[Regular Paper]

Catalytic Wet Oxidation of Phenol Using Regeneration of Pt/Al₂O₃

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(Received October 14, 2009)

Removal of phenol by wet air oxidation was conducted with 1 wt% Pt/Al₂O₃ catalyst in a batch reactor and in a continuous flow fluidized bed reactor with air lift tube operated at 423 K and 1.4 MPa. After 60 min in the batch reactor with initial phenol concentration of 1000 mg/l, almost complete conversion into CO₂ and H₂O was achieved. Pt/Al₂O₃ catalyst deactivation was observed during the wet oxidation reaction. TEM, EDX, XPS and TPO analyses showed the deactivation was caused by formation and deposition of carbonaceous materials on the catalyst surface. TEM of the deactivated Pt/Al₂O₃ showed formation of filamentous materials, which linked Pt particles, and some Pt particles were completely encapsulated by deposited material. XPS analysis showed that the carbonaceous materials on the catalyst consisted of four different morphologies (C₁, C₂, C₃, C₄). As the wet oxidation proceeded, the C₁ peak increased gradually with reaction time, whereas the C₂ and C₃ peaks passed through maxima. At around the C₂ and C₃ peak maxima, the C₄ peak began to appear and increased continuously up to 10 h reaction. This result indicates that at least two carbonaceous materials of C₂ and C₃ were transformed morphologically into C₄ material. The broad profiles of CO₂ formation from the TPO experiment implied that at least two types of carbon deposits were oxidized at different temperatures, one type on Pt particles, the other type on Al₂O₃. The carbonaceous deposit was formed on Pt particles and migrated continuously onto the support. The continuous flow fluidized bed reactor showed very stable wet oxidation performances in the presence of the air lift tube. The air lift tube was important in continuously regenerating the deactivated catalyst. The accumulated carbon deposits were reduced drastically by the action of the air lift tube.

Keywords

Carbonaceous material, Wet oxidation, Phenol, Platinum catalyst, Catalyst regeneration

1. Introduction

Many wastewater streams in the chemical process industry contain high concentrations of organic materials which are difficult to oxidize biologically. Phenol is one of the most common and important of such pollutants and is extremely toxic to the environment even at very low concentrations.

Wet air oxidation (WAO) is a very attractive and useful process for the treatment of effluents containing concentrations of organic pollutants that are too low for incineration and resistant to biological treatments, especially toxic effluents^{1)~3)}. WAO has been applied to removing total organic carbon (TOC) consisting of insoluble polymers⁴⁾, wastewaters^{5)~8)}, and certain organic compounds^{9),10)}. The efficient removal of pollutants *via*

the WAO process requires very high temperature and pressure, typically in the range of 473–573 K and 7–15 MPa, respectively¹¹⁾. However, such severe reaction conditions can lead to high installation costs, and practical applications of this process are limited. Therefore, catalytic wet air oxidation (CWAO) has been investigated to reduce the severity of the oxidation conditions. The use of catalysts improves the process by achieving high conversion at considerably lower temperature and pressure^{2),12),13)}.

Many studies have investigated heterogeneously catalyzed WAO, but catalyst deactivation during WAO is mainly unknown. The present study investigated the CWAO of phenol in batch and continuous flow fluidized bed reactors at 423 K and 1.4 MPa with Pt/Al₂O₃ catalyst. Formation/migration of carbonaceous deposits on the catalyst surface was investigated, and a new method to regenerate the deactivated catalysts was tested in the fluidized bed reactor.

This paper was presented at the 12th Japan-Korea Symposium on Catalysis, Akita, Japan, Oct. 14–16, 2009.

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Fig. 1 Continuous Flow Fluidized Bed Reactor

2. Experimental

Platinum (II) acetylacetonate (Aldrich Co.) was used as the precursor of the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. $\gamma\text{-Al}_2\text{O}_3$ (Strem Chemicals, Inc.) was used as the support for the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. All other chemicals were analytical reagent grade.

1 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ was prepared by the incipient wetness method. The platinum particles were located mainly at the exterior surface of the supports by pretreatment of the pores of $\gamma\text{-Al}_2\text{O}_3$ with *n*-hexane. The required amount of platinum (II) acetylacetonate solution was added to the supports dropwise. The prepared samples were then dried *in vacuo* at 323 K. These preparation steps were repeated ten times to obtain 1 wt% Pt loading. The prepared powder sample was then pressed into near-spherical particles with mean diameter of 80 μm and mean apparent density of 1.03 g/cm^3 . The samples were then calcined at 673 K for 4 h in a programmable furnace. The linear rate of heating up to 673 K was 0.5°C/min. The calcined samples were reduced under H_2 flow at 573 K for 4 h and finally passivated at 298 K under 0.96% O_2/He gas mixture.

Oxidation of phenol solution was performed in a batch reactor and in a continuous flow fluidized bed reactor. An 11 SS316 autoclave (Parr Instrument Co.) equipped with a teflon liner and a gas entrainment impeller with a variable-speed arrangement was used as the batch reactor. The continuous flow tubular fluidized bed reactor had 75 cm inside diameter and 2.25 m effective height as shown in **Fig. 1**. Generally 800 g of catalyst was used for the reaction. Phenol solution was fed into the reactor through a high pressure metering pump (Bran + Lube) at the bottom of the reactor. Air was introduced into the reactor with a compressor. The pressure inside the reactor was maintained at 1.4 MPa with a back pressure regulator installed at the

exit stream. A specially designed air lift tube (1 mm inside diameter) was placed at the center of the reactor. Catalyst particles deactivated by accumulation of carbonaceous materials fell down to the bottom of the reactor. The upflowing air inside the air lift tube carried the deactivated catalyst particles up into the water-free space at the top of the reactor where the carbonaceous materials were oxidized with air. The regenerated catalyst particles were then returned to the fluidized bed. The volume of the water-free space was about 0.18 m^3 .

The dispersion of both platinum particles and carbonaceous materials in the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst were observed by transmission electron microscopy (JEOL 200CX) at 160 keV. X-ray photoelectron spectroscopy (XPS) spectra of carbonaceous deposits were recorded by a VG ESCALAB 220 iXL spectrometer with a $\text{MgK}\alpha$ -source operating at 20 mA and 13 kV at room temperature.

The carbonaceous materials deposited on the catalyst during the wet oxidation reaction were analyzed by the temperature-programmed oxidation (TPO) method using a mass spectrometer (HP 5970). In a typical TPO experiment, 0.2 g of the used catalyst was loaded in a quartz microreactor which was then installed in a furnace coupled to a temperature programmer. The catalyst was first exposed to helium flow (100 ml/min) and the temperature was raised at 10 K/min to 393 K and kept at this temperature for 1 h before cooling to room temperature. Subsequently the catalyst was heated under a gas flow of 0.96% oxygen in helium at 10 K/min to 973 K. Analysis of the microreactor outlet gas was performed by mass spectrometry.

Reaction intermediates and phenol residue were identified and quantified with high performance liquid chromatography (HPLC) (Nihon Waters K.K.) using a Nova-Pak C18 column, and equipped with a tunable absorbance detector and MS spectrometer (HP 5970). Elution was performed at 1 ml/min flow rate of the mobile phase ($\text{MeOH} : \text{H}_2\text{O} : \text{H}_3\text{PO}_4 = 40 : 60 : 0.5 \text{ vol}\%$).

Total organic carbon (TOC) was measured with a Shimadzu 5000A TOC analyzer based on combustion/non-dispersive infrared (NDIR) gas analysis.

3. Results and Discussion

3.1. Wet Oxidation of Phenol with $\text{Pt}/\text{Al}_2\text{O}_3$

To assess the extent of the uncatalyzed thermal oxidation of phenol and the effect of the support, WAO tests were performed without catalyst and with metal-free support using the initial phenol concentration of 1000 mg/l. Uncatalyzed thermal oxidation did occur up to 5% in 3 h, and the use of metal-free Al_2O_3 support resulted in somewhat lower oxidation efficiency than uncatalyzed oxidation (**Fig. 2**). Elevated temperature can lead to the formation of oxygen radicals ($\text{O}\cdot$), which can react with water to form hydroxyl radicals

Fig. 2 Catalytic Wet Oxidation of Phenol at 423 K and 1.4 MPa (▲: uncatyzed reaction, ▼: reaction with metal-free Al_2O_3 , ●: reaction with 3 g 1 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst)

Fig. 3 Change in TOC Concentration during CWAO of Phenol at 423 K and 1.4 MPa (▲: uncatyzed reaction, ▼: reaction with metal-free Al_2O_3 , ●: reaction with 3 g 1 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst)

($\text{HO}\cdot$) that may have oxidized phenol. However, the metal-free Al_2O_3 support acts to scavenge some of the hydroxyl radical formed. In contrast, use of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst enhanced the oxidation appreciably, and almost complete conversion of phenol could be obtained in 60 min. Analysis of the results of TOC showed that more than 95% of the initial phenol was removed after 60 min reaction with $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst (Fig. 3), and most phenol in Fig. 2 was completely oxidized into CO_2 and water.

The effect of initial phenol concentration was investigated in the range 500–10,000 mg/l in the presence of 3.0 g $\text{Pt}/\text{Al}_2\text{O}_3$. The results in Fig. 4, showing the changes in phenol dimensionless concentration as a function of reaction time, indicate that higher initial phenol concentration resulted in lower conversion. Complete phenol conversion was obtained within 60 min with an initial phenol concentration of 1000 mg/l

Fig. 4 Effect of Initial Phenol Concentration on Wet Oxidation of Phenol at 423 K and 1.4 MPa with 3 g $\text{Pt}/\text{Al}_2\text{O}_3$ Catalyst

Fig. 5 Time Dependence of Relative Phenol and TOC Concentrations during CWAO of Phenol at 423 K and 1.4 MPa with 2 g Fresh $\text{Pt}/\text{Al}_2\text{O}_3$ Catalyst (●) and 2 g Used $\text{Pt}/\text{Al}_2\text{O}_3$ Catalyst (▲)

or less, whereas only 50% conversion was achieved with the highest initial phenol concentration of 10,000 mg/l. In addition, the conversion of phenol did not proceed and remained almost constant after 60 min reaction. This implies that catalyst deactivation might have occurred during the reaction which was highly dependent on the initial phenol concentration.

After CWAO of phenol was completed in 3 h, the used catalyst sample was filtered and washed with distilled deionized water. The sample was then dried at 353 K for 24 h, and the CWAO of phenol was repeated with initial phenol concentration of 1000 mg/l in the presence of the dried catalyst. As can be seen in Fig. 5, the efficiency of phenol removal and TOC removal could not successfully be restored. This deactivation of used catalyst might be due to either leaching of the active component (Pt) of the catalyst during the reaction and/or accumulation of carbonaceous materials

Fig. 6 TEM Micrographs of the Fresh 1 wt% Pt/Al₂O₃ (left) and 1 wt% Pt/Al₂O₃ (right) Catalysts after 3 h Reaction with Initial Phenol Concentration of 5000 mg/l

Fig. 7 Detailed TEM Micrographs of the Pt/Al₂O₃ Catalysts after 3 h Reaction with Initial Phenol Concentration of 5000 mg/l

deposited on the catalyst.

To investigate the stability of the Pt/Al₂O₃ catalyst with respect to metal leaching, catalyst samples were taken after the reaction at various temperatures. The concentrations of the dissolved Pt and Al metals were analyzed using inductively coupled plasma (ICP), but no detectable amount of dissolved Pt and Al metals could be measured. Accordingly, no leaching occurred under the reaction conditions employed.

3. 2. Analysis of the Deactivated Catalysts

Figure 6 shows transmission electron microscope (TEM) images of fresh and used Pt/Al₂O₃ catalysts after wet oxidation of phenol for 3 h with initial concentration 5000 mg/l. The fresh Pt/Al₂O₃ catalyst is clean and free of any deposited materials, whereas the used Pt/Al₂O₃ catalyst incorporates huge amounts of deposited material, especially on the surface. Detailed observation of the deactivated Pt/Al₂O₃ catalyst clearly shows the formation of filamentous materials linking the Pt particles (Fig. 7A). In addition, some of the Pt particles are completely encapsulated by deposited material (Fig. 7B).

Energy dispersive X-ray fluorescence spectrometer (EDX) analysis of the used catalysts demonstrated that the dominant component of the deposited material was carbon. XPS spectra of the used catalysts after reaction with different initial phenol concentrations and reaction times indicated the emergence of a strong C1s peak, confirming the presence of carbonaceous deposits on the catalyst surface. Figure 8 shows representative XPS C1s spectra of the Pt/Al₂O₃ catalyst after reaction

Fig. 8 XPS C1s Spectra of Pt/Al₂O₃ after Reaction for 1 h (A) and 4 h (B) with Initial Phenol Concentration of 1000 mg/l

Fig. 9 Changes in the XPS Peak Intensities with Reaction Time for Pt/Al₂O₃ Catalyst

for 1 h (A) and 4 h (B) with initial phenol concentration of 1000 mg/l. The maximum intensity of the C1s peak appears at binding energy of 286.3 eV. The peak intensity of C1s in Pt/Al₂O₃ catalysts increased with higher initial phenol concentration, but the shape and binding energy of the peak were almost unchanged. Deconvolution of the XPS spectrum obtained after 1 h reaction (A) showed that the C1s peak consisted of C1 (286.4 eV), C2 (288.2 eV) and C3 (292.9 eV) peaks. A new peak of C4 appeared at the binding energy 289.3 eV after reaction for another 3 h (B).

Figure 9 plots the changes in the intensities of four representative peaks of C1s spectra with reaction time. The C1 peak gradually increased with reaction time, whereas the C2 and C3 peaks passed through maxima. The C4 peak began to appear at around the time of the C2 and C3 maxima, and increased continuously up to 10 h reaction time. This result indicates that at least two carbonaceous materials, C2 and C3, transformed morphologically into C4.

Carbonaceous deposits on the catalysts were analyzed with TPO. Burn-off profiles of carbonaceous deposits on the catalysts after reaction for 3 h with ini-

Fig. 10 Profiles of O₂ Consumption and CO₂ Formation during TPO Experiments with Pt/Al₂O₃ (left) and Pt Powder (right) after Reaction for 3 h with Initial Phenol Concentration of 5000 mg/l

tial phenol concentration of 5000 mg/l are shown in **Fig. 10**. Formation of CO₂ over a broad temperature ranges from 250 to 700°C over Pt/Al₂O₃ catalyst in accordance with the consumption of oxygen. The carbonaceous deposit on Pt powder was burned off over narrow temperature range around 250°C and was completely removed below 300°C. Therefore, carbonaceous materials must have been deposited on the catalyst during the wet oxidation of phenol, and concurrent catalyst deactivation was caused by the deposition of carbonaceous materials.

Assuming that the carbonaceous deposits on Pt/Al₂O₃ and Al₂O₃ support have the same chemical composition and configuration, carbonaceous deposits on both catalysts are expected to be oxidized at the same narrow temperature range during the TPO experiment. However, the carbonaceous deposits on Pt/Al₂O₃ were less reactive toward oxygen (or more difficult to oxidize) than those on Al₂O₃ support. Carbon deposits on alumina support are reported to be oxidized at temperatures higher than 440°C¹⁴⁾. The presence of Pt metal could catalyze the oxidation of carbon deposits, and Pt-catalyzed oxidation of carbon is known to occur generally at temperatures around 280°C^{15),16)}.

The broad profile of CO₂ formation over Pt/Al₂O₃ implies at least two types of carbon deposits oxidizing at different temperatures. One type of deposit on the surface of Pt particles is oxidized at around 250°C, whereas the other type on Al₂O₃ will oxidize at much higher temperatures. The presence of filamentous carbons linking Pt particles on Al₂O₃ was confirmed by TEM as shown in **Figs. 6** and **7**.

3.3. Migration of Carbonaceous Deposits

Since the conversion of phenol on Pt-free Al₂O₃ support was almost negligible as shown in **Fig. 2**, both wet oxidation of phenol and initial formation of carbonaceous deposits occur predominantly on the surface of Pt particles. These carbon deposits will then migrate onto the surface of Al₂O₃ in the vicinity of the Pt parti-

Fig. 11 Effect of Initial Phenol Concentration on CO₂ Formation Profiles of Pt/Al₂O₃

cles. To investigate the migration of carbonaceous deposits, TPO experiments used oxidation of phenol for 3 h over Pt/Al₂O₃ with initial phenol concentrations of 10, 50, 100, 500 and 1000 mg/l. The profiles of CO₂ formation for Pt/Al₂O₃ are shown in **Fig. 11**. At initial phenol concentration of 50 mg/l or less, most CO₂ was produced at temperatures below 300°C. These CO₂ peaks are nearly the same as the CO₂ peak from Pt powder (**Fig. 10**), indicating that carbonaceous deposits are primarily formed on the surface of Pt particles. At initial phenol concentration of 100 mg/l, new higher temperature peaks occurred which increased with higher initial phenol concentration. The changes in the profiles of CO₂ formation with initial phenol concentration indicate that the carbonaceous deposits formed on Pt particles migrated onto the surface of Al₂O₃. Furthermore, careful examination of the TEM micrographs of Pt/Al₂O₃ (**Figs. 6** and **7**) indicates that the carbonaceous materials on the supports acted as bridges connecting the Pt particles.

Fig. 12 Phenol Conversions in the Continuous Flow Fluidized Bed Reactor without Air Lift Tube at Different Phenol Solution Flow Rates

Fig. 13 Phenol Conversions in the Continuous Flow Reactor with Air Lift Tube at Different Phenol Solution Flow Rates

3. 4. Continuous Flow Wet Oxidation

Figure 12 shows the performances of the fluidized bed reactor without the air lift tube. More than 97% phenol can be removed up to 10 h continuous operation under flow rate of 3.5 l/min. However, conversion then decreased continuously due to catalyst deactivation by carbon deposits. Similar results were obtained at higher flow rates of 7.0 l/min and 10.5 l/min. In the presence of the air lift tube (Fig. 13), the conversions decreased slightly, which indicates that the air lift tube is important in the oxidation of the carbon deposits, so regenerating the catalysts.

The TPO results in Fig. 14 demonstrate that the air tube must operate somewhat successfully to regenerate the deactivated catalysts. In the absence of the air lift tube, two main CO₂ peaks were produced at around 170°C and 300°C at the flow rate of 3.5 l/min. With increasing flow rate, the low temperature peak intensity decreased due to lower phenol conversion at higher flow rates. In the reaction with just Al₂O₃, one representative CO₂ peak appeared at 140°C. In the presence of the air lift tube, CO₂ production decreased drastically. In the case of only Al₂O₃, no detectable

Fig. 14 TPO Profiles of the Pt-free Al₂O₃ and 1 wt% Pt/Al₂O₃ Catalysts after Use in the Continuous Flow Fluidized Bed Reactor

amounts of CO₂ were observed.

4. Conclusions

Catalytic wet oxidation of phenol was carried out with 1 wt% Pt/Al₂O₃ in a batch reactor and in a continuous flow fluidized bed reactor with air lift tube operated at 423 K and 1.4 MPa.

Catalyst deactivation was observed especially on Pt/Al₂O₃ during the wet oxidation reaction. TEM, EDX, XPS and TPO analyses suggested the deactivation was caused by the formation and deposition of carbonaceous materials on the catalyst surface. The profiles of CO₂ formation in TPO experiments on Pt/Al₂O₃ and Al₂O₃ free Pt metal were different.

Carbonaceous deposits were located on the surface of Pt particles as well as supports. The deposits on Pt particles rather than the deposits on the support were much more reactive to oxygen. The different reactivities of these deposits to oxygen resulted in the appearance of broad CO₂ formation profiles in the temperature range 250–700°C for Pt/Al₂O₃.

Sequential CO₂ formation profiles showed that the carbonaceous deposits were primarily formed on the surface of the Pt particles and then migrated continuously onto the surface of Al₂O₃ in the vicinity of the Pt particles.

The continuous flow fluidized bed reactor showed very stable wet oxidation performances in the presence of the air lift tube. The accumulated carbon deposits were reduced drastically due to the action of the air lift tube.

Acknowledgments

This work was supported by a grant from the KOSEF/MOST to the Environmental Biotechnology National Core Research Center (grant #: R15-2003-012-02002-0).

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要 旨

再生可能な Pt/Al₂O₃ 触媒を用いるフェノールの湿式酸化反応

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1 wt% Pt/Al₂O₃ 触媒を用い湿式酸化によるフェノール除去を行った。バッチ式反応器による処理では初期濃度 1000 mg/l のフェノールを 60 分でほとんど全て二酸化炭素と水に酸化することができたが、Pt/Al₂O₃ 触媒の劣化が起こった。種々のキャラクタリゼーションにより、活性の劣化は触媒表面への炭素質の堆積が原因であることを示した。TEM 観察では、劣化した Pt/Al₂O₃ 触媒にはフィラメント状の堆積物が白金粒子と結合している像や、白金粒子が堆積物に完全に埋まっている像が示された。XPS 分析では炭素質堆積物として、湿式酸化の進行に伴い増大するもの (C₁)、極大をもつもの (C₂, C₃)、そして C₂

と C₃ が極大値を示す時から観測されその後増加するもの (C₄) などの 4 種類が存在すること、また反応中に C₂ と C₃ の炭素質堆積物が C₄ へと構造変化することが示された。TEM, EDX, XPS および TPO 分析から、炭素質堆積は白金上に存在するものとアルミナ上の二種類存在し、白金粒子上の炭素質堆積物は担体上に移動することが示された。423 K, 1.4 MPa で駆動するエアリフト管を備えた連続流動床反応器による湿式酸化反応実験から、空気処理により Pt/Al₂O₃ 触媒上の炭素質堆積物が除かれ、活性が安定することが示された。