Selective Oxidative Decomposition of Ammonia in Water to Nitrogen Catalyzed by Platinum-supported Titania

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Selective oxidative decomposition of NH_3 (or NH_4^+) in water to N_2 was achieved with 0.5 wt%Pt/TiO_2 catalyst at 433 K under 8 atm of O_2 without alkalization of the solution; NH_3 of 1000 ppm was exclusively converted to N_2 and undesirable products, NO_2^- and NO_3^- in the solution and N_2O in the gas phase were little formed.

Ammonia in waste-water is a serious pollutant which brings about eutrophication of river, lake, etc.;[1] its removal is thus becoming important. The removal of NH_3 has conventionally been conducted by biological treatment, adsorption, thermal incineration, etc. As a more economical and environmentally benign technology, catalytic removal of NH_3 in waste-water using solid catalysts has recently attracted attention. NH_3 has been oxidatively decomposed over solid catalysts[3–5] after transferring it from waste-water to a gas phase by air stripping,[2] although this process is still costly. Kurita Water Ind. Ltd. has commercialized a new process, in which NH_4^+ reacts with NO_2^- to form N_2 over Pt/TiO_2 in waste-water.[6] This system requires precise adjustment of the concentrations of the reactants.

A desirable method is selective oxidative decomposition of NH_3 with O_2 (or air) to N_2 (eq. (1)). There are some reports

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

about wet-air-oxidation (WAO) of NH_3 along this line. Imamura et al.[7] reported WAO of NH_3 (1000 ppm) over Mn-Ce oxides at 536 K and 40 atm of air. A large part of NH_3 disappeared at pH = 12, while NO_2^- and NO_3^- ions were formed with the total concentration of about 50 ppm. Chakchouk et al.[8] confirmed the above result. Recently Qin and Aika[9] found that RuO_2/Al_2O_3 exhibited the highest activity for WAO of NH_3 among various supported catalysts. NH_3 (1500 ppm) disappeared entirely at 503 K and pH = 12 under 15 atm of air.

However, these WAO systems still have two unsolved problems; (i) there is no evidence for the selective formation of N_2; the selectivity has not been determined experimentally, and (ii) it is necessary to alkalize the solution to accelerate the reaction. Quantitative analysis of N_2 formed is indispensable, and the excess alkalization of solution should be avoided, since such alkalized solution must be neutralized for disposal in environmentally acceptable way.

Here we wish to report the selective O_2 oxidation of NH_3 (NH_4^+) in water catalyzed by a Pt/TiO_2 catalyst at a moderate temperature, 433 K, without alkalization of the solution.[10]

Pt-supported catalysts containing 0.5 wt%Pt were prepared from H_2PtCl_6 and TiO_2 (P–25, 46 $m^2 \cdot g^{-1}$), ZrO_2 (by calcination of $Zr(OH)_4$ at 773 K, 55 $m^2 \cdot g^{-1}$), or γ-Al_2O_3 (JRC–ALO–4, 166 $m^2 \cdot g^{-1}$). Pt–H-ZSM-5 (Pt: 0.5 wt%) was prepared by an ion-exchange method from H-ZSM-5 (Tosoh, HSZ–860HOA, 410 $m^2 \cdot g^{-1}$) and $Pt(NH_3)_4Cl_2$. All the catalysts were pretreated in a flow of O_2 and then in a flow of H_2 at 723 K for each 3 h and were stored under ambient conditions.

Catalytic oxidation of NH_3 (NH_4^+) was performed in a glass autoclave (250 cm^3, Taiatsu Techno TEM–V200). Hereafter, NH_3 and/or NH_4^+ in the solution will be described as NH_3. An aqueous solution (150 cm^3) of NH_4Cl (containing 1000 ppm in weight as NH_3 (8.8 mmol)) and a catalyst (1 g) were charged into the reactor. An O_2 gas was introduced into the reactor to give 5 atm of pressure at 298 K (about 100 cm^3 (21 mmol)). The reactor was heated up to 433 K and kept at this temperature with stirring; the oxygen pressure became about 8 atm at this temperature.

A small portion of the gas was sampled into a syringe through a needle valve, and was analyzed by GC with columns of Molecular Sieves 5A (for N_2 and O_2) and Porapak Q (for N_2O). NH_3, NO_2^- and NO_3^- in the aqueous phase were analyzed quantitatively by a flow injection analysis system (FIA) (consisting of a Soma Optics S-3250 detector and a Sanuki Industry FI-710 analyzer equipped with a RX-703T pump and a R-5000C reactor) after withdrawing a small amount of liquid. After the filtration and drying (at room temperature) of the catalyst used at the first run, the number of N atom remained on the surface was determined by elementary analysis.

It was found that a key point to proceed the reaction is vigorous stirring the solution at both the upper and the bottom portions of the reactor to make a nearly uniform suspension in which the catalyst powder is well fluidized under the reaction conditions. A blank test showed that the decrease in NH_3 was only about 5% in the absence of catalyst under the O_2.

Figure 1 shows time courses of the conversion of NH_3 (the upper) and the conversion to N_2 (the bottom) over 0.5 wt%Pt/TiO_2, where the conversions of NH_3 and to N_2 are defined as 100 × (mol of NH_3 which disappeared)/(mol of NH_3 present initially) and 200 × (mol of N_2 formed)/(mol of NH_3 present initially), respectively. For some cases, the reaction was repeated three times. Between the runs, solid NH_4Cl was added to reform 1000 ppm NH_3 solution at room temperature. At the first run over 0.5 wt%Pt/TiO_2, about 70% and 98.5% of NH_3 disappeared after 1 h and 6 h, respectively. The time courses of the second and third runs were similar to that of the first run, suggesting that the catalyst deactivation was small under the reaction conditions. The conversion to N_2 was 65% at 6 h, while the conversion of NH_3 was 98.5%. It is noted that the yield of N_2 increased to 83% at 6 h of the third run.

Table 1 summarizes the yields of products in the oxidation of NH_3 over various Pt-supported catalysts. Over 0.5 wt%Pt/TiO_2, N_2 was the main product, and N_2O, NO_2^-, and NO_3^- little formed; the concentrations of NO_2^- and NO_3^- corresponded to 1.3 and 2.4 ppm at 6 h at the first run. On the other hand, 0.5 wt%Pt/Al_2O_3 was not efficient; the N_2 yield was 26% and 43% of 6 h for the first and second runs, respectively. Since the amounts of remaining NH_3 and NO_2^-, NO_3^-, and N_2O formed were also very small over 0.5 wt%Pt/Al_2O_3, undetected nitrogen

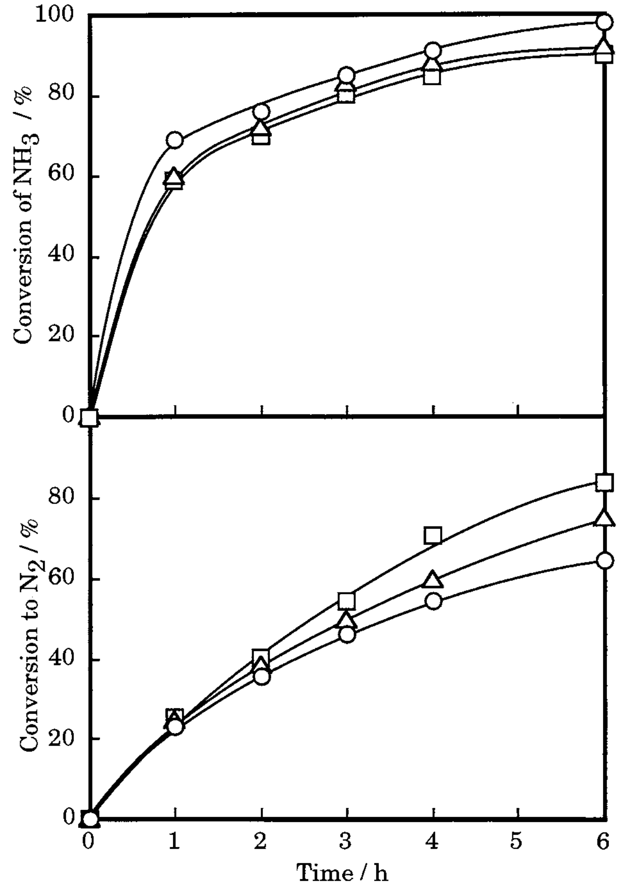

Figure 1. Time courses of the conversion of NH_3 (the upper) and the conversion to N_2 (the bottom) in oxidative decomposition of NH_3 over 0.5wt%Pt/TiO_2 at 433 K. NH_3; 1000 ppm (8.8 mmol), O_2; 5 atm at 298 K (21 mmol), and catalyst; 1 g. ○: 1st run, △: 2nd run, □: 3rd run.

atoms would be present as certain N-containing species on the surface. It should be emphasized that TiO_2 was a superior support in the N_2 yield among the oxide supports used in the present study. The selectivities to N_2 in the products of both the gas and liquid phases were higher than 99.6% for all cases.

The N-containing species adsorbed on the catalysts were examined by IR (KBr method). Both Pt/TiO_2 and Pt/Al_2O_3 after the first runs showed sharp peaks at 1383 cm^{-1} which are assigned to the ν_{as}(NO) band due to NO_3^- species.[11,12] Absorption bands due to NH_3 and NH_4^+ (3100~3330 cm^{-1} (ν(NH)) and 1390~1480 cm^{-1} (δ(NH))[11,12] were not detected on both the catalysts. In fact, when 0.5 wt%Pt/Al_2O_3 was added to the aqueous solution of NH_4Cl (1000 ppm) at 433 K under the N_2 atmosphere, no IR peak due to NH_3 and NH_4^+ on the surface was observed and N atoms were not detected in the catalyst by elementary analysis after the catalyst was washed with water at room temperature. Thus the surface N-containing species during the catalytic reaction would be mainly NO_3^- species. As shown in Table 1, the N atom was well balanced for all cases if the amounts of N atom on the surfaces were taken into account. To elucidate the role of the N-containing species on the surface in the reaction is an important subject of the next step.

Table 1. Activity of Pt-supported catalysts for selective oxidation of NH_3 in water to N_2

Catalysts[a]	Run[b]	Conv./%[c]	Yield / %[d]				N-surface/%[e]
			N_2	N_2O	NO_2^-	NO_3^-	
Pt/TiO_2	1	98.5	65	0	0.1	0.1	38.4 (102)[f]
	2	92.0	76	-	0.1	0.1	-
	3	90.1	83	-	0.2	0.1	-
Pt/Al_2O_3	1	99.8	26	0	0	0	62.0 (88)[f]
	2	99.9	43	-	0.1	0.1	-
	3	99.9	44	0	0.1	0.1	-
Pt/ZrO_2	1	98.5	54	0	0	0	45.0 (99)[f]
	2	92.1	71	-	0.1	0	-
Pt-H-ZSM-5	1	94.1	34	0	0	0	55.0 (89)[f]

[a] Pt: 0.5 wt%. [b] The reaction was repeated by the addition of NH_4Cl. [c] 100 × (mol of NH_3 which disappeared)/(mol of NH_3 present initially). Reaction conditions: NH_3, 1000 ppm; O_2, 5 atm (at 298 K); catalyst, 1 g; 433 K, 6 h. [d] Based on N atom. [e] 100 × (mol of N atom remaining on the surface)/(mol of NH_3 present initially)(see text). [f] Figures in parentheses are 100 × [(mol of $2N_2 + 2N_2O + NO_2^- + NO_3^-$) + (mol of N atom remaining on the surface) + (mol of remaining NH_3)]/(mol of NH_3 present initially).

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