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Catalytic wet air oxidation of wastewater containing ammonia and phenol over activated carbon supported Pt catalysts

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Abstract

Noble metal catalysts on activated carbon (AC) (Pt/AC and Ru/AC) and base metal catalysts (Cu/AC, CoMo/AC, Mo/AC, Mn/AC, Ru/Al_2O_3) were developed and examined for the simultaneous removal of organic pollutants and ammonia from wastewater using the wet air oxidation (WAO) process in the liquid phase. The noble metal catalysts were much more active than were the base metal catalysts. Ammonia removal was the rate-controlling step. Nitrate and nitrite accounted for a minor portion of the decomposed ammonia ($<5\%$ for Ru/AC and $<3\%$ for Pt/AC). Pt/AC was superior to Ru/AC in terms of ammonia removal, pH sensitivity and stability. Activated carbon was a better support for Pt than was TiO_2, Al_2O_3 or MCM-41.

The optimal preparation conditions of Pt/AC were: calcination at 300 °C for 6 h followed by H_2 reduction at 600 °C without pretreatment of AC. The catalyst so prepared, Pt(opt)/AC, produced ammonia removals of 52 and 88% at 200 °C, initial pH of 5.6 and 12, respectively. The experimental results based on the Pt(opt)/AC showed that the Pt/AC catalyst was able to remove ammonia (>50%) and phenol (≈100%) simultaneously from highly polluted wastewater containing up to 1500 mg/l N ammonia and up to 8000 mg/l COD.

Keywords: Catalysts; Base metals; Noble metals; Wastewater; Landfill leachate

1. Introduction

Ammonia in wastewater discharged from petrochemical plants, paper mills, textile plants and landfill sites is a major environmental concern. It causes eutrophication in rivers and lakes. There are various ways to eliminate ammonia from wastewater, including biological nitrification and denitrification, air stripping, break-point chlorination, ion exchange, etc. Biological treatment is widely used at many treatment sites, but this process is inhibited when the ammonia concentration is high or some toxicants are present in the feed [1]. In the air stripping process, ammonia is not ultimately eliminated, but transferred from the liquid phase (wastewater) to the gas phase (air). Subsequent catalytic oxidation is necessary to convert it to N_2. Break-point chlorination and ion exchange are very effective in removing ammonia ions from wastewater but are feasible only when the concentration of the ammonia is low.

Ammonia usually exists in wastewater along with various organic pollutants. For example, typical municipal wastewater contains 300 mg/l of COD (chemical oxygen demand) and 40 mg/l of NH_4–N [2]. Using a two-stage process with wet air oxidation (WAO) or catalytic wet air oxidation (CWAO) makes it possible to remove COD in the liquid phase, followed by air stripping and vapor phase oxidation of

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the ammonia. A great deal of effort has been devoted to creating various heterogeneous catalysts to promote the necessary oxidation reaction at temperatures from 250 to 600 °C [3–6]. In many cases, nitrous oxide and nitric oxide are formed in the oxidation processes as unfavorable by-products. Other ammonia abatement techniques such as supercritical water oxidation [7,8], ozone and hydrogen peroxide oxidation [9] and catalytic photooxidation [10] have been investigated.

Simultaneous removal of COD and ammonia in a single-stage is a very attractive solution with the use of catalytic wet air oxidation. This technique has several advantages such as a relatively short reaction time by the cheapest and most abundant oxidant, O_2 (or air), and applicability to a broad range of COD, toxicity, pH and ammonia concentrations, from municipal wastewater to heavily loaded landfill leachate.

The selection of the catalyst is the key issue in utilizing this simple process. The catalysts used for organic pollutant degradation function well at neutral pH [11–13] but suffer a significant drop in efficiency when ammonia is present. Nitrogen-containing organic compounds can be readily oxidized to ammonia at 200 °C [14]. Further decomposition of ammonia, however, is very difficult. Clearly, ammonia oxidation is the rate-limiting step in the whole process. Therefore, catalytic wet oxidation of ammonia has become the focus of several researchers. Imamura and Dol [15] discovered that the Co/Ce and Mn/Ce composite oxides were remarkably active in ammonia oxidation. At 263 °C, about 50 and 70% of ammonia were removed in 1 h with Co/Ce and Mn/Ce oxides, respectively. Deiber et al. [16] obtained removal efficiency of 66–81% at temperatures from 260 to 300 °C with the help of a Mn/Ce composite oxide catalyst. It has been suggested that the combination of a Group VIII with a Group VIB metal or metal compound on a support would be suitable for treating wastewater containing phenol, ammonia and other offensive substances in a packed bed reactor [17]. NiMo, NiW and CoMo were found to be more active and capable of removing 50–70% of ammonia and 60–90% of phenol simultaneously. Qin and Aika [18] investigated various metal catalysts supported on alumina and found that Ru/Al_2O_3 could remove more than 99% of ammonia in 2 h. Base metal catalysts, such as Co, Ni, Fe, etc. were much less effective than noble metal catalysts at 230 °C and $pH = 12$. Although Qin and Aika claimed that Pt/Al_2O_3 was not effective, Ukropec et al. achieved an efficiency of about 40% with Pt supported on graphite in a continuous stirred tank reactor at 180 °C [19]. It was also reported that Pt catalysts supported on TiO_2 (P-25), Al_2O_3, ZrO_2 and H-ZSM-5 could decompose at least 90% of ammonia in 6 h at 160 °C [20]. Obviously, there is still not a consensus regarding catalysts in WAO of ammonia.

In this paper, we report our recent findings on catalytic wet air oxidation of ammonia. Several transition metals (Cu, Co, Mo, Mn, Ru and Pt) were supported on inert porous materials (activated carbon (AC), TiO_2, Al_2O_3 and MCM-41). Among the catalysts prepared, activated carbon supported Pt was found to be the most effective catalyst. Consequently, its development, evaluation and application in the simultaneous oxidation of ammonia and phenol were investigated in detail.

2. Experimental

2.1. Catalyst preparation

Heterogeneous catalysts were prepared by impregnation or co-impregnation methods. Activated carbon, TiO_2, alumina and MCM-41 were selected as the catalyst supports for the test. TiO_2 (Degussa, P-25) and alumina (pure Al_2O_3, active neutral, 60–80 mesh, BDH) were used as received. MCM-41 was synthesized using a dodecyltrimethylammonium bromide (Aldrich) solution as the template [21,22]. The activated carbon was Norit ROW 0.8 Supra extrudes (American Norit Company). It was ground into fine particles and separated in a series of sieves. Particles with sizes ranging from 0.125 to 0.3 mm were employed as the catalyst support. The fine carbon particles were further treated by HCl solutions (5 wt.%) to remove impurities on the carbon surface [12], followed by oven drying at 105 °C 24 h under ambient pressure and then vacuum drying at room temperature for 24 h.

Aqueous solutions of $Cu(NO_3)_2\cdot 2.5H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Mn(NO_3)_2\cdot 4H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ from Riedel–deHaën, and $RuCl_3\cdot xH_2O$ and $H_2PtCl_6\cdot xH_2O$ from Aldrich were used as the source of the active catalytic elements. After impregnation for 24 h, the catalysts were dried at 80 °C overnight.

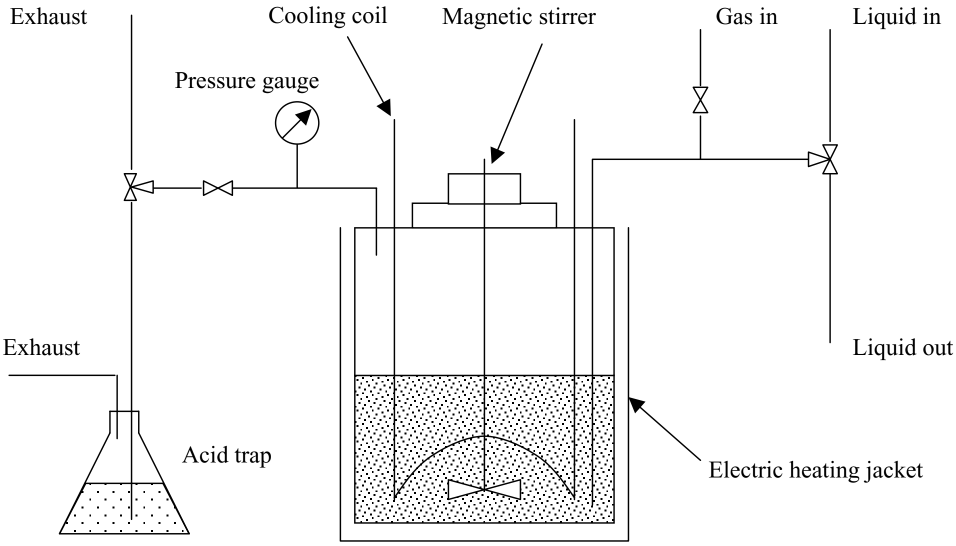

Fig. 1. Reactor for catalytic wet air oxidation of ammonia.

Further treatment by calcination and/or reduction was carried out if necessary.

2.2. Apparatus and experimental procedures

Most of the catalytic wet air oxidation was performed in a 1 l stainless steel Parr reactor (Fig. 1). In a typical run, 500 ml of synthetic wastewater containing 1000 mg/l N of ammonium sulfate (BDH) and 2.5 g of catalyst were charged into the reactor. When necessary, sodium hydroxide (Riedel–deHaën) or sulfuric acid (ARCOS) solution was added to adjust the initial pH. Phenol (RDH) was added as the source of COD. Argon was used to purge the reactor for 5 min to ensure there was no O_2 left in the reactor. Then, all the valves were closed and the reactor was heated by an automatic electric heater. Meanwhile, the solution was mixed by stirring at 500 rpm. After the temperature reached the set point (200 °C), 4.2 bar of O_2 (200 °C, 0.054 mol, equivalent to twice the stoichiometric amount) was introduced into the reactor and this point was taken as the starting point of the reaction. After 2 h reaction, the reactor was quickly cooled down to 40 °C with chilled water. Then, the gas and liquid samples were taken. Gas from the reactor was trapped with 80 ml of 0.05 M H_2SO_4 solution. Further oxidation was insignificant in the cooling process because it took only about 10 min to cool down the reactor from 200 to 40 °C. Some early experiments were performed in a similar reactor with a total volume of 2 l (as reported in Sections 3.1 and 3.2). The switching of reactors was because non-repairable leakage of the 2 l reactor was detected after a few trials.

2.3. Analysis

Concentrations of ammonia in the gas and liquid phases were measured with an Orion ammonia electrode (Model 95–12) with a range up to 14,000 mg/l N. Nitrate (NO_3^-) and Nitrite (NO_2^-) were analyzed by Ion Chromatography (Dionex LC20). Leaching of metals from the catalyst surface was determined by inductively coupled plasma (ICP) spectroscopy (Optima 3000XL). Concentrations of phenol were measured by a Shimadzu UV-1206 Spectrophotometer at a wavelength of 500 nm after proper solution dilution. The specific surface area of the catalysts was estimated at 77 K by an Omnisorp 100CX BET machine manufactured by Coulter Science Instruments. The catalyst morphologies were analyzed by a Philips High Resolution X-ray Diffraction System (Model PW1825, 3 kW) using Cu Kα radiation (1.54 Å). The analyses were performed over an angular range of $2\theta = 25$–70° at a speed of 0.05°/min with a step of 0.05°.

3. Results and discussion

3.1. Ammonia equilibrium at elevated temperatures

Ammonia (NH_3) is highly soluble in water, forming an alkaline solution called ammonium hydroxide (NH_4OH). Ammonium hydroxide is a weak base. The following equilibrium exists in a closed system:

$$\begin{aligned} NH_4^+ + OH^- &\Leftrightarrow NH_4OH \Leftrightarrow NH_3(l) + H_2O \\ &\Leftrightarrow NH_3(g) + H_2O \end{aligned}$$

pH is a critical factor affecting the quantity of ammonia in different forms. Although the ammonia–water vapor–liquid equilibrium at various temperatures and pressures has been studied [23,24], its behavior at different pH at elevated temperatures is still not well understood. In a batch reactor, ammonia (or ammonium) exists in the gas phase as well as the liquid phase. From Fig. 2, it is obvious that at 200 °C most ammonia remained in the liquid phase at a pH of 3 but existed in the gas phase when the pH was higher than 9. On the contrary, ammonia in the gas phase only accounted for less than 1% of the total amount at room temperature (22 °C) even if the pH was as high as 11.80. These results suggest that samples could only be withdrawn at the end of the reaction after the system was cooled down to the ambient temperature when running WAO under alkali conditions. Otherwise, sampling from the liquid phase would increase the volume of the headspace, which in turn caused the limited amount of ammonia in the liquid phase to evaporate. Consequently, the ammonia concentration in the liquid phase would be highly biased by the sampling process.

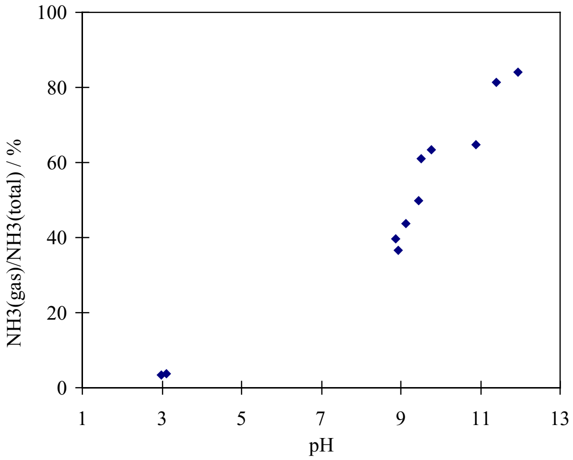

Fig. 2. Ammonia equilibrium at 200 °C in a closed batch reactor. NH_3 (gas)/NH_3 (total) was defined as the percentage of ammonia in the gas phase to the total ammonia in the reactor; reactor volume: 2000 ml (liquid: 1400 ml, gas: 600 ml); initial ammonia concentration in the liquid: 1000 mg/l N ($(NH_4)_2SO_4$ as the source of N).

3.2. Screening of active catalytic elements for CWAO of ammonia

The catalyst plays a vital role in CWAO of ammonia. Five transition metal catalysts were prepared using impregnation methods and tested in the 2 l reactor. The preparation conditions of CoMo/AC and Ru/Al_2O_3 were similar to previous work [17,18]. The results are listed in Table 1. Eight hundred ml of ammonia sulfate solution, 0.8 g of catalysts and 0.3 MPa of oxygen (about twice the stoichiometric amount) were used except for the case of the Cu/AC catalyst when the initial volume of the ammonia sulfate solution was 1400 ml and the oxygen was 1.05 MPa. The ammonia removal efficiency was defined as the ratio

Table 1
Heterogeneous catalyst preparation conditions and test results (230 °C, initial pH: 12)

Catalyst no.	Metal and loading	Support	Calcination	Reduction (H_2)	NH_3 removal efficiency (%)
1	Cu (5 wt.%)	AC	550 °C, 18 h (N_2)	300 °C, 3 h	13
2	Co (2 wt.%), Mo (5 wt.%)	AC	450 °C, 18 h (N_2)	300 °C, 3 h	18
3	Mo (5 wt.%)	AC	450 °C, 18 h (N_2)	300 °C, 3 h	20
4	Mn (5 wt.%)	AC	600 °C, 18 h (N_2)	300 °C, 3 h	20
5	Ru (3 wt.%)	Al_2O_3	300 °C, 3 h (air)	NA	39

of the missing ammonia to the initial amount of ammonia in the reactor.

It is clear that base metal catalysts were not active, which is consistent with Okada et al. [25], who found that base metal catalysts on Al_2O_3 were not active at oxidation temperatures below 250 °C. CoMo/AC was claimed to have good activity for ammonia removal [17], which was 45–67% when the synthetic wastewater (150 mg/l NH_3, pH = 8.4) was fed into a 3/8 in. o.d. stainless steel tube reactor at 110–120 °C. However, this catalyst showed a low efficiency for concentrated ammonia removal in the 2 l batch reactor in our experiments. In contrast, the noble metal catalyst, Ru/Al_2O_3, showed reasonable removal activity even at 230 °C. Qin and Aika obtained 99% ammonia removal with 2 g of an Ru (3 wt.%)/Al_2O_3 catalyst for 100 ml of synthetic ammonium chloride solution (NH_3: 1500 mg/l, pH = 12.3) at 230 °C in a batch reactor [18]. We obtained medium efficiency (39%) with 1 g/l of the Ru (3 wt.%)/Al_2O_3 catalyst. This result indicates that it is still possible for noble metal catalysts to promote wet oxidation at relatively low temperatures. Other researchers also found that base metal catalysts (Cr, Fe, Co, Ni, Cu, etc.) had much lower activities than did noble metal catalysts (Pt, Pd, Ru, etc.) under the same reaction conditions [18,20], which illustrates the necessity of employing noble metals as the active catalytic elements.

Since the performance of either Pt or Ru on activated carbon was not studied previously, we prepared and tested Ru and Pt supported on AC in this project. Ru and Pt were first impregnated and deposited on Norit activated carbon with the metal loading of 0.5 wt.%. Then, they were calcined at 450 °C in a flow of N_2 for 2 h before being reduced by H_2 at 450 °C for another 2 h. The 1 l Parr reactor was used for the CWAO experiments following the reaction conditions and procedures described in Section 2.2. Table 2 presents the performances of the two catalysts at three temperatures. The initial pH was 12 in all tests. The concentrations of NO_3^- and NO_2^- were based on the mass concentration of N (mg/l N). It is encouraging to note that fairly high efficiencies were obtained at 200 °C for both Ru and Pt catalysts, although the metal loading was only 0.5 wt.%. Nitrate and nitrite were detected after the treatment, but their total amount only accounted for a minor portion of the decomposed ammonia (<5% for Ru/AC and <3% for Pt/AC). Most of the ammonia was oxidized to N_2. This is very important for CWAO of ammonia because nitrate and nitrite are still toxic pollutants. On the other hand, Pt/AC had higher activity than did Ru/AC at all temperatures tested, and the difference increased with the temperature. It is impressive that 79% of ammonia removal was achieved by applying Pt/AC in CWAO. Moreover, elementary analysis by ICP revealed 0.6–4.2 mg/l of Ru in the treated water, whereas dissolution of Pt did not occur, indicating the high stability of the Pt/AC catalyst under the conditions employed. Therefore, the wastewater after wet air oxidation was free from contamination by the toxic Pt complex ion and could be discharged without further treatment.

pH sensitivity analysis is also necessary for screening a suitable CWAO catalyst of ammonia. Qin and Aika [18] reported that an Al_2O_3-supported Ru catalyst was highly pH-sensitive. The ammonia oxidation hardly occurred in the acidic region although the reaction proceeded quickly when the pH was higher than 10. In our experiments, the Ru/AC catalyst exhibited some activity under acidic conditions, but it was much lower than that for the Pt/AC catalyst. Ammonia removal with the Pt/AC catalyst was less pH sensitive, as can be seen from Table 3 (runs 1 and 2). Run 3 in Table 3 indicates the simultaneous oxidation of ammonia (1000 mg/l N) and phenol (1000 mg/l, as

Table 2
Performance of Ru/AC and Pt/AC catalysts at different temperatures (initial pH: 12)

Temperature (°C)	Ru/AC				Pt/AC			
	Efficiency (%)	$[NO_3^-]$ (mg/l N)	$[NO_2^-]$ (mg/l N)	Final pH	Efficiency (%)	$[NO_3^-]$ (mg/l N)	$[NO_2^-]$ (mg/l N)	Final pH
230	59	8.96	2.02	7.58	79	5.92	0.16	7.11
200	40	6.18	8.16	9.30	50	7.2	7.56	9.08
160	17	4.78	2.72	10.16	28	5.46	2.26	10.04

Table 3
Comparison of the activities between Pt/AC and Ru/AC catalysts

Run no.	Temperature (°C)	pH	Removal efficiency (%)		
				Pt/AC	Ru/AC
1	200	5.6	Ammonia	42	16
2	200	12	Ammonia Ammonia	50 61	40 62
3	230	12	Phenol COD	99.8 84	99.6 89

the initial source of COD) with an excess supply of O_2 (1.06 MPa) at 230 °C. The initial pH was 12. The ammonia removal was almost the same. The removal of phenol and COD reduction were highly efficient for both catalysts. The slightly lower COD removal than phenol degradation is believed to result from the formation of refractory intermediates in the oxidation process [26]. The results obtained in this section clearly show that Pt is the better element for ammonia removal.

3.3. Supports for Pt catalysts

The support is another important aspect of heterogeneous catalysts. Catalysts were prepared using AC, TiO_2, Al_2O_3 and MCM-41 as supports. The calcinations of Pt/AC and Pt/TiO_2 were conducted at 450 °C for 2 h in N_2 and O_2 environments, respectively. The Pt/Al_2O_3 and Pt/MCM-41 were calcinated at 300 °C for 6 h in an N_2 environment. All the catalysts were reduced by hydrogen gas for 2 h at 450 °C. With the same amount of Pt loading of 0.5 wt.%, Pt/MCM-41 exhibited only 12% ammonia removal after 2 h at 200 °C with an initial pH of 5.6. Using Al_2O_3 as the support yielded a 20% ammonia removal. Under the similar preparation conditions as reported in [20], Pt/TiO_2 yields slightly better activity of 25% ammonia removal. This finding is not consistent with results reported by Taguchi and Okuhara [20]. They reported that Pt/TiO_2 was able to oxidize 70% of ammonia in 1 h and 98.5% in 6 h at 160 °C. This high activity was also found for Pt deposited on other supports, Pt/Al_2O_3 (99.8%), Pt/ZrO_2 (98.5%), Pt/H-ZSM-5 (94.1%) and Pt/pure rutile TiO_2 (86.8%). However, Ukropec et al. [19] reported that the reaction rates of Pt catalysts on different supports varied greatly from 0.22 mol/(kg h) (Pt/Al_2O_3) to 25.2 mol/(kg h) (Pt/graphite), and Pt/TiO_2 was not active with a reaction rate of 4.19 mol/(kg h). At 171 °C, the ammonia removal was less than 5% on Pt/TiO_2 but about 50% on Pt/graphite in a continuous stirred tank reactor. Our results are consistent with those of Ukropec et al. [19]. In our experiments, Pt/AC exhibited the highest ammonia removal efficiency (42%) among all the catalysts. AC was therefore chosen as the support to make Pt catalysts for subsequent tests.

It is worth noting that under the same conditions, only 3% of ammonia disappeared in the blank test. Deposition of Pt on the AC surface could greatly enhance the activity of Pt in ammonia removal. This result was not due to the relatively large surface area of the AC (≈1200 m^2/g), because the MCM-41 we prepared possessed an even larger surface area (≈1400 m^2/g) but exhibited much lower activity (12%) compared with Pt/AC (42%). Takayama et al. proposed that the hydrophobicity of the surface of AC provided a better medium for the reaction of neutral ammonia (NH_3) and oxygen, which contributed to the high activity of the Pd/AC catalyst in ammonia removal under basic conditions [27]. However, this may not apply to our cases. In our tests, pH started from 5.6 and dropped to 2–3 at the end of the reaction. In this pH range, most ammonia exists in the form of ammonium ions (NH_4^+) because the pK_a value of ammonia is 9.27. Therefore, the ammonia oxidation might proceed via a way other than the Langmuir–Hinshelwood (L–H) mechanism proposed by Qin and Aika [18]. In addition, the hydrophobicity may contribute little to ammonia oxidation in the pH range of 2–5.6. Because AC and the homogeneous catalyst H_2PtCl_6 exhibited much lower efficiencies than did Pt/AC, 10 and 7%, respectively, the high activity of Pt/AC could be due to the interaction between Pt and the AC surface, although this interaction has not yet been elucidated.

3.4. Conditions optimization for Pt/AC catalysts preparation

The activity of a catalyst can be greatly affected by its preparation conditions. A three-level, four-factor orthogonal collocation chart was therefore employed to find the optimum preparation conditions for Pt/AC catalysts (Table 4). The prepared Pt catalysts were tested at 200 °C for ammonia oxidation at two initial

Table 4
Three-level, four-factor orthogonal collocation chart

Level	Factor			
	A Calcination temperature (°C)	B Calcination time (h)	C Reduction temperature (°C)	D AC pretreatment
1	300	10	300	None
2	450	6	450	Reduced in H_2 at 450 °C for 9 h
3	600	2	600	Calcined in N_2 at 450 °C for 9 h

pHs (Table 5). In the liquid phase, the major reactant was ammonium ions (NH_4^+) at pH of 5.6 and free ammonia (NH_3) at pH of 12. The average efficiency was calculated as follows. To take level 3 and factor C at pH of 5.6 for an example, under factor C, runs 1, 5 and 9 were carried out using the catalysts prepared at level 3, i.e., reduction temperature of 600 °C. The ammonia removal efficiencies for runs 1, 5, and 9 at pH of 5.6 are 41, 50 and 44%, respectively. The average of the three removal efficiencies is 45%. The importance of the four factors is reflected by the maximum difference among the averaged value for each level. The larger this value, the more important the factor. Interactions between different factors are not considered.

As shown in Table 5, the calcination time and reduction temperature had greater effects on catalyst activity. Pretreatment of the AC was of negligible advantage and seemed unnecessary. The pH of most wastewater is much lower than 12 [28–30]. Hence, the best condition for Pt/AC preparation can be determined as the levels corresponding to the largest average removal efficiency. That is calcination temperature: 300 °C (level 1); calcination time: 6 h (level 2); reduction temperature: 600 °C (level 3); no AC pretreatment. The catalysts were then prepared under these optimal conditions. They yielded ammonia removal of 52 and 88% at the initial pH of 5.6 and 12, respectively. As expected, the removal efficiency was higher than the

Table 5
Orthogonal collocation experiments and results (200 °C)

Run no.	Factor				NH_3 removal efficiency (%)	
	A	B	C	D	pH = 5.6	pH = 12
	Level					
1	1	1	3	2	41	45
2	2	1	1	1	18	36
3	3	1	2	3	34	42
4	1	2	2	1	44	69
5	2	2	3	3	50	68
6	3	2	1	2	35	46
7	1	3	1	3	33	53
8	2	3	2	2	41	66
9	3	3	3	1	44	48

Level	Average efficiency (%)							
	pH = 5.6				pH = 12			
	A	B	C	D	A	B	C	D
1	39.3	31	28.7	35.3	55.7	41	45	51
2	36.3	43	39.7	39	56.7	61	59	52.3
3	37.7	39.3	45	39	45.3	55.7	53.7	54.3
Maximum difference	3	12	16.3	3.7	11.4	20	14	3.3

results listed in Table 5. The catalysts prepared under the optimal conditions are denoted as Pt(opt)/AC in subsequent analyses. These catalysts have the BET surface area of 1225 m^2/g at Pt loading of 0.5 wt.%. XRD measurement indicated that no Pt crystallite was present, suggesting Pt was highly dispersed on the surface of the activated carbon. Ion chromatography analysis of the treated wastewater revealed that Pt(opt)/AC still retained high selectivity for N_2. Furthermore, leaching of Pt from the catalysts was not detected.

3.5. Performance of used Pt(opt)/AC

The Pt(opt)/AC catalysts were recycled after treatment. The used catalysts were washed, dried overnight at 80 °C, and then treated in H_2 at 600 °C for 4 h. Reactions were carried out with the used catalysts. A slight deactivation was observed in the second run: the removal efficiency was 43% compared with 52% of the fresh catalyst. But no further deactivation occurred in the third run, with a removal efficiency of 44%. A similar ammonia removal efficiency (39%) was obtained with the used catalyst without pretreatment in H_2. These results indicate that Pt(opt)/AC is reusable and maintains its high activity after reactions at elevated temperatures. Therefore, it is potentially employable for continuous CWAO process.

3.6. CWAO of ammonia with Pt(opt)/AC catalysts

The Pt(opt)/AC catalyst was tested in a series of experiments under different reaction conditions. As illustrated in Fig. 3, a higher reaction temperature considerably improved the ammonia oxidation. At 180 °C, the reaction proceeded rather slowly and only about 20% of the ammonia was oxidized after 105 min. However, the activity was greatly enhanced when the temperature was increased by 40 °C. At 220 °C, removal of most of the ammonia (≈80%) could be achieved. This high temperature dependence may be attributed to the refractory property of ammonia, which results in the high activation energy in this process.

Table 6 shows the effects of different parameters on the ammonia removal efficiency after 2 h of reaction at 200 °C. It is very clear that higher catalyst loading enhanced the oxidation of ammonia. When the catalyst loading was increased to 10 g/l, 83% of the initial ammonia was removed in 2 h. Reducing the initial ammonia concentration resulted in an increased removal efficiency with 89% of ammonia removal after the reaction when the initial ammonia concentration was 500 mg/l N. It should be noted that, in the case of high concentrations (2000 mg/l N), the removal did not change much with variation in the initial ammonia concentration. The improvement of the oxidation efficiency by using higher metal loading was not

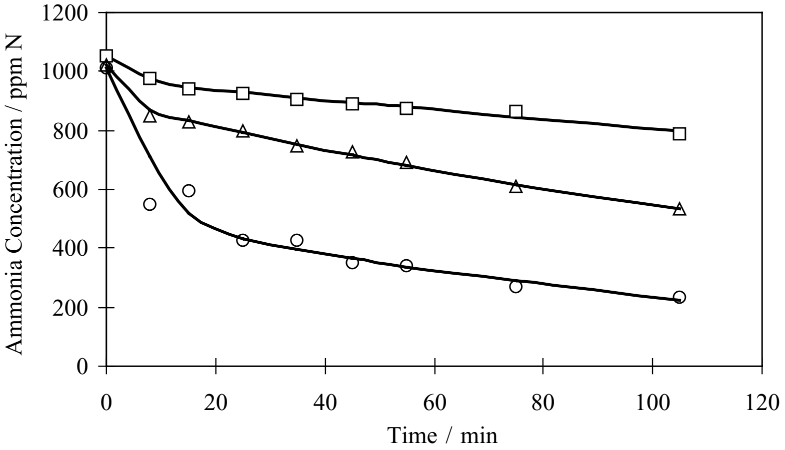

Fig. 3. Ammonia removal at different reaction temperatures. (□) 180 °C; (△) 200 °C; (○) 220 °C; catalyst: Pt(opt)/AC, 0.5 wt.%; catalyst loading: 5 g/l; initial pH: 5.6; O_2: stoichiometric amount × 2; initial ammonia concentration: 1000 mg/l N.

Table 6
Ammonia removal under different conditions (200 °C)

Run no.	Catalyst loading (g/l)	Initial ammonia concentration (mg/l N)	Pt loading on AC (wt.%)	Initial pH	O_2 loading (MPa)	NH_3 removal efficiency (%)
1	2.5	1000	0.5	5.6	0.42	41
2	5	1000	0.5	5.6	0.42	52
3	10	1000	0.5	5.6	0.42	83
4	5	500	0.5	5.6	0.21	89
5	5	1000	0.5	5.6	0.42	52
6	5	2000	0.5	5.5	0.85	54
7	5	1000	0.5	5.6	0.42	52
8	5	1000	0.5	12	0.42	88
9	5	1000	1	5.6	0.42	60
10	5	1000	1	12	0.42	98
11	5	1000	0.5	5.6	0.21	79
12	5	1000	0.5	5.6	0.42	52
13	5	1000	0.5	5.6	0.63	51

significant under both acidic and basic conditions, although 0.5 wt.% of metal loading was extremely low for most of heterogeneous catalysts. Higher metal loading was of little advantage, suggesting 0.5 wt.% of Pt loading was already sufficient.

It is interesting to note that when the O_2 supply was much greater than the stoichiometic amount (e.g. two times the stoichiometic amount), the efficiency changed little with variation in the O_2 loading. However, when the stoichiometric amount of O_2 (0.21 MPa) was provided, a higher removal efficiency was observed, which was quite different from most of the cases encountered in the wet air oxidation of organic pollutants. Further experiments showed that ammonia oxidation could be greatly improved by gradual addition of O_2 into the reactor although the total O_2 supply was the same. Specifically, when half of the stoichiometric amount of O_2 was supplied to the reactor at half hour intervals, i.e., at $t = 0$, 30, 60, 90 min, the ammonia removal efficiency was 70% instead of 52%. Ukropec et al. [19] observed a similar phenomenon in their experiments. A gradual decrease of the activity of the 5 wt.% Pt/graphite catalyst occurred in a continuous stirred tank reactor when the oxygen concentration in the gas feed was increased from 3.75 to 7.5%. Nevertheless, if the oxygen supply was ceased for 30 min, the activity of the Pt/graphite catalyst could be restored. Therefore, they proposed that the Pt/graphite catalyst underwent a reversible deactivation/over-oxidation process under higher oxygen concentrations. Our results here are consistent with their observation and may be due to the effect of Pt over-oxidation.

3.7. *CWAO of concentrated ammonia and phenol with Pt(opt)/AC catalysts*

Although the Pt(opt)/AC catalyst exhibited satisfactory activity in ammonia oxidation, the ability to remove simultaneously ammonia and organic pollutants is indispensable in a one-stage wet air oxidation system. In this test, the oxidations were performed at 200 °C with the synthetic wastewater instead of real industrial effluents and landfill leachate under three different initial conditions, noted as runs 1–3. Ammonia sulfate served as the source for the ammonia. Phenol was chosen to represent the various organic compounds. The ammonia concentration and COD (initially in the form of phenol) were 500 mg/l N/1000 mg/l, 1000 mg/l N/4000 mg/l and 1500 mg/l N/8000 mg/l, respectively, for runs 1–3. The oxygen pressure was 1.5 times the stoichiometric amount, i.e. 0.34, 1.04 and 1.93 MPa, respectively. The initial pH of the synthetic wastewater was adjusted to 7.0 (6.5–7.5). Metal loading of Pt(opt)/AC was controlled to be 0.5 wt.%.

The removal of phenol was demonstrated to be quite rapid and complete, more than 99.9% in all three runs.

The residual COD and TOC accounted for only a minor percentage of the initial amount, 2–5 and 5–8%, respectively. This indicates that few intermediates were formed in this process, showing that Pt(opt)/AC is also a good catalyst for the mineralization of organic pollutants.

Ammonia removal was 71, 49 and 53%, respectively for runs 1–3. It is worth noting that phenol and other organic intermediates did not interfere with the ammonia oxidation over the Pt(opt)/AC catalyst despite their initially high concentration ($[NH_3] > 1000$ mg/l N and COD > 4000 mg/l). In contrast, carbon supported Cu catalysts, which are very popular and effective in the degradation of various organic pollutants, were no longer effective for ammonia oxidation when phenol was present [17], which is not desirable in a one-stage catalytic wet air oxidation process.

4. Conclusions

Pt/AC is a suitable catalyst in a single-stage catalytic wet air oxidation process to remove ammonia and COD at the same time. In our tests, this catalyst could remove ammonia much more efficiently than could other noble and base metal catalysts (Ru, Cu, Co, Mo, Mn) at 230 °C and initial pH of 12. In addition, little nitrate and nitrite were formed after the reaction and leaching of Pt was not detected. The pH affected the catalyst's efficiency but it was less pH-sensitive than was Ru/AC. The preparation conditions had great effects on the catalyst's activity, especially the calcination time and reduction temperature. The optimal preparation conditions were determined by an orthogonal collocation chart. The highest efficiency was obtained with the optimal catalyst, Pt(opt)/AC, among all the Pt/AC catalysts that we prepared. Its performance was greatly enhanced with increased temperature, catalyst loading and pH, whereas high initial ammonia concentrations (>1000 mg/l N) and Pt loading on AC (>0.5 wt.%) did not have much effect. Lower oxygen loading or gradual addition of oxygen significantly increased the catalyst's efficiency, which might be related to Pt over-oxidation. This catalyst was reusable and capable of simultaneously removing high concentrations of ammonia and phenol at 200 °C.

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References

[1] N.G. Love, R.J. Smith, K.R. Gilmore, C.W. Randall, Water Environ. Res. 71 (4) (1999) 418–426.

[2] U. Wiesmann, Adv. Biochem. Eng. Biotechnol. 51 (1994) 113–154.

[3] Y. Li, J.N. Armor, Appl. Catal. B: Environ. 13 (1997) 131–139.

[4] M. Amblard, R. Burch, B.W.L. Southward, Appl. Catal. B: Environ. 22 (1999) L159–L166.

[5] L. Lietti, G. Ramis, G. Busca, F. Bregani, P. Forzatti, Catal. Today 61 (2000) 187–195.

[6] T. Curtin, F.O. Regan, C. Deconinck, N. Knuttle, B.K. Hodnett, Catal. Today 55 (2000) 189–195.

[7] P.A. Webley, J.W. Tester, H.R. Holgate, Ind. Eng. Chem. Res. 30 (1991) 1745–1754.

[8] Z.Y. Ding, L. Li, D. Wade, E.F. Gloyna, Ind. Eng. Chem. Res. 37 (1998) 1707–1716.

[9] C.H. Kuo, F. Yuan, D.O. Hill, Ind. Eng. Chem. Res. 36 (1997) 4108–4113.

[10] A. Wang, J.G. Edwards, J.A. Davies, Solar Energy 52 (6) (1994) 459–466.

[11] L. Lei, X. Hu, H.P. Chu, G. Chen, P.L. Yue, Water Sci. Technol. 35 (4) (1997) 311–319.

[12] X. Hu, L. Lei, H.P. Chu, P.L. Yue, Carbon 37 (1999) 631–637.

[13] H.P. Chu, L. Lei, X. Hu, P.L. Yue, Energy Fuels 12 (1998) 1108–1113.

[14] M.M. Ito, K. Akita, H. Inoue, Ind. Eng. Chem. Res. 28 (1989) 894–899.

[15] S. Imamura, A. Dol, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 75–80.

[16] G. Deiber, J.N. Foussard, H. Debellefontaine, Environ. Pollut. 96 (3) (1997) 311–319.

[17] T.Y. Yan, P.A. Wayne, US Patent 5,552,063 (1996).

[18] J.Y. Qin, K. Aika, Appl. Catal. B: Environ. 16 (1998) 261–268.

[19] R. Ukropec, B.F.M. Kuster, J.C. Schouten, R.A. Santen, Appl. Catal. B: Environ. 23 (1999) 45–57.

[20] J. Taguchi, T. Okuhara, Appl. Catal. A: Gen. 194 (2000) 89–97.

[21] X.S. Zhao, G.Q. Lu, X. Hu, Micropor. Mesopor. Mater. 41 (2000) 37–47.

[22] Q. Wu, X. Hu, P.L. Yue, X.S. Zhao, G.Q. Lu, Appl. Catal. B: Environ. 32 (2001) 151–156.

[23] T.M. Smolen, D.B. Manley, B.E. Poling, J. Chem. Eng. Data 36 (1991) 202–208.

[24] R.M. Enick, G.P. Donahey, M. Holsinger, Ind. Eng. Chem. Res. 37 (1998) 1644–1650.

[25] N. Okada, Y. Nakanishi, Y. Halada, US Patent 4,141,828 (1977).

[26] L. Li, P. Chen, E.F. Gloyna, AIChE J. 37 (11) (1991) 1687–1697.

[27] H. Takayama, J.Y. Qin, K. Inazu, K. Aika, Chem. Lett. 5 (1999) 377–378.

[28] G. Tchobanoglous, E.D. Schroeder, Water Quality: Characteristics, Modeling, Modification, Addison-Wesley, Reading, MA, 1985, pp. 163–165.

[29] M.J. Hammer, Water and Wastewater Technology, Wiley, New York, 1986, pp. 330–343.

[30] T.H. Christensen, R. Cossu, R. Stegmann, Landfilling of Waste: Leachate, Elsevier, London/New York, 1992, pp. 65–88.