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Catalytic decomposition of N_2O over supported rhodium catalysts: high activities of Rh / USY and Rh / Al_2O_3 and the effect of Rh precursors

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The catalytic decomposition of nitrous oxide to nitrogen and oxygen has been studied over Al_2O_3-supported and zeolite-supported Rh catalysts. The activities of Rh / Al_2O_3 and Rh / USY (ultrastable Y zeolite) catalysts prepared from $Rh(NO_3)_3$ were higher than those of Rh / ZSM-5 and Rh / ZnO reported in the literature, while the activity of a Rh / Al_2O_3 catalyst prepared from $RhCl_3$ was suppressed severely in spite of the high H / Rh and CO / Rh values. 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.

Keywords: N_2O decomposition, Rh / Al_2O_3, Rh / USY, TOF values

1. Introduction

Nitrous oxide (N_2O) is one of the environmental pollutants because it contributes to the catalytic destruction of stratospheric ozone and is a greenhouse gas. To protect our environment there is a need to decompose N_2O. Recently, Li and Armor [1] reported that Rh (or Ru)/ zeolite (ZSM-5) catalysts are very active for catalytic decomposition of N_2O (to N_2 and 1/2 O_2) at low temperatures (e.g., 300°C). Since then, several works [2–6] have been reported for the catalytic decomposition of N_2O over metal (Rh, Ru, Fe, Co, and Ni) catalysts. Oi et al. [5] have studied the activities of Rh catalysts supported on various oxides, and reported that Rh / ZnO was the most active catalyst. However, little is known about the effects of Rh dispersion (the percentage exposed) and preparation variables such as Rh precursors ($RhCl_3$, $Rh(NO_3)_3$). In fact, they [1,5] failed to report TOF values based on the percentage exposed. We have studied the activities (and TOF values) of N_2O decomposition over Al_2O_3-supported and zeolite-supported Rh catalysts, and found that Rh / Al_2O_3 and Rh / USY (ultrastable Y zeolite) catalysts prepared from $Rh(NO_3)_3$ are more active than those reported so far [1,5] and the activity of Rh / Al_2O_3 is very sensitive to the Rh precursors.

2. Experimental

The catalyst supports used are Japan Reference alumina (JRC-ALO-4, BET: 168.2 m^2/g), NaY (SK-40, GL SCIENCE, BET: 765.1 m^2/g) and USY (TOSO, Si/ Al_2 = 14.6, BET: 695.1 m^2/g). The NaY and USY supports were precalcined in air for 3 h at 600 and 700°C, respectively. Rh / NaY and Rh / USY catalysts were prepared by incipient wetness impregnation with aqueous solutions of $RhCl_3$ or $Rh(NO_3)_3$, followed by air calcination at 600°C for 3 h. A Rh / NaY catalyst was also prepared by an ion exchange method using an aqueous solution of $RhCl_3$ [7], followed by air calcination at 400°C for 3 h. Shannon et al. [7] reported that ion exchange with hexa-aquoion, $Rh(H_2O)_6^{3+}$, using $RhCl_3$(aq) solution (pH 4–5) could be used to prepare highly dispersed Rh in NaY zeolite [7]. Rh / Al_2O_3 catalysts were prepared by incipient wetness impregnation with aqueous solution of $RhCl_3$ or $Rh(NO_3)_3$, followed by air calcination at 500°C for 3 h. The Rh loading was 2 wt% for all the catalysts studied. The 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 microcatalytic reactor [8]. Unless otherwise stated, N_2O concentration was 950 ppm in helium. The catalysts were pretreated in H_2 at 500°C before use. The H_2 and CO chemisorption measurements were performed by a conventional volumetric adsorption apparatus [9,10]. The total adsorption of H_2 (H / Rh) as well as irreversible adsorption of CO (CO / Rh) were measured after H_2 reduction at 500°C [10]. The TOF values (molecules of N_2O converted per number of surface Rh per s) were calculated by assuming that the adsorption stoichiometry (H / surface Rh) is unity.

3. Results and discussion

Figure 1 shows the activities of N_2O decomposition over Rh catalysts as a function of temperature. The Rh / Al_2O_3 (NO_3) prepared from $Rh(NO_3)_3$ showed higher activity, while the Rh / Al_2O_3 (Cl) prepared from $RhCl_3$

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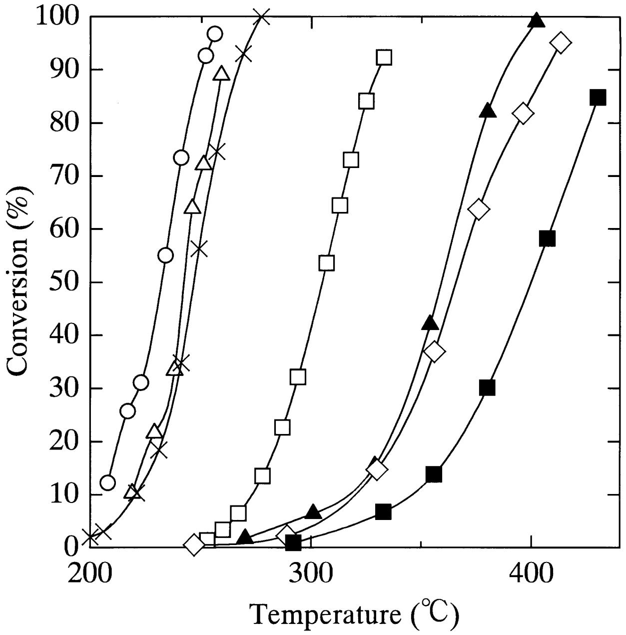

Figure 1. N_2O conversion on Rh/USY (NO_3) (○), Rh/Al_2O_3 (NO_3) (△), Rh/NaY (IE) (×), Rh/NaY (NO_3) (□), Rh/Al_2O_3 (Cl)(▲), Rh/NaY (Cl)(■), and Rh/NaY (Cl-washed)(◇) as a function of catalyst temperature (NO_3: $Rh(NO_3)_3$; Cl: $RhCl_3$). N_2O concentration was 950 ppm except for (▲, ◇, ■) 5000 ppm N_2O.

exhibited much lower activity. The activity of the Rh/NaY (Cl) prepared from $RhCl_3$ was also much lower than that of the Rh/NaY (NO_3) prepared from $Rh(NO_3)_3$. While the Rh/NaY (IE) catalyst prepared by the ion exchange with $Rh(H_2O)_6^{3+}$ showed higher activity than the Rh/NaY (NO_3) catalyst, the Rh/USY (NO_3) showed much higher activity than the Rh/NaY (NO_3) and the highest activity of all the catalysts studied. Table 1 summarizes the H/Rh and CO/Rh values and the TOF values of the catalysts. All kinetic data were taken from the N_2O conversion below 20%. For comparison, the TOF values are calculated from the activities of the Rh catalysts reported in the literature [1,5]. The Rh/USY (NO_3) catalyst showed the highest TOF value. 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 activity of Rh/USY (NO_3) did not decrease during the reaction for more than 8 h. The effects of N_2O pressure and O_2 pressure on the rate of N_2O decomposition were also studied: 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, but under similar experimental conditions the activity of the Rh/USY (NO_3) catalyst was higher than those of Rh/ZSM-5 and Rh/ZnO reported in the literature (see table 1).

Table 1
Comparison of the Rh dispersion and the activities of Rh catalysts (950 ppm N_2O)

Catalyst	H/Rh	CO/Rh	TOF($\times10^{-3}$ s^{-1})[a]
2% Rh/Al_2O_3 (NO_3)	0.83	0.75	14.0
2% Rh/Al_2O_3 (Cl)	1.16	1.10	0.48[b]
2% Rh/USY (NO_3)	0.62	0.47	26.0
2% Rh/NaY (IE)	0.95	1.00	10.9
2% Rh/NaY (NO_3)	0.27	0.19	1.91
2% Rh/NaY (Cl)	0.11	0.03	0.06
1% Rh/ZnO[c]	–	–	6.81[d]
0.6% Rh/ZSM-5[e]	–	–	6.60[d]

[a] At 280°C, based on the H/Rh value.
[b] 5000 ppm N_2O.
[c] From ref. [5].
[d] Calculated by assuming H/Rh = 1.
[e] From ref. [1].

The activity of the Rh/Al_2O_3 (NO_3) catalyst was also higher than those of the Rh catalysts reported so far [1,5]. For the Rh/Al_2O_3 (Cl) catalyst, the Rh is highly dispersed judging from the high H/Rh and CO/Rh values, but the catalytic activity was severely suppressed probably due to the effect of residual Cl in the catalyst. It should be noted that the presence of Cl appears not to affect the H_2 and CO adsorption in the case of Rh/Al_2O_3 catalysts [11], but the present results show that the catalytic activity of N_2O decomposition is quite sensitive to the presence of Cl. The activity of the Rh/NaY (Cl) may also be suppressed by the effect of Cl. In practice, the activity was increased after the Rh/NaY (Cl) catalyst was washed with hot water (see figure 1), but it was still lower than that of the Rh/NaY (NO_3) catalyst.

As shown in table 1, there is a good correlation between the activities and the Rh dispersion when compared with the catalysts on the same support (NaY). However, the Rh/USY (NO_3) catalyst showed the higher activity of N_2O decomposition in spite of the lower H/Rh and CO/Rh values. The USY-supported Rh catalysts seem to be a promising system for the catalytic decomposition of N_2O, and further work will be needed to elucidate the effect of the USY support and the nature of the active Rh surface for the development of high-performance catalysts.

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