CATALYTIC WET OXIDATION OF AMMONIA SOLUTION WITH PLATINUM-PALLADIUM-RHODIUM COMPOSITE OXIDE CATALYST

Chang-Mao Hung*
Department of Industry Engineering and Management
Yung Ta Institute of Technology & Commerce
Pingtung 909, Taiwan.

Key Words: Catalytic wet oxidation (CWO), ammonia, trickle-bed reactor (TBR), platinum-palladium-rhodium composite oxide catalyst

ABSTRACT

This study adopted high concentration aqueous solutions of ammonia for use in catalytic liquid-phase oxidation in a trickle-bed reactor with platinum-group metals (platinum-palladium-rhodium), prepared by the co-precipitation of H₂PtCl₆, Pd(NO₃)₃ and Rh(NO₃)₃. The experimental results revealed that a minimal amount of ammonia was removed from the solution by wet oxidation in the absence of any catalyst, while around 99% of the ammonia was removed by wet oxidation over the platinum-palladium-rhodium composite oxide catalyst at 230 °C with an oxygen partial pressure of 2.0 MPa. A synergistic effect is evident in the platinum-palladium-rhodium composite oxide structure, which has the greatest capacity to reduce ammonia. The particles were characterized by UV-Vis and particle size analyzer. The effluent streams were at a liquid hourly space velocity of under 9 h⁻¹ in the wet catalytic processes, and a reaction pathway was linked the oxidizing ammonia to nitric oxide, nitrogen and water. The solution contained by-products, including nitrate and nitrite. Nitrite selectivity was minimized and ammonia removal maximized when the feed ammonia solution had pH about 8.2.

INTRODUCTION

Ammonia is utilized 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 commonly present in industrial wastewaters. Additionally, wastewaters that contain ammonia are commonly either toxic or have concentrations or temperatures that prevent direct biological treatment. Aqueous solutions primarily contain two forms of ammonia, unionized ammonia and ammonium ion; both of which are in equilibrium.

The removal of ammonia from industrial effluent represents an important and dynamic field 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. Therefore, the removal of ammonia from air and waste streams is important.

Several nitrogen-containing compounds are present in the environment, and affect the acidification and eutrophication of ecosystems. The nitrogen cycle characterizes the motion and transformation of these nitrogen compounds through the biosphere. The key concern associated with the use of ammonia-contaminated water with excessive nitrate concentrations involves its effect on human health, especially that of infants [1].

Wet oxidation (WO) technology was originally designed to oxidize organic substances, yielding intermediate products with small molecular weights at temperatures between 125 and 350 °C and pressures of between 0.5 and 20.0 MPa in the aqueous phase. However, ammonia is usually 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. However, catalytic WO (CWO) is known to increase the range of uses of WO technology if appropriate catalysts are used; such catalysts have the potential to promote oxidation with shorter reaction times and under milder operating conditions. The selective catalytic oxidation

*Corresponding author
Email: hungcm1031@gmail.com
of ammonia-containing water to yield molecular nitrogen and water can be adopted to eliminate ammonia pollution [4-7].

Various catalysts have also been used for ammonia oxidation in the liquid phase. For instance, Levec and Pintar [8] showed that the WO of aqueous solutions of organics from wastewaters at low temperatures and pressures was easier in the presence of heterogeneous catalysts than in a non-catalytic WO processes. Also, Imamura et al. [9], who designed various heterogeneous catalysts of WO, found that the Mn/Ce (1:1, molar/molar) composite catalyst was more active than a Co/Bi catalyst for the WO of ammonia. These catalysts were active in reactions at temperatures of over 260 °C with 4.0 MPa. Imamura [10] published a review paper that summarized recent works on CWO and noncatalytic WO.

Platinum-based group metal additives as three-way catalysts are the most active components in hydrocarbon oxidation and are also active in all other reactions [11,12]. However, little research has been performed on the use of platinum-palladium-rhodium (Pt-Pd-Rh) based alumina-supported catalyst to elucidate the reactive characteristics of these active metals in CWO. The activity of the Pt-Pd-Rh composite oxide catalyst in the oxidation of ammonia solutions, given various values of relevant parameters, and its effect on the removal of ammonia in CWO, were studied.

MATERIALS AND METHODS

1. Materials and Chemicals

The Pt-Pd-Rh composite oxide catalysts that were used in this study were prepared by the co-precipitation, which involved aqueous H2PtCl6, Pd(NO3)2 and Rh(NO3)3 (all grade, Merck, Darmstadt, Germany). A Pt-Pd-Rh 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 500 °C in an air stream for 4 h. The resulting powder was formed into tablets using acetic acid as a binder.

2. Experimental Methods

All feed solutions were made using Millipore (Bedford, MA) water (18 MΩ cm), and the pH value of the ammonia aqueous solution was adjusted to 12.0 using 1 M sodium hydroxide. The CWO was conducted in a continuous trickle-bed reactor (TBR) that was constructed from 45 cm of stainless steel tubing (SS-316), 25 mm I.D., which was resistant to high pressures and temperatures of up to 10 MPa and 350 °C, respectively, and to corrosion at pHs of between 5 and 12.5. The main operating parameters were a liquid feed rate given by a liquid hourly space velocity (LHSV) of 1.5 to 9 h⁻¹, reaction temperatures of 150, 200 and 230 °C, and ammonia concentrations in the inlet between 400 and 1000 mg L⁻¹. The partial pressure of oxygen in the reactor was maintained at a constant 2.0 MPa, and the pH of the buffer ammonia solution in the inlet was maintained at 12.0.

Before each experiment, the reactor was heated for around 2 h to a steady reaction temperature. Each temperature was maintained for 60 min to allow the system to enter a steady state. When the desired reaction temperature was reached, the desired feed flow rate was initiated. After a constant reaction temperature had been reached, the reaction pressure was adjusted to the desired value using a backpressure regulator. This change took about 15 min. Additionally, the sample cooling system started at the same time as the heating system of the reactor. Reducing the temperature of the recirculation took about 15 min. The cooled mixed stream was directed to the sampling vessel and separated immediately. Therefore, the liquid and gas samples could be collected. The reproducibility of experiments was acceptable, since differences between ammonia conversions from duplicate experiences were found always to be less than 5%.

3. Analyses

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 0.03-3 mg L⁻¹ (Spectroquant 14752). Also, the concentrations of two other compounds in the samples, namely NO3⁻ between 0.2 and 20 mg L⁻¹ (Spectroquant 14773) and NO2⁻ between 0.005 and 1 mg L⁻¹ (Spectroquant 14776), were determined using a Merck kit, as described above. The residual ammonia in the vapor gas was scrubbed by dilute sulfuric acid solution and measured using a Merck Kit. No residual NH3 was found in the outlet. Thus, we found that the residual ammonia in the gas phase could be ignored for the TBR 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. Meanwhile, the amounts of NO and NO2 in the gas sample were determined using a gas analyzer unit (IMR3000, IMR, Germany). Furthermore, the levels of O2, N2 and N2O were determined using a Shimadzu GC-14A that was equipped with a TCD (Shimadzu, Kyoto, Japan).

UV-Vis absorption spectra were obtained from the solid sample using a photo spectrophotometer (MCPD-3000, OTSUKA Electronics, Osaka, Japan). The reflectance was measured relative to that of a BaSO4 standard. The changes in the sizes of the catalytic particles were measured using a laser light-
scattering particle size analyzer (PSA, Coulter LS100, USA).

RESULTS AND DISCUSSION

1. Product Selectivity

The removal of ammonia from the water was followed by the liquid-phase oxidation of ammonia over the Pt-Pd-Rh composite oxide catalyst. All of the possible products, in the gas or liquid phases, of ammonia oxidation obtained using a Pt-Pd-Rh composite oxide catalyst, were identified. Specifically, the treated water contained small amounts of nitrate and nitrite, and the gaseous samples also contained nitrogen and traces of nitrous oxide (N₂O) and nitrogen dioxide (NO₂). Table 1 shows the product selectivity of ammonia oxidation. The overall selectivity of the production of nitrates and nitrites was about 16% (84% as N₂) with 99% ammonia conversion at 230 °C. Nitrogen was thus the main product of ammonia oxidation. Therefore, Pt (IV) oxide is posited be important in the CWO of ammonia, while Pd (IV) and Rh (III) oxide only provide active sites for the reaction during a CWO run. A synergistic effect occurs in the Pt-Pd-Rh composite oxide structure, which is the material interest with the highest ammonia reduction activity. This result is similar to that of Rogemond et al. [13]. Hu et al. [14] observed a Pt-Rh synergism: Rh particles are the main active sites of the three-way catalyst performance and the Pt maintains the Rh in active Rh metal particles by regenerating nonactive Rh-Al-oxide species. Lecomte et al. [15] demonstrated that platinum is more stable when dispersed in a metallic matrix, and that platinum clusters that formed on a support appear to be the most active components of the catalyst. The effect of metal oxide is discussed below.

2. Characterization by UV-Vis and PSA

Figure 1 presents UV-Vis spectra and thus provides further information on the states of platinum and rhodium species in these catalysts. The bands associated with such octahedral Pd (IV) species were observed in the ranges 325-350. The band at 325-350 nm corresponds to d-d transitions [16,17]. No rhodium-containing species are detected by UV-Vis. These results indicate that rhodium may exist in a highly dispersed form.

The change in the sizes of particles of the catalyst was determined using the laser light-scattering approach, as shown in Fig. 2. The mean particle size converged at approximately 18 μm for fresh Pt-Pd-Rh composite oxide catalyst. However, the diameters of the catalyst decreased during the activity test and the mean particle size was about 9 μm. Such changes in the sizes of particles of the catalyst after the reaction can be attributed to over-oxidation of the Pt-Pd-Rh composite oxide surface during the reaction. The emergent technology of CAO, which uses catalysts of the oxidation NH₃ into N₂, enables the operation under temperature and pressure conditions that are milder than those required without a catalysts. As a result, the stability of heterogeneous catalysts in the oxidizing reaction medium is critical to WAO processes. Without this stability, the possible leaching of the active species should be separated from the treated liquid phase.

3. Effect of Experimental Parameters on Catalytic of Ammonia

As illustrated in Figs. 3 and 4, nitrite production was substantially lower than nitrate production, and was significant, only at a high operating temperature of 230 °C and a high ammonia conversion efficiency (99%). The concentration of accumulated nitrates in the aqueous solution decreased as the ammonia conversion increased above 78%, reaching approximately 0.5 mM. The treated water was also found to contain nitrate and nitrite, resulting from NO compounds. In this work, reactions that were conducted with excess oxygen were passed over Pt-Pd-Rh composite oxide catalyst to produce N₂O and water, before a subse-

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>Ammonia Conversion (%)</th>
<th>NO₃⁻ + NO₂⁻</th>
<th>N₂O</th>
<th>N₂</th>
<th>Product Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>99</td>
<td>16</td>
<td>ND</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>95</td>
<td>19</td>
<td>ND</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>63</td>
<td>24</td>
<td>ND</td>
<td>76</td>
<td></td>
</tr>
</tbody>
</table>

ND: not detected
Fig. 2. Changes in particle sizes distribution of the Pt-Pd-Rh composite oxide catalyst showing: (a) fresh, (b) after activity test. Test conditions: temperature = 230 °C, pH = 12.0, partial pressure of O2 P02: 2.0 MPa, initial concentration of ammonia = 400 mg L⁻¹.

Fig. 3. NO₂⁻ and NO₃⁻ formation at 200 °C in the trickle-bed reactor (P02: 2.0 MPa, ammonia in feed: 19.6 mM, LHSV: 1.5-9.0 h⁻¹).

Fig. 4. NO₂⁻ and NO₃⁻ formation at 230 °C in the trickle-bed reactor (P02: 2.0 MPa, ammonia in feed: 19.6 mM, LHSV: 1.5-9.0 h⁻¹).

sequent reaction formed nitrogen. Some of the N₂O oxide may desorb from the Pt-Pd-Rh composite oxide catalyst and further react with the surrounding oxygen to produce NO₂. This reaction is spontaneous and reversible and does not involve any catalyst.

Within a TBR, the formation of nitrates and nitrites in the resultant solution from ammonia oxidation with a Pt-Pd-Rh composite oxide catalyst proceeds by the same reactions and mechanisms. The mass transfer of nitrites and ammonia between the gas and liquid phases affects the selectivity of by-products when the pH of the treated water is less than 8.2, resulting from a high ammonia conversion efficiency of 99% (Fig. 4). The nitrate profile has a peak at pH 8.4 with 89% ammonia conversion. The peak declines as the ammonia conversion increases, indicating that further removal of the aqueous nitrates is possible. In this step, atomic oxygen may be generated and may adsorb to the catalyst surface, blocking the active sites and reducing the activity. This additional atomic oxygen on the catalyst surface reduced the recombination of atomic nitrogen to form N₂. Therefore, the nitrogen formation activity enables the action of the catalyst. The removed nitrite can be regarded as decomposed to NO and NO₂ in the gas phase, following a reversible reaction. The NO₂ reacts with gaseous ammonia to produce N₂ at the active sites of the Pt-Pd-Rh composite oxide catalyst. Accordingly, in the reaction system, the reaction of ammonia and oxygen generated NO and H₂O, after which some NO was converted to NO₂ in an environment of excess oxygen producing a gaseous environment of NH₃, NOₓ and H₂O, which in turn produced an ammonia salt.

In the TBR, the N₂O was converted to aqueous NO₃⁻ and NO₂⁻. However, nitrate exhibits a sudden change in their concentration profiles. Clearly, further removal of nitrite is more difficult than that of nitrate. Although the concentration of nitrite increases with ammonia conversion (Fig. 4), nitrite selectivity actually decreases (Fig. 5). Comparing Figs. 5 and 6 data reveals that a lower liquid flow rate resulted in increased ammonia conversion, lower resultant pH, and ultimately lower nitrite selectivity. Consequently, the profile of nitrate selectivity was also consistent with that of pH (Figs. 5 and 6). The activity and selectivity of the ammonia reduction thus depends strongly on the pH value. The above results are consistent with those of Huang et al. [18]. Huang et al. [19] also
found that a higher pH favors the formation of aqueous molecular ammonia, increasing the partial pressure of ammonia in the gas phase. Therefore, in a present study, a higher reaction rate can be achieved by the Pt-Pd-Rh composite oxide catalyst. However, the gas flow rate did not influence the ammonia removal efficiency.

Nitrite selectivity was low, remaining under 12% for various liquid flow rates. This result reveals that in this study, nitrite selectivity is significantly lower than nitrate selectivity, even at a pH range of above 9.0. However, this study found that to achieve an ammonia conversion of more than 99%, the feed liquid flow rate would have to be as low as 1.5 mL min⁻¹ at 230 °C. Such a low liquid flow rate may cause an uneven liquid distribution within the catalyst bed, possibly resulting in poor local mass transfer. Under such conditions, ammonia cannot be removed completely, as presented in Figs. 7-9. This phenomenon occurs because, under these conditions, ammonia cannot react with the active sites of the Pt-Pd-Rh composite oxide catalyst. Hence, the nitrite selectivity was lower, because of the poor distribution of the aqueous phase, which is caused by the partial soaking of the outer surface of the catalysts, since the ammonia was preferentially transformed to nitrate. Furthermore, the resultant pH of the treated water significantly influences the selectivity towards nitrate by-products of ammonia oxidation. Higher ammonia conversion is responsible for lower pH because of the reduction in alkalinity and the production of nitrites and nitrates. This phenomenon reveals that the inactivation was probably caused by increased pH, which occurred when ammonia was oxidized by Pt-Pd-Rh composite oxide catalyst. The above results are consistent with those of Huang et al. [19].
A lower pH promotes the further removal of by-product NO$_2^-$, but not the removal of ammonia. The results in Figs. 7, 8 and 9 indicate that both NO$_2^-$ selectivity was minimized and ammonia removal maximized when the resultant pH of the reaction solution approached 8.2 for a given ammonia solution feed. Imamura et al. [9] demonstrated that the reactions did not proceed at all in acidic solution in the presence of Co/Bi catalysts, but proceeded only at a pH of over 9.0. Thus, they concluded that ammonia was more reactive than ammonium when Co/Bi catalysts were used. The reactions must occur in the liquid phase when catalysts are used. Therefore, the data presented here indicate that a low pH promotes nitrite reduction. However, when a Pt-Pd-Rh composite oxide catalyst was used, the reactions occurred in the gas phase. However, at a pH of under 8.2, substantially more ammonia can exist in high conversions at 230 °C, and NO$_2^-$ selectivity is minimized. Although some parts of the primarily pathways are poorly understood, this study clarified the possible mechanisms of ammonia oxidation, and provided significantly new information on this process.

**CONCLUSIONS**

The overall by-product selectivity of nitrate and nitrite production varied from 16-24% with 63-99% ammonia conversion over a Pt-Pd-Rh composite oxide catalyst. The results of this study reveal that pH is a critical parameter for controlling the reduction of ammonia over a Pt-Pd-Rh composite oxide catalyst. Nitrite selectivity was minimized and ammonia removal was maximized when the resultant pH of the treated water was around 8.2 for in an ammonia solution feed. Therefore, catalyst reduction can be a cost-effective scheme of treating wastewater at high temperature or high concentrations of ammonia.

**ACKNOWLEDGMENTS**

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**


Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.

Manuscript Received: October 25, 2007
Revision Received: February 14, 2008
and Accepted: February 18, 2008