yagita, S. Kushiyama, K. Mizuno, Appl. Catal. B 12 (1997) 277.
[7] J.N. Armor, T.A. Braymer, T.S. Farris, Y. Li, F.P. Petrocelli, E.L. Weist, S. Kannan, C.S. Swamy, Appl. Catal. B 7 (1996) 397.
[8] S. Inagaki, Y. Fukushima, K. Kuroda, J. Chem. Soc., Chem. Commun. (1993) 680.
[9] R.D. Shannon, J.C. Vedrine, C. Naccache, F. Lefebvre, J. Catal. 88 (1984) 431.
[10] K. Yuzaki, T. Yarimizu, S. Ito, K. Kunimori, Catal. Lett. 47 (1997) 173.
[11] K. Kunimori, K. Yuzaki, T. Yarimizu, M. Seino, S. Ito, Stud. Surf. Sci. Catal. 105 (1997) 2083.
[12] K. Kunimori, Y. Ikeda, M. Soma, T. Uchijima, J. Catal. 79 (1983) 185.
[13] K. Kunimori, T. Uchijima, M. Yamada, H. Matsumoto, T. Hattori, Y. Murakami, Appl. Catal. 4 (1982) 67.
[14] E.R.S. Winter, J. Catal. 15 (1969) 144.
[15] E.R.S. Winter, J. Catal. 19 (1970) 32.
[16] E.R.S. Winter, J. Catal. 34 (1974) 431.
[17] C.M. Fu, V.N. Korchak, W.K. Hall, J. Catal. 68 (1981) 166.
[18] J. Leglise, J.O. Petunchi, W.K. Hall, J. Catal. 86 (1984) 392.