Purification of Ammonia-Containing Water by Catalytic Selective Decomposition with Novel Pd-Supported Zirconia

Junji Taguchi, Yusuke Yoshinaga, and Toshio Okuhara*
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810

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Pd-Supported ZrO_2 prepared through a hydrothermal treatment was found to be pronouncedly effective for purification of waste water containing ammonia; NH_3 (1000 ppm) was exclusively converted to N_2 at 433 K in the presence of O_2 and undesirable NO_2^- and NO_3^- were not detected. It was further demonstrated that the Pd/ZrO_2 was insoluble during the reaction and was reusable without any treatment.

Removal of NH_3 in waste water is becoming more important, since NH_3 is a serious pollutant because of eutrophication of river, lake, etc.[1] The selective oxidative conversion of NH_3 to N_2 using solid catalysts has recently attracted much attention as an alternative to the current NH_3 removal methods such as biological treatment, absorption and thermal incineration, because this catalytic process has the possibility of a single operation with a relatively small expense. Kurita Kogyo Co. has recently commercialized a new process, in which NH_3 in waste water reacts with NO_2^- to form N_2 over Pt/TiO_2.[2]

A most desirable method is recognized to be selective oxidative decomposition of NH_3 with O_2 (or air) to N_2 (eq. (1)).

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (1)$$

There are some reports about the wet air oxidation (WAO) of NH_3 along this line. Imamura et al.[3] and Chakchouk et al.[4] examined WAO of NH_3 (1000 ppm) over Mn–Ce oxides at 536 K and 40 atm of air. When pH of the solution was adjusted to 12, a large part of NH_3 was converted, while undesirable NO_2^- and NO_3^- were detected at the concentration of about 50 ppm. Qin and Aika[5] claimed that RuO_2/Al_2O_3 exhibited the highest activity for WAO of NH_3 at pH = 12 among various supported catalysts. Recently, we reported that Pt/TiO_2 catalyzed WAO at a moderate temperature, 433 K, without alkalization of the solution.[6] However, there are still issues to be solved, that is, the formation of the undesirable NO_3^- and NO_2^- and dissolution of the active components into the solution during the reaction.

Here we wish to report that Pd supported on a high surface area ZrO_2 prepared through the hydrothermal treatment catalyzed very efficiently WAO to N_2 without the formation of NO_3^- and NO_2^-.

As ZrO_2 supports, two kinds of ZrO_2 were prepared. The first one was obtained conventionally from $ZrOCl_2$ (Wako Pure Chem.) and an aqueous solution of NH_3 (25 wt%) at pH = 10. The ZrO_2 obtained after calcination at 723 K (surface area = 55 $m^2 \cdot g^{-1}$) is denoted to ZrO_2(C). XRD of ZrO_2(C) showed a monoclinic phase of ZrO_2. The second was prepared with modifications of the method in the literature.[7,8] $ZrOCl_2$ (7.7 g) was dissolved in distilled water (600 cm^3) and 50 cm^3 of ammonium aqueous solution (25 wt%) was added dropwise to the solution to form precipitates (pH = 10). The suspension was hydrothermally treated at 363 K for 90 h, and then the precipitate separated was washed with distilled water until no chloride ion was detected. The obtained ZrO_2 after the calcination at 723 K for 2 h is denoted to ZrO_2(H) (surface area = 283 $m^2 \cdot g^{-1}$, amorphous from XRD). Besides ZrO_2, TiO_2 (P-25, 46 $m^2 \cdot g^{-1}$), SiO_2 (Aerosil 300, 300 $m^2 \cdot g^{-1}$), mesoporous SiO_2 (FSM-16, 970 $m^2 \cdot g^{-1}$, supplied from Dr. S. Inagaki, Toyota Central R&D Lab.), Active Carbon (AC, 1155 $m^2 \cdot g^{-1}$, Wako Pure Chem.) and γ-Al_2O_3 (JRC-ALO-4, 166 $m^2 \cdot g^{-1}$) were used. All Pd-supported catalysts, containing 1.0 wt% Pd, were prepared by incipient wetness impregnations with an aqueous solution (0.115 $mol \cdot dm^{-3}$) of $PdCl_2$ (Wako Pure Chem.). After drying at 373 K for 6 h, they were calcined in air at 723 K for 2 h and reduced in a flow of H_2 at 673 K for 2 h.

The oxidation of NH_3 was performed in a glass autoclave (Taiatsu Techno TEM-V200, 250 cm^3) at 433 K as described in the literature.[6] After an aqueous solution (150 cm^3) of NH_4Cl (containing 1000 ppm of NH_3) and a catalyst (1 g) were put into the reactor, O_2 (about 100 cm^3) was introduced into the reactor at 5 atm at room temperature (8 atm at 433 K). The gas and liquid phases were analyzed with GC and FIA, respectively.[6,9] For NO_3^- and NO_2^-, the lower limit of detection was 0.01 ppm in the FIA. After the reaction, the concentrations of Pd and Zr dissolved in the solution were analyzed with ICP (SPS3000 Seiko Instrument Inc.).

Table 1 shows the results of NH_3 oxidation over 1wt%Pd supported catalysts. Among these catalysts, Pd/ZrO_2(H) and Pd/FSM-16 gave the higher conversions (close to 95%) of NH_3. In addition, the yields of N_2 reached 92–94% over both the cat-

Table 1. Conversion and product yield of selective oxidation of NH_3 in water over Pd-supported catalysts

Catalyst[a]	Conversion /%[b]	Yield/%[c]		
		N_2	NO_2^- [ppm]	NO_3^- [ppm]
Pd/ZrO_2(H)	94.5	91.9	0.0 [0.0]	0.0 [0.0]
Pd/FSM-16	95.4	94.0	0.1 [2.8]	0.0 [1.5]
Pd/AC	89.0	63.8	3.5 [84.1]	5.6 [182.2]
Pd/ZrO_2(C)	61.5	57.1	0.0 [0.0]	0.0 [0.0]
Pd/Al_2O_3	82.7	78.4	0.0 [1.2]	0.1 [3.6]
Pd/TiO_2	87.4	73.1	0.0 [0.0]	0.0 [0.0]
Pd/SiO_2	78.7	75.0	5.0 [121.1]	6.5 [210.4]
blank[d]	5.8	-	-	-

[a] 1 wt%Pd. [b] Conversion is defined as 100 × (mol of NH_3 which disappeared)/(mol of NH_3 present initially)/%. Reaction conditions: NH_3, 1000 ppm (150 cm^3; 8.8 mmol); O_2, 8 atm (20.4 mmol); catalyst, 1 g; temperature, 433 K; time, 6 h. [c] Yield was calculated on the basis of the number of N atom. The figures in the brackets are the concentrations in the unit of ppm. N_2O was not detected in the gas phase over all the catalysts. [d] Without catalyst.

alysts. It should be noted that NO_2^- and NO_3^- were not detected over Pd/ZrO_2(H), while Pd/FSM-16 produced small amounts of NO_2^- and NO_3^-. Pd/ZrO_2(C), Pd/Al_2O_3 and Pd/TiO_2 were less active than Pd/ZrO_2(H) and Pd/FSM-16 (Table 1). On the other hand, Pd/AC and Pd/SiO_2 were rather active, but produced large amounts of NO_2^- and NO_3^-. As reported previously,[9] NO_3^- species was present on supported Pd catalysts in only a few % of the amount of initial NH_3.

Then we examined the reusability of Pd/ZrO_2(H) as a indispensable function of environmental catalyst. Figure 1 provides the changes in the conversion of NH_3 by repeating the reaction, where the reaction was carried out using the catalyst separated by filtration without any pretreatment. It was found that the conversion of NH_3 on Pd/ZrO_2(H) was almost unchanged when the reaction was repeated at least three times. On the other hand, the conversions of NH_3 on both Pd/FSM-16 and Pd/AC were greatly declined by repeating the reaction. NO_2^- and NO_3^- were not detected at the second and third runs over Pd/ZrO_2(H). These results clearly indicate that Pd/ZrO_2(H) is reusable, keeping the high catalytic performance for the purification of NH_3-containing water.

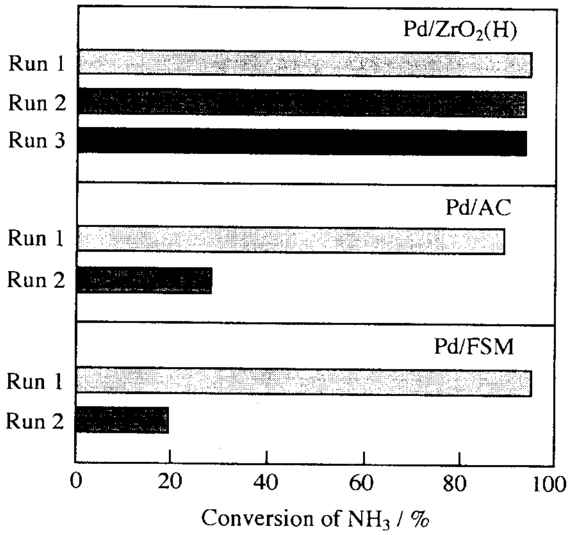

Figure 1. The changes in the conversion of NH_3 by repeating the reaction. Reaction conditions: NH_3, 1000 ppm (150 cm^3); O_2, 8 atm; catalyst, 1 g; temperature, 433 K; time, 6 h. The second reaction was performed with the used catalyst at the first run without any treatment. The third reaction was performed with the used catalyst at the second run without any treatment.

Table 2. Amount of Pd dissolved into the reactant solution after the reaction

Catalyst[a]	Amount of Pd dissolved /%[b]		
	Run 1[c]	Run 2[d]	Run 3[e]
Pd/ZrO_2(H)	0.0	0.0	0.0
Pd/FSM-16	44.6	-	-
Pd/AC	17.4	0.0	-
Pd/ZrO_2(C)	0.9	-	-
Pd/TiO_2	5.1	-	-
Pd/SiO_2	13.7	2.6	-

[a] 1wt%Pd. [b] ICP Analysis. 100×(amount of Pd atom dissolved)/(total amount of Pd atom in the catalyst)/%. [c] Reaction conditions: NH_3, 1000 ppm (150 cm^3); O_2, 8 atm; catalyst, 1 g; temperature, 433 K; time, 6 h. [d] The reaction was carried out by using the catalyst without any treatment after the catalyst was separated from the suspension at the first run. [e] The reaction was carried out with the catalyst without any treatment after the catalyst was separated from the suspension at the second run.

Insolubility of catalyst components during the reaction is also important for the environmental catalyst. Table 2 shows the amount of Pd dissolved from the solid catalyst into the aqueous solution during the reaction (433 K and 6 h). After the solid catalyst was separated by centrifugation, the solution was analyzed by ICP. It was clearly revealed that the amounts of Pd dissolved from Pd/ZrO_2(H) were zero within the experimental error (the lower limit is 0.03%) in all the runs. Furthermore, through were not shown in this table, the amounts of Zr dissolved in the solution were confirmed to be also negligible for Pd/ZrO_2(H). On the other hand, large amounts of Pd were dissolved in the cases of Pd/AC, Pd/FSM-16, and Pd/SiO_2 (Table 2). Pd/TiO_2 was also unfavorable for use because of the slight releasing of Pd. While ZrO_2(C) has the surface area similar to TiO_2, the amount of Pd dissolved from the Pd/ZrO_2(C) was much smaller than that from Pd/TiO_2, indicating that the surface of ZrO_2 can stabilize the Pd particles against the dissolution. This is a reason for the insolubility of Pd on the high surface area ZrO_2(H). XRD measurement of Pd/ZrO_2(H) showed that no Pd crystallite was present, suggesting the high dispersion of Pd on Pd/ZrO_2(H).

There are some reports[7,8,10–13] as for preparation of high surface area ZrO_2. A sol–gel method using the alkoxide gave ZrO_2 with relatively high surface areas; 120 $m^2 \cdot g^{-1}$ by Ward et al.,[10] and 380 $m^2 \cdot g^{-1}$ by Chuah et al.[11] after the calcination at 773 K. In addition, surfactant-aided synthesis was recently reported.[12,13] The obtained ZrO_2 by this method had about 300 $m^2 \cdot g^{-1}$ of the surface area after the calcination at 723 K. Considering the above reports, the hydrothermal treatment method used in the present study is a promising method for the preparation of ZrO_2 with the high surface area from the viewpoints of convenience.

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