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Catalysis Today 93–95 (2004) 263–271
CATALYSIS TODAY
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Decomposition of ammonium nitrate in aqueous solution using supported platinum catalysts

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Abstract

Supported metal catalysts for wet decomposition of ammonium nitrate were investigated in order to develop the catalysts, which can convert both ammonium ion and nitrate ion selectively to N_2 and H_2O under mild conditions, and to investigate the possible reaction pathways for simultaneous decomposition of ammonium and nitrate. Pt/active carbon (AC) catalysts were revealed to be the most active among the catalysts examined in this study. Effects of the reaction conditions such as metal loading, reaction temperature, and gas-feed pressure on the conversion and selectivity for N_2 were also investigated. 2 wt.% Pt/AC decomposed ammonium nitrate effectively under 0.5 MPa of air at 453 K showing the conversion of 99% or higher and N_2 selectivity of 95% or higher. While N_2O was the main byproduct with selectivity of 5% or lower in the reaction using Pt/AC catalysts, CO_2 was also formed at different yield depending on the activity, indicating AC support worked as a reducing agent, i.e. AC played an important role in formation of N_2 as well as in dispersion of the active metal as the support. NO_2^-, CO, NO, and NO_2 were hardly formed. A series of experiments using isotope-labeled ammonium nitrate revealed that simultaneous removal of ammonium ion and nitrate ion did not take place via independent reactions of the two ions but via the equimolecular reaction between the two and that wet air oxidation of ammonium ion competed with the reaction of ammonium ion with nitrate ion. N_2O was the major intermediate of the reaction for all the reactions studied.

Keywords: Selective decomposition of ammonium nitrate to N_2; Pt/AC; Equimolecular reaction

1. Introduction

A number of investigations on catalytic wet air oxidation (WAO) of ammonia [1–6] and catalytic hydrogenation of nitrate have been reported in the last decades in order to remove nitrogenous pollutants from industrial wastewater, groundwater, or drinking water. Excess amount of ammonia in water system causes eutrophication, while excess nitrate is toxic to human beings to cause serious health problems such as blue baby syndrome. Catalytic reduction of nitrate is a relatively new technique, first described in 1989 by Vorlop and Tacke [7], and followed by many other groups to develop more active and selective catalysts or systems [6,8–13]. Nitrate can be effectively hydrogenated only over bimetallic catalysts such as Pd–Cu, while nitrite can be reduced over monometallic catalysts. However, excess hydrogenation of nitrate produces undesirable ammonium as a byproduct [9].

On the other hand, few fundamental studies have been reported regarding simultaneous removal of ammonium and nitrate. Asano et al. reported a wastewater treatment process catalyzed by molybdenum ion to remove aqueous ammonium and nitrate simultaneously [14]. Harada et al. also studied catalytic decomposition of ammonium nitrate in aqueous phase with addition of both ammonia and COD (chemical oxygen demanding) compounds as reducing agent in the last decades [15,16]. However, both processes are performed at high reaction temperatures as 473–563 K and under high pressures as 4.0–8.0 MPa to achieve complete conversion. Moreover, even when such severe conditions are employed, selective conversion of nitrogenous species to N_2 is not guaranteed. Hence, more effective catalysts, which enable ammonium ion and nitrate ion in aqueous phase to react each other to form N_2 as well as to be decomposed under mild conditions, are still required. Simultaneous catalytic decomposition of ammonium and nitrate is also a good candidate

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doi:10.1016/j.cattod.2004.06.055

to simplify wastewater treatment process to reduce energy consumption for the treatment as well as the cost of the operation compared to the conventional ones such as biological treatment or multi-step processes.

The objective of this study is to develop the catalyst, which converts ammonium and nitrate simultaneously and selectively to N_2 under mild conditions. Since the stoichiometric reaction between ammonium and nitrate produces undesired product, N_2O, whose greenhouse forcing factor is 315 times as great as that of CO_2 [17], a reducing additive will be needed for selective decomposition to N_2 as following Eq. (1).

$$NH_4{}^+ + NO_3{}^- + \text{reducing additive} \rightarrow N_2 + 2H_2O + \text{oxidized product} \quad (1)$$

From this point of view, active carbon, which can work as reducing agent, was employed as support. In addition to development of the catalysts, the possible reaction pathways for selective N_2 formation are also proposed.

2. Experimental

2.1. Catalyst preparation

A commercial ball-shaped active carbon (AC, Kureha Chemicals, G-BAC-70R) was treated with hydrogen at 1173 K for 90 h to remove impurities and used as one of the support. Metal oxide supports employed in this study were a commercial Al_2O_3 (Aerosil Co.), ZrO_2 (GIMEX, RC-100), TiO_2 (Aerosil Co., P-25), and MgO (Ube Materials Co.). All the supported catalysts were prepared to have metal loadings of 1–3 wt.% by impregnation method with aqueous solution of palladium chloride (Wako Pure Chemical Co., 99.9%), hexachloroplatinic acid hexahydrate (Wako Pure Chemical Co., >98.5%), or rhenium trichloride (Mitsuwa Pure Chemical Co., Re: 63.5%). For ruthenium catalysts, acetone solution of ruthenium trichloride hydrate (Wako Pure Chemical Co., 99.9%) was used. After the impregnation, catalysts were dried in oven overnight at 373 K and hydrogen-treated in a closed glass vacuum system at 773 K (823 K for Re/AC) for 3 h followed by evacuation at the same temperature for 1 h.

3. Reaction apparatus and procedure

All reactions were performed using a batch type closed high-pressure system (autoclave). A given amount of the catalyst (1.0–2.0 g) and 100 mL of aqueous solution of ammonium nitrate (Kanto Chemical Co., >99.0%; 0.1 mL/L, pH = 5–6, no additive) were put into a Pyrex glass inner reactor and set to the autoclave. After the reaction gas was introduced at a given pressure between 0.1 and 3.5 MPa, the reactor was heated to reaction temperatures ranging between 403 and 453 K. After the reaction for 2 h, the autoclave was cooled down to ambient temperature and ammonia in the gas phase was trapped into 0.1 M sulfuric to be analyzed. Labeled ammonium nitrates, ${}^{15}NH_4NO_3$ (Aldrich, isotope purity of 98 atom% ${}^{15}N$) and $NH_4{}^{15}NO_3$ (Aldrich, isotope purity of 99 atom% ${}^{15}N$), were also used in the experiments to investigate the reaction pathways for N_2 formation.

3.1. Analysis

An ion chromatograph (IC; Dionex, DX 120) was used for determination of $NH_4{}^+$, $NO_3{}^-$, and $NO_2{}^-$. CO_2, N_2O, and N_2 which were formed during decomposition of ammonium nitrate, were also analyzed by gas chromatography (Hewlett-Packard, HP 5890 series II equipped with a thermal conductivity detector) on a stainless column packed with Porapak Q or Molecular Sieve 5A at 333 K. CO, NO, and NO_2 were not detected by GC–TCD and GC–MS thorough all reactions at all. Conversions and selectivity were calculated using following equations (2)-(6),

$$\text{conversion}_{(NH_4{}^+)}(\%) = \frac{[NH_4{}^+]_{init} - [NH_4{}^+]_{final}}{[NH_4{}^+]_{init}} \times 100 \quad (2)$$

$$\text{conversion}_{(NO_3{}^-)}(\%) = \frac{[NO_3{}^-]_{init} - [NO_3{}^-]_{final}}{[NO_3{}^-]_{initial}} \times 100 \quad (3)$$

$$\text{selectivity}_{(NO_2{}^-)}(\%) = \frac{[NO_2{}^-]_{final}}{2([NH_4NO_3]_{init} - [NH_4NO_3]_{final})} \times 100 \quad (4)$$

$$\text{selectivity}_{(N_2O)}(\%) = \frac{[N_2O]_{final}}{([NH_4NO_3]_{init} - [NH_4NO_3]_{final})} \times 100 \quad (5)$$

$$\text{selectivity}_{(N_2)}(\%) = \frac{[N_2]_{final}}{([NH_4NO_3]_{init} - [NH_4NO_3]_{init})} \times 100 \quad (6)$$

where $[X]_{init}$ and $[X]_{final}$ denote molar concentrations of species X before and after the reaction, respectively. GC–MS (Hewlett-Packard, HP 5890 series II plus/HP 5972) was used in addition to GC–TCD to determine the extent of ${}^{15}N$ incorporation into N_2 and N_2O in the isotope labeling experiments.

3.2. Characterization of catalysts

The catalysts were characterized with X-ray diffraction (Rigaku Multiflex-S, Cu Kα monochromated radiation source). TEM observation (JEOL, JEM-2010F, accelerating voltage of 200 keV and magnification ranged between 20,000 and 100,000) and elemental analysis were carried out for some of the catalysts to measure the size of metal particles and to determine the amount of adsorbed species on the catalysts before and after use, respectively. The dissolution of Pt during the reaction was examined by the analysis of solution after reaction with ICP-AES (SII, SPS-4000).

4. Results

4.1. Decomposition of ammonium nitrate using supported noble metal catalysts

Fig. 1 shows the conversion of NH_4^+ and NO_3^-, and the selectivity to N_2O formation over various metal catalysts supported on active carbon (AC) in the decomposition of NH_4NO_3 at 453 K with air-feed pressure of 1.0 MPa. N_2 was the major product and N_2O was detected as a major nitrogenous byproduct for all the catalysts used. The highest conversions of 60–70% was obtained by using Pt/AC, and decreased in the order; Pt/AC > Pd/AC > Ru/AC > Re/AC ≈ AC. NO_3^- conversion was higher than NH_4^+ conversion except for Ru/AC. On the other hand, selectivity to N_2O decreased by the following order: Re/AC > Pt/AC > Pd/AC > Ru/AC > AC. Since air was used as reaction gas, selectivity to N_2 cannot be determined. CO_2 was also formed through all the cases although quantitative determination was not carried out. The decomposition did not proceed at all without catalyst and hardly occur over other transition metal catalysts supported on AC.

Since Pt and Pd showed higher activity than other metals on AC, these two were chosen as active metal and four other kinds of support materials, MgO, Al_2O_3, ZrO_2, and TiO_2 were examined for ammonium nitrate decomposition. The supports were selected based on previous reports regarding catalytic wet conversion of ammonium or nitrate. We have recently found that Pd/MgO exhibited extremely high performance in wet air oxidation (WAO) of ammonia and Okuhara et al. reported that Pd/ZrO_2 also exhibited high activity for WAO of ammonia [5,6] while Pt/TiO_2 has been in practical use for catalytic oxidation of ammonia by nitrite in Kurita process [18]. Furthermore, other papers reported that Pd/Al_2O_3 catalysts doped with other metals represented high activity for liquid-phase hydrogenation of nitrate [7–12]. The results are shown in Fig. 2. Though MgO supported catalysts exhibited higher NH_4^+ conversion than AC supported catalysts, conversion of NO_3^- by MgO supported catalysts was much lower than that by AC supported ones. Other metal oxide supported catalysts did not have such a high activity as MgO supported catalysts, with the exception of high NO_3^- conversion by Pt/TiO_2. Most of Pt catalysts exhibited higher activity to ammonium nitrate decomposition than Pd catalysts. With respect to the selectivity to N_2O, remarkable decrease was observed when metal oxides were used as support instead of active carbon, especially for MgO. The formation of NO_2^- was negligible for all the catalysts. The pH of the solution after reaction was also measured and it was found that the pH decreased after the reaction. In the case of Pd/MgO and Pt/MgO, increase in pH was probably due to strong basicity of MgO (as in the form of $Mg(OH)_2$ during the reaction in aqueous phase).

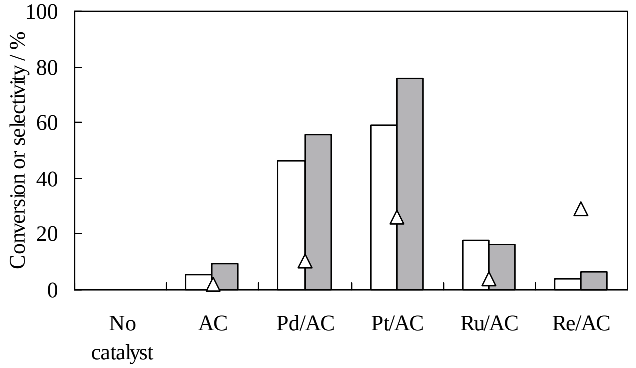

Fig. 1. Decomposition of ammonium nitrate by active carbon supported catalysts. Air-feed pressure, 1.0 MPa; metal loading, 3 wt.%; initial ammonium nitrate concentration, 0.1 mol/L; reaction time, 2 h. (☐) NH_4^+ conversion; (■) NO_3^- conversion; (△) N_2O selectivity.

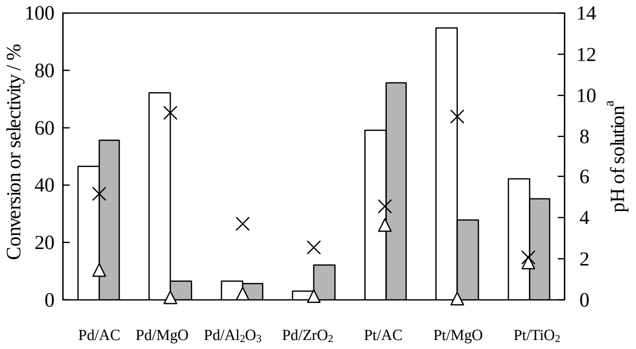

Fig. 2. Decomposition of ammonium nitrate by supported palladium and platinum catalysts. Air-feed pressure, 1.0 MPa; metal loading, 3 wt.%; initial ammonium nitrate concentration, 0.1 mol/L; reaction time, 2 h. (☐) NH_4^+ conversion; (■) NO_3^- conversion; (△) N_2O selectivity; (×) pH. (a) Initial pH of 5.8.

The time course of the reaction at 453 K with air-feed pressure of 1.0 MPa are illustrated for Pd/AC and Pt/MgO catalysts in Figs. 3 and 4, respectively. In the case of Pd/AC, conversions of NH_4^+ and NO_3^- increased with an increase in reaction time and then reached around 95% with higher conversions of NO_3^- than those of NH_4^+. The selectivity to N_2O was constantly around 10% and pH of the solution slightly decreased as the reaction proceeded. As for Pt/MgO, NH_4^+ conversion reached almost 100% after 4 h, whereas NO_3^- conversion was about 15% and N_2O formation was negligible.

The contribution of residual adsorbed nitrogen-containing species on the catalysts to the calculated conversions, selectivities, and thus mass balance on nitrogen were inspected for active catalysts, Pd/AC, Pt/AC, and Pt/MgO. The amount of residual adsorbed nitrogen on the whole catalysts ranged between 0.6 and 1.1 mmol, which was 3–6 mol%

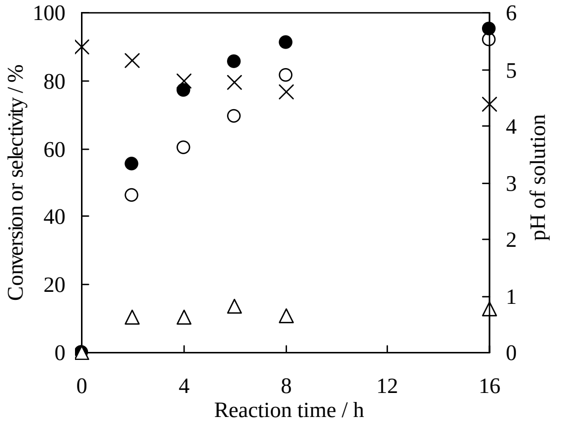

Fig. 3. Time course of ammonium nitrate decomposition by 3 wt.% Pd/AC. Reaction time, 2, 4, 6, 8, or 16 h; air-feed pressure, 1.0 MPa; initial ammonium nitrate concentration, 0.1 mol/L. (●) NH_4^+ conversion; (○) NO_3^- conversion; (△) N_2O selectivity; (×) pH.

of initially introduced nitrogen. For other elements, slight decrease of carbon (1.6–3.3 mmol) and increase of oxygen (5.0–6.3 mmol) were found for Pd/AC and Pt/AC. Such changes in elemental composition of the catalysts after the reaction can be attributed to oxidation of active carbon support during the reaction. Chlorine was also detected for all catalysts, which probably came from precursors of supported metals. The remarkable increase was found for hydrogen and oxygen in Pt/MgO after the reaction. It should be due to formation of $Mg(OH)_2$ by hydration of MgO during the reaction in aqueous solutions.

4.2. Decomposition of ammonium nitrate using active carbon supported platinum catalysts

To investigate the oxygen-partial pressure dependence of ammonium nitrate decomposition, the experiments were performed with air-feed pressure of 0.5 MPa using Pd/AC, Pt/AC, Pt/MgO, and Pt/TiO_2. The results are shown in Fig. 5 in comparison of the result with that of 1.0 MPa. While employing air-feed pressure of 0.5 MPa made conversions decreased for Pd/AC and Pt/TiO_2, conversions for Pt/AC and Pt/MgO increased to be almost 100% in the case of Pt/AC. Moreover, the selectivity to undesirable N_2O formation significantly decreased for all the catalysts. Thus, under these conditions, Pt/AC is the most suitable catalyst for ammonium nitrate decomposition, and further investigations using Pt/AC were carried out in the following sections.

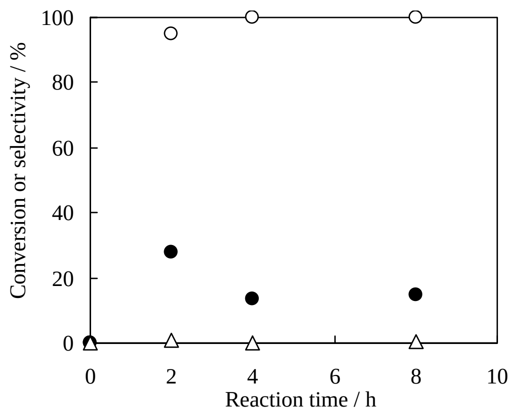

Fig. 4. Time course of ammonium nitrate decomposition by 3 wt.% Pt/MgO. Reaction time, 2, 4, or 8 h; air-feed pressure, 1.0 MPa; initial ammonium nitrate concentration, 0.1 mol/L. (●) NH_4^+ conversion; (○) NO_3^- conversion; (△) N_2O selectivity.

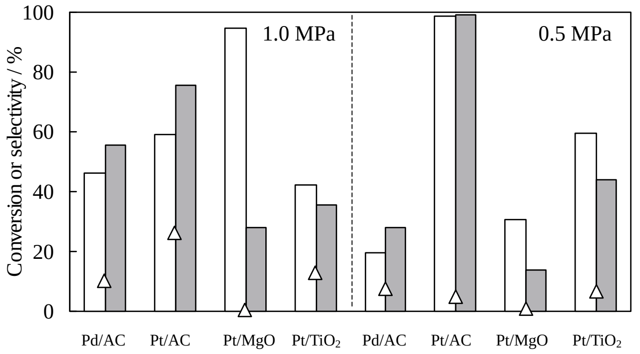

Fig. 5. Effects of air-feed pressure on ammonium nitrate decomposition by supported palladium and platinum catalysts. Air-feed pressure, 1.0 and 0.5 MPa; metal loading, 3 wt.%; initial ammonium nitrate concentration, 0.1 mol/L; reaction time, 2 h. (☐) NH_4^+ conversion; (■) NO_3^- conversion; (△) N_2O selectivity.

4.3. Reaction temperature dependence of the decomposition

The temperature dependence of ammonium nitrate decomposition is shown in Fig. 6. While reaction hardly proceeded at 403 K, the conversions increased with an increase in reaction temperature and almost complete conversions were obtained in the reaction at 443 K. It should be noted that NO_3^- conversions were higher than NH_4^+ conversions

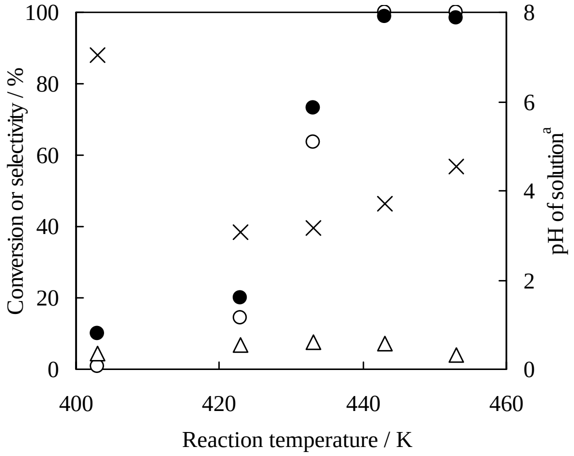

Fig. 6. Temperature dependence of decomposition of ammonium nitrate by 2 wt.% Pt/AC. Reaction temperature, 403, 423, 433, 443, or 453 K; air-feed pressure, 0.5 MPa; initial ammonium nitrate concentration, 0.1 mol/L; reaction time, 2 h. (●) NH_4^+ conversion; (○) NO_3^- conversion; (△) N_2O selectivity; (×) pH. (a) Initial pH of 5.8.

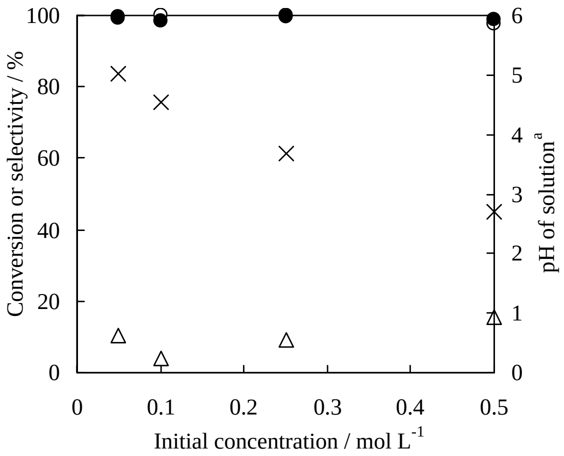

Fig. 7. Effects of initial ammonium nitrate concentration on decomposition of ammonium nitrate by 2 wt.% Pt/AC. Initial ammonium nitrate concentration, 0.05, 0.1, 0.25, or 0.5 mol/L; air-feed pressure, 0.5 MPa; reaction temperature, 453 K; reaction time, 2 h. (●) NH_4^+ conversion; (○) NO_3^- conversion; (△) N_2O selectivity; (×) pH. (a) Initial pH of 4.0–5.5.

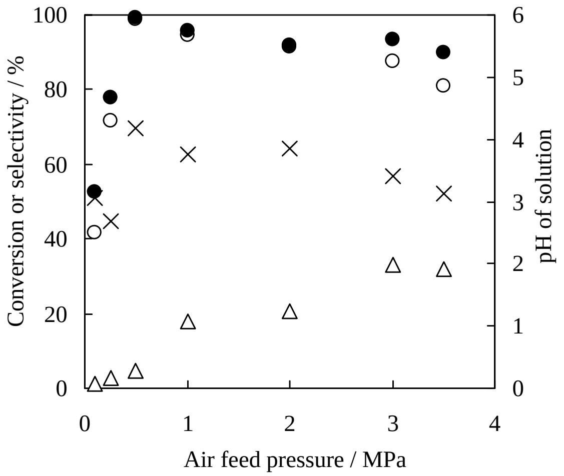

Fig. 8. Air-feed pressure dependence of decomposition of ammonium nitrate by 3 wt.% Pt/AC. Air-feed pressure, 0.1, 0.25, 0.5, 1.0, 2.0, 3.0, or 3.5 MPa; initial ammonium nitrate concentration, 0.1 mol/L; reaction temperature, 453 K; reaction time, 2 h. (●) NH_4^+ conversion; (○) NO_3^- conversion; (△) N_2O selectivity; (×) pH.

under the conditions where ammonium nitrate was not completely decomposed (<443 K). In addition, the decrease of pH during the reaction was large at low conversions except for the reactions at 403 K. In spite of the decrease of pH, no other anion than NO_3^-, which should exist as counter anion of H^+, was detected. The selectivity to N_2O was around 5% and the formation of NO_2^- was negligible at all employed temperatures.

4.4. *Effects of initial ammonium nitrate concentration*

Fig. 7 shows the effects of initial ammonium nitrate concentration. No remarkable difference in the conversions was found with the initial ammonium nitrate concentration ranging from 0.05 to 0.5 mol/L, i.e. 2.0 g of 2 wt.% Pt/AC was applicable for almost complete conversions even at the initial concentration of 0.5 mol/L. However, the selectivity for undesirable N_2O formation slightly increased with an increase in the initial concentration and large amounts of CO_2 (7.1 and 20.0 mmol for 0.25 and 0.5 mol/L, respectively) was evolved, indicating active carbon support was oxidized during the reactions. With respect to the lower initial concentration of 0.05 mol/L, a slight increase of N_2O selectivity was also observed. The decrease of pH during the reaction was larger with higher initial concentrations.

4.5. *Effects of gas-feed pressure*

Fig. 8 exhibits the dependence of air-feed pressure on ammonium nitrate decomposition using 3 wt.% Pt/AC. NH_4^+ and NO_3^- conversions were about 40 and 50% with air-feed pressure of 0.1 MPa, and increased to reach the maximum with that of 0.5 MPa, then decreased slightly with an increase in air-feed pressure. Since it was not obvious on which the activity depended, total pressure or oxygen-partial pressure, further study was performed in the next section. Moreover, the N_2O selectivity increased with an increase in air-feed pressure, reaching about 30% at 3.0 MPa. Thus, air-feed pressure of 0.5 MPa was the optimum condition considering both the conversions and the selectivity to N_2. The decrease in pH was also observed in these experiments.

4.6. *Effects of oxygen partial pressure*

In order to clarify the effects of oxygen partial pressure on the activity shown in Fig. 8 (from 0.1 to 0.5 MPa), reactions were carried out using O_2–Ar as reaction gas with various O_2/Ar ratios. The total gas-feed pressure was fixed to 1.0 MPa and the oxygen partial pressures of the gas was varied with O_2/Ar of 0.02, 0.03, 0.1, and 0.2 corresponded to those of 0.1, 0.15, 0.5, and 1.0 MPa of air, respectively.

The results in Table 1 indicate that neither NH_4^+ conversion nor NO_3^- conversion depend upon oxygen partial pressure. They were almost 100% at any oxygen partial pressure, even in the absence of oxygen in gas phase ($O_2/Ar = 0$). In order to eliminate the effects of dissolved oxygen in the reaction solution, the solution was bubbled and the inside of the autoclave was purged thoroughly with highly pure nitrogen (>99.999%) or Ar, and then the reactions were performed after pressurized with O_2/Ar gas. As a result, conversions of both NH_4^+ and NO_3^- exceeded 99% in the presence of oxygen, but they dropped down to only 80% under pure nitrogen. This fact implies that oxygen plays an important role in the ammonium nitrate decomposition while trace amount of oxygen is enough to promote or initiate the reaction.

The results in Table 1 also suggest that the activity shown in Fig. 8 was dependent upon the total gas-feed pressure. Thus, reactions with gas-feed pressure of 0.1 MPa were performed to verify the dependence of the decomposition on

Table 1
Effects of oxygen partial pressure on decomposition of ammonium nitrate by 3 wt.% Pt/AC

O_2/Ar ratio	Conversion (%)		Selectivity (%)			Mass balance on nitrogen (%)	CO_2 formation (mmol)
	NH_4^+	NO_3^-	N_2	N_2O	NO_2^- [a]		
0.00	77.0	80.4	83.2	4.6	0.8	83.0	0.4
0.02	99.8	99.0	87.1	3.5	0.2	91.6	1.4
0.03	99.7	99.6	79.6	3.2	0.2	83.0	1.4
0.1	100.0	99.6	91.2	4.8	0.0	96.0	2.8
0.2	99.1	99.2	55.8	23.9	0.1	79.8	2.6

Catalyst weight, 2.0 g; total gas-feed pressure, 1.0 MPa; initial ammonium nitrate concentration, 0.1 mol/L; reaction time, 2 h; reaction temperature, 453 K.

[a] Including HNO_2 in gas phase.

total air-feed pressure. 20% O_2–Ar was used for these experiments containing the same amount of oxygen as 1.0 MPa of 2% O_2–Ar. Remarkable decrease of conversions of NH_4^+ and NO_3^- was observed in the reactions at 0.1 MPa O_2–Ar although the oxygen partial pressure was same as 2% O_2–Ar at 1.0 MPa, showing that the decomposition is dependent on the total gas-feed pressure. Although the selectivity to N_2 reached 91.2% at maximum with 10% O_2–Ar with high nitrogen mass balance of 96%, HNO_2 emission was examined: 0.1 mol/L NaOH aqueous was used as absorber instead of diluted H_2SO_4. Small amount of NO_2^- was detected and resulting selectivity to HNO_2 was ca. 0.8%. The amount of CO_2 formed in the reaction was 1–3 mmol.

4.7. Possible reactions pathways for decomposition of NH_4NO_3

To investigate the reaction pathways for selective decomposition of ammonium nitrate, several possible reaction to result N_2 formation were considered. The possible reactions to give intermediate, if it exists, were studied. Since simple stoichiometric decomposition of ammonium nitrate does not yield N_2 but N_2O due to an excess oxygen Eq. (7), reduction of NO_3^- to NO_2^- followed by reaction with NH_4^+ such as Eqs. (9) and (10) or reduction of N_2O to N_2 after formation of N_2O as Eq. (8) is necessary to yield N_2.

$$NH_4^+ + NO_3^- \rightarrow N_2O + 2H_2O \quad (7)$$

$$2N_2O + C \rightarrow 2N_2 + CO_2 \quad (8)$$

$$2NO_3^- + C \rightarrow 2NO_2^- + CO_2 \quad (9)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (10)$$

The role of AC as reducing agent was proved by CO_2 formation during reactions accompanying N_2 formation as described above. In order to confirm the possibility of the reaction of Eq. (10), the reactions of ammonium with nitrite, which has been investigated [18], were performed under the same conditions as those for NH_4NO_3 decomposition. Ammonium and nitrite reacted completely to form N_2, with little formation of N_2O and NO_3^-. Thus, NO_2^- can be an intermediate in decomposition of NH_4NO_3. Next, the possibility of Eq. (8) was studied by performing the reaction of pure N_2O in the presence of Pt/AC catalyst under the same condition as decomposition of NH_4NO_3. To exclude the contribution of N_2O and N_2 inadvertently into the reaction system, highly purified water and feed gas were introduced into the autoclave. As a result, N_2O was reduced to N_2 by Pt/AC with N_2O conversion of 31% and N_2 selectivity of 100%. Accordingly, N_2O should be the intermediate product of decomposition of NH_4NO_3. On the other hand, while a little NO_3^- was detected in the reaction solution after the reaction, the amount of NH_4^+ was under detection limit of the analysis suggesting that the contribution of the inverse reaction of ammonium nitrate decomposition as Eq. (11) cannot substantially occur.

$$N_2O + 2H_2O \rightarrow NH_4^+ + NO_3^- \quad (11)$$

Since air was used as reaction gas, wet air oxidation of ammonia can proceed in decomposition of NH_4NO_3 (Eq. (12)).

$$NH_4^+ + \frac{3}{4}O_2 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O + H^+ \quad (12)$$

Therefore, the individual reactions of oxidation of ammonium and reduction of nitrate were investigated using Pt/AC catalyst. Both reactions hardly proceeded with N_2O selectivity higher than that in ammonium nitrate decomposition.

The experiments using isotope-labeled ammonium nitrate with ^{15}N, i.e. $^{15}NH_4NO_3$ or $NH_4{}^{15}NO_3$ were carried out to confirm the pathways for N_2 formation in NH_4NO_3 decomposition. The initial concentrations were 0.05 mol/L for $^{15}NH_4NO_3$ solution and 0.1 mol/L for $NH_4{}^{15}NO_3$ solution. The feed-gas was N_2-free O_2–Ar ($O_2/Ar = 0.2$). The conversions and selectivity in these experiments are shown in Table 2. The conversions were almost 100% for

Table 2
Decomposition of ^{15}N isotope labeled ammonium nitrates by 2 wt.% Pt/AC

	Initial concentration (mol/L)	Conversion (%)		Selectivity (%)	
		NH_4^+	NO_3^-	N_2	N_2O
$^{15}NH_4NO_3$	0.05	100.0	99.3	76.5	8.2
$NH_4{}^{15}NO_3$	0.1	100.0	99.9	77.9	5.3

Catalyst weight, 2.0 g; gas-feed pressure, 0.5 MPa (O_2/Ar); reaction time, 2 h; reaction temperature, 453 K.

Table 3
Isotopic distribution of products in decomposition of ^{15}N isotope labeled ammonium nitrates by 2 wt.% Pt/AC

	Isotopic ratio in N_2			Isotopic ratio in N_2O		
	$^{14}N_2$	$^{14}N^{15}N$	$^{15}N_2$	$^{14}N_2O$	$^{14}N^{15}NO$	$^{15}N_2O$
$^{15}NH_4NO_3$[a]	0.0	1	0.145	n.d.[c]	1	0.192
$NH_4{}^{15}NO_3$[b]	n.d.[c]	1	0.005	n.d.[c]	1	0.238

Initial ammonium and nitrate concentration, 0.05 and 0.1 mol/L; catalyst weight, 2.0 g; O_2/Ar-feed pressure, 0.5 MPa; reaction time, 2 h; reaction temperature, 453 K.

[a] Initial concentration, 0.05 mol/L.

[b] Initial concentration, 0.1 mol/L.

[c] Not determined.

both $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$, while the N_2O selectivity was somewhat higher in the reaction of $^{15}NH_4NO_3$. The isotopic ratio of N_2 and N_2O was determined by mass spectrometry and presented in Table 3. Background N_2 and CO_2 (mass number is 44; the same as $^{14}N_2O$) in the mass spectrometer prevented reliable quantification of $^{14}N_2$ and $^{14}N_2O$. $^{14}N^{15}N$ and $^{14}N^{15}NO$ were the main products (>80%) for N_2 and N_2O, respectively. This result indicates that ammonium ion and nitrate ion react each other primarily in ammonium nitrate decomposition while the yield of about 13% for $^{15}N_2$ formation was observed in $^{15}NH_4NO_3$ decomposition. $^{15}N_2O$ was formed at the yield of 16–19% for both $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$.

ICP analysis of the reaction solution after the reaction confirmed that platinum dissolution to liquid phase did not occur during decomposition of ammonium nitrate at any temperature used. This observation is consistent with stable activity in repeated experiments with same catalysts.

5. Discussion

5.1. Factors influencing the conversion and the selectivity to nitrogen

As described above, almost complete conversion of 0.1 mol/L ammonium nitrate in aqueous phase to N_2 has been achieved using 2 wt.% Pt/AC under 0.5 MPa of air at 453 K for 2 h. The complete decomposition was attained even in the reactions at 443 K in 2 h and the initial ammonium nitrate concentration can be increased to at least 0.5 mol/L maintaining the high conversions as observed in Fig. 7. If WAO of ammonia is applied for these concentrations (0.1–0.5 mol/L) of ammonia, much more air including stoichiometric amount of oxygen and longer reaction time is necessary to obtain complete decomposition. On the other hand, if nitrate is reduced by the methods for hydrogenation, the process needs costly hydrogen gas and form undesirable ammonia as byproduct. Furthermore, the catalysts so far studied for nitrate reduction are mainly supported bimetallic catalysts, which need complicated process to prepare, because monometallic catalysts do not show the sufficient high activity [7–13]. Considering above, this synergistic ammonium nitrate decomposition in aqueous phase by Pt/AC is an attractive new process that has many advantages compared to conventional wastewater treatment technology.

Several factors, other than reaction temperature and time, were revealed to affect on the conversion of ammonium and nitrate. One of the most important factors is partial pressure of oxygen in the system. As shown in Table 1, significant decreases of conversion were observed when oxygen was thoroughly eliminated from the system, suggesting oxygen is essential for this reaction. However, high conversions were observed with a trace amount of oxygen. This fact indicates very small amount of oxygen is enough to promote the reaction. Another possible factor influencing the conversion is partial pressure of N_2 in gas phase. Since the ammonium nitrate decomposition is N_2-formation reaction, the equilibrium of the decomposition can shift to reactant side by dissolution of N_2 into water. The decrease of conversions under air-feed pressures higher than 0.5 MPa (Fig. 8) can be explained with this assumption. That is, the equilibrium changed resulting in apparent low conversion since more N_2 dissolves into water under higher air-feed pressures.

The total gas-feed pressure is also an important factor to affect the activity of the catalysts, as observed in Fig. 8. However, the reason of total gas-feed pressure dependence has not been clarified yet. A conceivable change caused by difference of the total gas-feed pressure is water vapor pressure in the system, which is expected to be larger under lower pressure. However, the relationship between conversions and water evaporation is obscure. On the other hand, by the fact that $NH_4{}^+$ conversion was higher than $NO_3{}^-$ conversion in the reaction by Pd/MgO and Pt/MgO, the oxidation of $NH_4{}^+$ by oxygen (Eq. (12)) should occur as well as the oxidation by $NO_3{}^-$.

N_2O selectivity increased with an increase in air-feed pressure and concentration of oxygen in the gas phase. It is considered that when the oxygen partial pressure increases, the concentration of oxygen on the catalyst surface also increases, then consequently, the reaction pathway to N_2O formation becomes more favorable. The increase of byproduct formation with an increase in air-feed pressure also reported in WAO of ammonia [3]. Thus, it is important to conduct the reaction with feeding an appropriate oxygen level to prevent formation of N_2O. In addition, a slight change of N_2O selectivity was observed in the reactions with different initial ammonium nitrate concentration as shown in Fig. 7. N_2O selectivity was at minimum with the initial concentration of 0.1 mol/L, and increased slightly both with lower and higher initial concentrations. The increase with lower initial concentration will be due to too much relative amount of oxygen to ammonium nitrate and the increase with higher initial concentration can be explained by increase of its concentration.

5.2. Effectiveness of supporting platinum catalyst on AC

By the facts that nitrate reduction proceeded efficiently only by AC supported catalysts as shown in Figs. 2–5, and CO_2 formation was observed through all the reactions using those catalysts, it is obvious that the role of AC as reducing agent is essential for this reaction. The result shown in Fig. 4 suggests that ammonium nitrate cannot be decomposed even for prolonged reaction over Pt/MgO, i.e. AC is also essential for effective N_2 formation. Since the ammonium nitrate decomposition hardly proceeded when Pt/MgO and AC were mixed and used for reaction, only AC in contact with Pt is considered to have the ability to act as reducing agent. The result of the reaction between AC and NH_4NO_3 in the absence of platinum (i.e. Pt loading = 0%) indicates that AC itself cannot promote the reaction. The amount of consumed AC can be estimated by the amount of CO_2 formed in the reaction, and it is around 1–2% of introduced amount (2.0 g) when 0.1 mol/L of ammonium nitrate is completely decomposed. Since it is regarded as negligible amount, it can be concluded that AC is an excellent support to complete ammonium nitrate decomposition at least for laboratory-scale experiments.

With respect to active metals, Pt showed the highest activity among the metals employed in this study as presented in Fig. 1. It was even more active than Pd, which had high catalytic activity for the reactions such as WAO of ammonia and nitrate hydrogenation. The order the activity among the supported metal catalysts can be explained by the oxygen affinity of metal surface which is represented by $-\Delta H_f{}^{\circ}$ (heat of formation of metal oxide) [19], as reported for some kinds of reactions [3,20–22]. Fig. 9 shows a plot of the activity to decomposition of NH_4NO_3 versus $-\Delta H_f{}^{\circ}$. The activity decreased with increasing the value of $-\Delta H_f{}^{\circ}$. This result may indicate weaker adsorption of oxygen onto metal surface is favorable in this reaction, that is, reactivity of surface oxygen is more important than surface oxygen concentration. Similar phenomena can be seen in the reactions of ethylene hydrogenation as reported in [20].

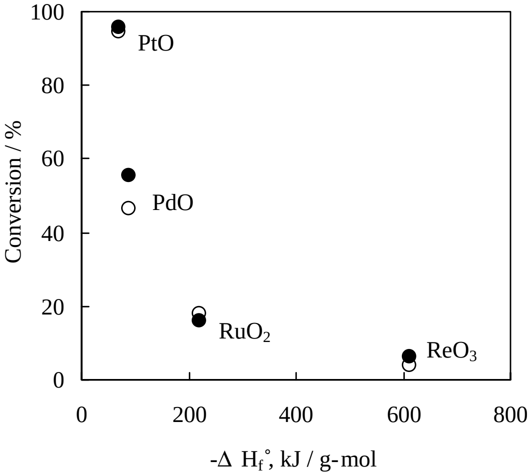

Fig. 9. Plot of conversions of ammonium nitrate decomposition by active carbon supported catalysts vs. the heat of formation of metal oxide. Air-feed pressure, 1.0 MPa; metal loading, 3 wt.%; initial ammonium nitrate concentration, 0.1 mol/L; reaction time, 2 h. (●) $NH_4{}^+$ conversion; (○) $NO_3{}^-$ conversion.

TEM images suggest Pt particles supported on AC are not so small as expected, even larger than Pt supported on MgO. This is possibly caused by metal sintering during H_2 treatment, which is performed at 773 K for 3 h in this study. Burguete et al. reported that the sintering of Pt (precursor; $H_2PtCl_6 \cdot 6H_2O$) supported on AC may start at 623 K and that the oxygen surface groups on AC may hinder the metal sintering. [23] Such oxygen groups were eliminated by hydrogen treatment in this study. In addition, methane formation by reaction between AC and H_2 during pretreatment was a possible reaction, resulting in Pt migration. The higher conversion of Pt/AC than Pt/MgO despite its larger particle size, shown in Figs. 2 and 5, suggested that the role of AC is more important than metal dispersion in this system. That is, though active metal is highly dispersed, ammonium nitrate decomposition hardly proceed without AC or other carbon source.

5.3. Possible reaction pathways for selective decomposition of ammonium nitrate

The possible intermediates of ammonium nitrate decomposition are $NO_2{}^-$ and N_2O, and the pathways of Eqs. (8) and (10) were experimentally ascertained to proceed. However, little $NO_2{}^-$ formation was seen in liquid phase after any reaction while N_2O was always detected. Moreover, the pathway of Eq. (9) was denied by the fact that $NO_2{}^-$ was not detected in the solution when the reaction was performed with Pt/AC using $NO_3{}^-$ as reactant. Thus, the major pathway for decomposition of NH_4NO_3 is not the reactions via $NO_2{}^-$ but those via N_2O.

In order to investigate whether N of $NH_4{}^+$ and N of $NO_3{}^-$ react mutually, each nitrogen was labeled with ^{15}N and the reactions were performed. The isotopic ratios shown in Table 3 can be approximately recalculated as following:

- N_2 formation: $NH_4{}^+ + NH_4{}^+ : NH_4{}^+ + NO_3{}^- : NO_3{}^- + NO_3{}^- = 13:87:0$;
- N_2O formation: $NH_4{}^+ + NH_4{}^+ : NH_4{}^+ + NO_3{}^- : NO_3{}^- + NO_3{}^- = 13:70:17$.

These results clearly indicate that $NH_4{}^+$ and $NO_3{}^-$ react each other mainly as expected. It is also revealed that $NH_4{}^+$ and $NH_4{}^+$ can react to form N_2 and N_2O. On the other hand, two $NO_3{}^-$ did not react to form N_2, while they could react to form N_2O. This is reasonable considering the electronic state of $NO_3{}^-$, and is supported by the results that N_2O selectivity increased with increase of $NO_3{}^-$ conversion as shown in Fig. 2.

Since simultaneous decomposition of ammonium and nitrate can proceed with trace amount of oxygen and oxygen is not required for stoichiometric reactions except for oxidation of NH_4^+, the role of oxygen is considered to initiate the reaction. Two kinds of initiation can be proposed: One is to oxidize ammonium ion slightly ($NH_4^+ \rightarrow NHx^+$; $x < 4$) followed by reaction with nitrate. The other is to oxidize AC to make it active as reducing agent. In both cases, the reactions will be able to proceed without oxygen once it starts to proceed.

6. Conclusions

Supported platinum catalyst on active carbon (Pt/AC) was highly active for decomposition of NH_4NO_3 into N_2 and H_2O under mild conditions. The selective decomposition was achieved within 2 h under air at 0.5 MPa and 453 K, which were very mild conditions compared to those for conventional wet air decomposition systems. Conversions of ammonium and nitrate and selectivity to N_2 were influenced by oxygen partial pressure or total gas-feed pressure although their effects have not been elucidated. The major byproduct was N_2O, which is formed by stoichiometric reaction between ammonium ion and nitrate ion at the molar ratio of unity. CO_2 was also detected after the reaction, indicating AC support also works as reducing agent. NO_2^-, CO, NO, and NO_2 were not in a significant quantity for all the reactions studied. Isotope-labeling experiments were performed and the expected ammonium-nitrate reaction was confirmed to proceed dominantly. The oxidation of ammonium by oxygen to form N_2 and N_2O was found to be a competing reaction with the reaction between ammonium and nitrate. N_2O was concluded to be the intermediate of nitrogen formation by decomposition of NH_4NO_3.

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