Hydrogen-Treated Active Carbon Supported Palladium Catalysts for Wet Air Oxidation of Ammonia

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Almost complete conversion of dilute aqueous ammonia (1.5 g-NH_3 dm^{-3}) to dinitrogen has been attained over a hydrogen-treated active carbon supported (3 wt%) Pd catalyst under a rather mild condition (2.0 MPa of air, 453 K). The hydrophobicity of the support surface is considered to be important to provide high activity and selectivity in Pd catalysis.

Removal of ammonia, which may cause eutrophication, from wastewater has been an emerging issue in aquatic environment. Recently a new legal regulation of ammonium ion has been effective. Although ammonia in wastewater can be removed by biological processes,[1] most of which need wide facility and are costly due to plural processes of nitrification and denitrification. They are hard to overcome the severe operating conditions of the low and narrow ammonia concentration. Catalytic wet air oxidation (WAO) of ammonia to dinitrogen has several advantages such as the faster reaction, wide operating range of ammonia concentration, and the simple one-step process[2] in comparison with biological processes, if an active and selective catalyst is developed.

Several effective catalysts for WAO of ammonia have been reported[3] including supported ruthenium catalysts.[4] The affinity of metal surface with oxygen represented by heat of formation of metal oxide per oxygen atom (ΔH^0_f) has also been pointed out to be the major factor of metal catalysis for WAO of ammonia, and metals having moderate ΔH^0_f value such as Ru or Pd were shown to be active.[4] Of course there are several other factors of reaction conditions such as temperature, air pressure, ammonia concentration, or pH which influence the activity and selectivity of the reaction. Even the excellent catalyst so far reported, for example Ru/Al_2O_3, can not give high selectivity at low temperature and under low ammonia concentration.[5] Thus, there is a room to improve catalysts especially in the selectivity for dinitrogen formation. Hence, we intended to explore more effective catalysts using Pd as another active metal.

The catalysts were prepared by impregnating supports such as active carbon (A.C.), TiO_2, Al_2O_3, MgO, CeO_2, Sm_2O_3, and La_2O_3 with aqueous solution of palladium chloride. Metal oxide supported catalysts were calcined in air at 773 K for 3 h before use. A.C. supported catalysts was treated with hydrogen at 773 K for 3 h followed by evacuation at 773 K for 1 h. Palladium loading was set to 3 wt% against the support for all the catalysts. WAO was carried out using a batch type closed high-pressure system (autoclave) equipped with a mechanical starrier made of corrosion-proof Hastelloy alloy. 100 mL of an aqueous solution which contains 1500 ppm of NH_3 (1.5 g-NH_3 dm^{-3}) originated from NH_4Cl was put into a glass container which fitted inside of the autoclave having 2 g of catalyst, then pH was adjusted to around 12 with NaOH. After introducing 2.0 MPa of air the reactor was heated to the given temperature, after which the reaction was performed for 2 h with continuous stirring. The system was cooled with a fan, and ammonia in the releasing gas was trapped into 0.1 mol dm^{-3} sulfuric acid. Usually no ammonia was detected in the gas phase. Concentrations of NH_4^+, NO_2^-, and NO_3^- in the liquid phase before and after the reaction were determined by ion chromatography. Conversion of ammonia was determined by the ratio of final concentration to initial one.

Table 1. Ammonia decomposition over 2.0 g of Pd (3 wt%) catalysts under 2.0 MPa of air at 453 K for 2 h[a]

Support	BET surface area $/m^2g^{-1}$	Conversion /%	Yield /%		Selectivity for N_2 /%
			NO_3^-	NO_2^-	
CeO_2	51	27.1	0.0	0.0	100.0
La_2O_3	35	13.8	13.5	0.0	2.3
Sm_2O_3	18	31.4	0.0	1.3	95.9
MgO	133	36.9	0.3	0.6	97.5
Al_2O_3	101	21.7	0.0	0.0	100.0
TiO_2	53	34.9	0.2	0.2	98.7
A.C.	1155	100.0	0.0	0.0	100.0
Ru/Al_2O_3[b]	88	99.9	9.9	0.0	90.1

[a] $[NH_4^+]_0$ =1443 ppm, pH = 11.65. [b] Former work, reference 4.

The reactivity of supported Pd catalysts for this reaction was found to be strongly dependent on the kind of support used. However, no product other than dinitrogen and nitrogen oxides was detected in GC/MS and ion chromatographic analysis. Table 1 shows the conversion and the selectivity of ammonia oxidation over supported Pd catalysts with different kinds of supports at 453 K. Metal oxide supports are not appreciably effective for this reaction when combined with palladium. However all the Pd catalysts, except La_2O_3 supported one, possessed the extremely high N_2 selectivity. The most interesting is that the A.C. supported Pd showed 100% of conversion and N_2 selectivity under these conditions. The Pd/A.C. is more effective than Ru/Al_2O_3 which has been reported as one of the most promising catalysts for this reaction.[4] Since A.C. has large surface area, this extremely high activity might be partially due to the large surface area. However, no obvious correlation was observed between surface area and their activity of catalysts employed.

The pH dependence of the reaction over Pd/A.C. was also studied, and the conversion and selectivity are plotted as a function of pH in Figure 1. When pH value was higher than 11, ammonia conversion at 423 K reached more than 80%, but it was less than 7% when below 3 of pH. The fact that the drastic increase of activity at pH value of 10 means that an active form of ammonia is not ammonium ion but ammonia molecule because pKa value of ammonia is 9.27. Since ammonia concentration in aqueous phase might decrease due to adsorption onto A.C. having such very high surface area, the

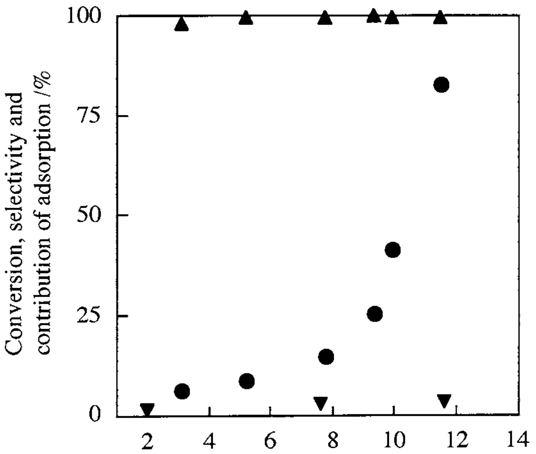

Figure 1. pH dependence of ammonia decomposition over Pd/A.C. at 423K. ● Conversion; ▲ selectivity for N_2; ▼ contribution of adsorption.

amount of ammonia adsorbed onto A.C. was measured under ambient condition by checking the ammonia content before and after the A.C. addition. The percentage of adsorbed ammonia was plotted as a function of pH in Figure 1. It was only 2 to 3% at ambient temperature through all the pH value. This result indicates that decrease of ammonia during the reaction is not due to physical adsorption onto A.C. because the adsorbed amount of ammonia at 423 K must be much lower than that at ambient temperature. Elemental analysis of Pd/A.C. after the use in the reaction at pH=11 also showed the increment of N atom was less than 0.2 wt%, which corresponded to that the lost (adsorbed) N atom onto the catalyst was less than 3% of initial amount of NH_3. Adsorption of by-products (NO_2^-, NO_3^-) was negligible at such pH condition, too.

Three factors of the effectiveness of Pd/A.C. are pointed out here. The first one may be the role of oxygen activation by A.C. itself, which is well known to have an ability of oxygen activation as in the case of H_2S oxidation.[6] An edge carbon of graphite structure in A.C. can generate active oxygen species such as O^- or O_2^-. In fact, A.C. itself showed some activity for WAO of ammonia (conversion of more than 35% and N_2 selectivity of 99.8% at 453 K). Thus, A.C. itself in Pd/A.C. may partly contribute to the activity.

The second one is the hydrophobicity of the surface of A.C. According to our previous works,[4] WAO of ammonia is considered to obey the Langmuir-Hinshelwood (L-H) mechanism. As shown in Figure 1 and above, the active form of ammonia is not ammonium ion but ammonia molecule. Hence, following L-H mechanism, high concentration of neutral molecule of ammonia near the surface must promote the reaction. While. the surface of metal oxide is ionic and hydrophilic, the surface of A.C. is hydrophobic and supplies a thin gas phase layer which protects the active site from H_2O adsorption and assures the space of reaction between ammonia and oxygen. Another evidence for the validity of hydrophobicity of the surface is shown in Table 2. Treating A.C. with hydrogen at 1073 K for more than 48 h, conversion of ammonia at 423 K increased from 66.9 to 82.8%. After this treatment, hydrophilic functional groups on A.C. such as -COOH, -C=O, or –OH are almost removed as evidenced by the elemental analysis data, and A.C. surface must get much more hydrophobic than the untreated A.C. and metal oxides.[7,8] Thus the increase of conversion is considered due to the increased hydrophobicity.

Table 2. Effect of hydrogen treatment of active carbon on ammonia decomposition over Pd/A.C. at 423 K

Support	Conversion /%	Selectivity for N_2 /%
A.C. (H_2 red.)	82.8	99.5
A.C. (No treat.)	66.9	100.0

Precursor : $PdCl_2$

The third factor is the electronic state of Pd. While Pd/A.C. was used after the hydrogen treatment, metal oxide supported catalysts were used after calcined in the air. Thus, the electronic state of Pd on these kinds of supports should be different and can affect on their activity. Actually hydrogen-treated Pd/MgO showed higher activity than calcined one although it was still less active than Pd/A.C. of which surface is hydrophobic.

Although further studies are necessary to evaluate the importance of these factors, it is evident Pd/A.C. is one of the most promising catalysts for WAO of ammonia.

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