

Catalytic wet oxidation of ammonia solution: Activity of the nanoscale platinum–palladium–rhodium composite oxide catalyst

Chang-Mao Hung*

Department of Industry Engineering and Management, Yung-Ta Institute of Technology & Commerce, 316 Chung-shan Road, Linlo, Pingtung 909, Taiwan

ARTICLE INFO

Article history:

Received 30 April 2007

Received in revised form 30 May 2008

Accepted 23 June 2008

Available online 2 July 2008

Keywords:

Catalytic wet oxidation (CWO)

Ammonia

Trickle-bed reactor (TBR)

Nanoscale platinum–palladium–rhodium composite oxide catalysts

ABSTRACT

Aqueous solutions of 400–1000 mg/L of ammonia were oxidized in a trickle-bed reactor (TBR) in this study of nanoscale platinum–palladium–rhodium composite oxide catalysts, which were prepared by the co-precipitation of H_2PtCl_6 , $\text{Pd}(\text{NO}_3)_2$ and $\text{Rh}(\text{NO}_3)_3$. Hardly any of the dissolved ammonia was removed by wet oxidation in the absence of any catalyst, whereas about 99% of the ammonia was reduced during wet oxidation over nanoscale platinum–palladium–rhodium composite oxide catalysts at 503 K in an oxygen partial pressure of 2.0 MPa. A synergistic effect exists in the nanoscale platinum–palladium–rhodium composite structure, which is the material with the highest ammonia reduction activity. The nanometer-sized particles were characterized by TEM, XRD and FTIR. The effect of the initial concentration and reaction temperature on the removal of ammonia from the effluent streams was also studied at a liquid hourly space velocity of under 9 h^{-1} in the wet catalytic processes.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Ammonia (NH_3) is adopted extensively and in large quantities for various purposes. Since ammonia is a useful chemical in the manufacture of ammonium nitrate, ammonia, urea, ammonium phosphate, petroleum refineries and coke, it is commonplace in industrial wastewaters. Furthermore, wastewaters that containing ammonia are commonly either toxic or have concentrations or temperatures such that prevent direct biological treatment.

The removal of ammonia from industrial effluent represents an important and dynamic area of research. Conventional biological, physical and chemical treatment processes, including biological nitrification, activated carbon fiber adsorption, ozonation and ion exchange processing, achieve only phase transformations and may yield contaminated sludge and/or adsorbent, both of which require further disposal. Hence, the removal of ammonia from air and waste streams is an important problem. Treatment of ammonia-contaminated discharge is an important challenge, because environmental laws and regulations governing safe discharge levels are becoming increasingly stringent.

Various nitrogen-containing compounds exist in the environment, and affect the acidification and eutrophication of ecosystems. The nitrogen cycle characterizes the movement and transformation of these nitrogen compounds through the biosphere. The key

concern that is related to the use of ammonia-contaminated water with excessive nitrate concentrations involves its effect on human health, especially that of infants [1]. Specifically, the major health effects are associated with the loss of oxygen transport/transfer capabilities in the blood. Nitrates are one of the main causes of methemoglobinemia in infants. Meanwhile, the large number of potential groundwater and surface water contaminants means that nitrates are very widespread. Nitrate test results can be expressed as either nitrate-nitrogen or nitrate (NO_3^-).

Wet oxidation (WO) technology was originally designed for the oxidation of organic substances, changing them into intermediate products with small molecular weights at temperatures between 398 and 623 K and pressures of between 0.5 and 20.0 MPa in the aqueous phase. However, ammonia is generally an end product of wet oxidation and is difficult to oxidize. In their review of the WO process, Mishra et al. [2] and Bhargava et al. [3] also offered suggestions for future work. The WO process has been verified to be a promising technique for pre-treating wastewater containing ammonia at concentrations as high as 600 mg/L [4]. However, the efficient removal of ammonia via a noncatalytic WO requires excessive pressures of up to 5.0 MPa, as well as a high temperature (513 K), making this technology rather uneconomical.

Catalytic wet oxidation (CWO) is known to increase the power of WO technology if dedicated catalysts are used: such catalysts have the potential to promote oxidation with shorter reaction times and under milder operating conditions. The selective catalytic oxidation (SCO) of ammonia-containing water to yield molecular nitrogen and water can be employed to eliminate problems of ammonia

* Tel.: +886 8 7233733x508; fax: +886 8 7228046.

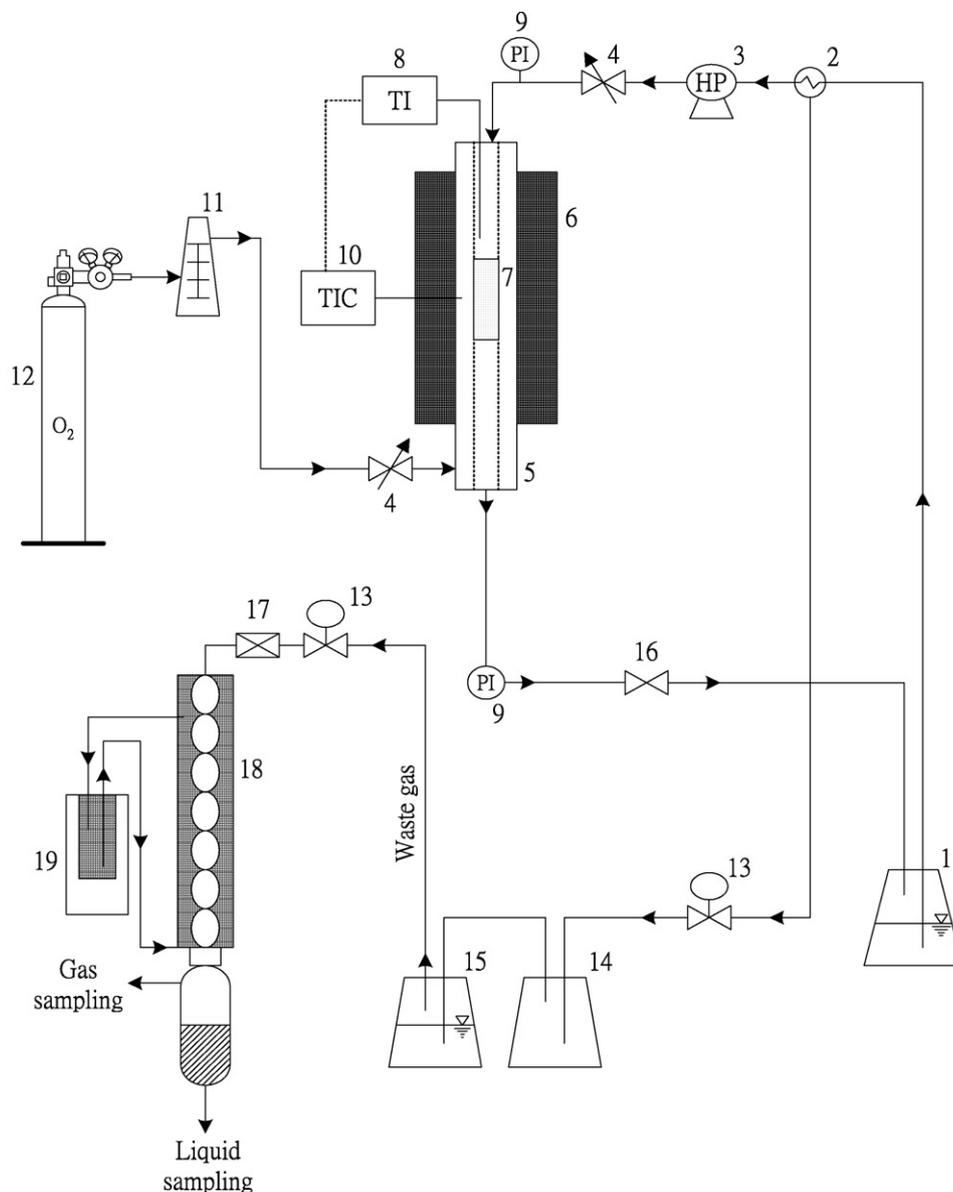
E-mail address: hungcm1031@gmail.com.

pollution [5–12]. Some reports also claim that the CWO of ammonia occurs through the following mechanism:



The SCO process involving ammonia should be selective for nitrogen (reaction (1)), and should prevent oxidation to further oxidation products of nitrogen (reactions (2) and (3)). Therefore, few catalysts have been used to oxidize ammonia in the liquid phase.

Various catalysts have also been used for ammonia oxidation in the liquid phase. For instance, Levec and Pintar [13] established that the WO of aqueous solutions of organics from wastewaters at very low temperatures and pressures was easier in the presence of heterogeneous catalysts than in a noncatalytic WO processes. Also, Imamura et al. [14], who designed numerous heterogeneous catalysts for WO, found that the Mn/Ce (1:1, molar/molar) composite catalyst was more active than a Co/Bi catalyst in the WO of ammonia. These catalysts were active for reactions at temperatures that exceeded 533 K with 4.0 MPa. Additionally, Ding et al. [15] investigated ammonia oxidation in supercritical water oxidation in the



1. Liquid feed tank ; 2. Heat exchanger ; 3. Pump ; 4. Check valve ; 5. Reactor ; 6. Heater
7. Catalyst bed ; 8. Temperature sensor ; 9. Pressure gauge ; 10. Temperature controller
11. Flow meter ; 12. Oxygen cylinder ; 13. Back pressure regulator ; 14. Buffering Bottle
15. Sample reservoir ; 16. Ball valve ; 17. Filter ; 18. Condenser ; 19. Refrigerator .

Fig. 1. Schematic diagram of catalytic wet oxidation employed to carry out ammonia oxidation over nanoscale platinum–palladium–rhodium composite catalyst in a trickle-bed reactor.

temperature range 683–743 K with 27.6 MPa. Ding observed that ammonia conversion reached 96% on a $\text{MnO}_2/\text{CeO}_2$ catalyst. Ima-mura [16] published a review paper summarized recent work on catalytic and noncatalytic WO.

Platinum-based group metal (PGM) additives in three-way catalysts (TWC) are the most active components in hydrocarbon oxidation and are also active in all other reactions [17]. Palladium-based metal is frequently recognized as the most active component for methane oxidation [18]. Rhodium-based metal improves the nitrogen oxide conversion properties of the catalysts and the selectivity towards dinitrogen; it also reduces self-poisoning by carbon monoxide [19,20]. Normal operating conditions are well within the ranges of stability of the elements platinum, palladium and rhodium as well as of the components that are used to stabilize the surface of the catalyst [21,22]. However, little research has been performed on the application of platinum–palladium–rhodium-based alumina-supported nanoparticle catalyst to elucidate the reactive characteristics of these active metals in catalytic wet oxidation. The activity of the nanoscale platinum–palladium–rhodium composite oxide catalyst in the oxidation of ammonia solutions given various values of relevant parameters, and its effect on the removal of ammonia from the effluent stream in catalytic wet oxidation processes, were studied. A transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Fourier transform infrared absorption spectra (FTIR), were used to characterize the nanoscale platinum–palladium–rhodium composite oxide catalyst.

2. Materials and methods

The nanoscale platinum–palladium–rhodium composite oxide catalysts that were used in this study were prepared by the co-precipitation, which involved aqueous H_2PtCl_6 , $\text{Pd}(\text{NO}_3)_2$ and $\text{Rh}(\text{NO}_3)_3$ (all grade, Merck, Darmstadt, Germany). A nanoscale platinum–palladium–rhodium catalyst was washcoated on gamma-alumina substrate with a high surface area with platinum, palladium and rhodium in weight ratios of 4:3:1, maintaining the ratio of catalytic active metals at a constant 6.4%. The catalysts were then calcined at 773 K in an air stream for 4 h. The resulting powder was formed into tablets using acetic acid as a binder. The tablets were later reheated at 573 K to burn the binder out of the platinum–palladium–rhodium composite tablets. The tablets were then crushed and sieved into various particle sizes ranging from 0.25 to 0.15 mm for use later.

All feed solutions were made using Millipore (Bedford, Massachusetts) water (18 M Ω), and the pH value of the ammonia aqueous solution was adjusted to 11.5 ± 0.2 using 1 M sodium hydroxide. Fig. 1 schematically depicts the catalytic wet oxidation system used in this study. The wet oxidation was conducted in a continuous trickle-bed reactor (TBR) that was constructed from 45 cm of stainless steel tubing (SS-316), 25 mm ID, which was resistant to high pressures and temperatures of up to 10 MPa and 623 K, respectively, and to corrosion at pHs of between 5 and 12.5. In each experiment, a fixed bed was created by measuring 25 g of the nanoscale platinum–palladium–rhodium composite oxide catalyst while maintaining a catalytic bed volume of approximately 15.6 mL. This bed was then installed in the reactor. An inert material based on $\gamma\text{-Al}_2\text{O}_3$ spheres (a hydrophilic inert material) was used to increase the interfacial area between the liquid and gas phases and thus enhance the mass transfer of ammonia from water. A heat exchanger maintained a constant temperature in the feed reservoir. The ammonia solutions were down-flowed into the reactor via a positive-displacement pump. Moreover, an electric heating belt attached to a laboratory direct-current power supply was used to maintain a constant temperature ($\pm 2^\circ\text{C}$) during the experi-

ment. An oxygen cylinder provided the oxygen required in the CWO runs; the oxygen flow rate was kept constant at 1.0 mL/min using a regulator and an electronic flow meter. Finally, liquid samples extracted periodically from the effluent streams of the reactor were filtered through a 0.2- μm pore-size polycarbonate filter (Nucleopore, Pleasanton, California, USA) after being cooled to ambient temperature and analyzed to determine pH, ammonia, NO_3^- and NO_2^- content.

The main operating parameters were a liquid feed rate given by a liquid hourly space velocity (LHSV) of 1.5–9 h^{-1} , reaction temperatures of 423, 473 and 503 K, and ammonia concentrations in the inlet from between 400 and 1000 mg/L. The partial pressure of oxygen in the reactor was maintained at a constant 2.0 MPa, and the pH of the ammonia in the inlet was maintained at 11.0 ± 0.2 .

The pH of the samples was measured using a pH meter (SP701, Sontex, Kaohsiung Taiwan). Meanwhile, the residual ammonia in the liquid sample was diluted and analyzed using a Merck kit (Merck, Spectroquant Vega 400, Darmstadt, Germany) over a range of concentrations from 0.03 to 3.00 mg/L (Spectroquant 14752). Also, the concentrations of two other compounds in the samples, namely NO_3^- between 0.2 and 20.0 mg/L (Spectroquant 14773) and NO_2^- between 0.005 and 1.00 mg/L (Spectroquant 14776), were determined using a Merck kit, as described above. Meanwhile, the amounts of NO and NO_2 in the gas sample were determined using a gas analyzer unit (IMR3000, IMR, Germany). Moreover, the levels of O_2 , N_2 and N_2O were determined using a Shimadzu GC-14A that was equipped with a TCD (Shimadzu, Kyoto, Japan). A stainless-steel column (Porapak Q 80/100 mesh) was used together with a refinery analyzer for isothermal separation. The residual ammonia in the vapor gas was scrubbed by dilute sulfuric acid solution and measured using a Merck kit. No residual NH_3 was found in the outlet. Thus, we found that the residual ammonia in the gas phase could be ignored for the trickle-bed reaction system operated at high pressure of about 2.0 MPa. Only the residual ammonia concentration in the liquid phase was determined and represented all the untreated ammonia.

The sizes of the catalytic particles were detected using a transmission electron microscopy (TEM) (Philips CM-200 Twin, Netherlands). TEM indicated a broad particle size distribution of 30–80 nm. X-ray diffractograms (XRD) were obtained using a Diano-8536 diffractometer with $\text{Cu K}\alpha$ radiation as the source. During analysis, the sample was scanned from 20 to 80° at a rate of 0.4°/min. Diffuse reflectance FTIR spectra of species adsorbed on the catalyst were measured at room temperature using a Bruker Vector 22 FTIR spectrometer equipped with a diffuse reflectance attachment with 4 cm^{-1} resolution.

3. Results and discussions

The removal of ammonia from the water was followed by the liquid-phase oxidation of ammonia over the nanoscale platinum–palladium–rhodium composite oxide catalyst. All of the possible products, in the gas or liquid phases, of ammonia oxidation produced using a nanoscale platinum–palladium–rhodium composite oxide catalyst, were identified. Specifically, the treated water was found to contain nitrates and nitrites, while the gaseous samples also contained nitrogen and trace amounts of nitrous oxide. Small amounts of nitrates (NO_3^-) and nitrites (NO_2^-) were detected in the treated water. Hence, nitrogen (N_2) and traces of nitrous oxide (N_2O) and nitrogen dioxide (NO_2) were detected in the gaseous samples. Table 1 shows the product selectivity of ammonia oxidation. The overall selectivity of the production of nitrates and nitrites varied from 22.6% to 99.9% ammonia conversion at 503 K. Nitrogen was thus the main product of ammonia oxidation. Accordingly,

Table 1

Product selectivity from ammonia oxidation using nanoscale platinum–palladium–rhodium composite catalysts at different temperature (initial concentration of ammonia = 400 mg/L, partial pressure of O₂ = 2.0 MPa)

Temperature (K)	Ammonia conversion (%)	Product selectivity (%)		
		NO ₃ ⁻ + NO ₂ ⁻	N ₂ O	N ₂
503	99.9	22.6	N.D.	77.4
473	94.5	24.1	N.D.	75.9
423	63.4	29.1	N.D.	70.9

platinum, palladium and rhodium oxide is providing active sites for the reaction in the catalytic wet oxidation of ammonia. A synergistic effect exists in the platinum–palladium–rhodium composite oxide structure, which is the material of interest with the highest ammonia reduction activity. This result is similar to that obtained by Rogemond et al. [23] and Hu et al. [19]. Lecomte et al. [24] demonstrated that platinum is more stable when dispersed in the metallic matrix, and that platinum clusters formed on a support appear to be the most active component of the catalyst. The effect of metal oxide is discussed below.

Fig. 2 presents the X-ray diffraction (XRD) patterns of fresh and used catalysts for comparison, confirming the PtO₂/Pt⁰, PdO/Pd⁰, and Rh₂O₃/Rh⁰ states of the nanoscale platinum–palladium–rhodium composite catalyst. As indicated, the catalyst changed after exposure to a catalytic wet oxidation environment. The dominant PtO₂ diffraction peaks were close to 2θ = 34.8, 42.5, and 54.9° for a nanoscale platinum–palladium–rhodium composite catalyst [25]. The dominant Pt⁰ diffraction peaks were close to 2θ = 67.4° for this catalyst following activity test. These results indicate that Pt⁰ may be present in a highly dispersed form. This finding agrees with data that were presented by Shin et al. [26] and García-Cortés et al. [27] for this system. The dominant PdO and Pd⁰ diffraction peaks were near 2θ = 41.9 and 40.4° for a nanoscale platinum–palladium–rhodium composite catalyst [28]. However, under oxidation conditions over the nanoscale

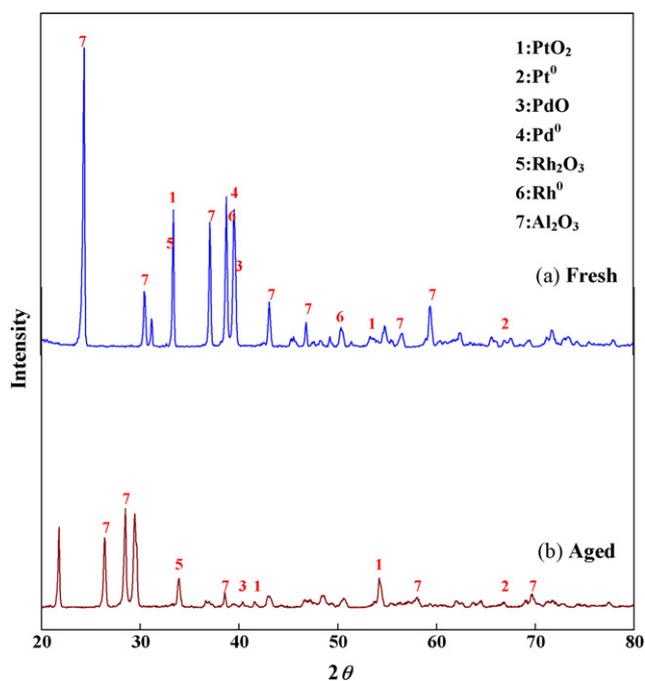


Fig. 2. X-ray diffraction pattern of nanoscale platinum–palladium–rhodium composite catalysts: (a) fresh; (b) after activity test.

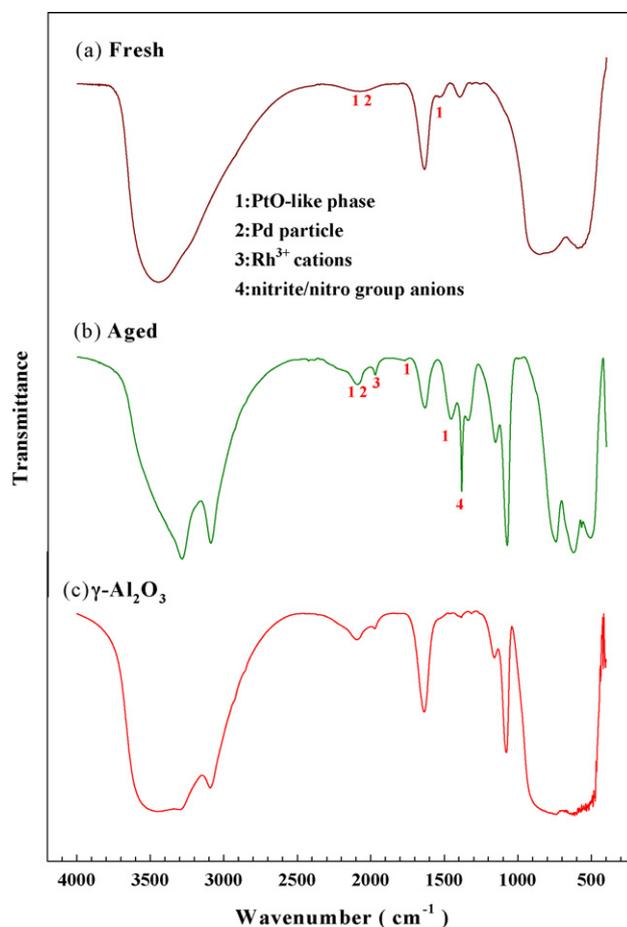


Fig. 3. Fourier transform infrared pattern of nanoscale platinum–palladium–rhodium composite catalysts: (a) fresh; (b) after activity test.

platinum–palladium–rhodium composite catalyst, the platinum and palladium were transformed from the oxide to the metal form.

The dominant Rh₂O₃ diffraction peaks were close to 2θ = 34.3 and 35.4° for an orthorhombic structure with hexagonal symmetry. This result is similar to that of Mulukutla et al. [29]. The dominant Rh⁰ diffraction peaks were in the range 2θ = 40–50° for the catalyst following the activity test [30]. However, under oxidation conditions, over a nanoscale platinum–palladium–rhodium composite catalyst, the oxidation state of rhodium may vary between Rh³⁺ and Rh⁰. An earlier work established that Rh₂O₃ is the most active phase in the catalytic reaction, because it is a good promoter of oxygen storage, although some noble metals are used as the major catalysts [31]. Rhodium dioxide in a platinum catalyst may be assumed to promote the formation of the active phase of PtO₂ and PdO under ammonia oxidation. Thus, the X-ray powder diffraction approach confirmed the formation of platinum (IV), palladium (IV) and rhodium (III) oxide active sites on the nanoscale platinum–palladium–rhodium composite catalyst.

Fig. 3 compares the FTIR spectra of fresh and used catalysts, also verifying the presence of the PtO-like phase, the Pd particle phase, Rh³⁺ cations and nitrite or nitro group anionic species on the surface of the nanoscale platinum–palladium–rhodium composite catalyst. As shown in Fig. 3(a), the peaks from the PtO-like phase are at 1530, 1553 and 2120 cm⁻¹ [32,33]. The peaks of the Pd particle phase are at 1979 and 2130 cm⁻¹, respectively [34]. The Rh³⁺ cations are adsorbed onto platinum oxide clusters at 1912 cm⁻¹ [23,35]. As illustrated in Fig. 3(b), the monodentate nitrite or nitro group anions on the framework are associated with a peak at about

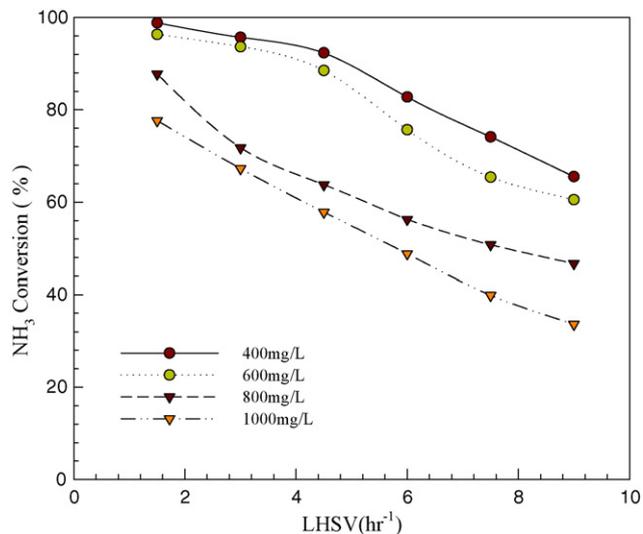


Fig. 4. Effect of initial concentration on ammonia removal of catalytic wet oxidation over the nanoscale platinum-palladium-rhodium composite catalyst (partial pressure of O₂ = 2.0 MPa; temperature = 503 K).

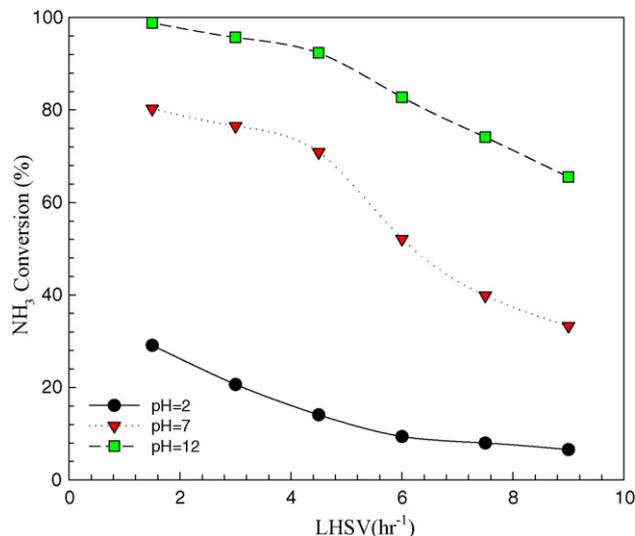


Fig. 6. Effect of initial pH on ammonia removal of the catalytic wet oxidation over the nanoscale platinum-palladium-rhodium composite catalyst (partial pressure of O₂ = 2.0 MPa; temperature = 503 K).

1490 cm⁻¹ for used catalysts [11,36]. As presented in Fig. 3(c), peak systems can be attributed to particular surface hydroxyl (OH⁻) group configurations, depending on the structure of Al₂O₃.

Fig. 4 plots the effect of the initial concentration of the ammonia to be reduced by catalytic wet oxidation runs over a nanoscale platinum-palladium-rhodium composite catalyst at 503 K at a partial pressure of oxygen of 2.0 MPa. The removal of ammonia decreased markedly as the LHSV of the influent stream increased, because the retention time during the catalytic wet oxidation process decreased. The effect on ammonia reduction was negligible in the influent stream with ammonia concentrations from 400 to 1000 mg/L, while the removal of ammonia was drastically suppressed by increasing the ammonia concentration to 400 mg/L. This difference suggests that the rate of reaction of ammonia in a catalytic wet oxidation continuous reactor was independent of the oxygen partial pressure above 2.0 MPa. This difference also

shows that the dissolved oxygen flux dominates the concentration of ammonia, and that the reaction is liquid-limited. Otherwise, oxygen that is dissolved in the liquid from the oxygen flow, might not suffice for use in the catalytic wet oxidation runs, which proceed at ammonia concentrations above 1000 mg/L in the influent stream.

Fig. 5 plots the effects of reaction temperature and space velocity of the influent stream on the reduction of ammonia. Increasing the reaction temperature or catalyst loading promoted the removal of ammonia. When the LHSV of the influent stream was set to 1.5 h⁻¹, around 99% of the ammonia was reduced at 503 K in the catalytic run. This result reveals that the removal of ammonia can be remarkably increased using a nanoscale platinum-palladium-rhodium composite catalyst. Generally, a strong chemical interaction between the catalytic support and water causes the rapid decomposition of existing WAO catalysts [37].

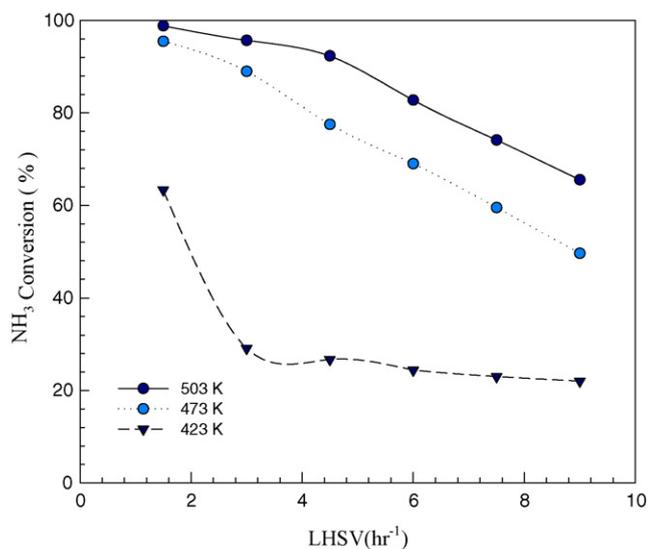


Fig. 5. Effect of reaction temperature and liquid hourly space velocity on removal of the catalytic wet oxidation of ammonia solution over the nanoscale platinum-palladium-rhodium composite catalyst (initial ammonia concentration = 1000 mg/L; partial pressure of O₂ = 2.0 MPa).

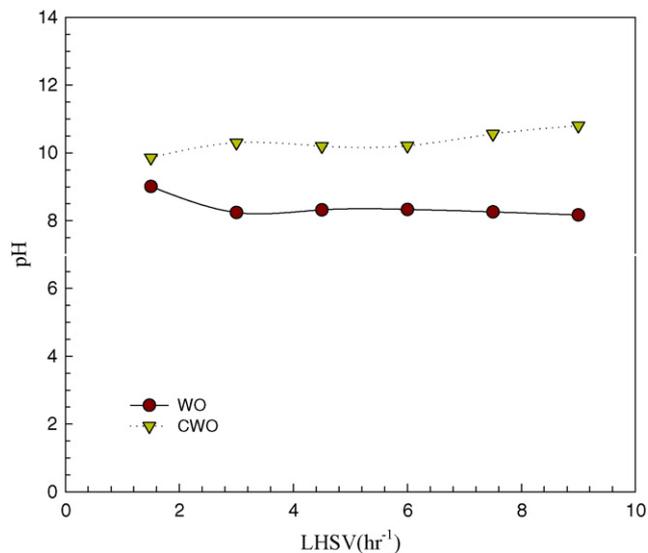


Fig. 7. pH fluctuation of the WO and CWO (over the nanoscale platinum-palladium-rhodium composite catalyst) of the ammonia solution (temperature = 503 K; partial pressure of O₂ = 2.0 MPa; initial concentration of ammonia = 400 mg/L).

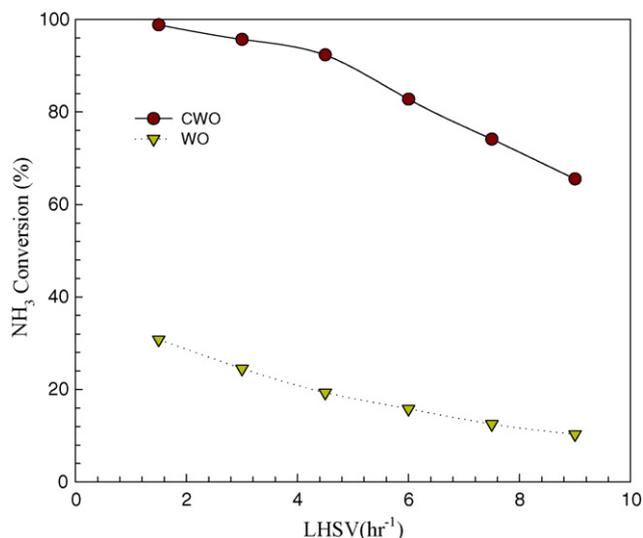


Fig. 8. NH₃ removal profiles during both the catalytic (over the nanoscale platinum–palladium–rhodium composite catalyst) and the noncatalytic wet oxidations of ammonia solution (initial ammonia concentration = 400 mg/L; partial pressure of O₂ = 2.0 MPa = 2.0 MPa; temperature = 503 K).

Fig. 6 plots the effect of pH on the decomposition of NH₃ profiles during both catalytic wet oxidations of ammonia solution at 503 K in the trickle-bed reactor. Molecular ammonia is volatile and a higher pH favors a higher NH₃/NH₄⁺ ratio in the aqueous solution. The fact that ammonia is more reactive than ammonium ion indicates that the reaction catalyzed by nanoscale platinum–palladium–rhodium composite catalyst should be significantly in the liquid phase on the catalyst surface, which fact is consistent with the literature [5]. Therefore, most ammonia under neutral or acidic conditions, is posited to exist in the form of NH₄⁺ salt, which cannot be stripped to the gas phase, such that reactants in the liquid phase diffuse to the nanoscale platinum–palladium–rhodium composite catalyst sites. Notably, the use of the nanoscale catalyst markedly promotes the conversion of ammonia and the catalytic removal of ammonia in this work. Fig. 7 plots the pH fluctuation during the catalytic WO of ammonia solution. The pH of the effluent changed insignificantly with LHSV in catalytic wet oxidation with a nanoscale platinum–palladium–rhodium composite catalyst. However, the CWO run involved a pH rise from the original value, 10.0, to the final value, 11.0. This phenomenon can be explained by the fact that the generation rates of molecular ammonia during CWO are in equilibrium with each other; however, the generation rate of ammonia may be higher during the noncatalytic run and result in a final pH of about 8.0 after the reaction.

The results plotted in Fig. 8 reveal the effect of the nanoscale platinum–palladium–rhodium composite catalyst of wet oxidation of ammonia solution, in terms of removal efficiency versus LHSV. Specifically, Fig. 8 reveals that the use of the nanoscale platinum–palladium–rhodium composite catalyst markedly promoted the conversion of ammonia, yielding a maximum conversion rate of 99% at a space velocity of 1.5 h⁻¹. Generally, the catalytic removal of ammonia proceeded around 99% further than the non-catalytic removal of ammonia at 503 K at a space velocity of under 1.5 h⁻¹.

4. Conclusions

The results of this study demonstrate that the CWO of ammonia over a nanoscale platinum–palladium–rhodium composite cata-

lyst removed more ammonia, particularly at low temperatures. The overall by-product selectivity of the produced nitrates and nitrites varied from 22.6% to 99.9% ammonia conversion when a nanoscale platinum–palladium–rhodium composite catalyst was used. CWO thus has potential for treating highly concentrated ammonia solutions, and can help industrial plants to meet discharge standards. Future research will identify the intermediate products that are formed during WO. Notably, nitrite production was significantly less than nitrate production, but was still significant at high reaction temperatures (503 K). The results of this work indicate that pH is critical to controlling the reduction of ammonia over a nanoscale platinum–palladium–rhodium composite catalyst.

Acknowledgment

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract No. NSC95-2211-E-132-001.

References

- [1] S.D. Hafner, J.J. Bisogni, W.J. Jewell, Measurement of un-ionized ammonia in complex mixtures, *Environ. Sci. Technol.* 40 (2006) 1597–1602.
- [2] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Wet air oxidation, *Ind. Eng. Chem. Res.* 34 (1995) 2–48.
- [3] S.K. Bhargava, J. Tardio, J. Prasad, K. Föger, D.B. Akolekar, S.C. Grocott, Wet oxidation and catalytic wet oxidation, *Ind. Eng. Chem. Res.* 45 (2006) 1221–1258.
- [4] T.L. Huang, K.R. Cliffe, J.M. Macinnes, The removal of ammonia from water by a hydrophobic catalyst, *Environ. Sci. Technol.* 34 (2000) 4804–4809.
- [5] J. Qin, K. Aika, Catalytic wet air oxidation of ammonia over alumina supported metals, *Appl. Catal. B: Environ.* 16 (1998) 261–268.
- [6] R. Ukropec, B.F.M. Kuster, J.C. Schouten, R.A. Van Santen, Low temperature oxidation of ammonia to nitrogen in liquid phase, *Appl. Catal. B: Environ.* 23 (1999) 45–57.
- [7] J. Taguchi, T. Nakato, T. Okuhara, Selective oxidative decomposition of ammonia in water to nitrogen catalyzed by platinum-supported titania, *Chem. Lett.* 28 (1999) 277–278.
- [8] J. Taguchi, T. Okuhara, Selective oxidative decomposition of ammonia in neutral water to nitrogen over titania-supported platinum or palladium catalyst, *Appl. Catal. A: Gen.* 194–195 (2000) 89–97.
- [9] C.M. Hung, J.C. Lou, C.H. Lin, Wet air oxidation of aqueous ammonia solution catalyzed by composite metal oxide, *Environ. Eng. Sci.* 20 (2003) 547–556.
- [10] C.M. Hung, J.C. Lou, C.H. Lin, Removal of ammonia solutions used in catalytic wet oxidation processes, *Chemosphere* 52 (2003) 988–995.
- [11] C.M. Hung, J.C. Lou, C.H. Lin, Catalytic wet oxidation of ammonia solution: activity of the copper–lanthanum–cerium composite catalyst, *J. Environ. Eng.* 130 (2004) 193–200.
- [12] D.K. Lee, J.S. Cho, W.L. Yoon, Catalytic wet oxidation of ammonia: why is N₂ formed preferentially against NO₃⁻? *Chemosphere* 61 (2005) 573–578.
- [13] J. Levec, A. Pintar, Catalytic oxidation of aqueous solutions of organics: an effective method for removal of toxic pollutants from waste waters, *Catal. Today* 24 (1995) 51–58.
- [14] S. Imamura, A. Dol, S. Ishida, Wet oxidation of ammonia catalyzed by cerium-based composite oxides, *Ind. Eng. Chem. Prod. Res. Dev.* 24 (1985) 75–80.
- [15] Z.Y. Ding, L. Li, D. Wade, E.F. Gloyna, Supercritical water oxidation of NH₃ over a MnO₂/CeO₂ catalyst, *Ind. Eng. Chem. Res.* 37 (1998) 1707–1716.
- [16] S. Imamura, Catalytic and noncatalytic wet oxidation, *Ind. Eng. Chem. Res.* 38 (1999) 1743–1753.
- [17] D.C. Chamber, D.E. Angove, N.W. Cant, The formation and hydrolysis of isocyanic acid during the reaction of NO, CO and H₂ mixtures on supported platinum, palladium, and rhodium, *J. Catal.* 204 (2001) 11–22.
- [18] S. Cimino, L. Lisi, R. Pirone, G. Russo, Dual-site Pd/perovskite monolithic catalysts for methane catalytic combustion, *Ind. Eng. Chem. Res.* 43 (2004) 6670–6679.
- [19] Z. Hu, F.M. Allen, C.Z. Wan, R.M. Heck, J.J. Stenger, R.E. Lakis, C.E. Lyman, Performance and structure of Pt–Rh three-way catalysts: mechanism for Pt/Rh synergism, *J. Catal.* 174 (1998) 13–21.
- [20] C. Larese, M.L. Granados, F.C. Galisteo, R. Mariscal, J.L.G. Fierro, TWC deactivation by lead: a study of the Rh/CeO₂ system, *Appl. Catal. B: Environ.* 62 (2006) 132–143.
- [21] M.L. Wanger, L.D. Schmidt, Model catalytic oxidation reaction: oxygen with H₂, NH₃, and N₂H₄ on Rh (1 1 1), *J. Phys. Chem.* 99 (1995) 805–815.
- [22] U. Lassi, R. Polvinen, S. Suhonen, K. Kallinen, A. Savimäki, M. Härkönen, M. Valden, R.L. Keiski, Effect of aging atmosphere on the deactivation of Pd/Rh automotive exhaust gas catalysts: catalytic activity and XPS studies, *Appl. Catal. A: Gen.* 263 (2004) 241–248.
- [23] E. Rogmond, R. Fréty, V. Perrichon, M. Primet, S. Salasc, M. Chevrier, C. Gauthier, F. Mathis, Preparation of alumina-supported ceria. II. Measurement of ceria

- surface area after impregnation with platinum or rhodium, *J. Catal.* 169 (1997) 120–131.
- [24] J.J. Lecomte, S. Haydar, P. Granger, L. Leclercq, G. Leclercq, J.P. Joly, Investigation of oxygen interaction with a Pt–Rh/Al₂O₃ catalyst by a differential temperature-programmed desorption method, *Langmuir* 19 (2003) 9266–9270.
- [25] J. Pérez-Ramírez, J.M. García-Cortés, F. Kapteijn, G. Mul, J.A. Moulijn, C. Salinas-Martínez de Lecea, Characterization and performance of Pt-USY in the SCR of NO_x with hydrocarbons under lean-burn conditions, *Appl. Catal. B: Environ.* 29 (2001) 285–298.
- [26] H.K. Shin, H. Hirahayashi, H. Yahiro, M. Watanabe, M. Iwamoto, Selective catalytic reduction of NO by ethene in excess oxygen over platinum ion-exchanged MFI zeolites, *Catal. Today* 26 (1995) 13–21.
- [27] J.M. García-Cortés, J. Pérez-Ramírez, J.N. Rouzaud, A.R. Vaccaro, M.J. Illán-Gómez, C. Salinas-Martínez de Lecea, On the structure sensitivity of deNO_x HC-SCR over Pt-beta catalysts, *J. Catal.* 218 (2003) 111–122.
- [28] P. Fornasiero, J. Kašpar, V. Sergio, Redox behavior of high-surface-area Rh-, Pt-, and Pd-loaded Ce_{0.5}Zr_{0.5}O₂ mixed oxide, *J. Catal.* 182 (1999) 56–69.
- [29] R.S. Mulukutla, T. Shido, K. Asakuru, T. Kogure, Y. Iwasawa, Characterization of rhodium oxide nanoparticles in MCM-41 and their catalytic performances for NO–CO reactions in excess O₂, *Appl. Catal. A: Gen.* 228 (2002) 305–314.
- [30] K.V. Prasad, R.V. Chavdhari, Activity and selectivity of supported Rh catalysts for oxidative carbonylation of aniline, *J. Catal.* 145 (1994) 204–215.
- [31] E. Ruckenstein, H.Y. Wang, Effect of support on partial oxidation of methane to synthesis gas over supported rhodium catalysts, *J. Catal.* 187 (1999) 151–159.
- [32] E. Sánchez, R. Gómez, A. Morales, O. Novaro, Synthesis and characterization of sol–gel Pt/TiO₂ catalyst, *J. Solid State Chem.* 122 (1996) 309–314.
- [33] P.T. Fanson, W.N. Delgass, J. Lauterbach, Island formation during kinetic rate oscillations in the oxidation of CO over Pt/SiO₂: a transient Fourier transform infrared spectrometry study, *J. Catal.* 204 (2001) 35–52.
- [34] A. Martínez-Arias, M. Fernández-García, A.B. Hungría, A. Iglesias-Juez, K. Duncan, R. Smith, J.A. Anderson, J.C. Conesa, J. Soria, Effect of thermal sintering on light-off performance of Pd/(Ce, Zr)O_x/Al₂O₃ three-way catalysts: model gas and engine tests, *J. Catal.* 204 (2001) 238–248.
- [35] P.J. Lévy, V. Pitchon, V. Perrichon, M. Primet, M. Chevrier, C. Gauthier, Characterisation of model three-way catalysts. II. Infrared study of platinum–rhodium alumina catalysts, *J. Catal.* 178 (1998) 363–371.
- [36] P.T. Fanson, M.W. Stradt, J. Lauterbach, W.N. Deglass, The effect of Si/Al ratio and copper exchange level on isothermal kinetic rate oscillations for N₂O decomposition over Cu-ZSM-5: a transient FTIR study, *Appl. Catal. B* 38 (2002) 331–347.
- [37] N.M. Dobrynkin, M.V. Batygin, A.S. Noskov, Solid catalysts for wet oxidation of nitrogen-containing organic compounds, *Catal. Today* 45 (1998) 257–260.