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Deactivation of Pt catalysts during wet oxidation of phenol

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ABSTRACT

Removal of phenol by wet air oxidation was conducted with 1 wt.% Pt/Al_2O_3 and 1 wt.% Pt/CeO_2 catalysts. During the reaction carbonaceous materials were formed and deposited on the catalyst surface, and the materials deactivated the catalysts. XPS analysis showed that the carbonaceous materials on the Pt/Al_2O_3 catalyst were composed of four different morphologies. As the wet oxidation proceeded, C_2 type and C_3 type carbonaceous materials transformed into C_4 material. In the Pt/CeO_2 catalysts, however, C_4 material was not formed through the reaction. The broad profiles of CO_2 formation from TPO experiment implied that there were at least two types of carbon deposits burning at different temperatures; one on Pt particles, the other Al_2O_3 and CeO_2. The primarily formed carbonaceous deposit on Pt particles migrated continuously onto the supports.

1. Introduction

Many wastewater streams originating in chemical process industries contain high concentrations of organic materials which are difficult to be oxidized biologically. Phenol is one of the most common and important pollutants because it is extremely toxic to the environment even at very low concentrations.

Wet air oxidation (WAO) process is a very attractive and useful technique for the treatment of effluents where the concentrations of organic pollutants are too low for incineration process and when biological treatments are ineffective, e.g., in the case of toxic effluents [1–3]. WAO was applied to remove total organic carbon (TOC) such as insoluble polymers [4], wastewaters [5–8], and certain organic compounds [9,10]. The efficient removal of pollutants *via* WAO process requires very high temperature and pressure, typically in the range of 473–573 K and 7–15 MPa, respectively [11]. However, the severe reaction conditions can lead to high installation costs, and practical applications of this process are limited. Therefore, development of catalytic wet air oxidation (CWAO) using various catalysts has been attempted in order to reduce the severity of the oxidation conditions. The use of catalysts makes the process more attractive by achieving high conversion at considerably lower temperature and pressure [2,12,13].

Although many investigations dealing with heterogeneously catalyzed WAO have been reported, study of catalyst deactivation during WAO has been mostly unexplored. In the present work CWAO of phenol was carried at 423 K and 1.4 MPa with Pt/Al_2O_3 and Pt/CeO_2 catalysts, and formation/migration of carbonaceous deposits on the catalyst surface were investigated.

2. Experimental

High purity phenol-d_6 (C_6D_5OD), supplied from Aldrich Co., was used without further purification. Platinum (II) acetylacetonate (Aldrich Co.) was used as the precursor of Pt/Al_2O_3 and Pt/CeO_2 catalysts. γ-Al_2O_3 (Strem Chemicals) and CeO_2 (Aldrich Co.) were used as the support of Pt/Al_2O_3 and Pt/CeO_2 catalysts, respectively. All other chemicals used were of analytical reagent grade.

1 wt.% Pt/Al_2O_3 and 1 wt.% Pt/CeO_2 catalysts were prepared by incipient wetness method. In order to locate platinum particles mainly at the exterior surface of the supports, the pores of γ-Al_2O_3 and CeO_2 had been *a priori* saturated with n-hexane. A certain amount of platinum (II) acetylacetonate solution was added to the supports drop by drop. The prepared samples were then dried *in vacuo* at 323 K. The above preparation steps were repeated 10 times to have 1 wt.% Pt loading. The samples were then calcined at 673 K for 4 h in a programmable furnace. The liner rate of heating up to 673 K was kept to be 0.5 °C/min. The calcined samples were reduced with flowing H_2 at 573 K for 4 h and were finally passivated at 298 K with flowing 0.96% O_2/He gas mixture.

The surface area and pore volume of Pt/Al_2O_3 catalyst were 190 m^3/g and 0.23 cm^3/g, respectively. Pt/CeO_2 catalyst had, however, much lower surface area (45 m^2/g) and pore volume (0.09 cm^3/g).

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The oxidation of phenol solution was performed in a 1 L SS316 autoclave (Parr Instrument Co.) equipped with a Teflon liner and a gas entrainment impeller having a variable-speed arrangement.

Not only the dispersion of platinum particles but also the carbonaceous materials in the Pt/Al_2O_3 and Pt/CeO_2 catalysts were observed with a transmission electron microscopy (JEOL 200CX) using 160 keV electrons. XPS spectra of carbonaceous deposits were recorded by a VG ESCALAB 220 iXL spectrometer with a Mg Kα-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 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 flowing helium (100 mL/min) and the temperature was raised at a rate of 10 K/min to 393 K and kept at this temperature for 1 h before being cooled to room temperature. Subsequently the catalyst was heated under a flowing gas mixture of 0.96% oxygen in helium at a rate of 10 K/min to 973 K. Analysis of the microreactor outlet gas was performed by mass spectrometry.

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

3. Results and discussion

3.1. Wet oxidation of phenol with Pt/Al_2O_3 and Pt/CeO_2

TEM micrographs of the 1 wt.% Pt/Al_2O_3 and 1 wt.% Pt/CeO_2 catalysts are shown in Fig. 1. Platinum particles were finely dispersed on the surface of Al_2O_3 and CeO_2 support, and the average Pt particle size was estimated to be 20 Å. To assess the extent of the uncatalyzed thermal oxidation of phenol and the effect of support, WAO tests were performed without catalyst and with metal-free support with phenol initial concentration 1000 mg/L. As can be seen in Fig. 2, the 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. The elevated temperature can lead to the formation of oxygen radical ($O^\bullet$), which in turn can read with water to form hydroxyl radical ($HO^\bullet$). This radical might have oxidized phenol. Metal-free Al_2O_3 support, however, scavenged some of the hydroxyl radical formed. The use of Pt/Al_2O_3 catalyst enhanced the oxidation appreciably. Almost complete conversion of phenol could be obtained in 60 min.

When analyzing the results of TOC that more than 95% of the initial TOC was removed in 60 min reaction with Pt/Al_2O_3 catalyst (Fig. 3), most phenol in Fig. 2 is believed to be completely mineralized into CO_2 and water.

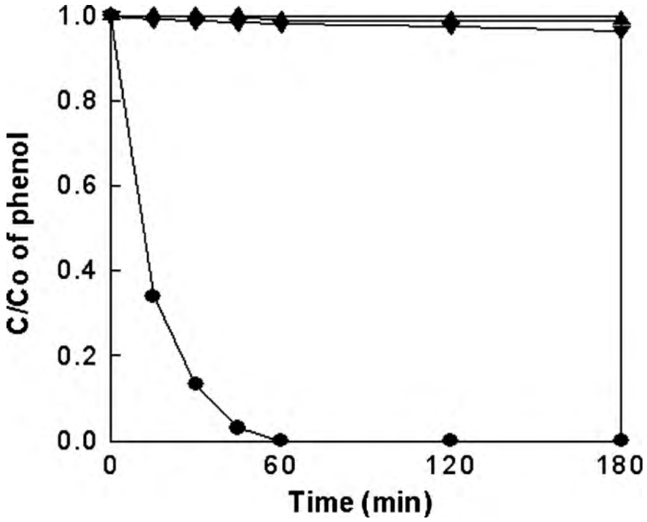

Fig. 2. Catalytic wet oxidation of phenol at 423 K and 1.4 MPa (▲: uncatalyzed reaction, ▼: reaction with metal-free Al_2O_3, ●: reaction with 3 g 1 wt.% Pt/Al_2O_3 catalyst).

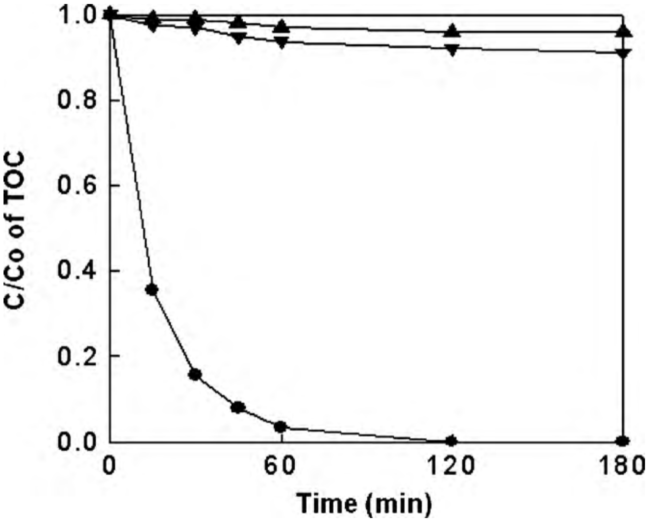

Fig. 3. Change in TOC concentration during CWAO of phenol at 423 K and 1.4 MPa (▲: uncatalyzed reaction, ▼: reaction with metal-free Al_2O_3, ●: reaction with 3 g 1 wt.% Pt/Al_2O_3 catalyst).

The effect of initial phenol concentration was investigated in the range 500–10,000 mg/L in the presence of 3.0 g Pt/Al_2O_3. The results in Fig. 4, showing the changes in phenol dimensionless concentration as a function of reaction time, indicate that the higher

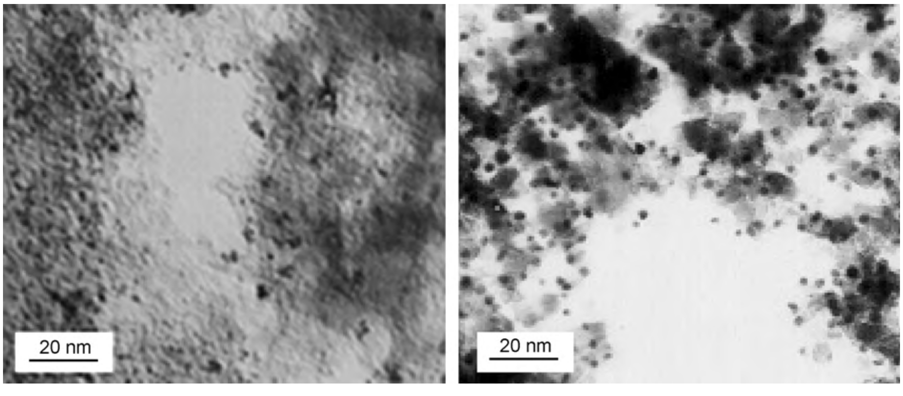

Fig. 1. TEM micrographs of the fresh 1 wt.% Pt/Al_2O_3 (left) and 1 wt.% Pt/CeO_2 (right).

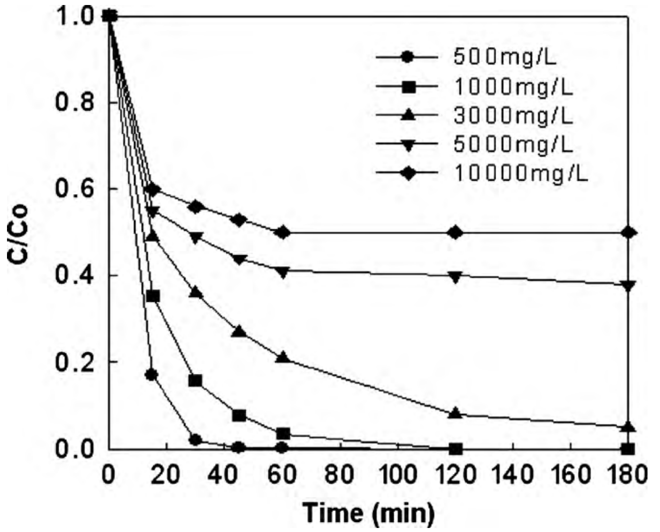

Fig. 4. Effect of phenol initial concentration on wet oxidation of phenol at 423 K and 1.4 MPa with 3 g Pt/Al_2O_3 catalyst.

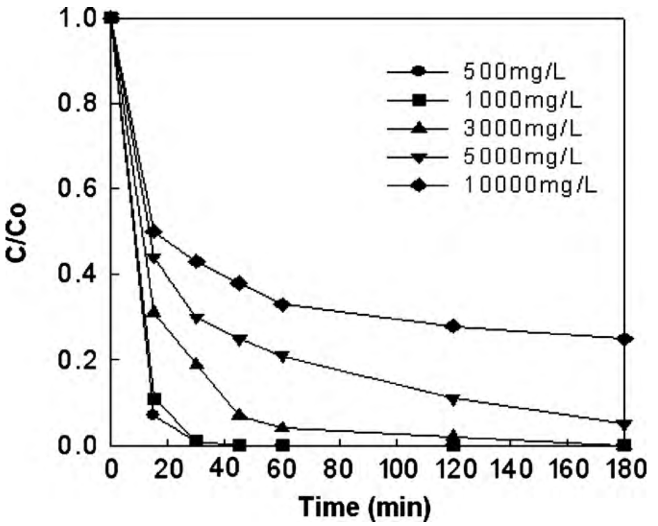

Fig. 6. Effect of phenol initial concentration on wet oxidation of phenol at 423 K and 1.4 MPa with 3 g Pt/CeO_2 catalyst.

the phenol initial concentration, the lower the conversion. While complete phenol conversion was obtained within 60 min operation with an initial phenol concentration of 1000 mg/L or less, only 50% conversion was achieved with the highest phenol initial concentration (10,000 mg/L). In addition after 60 min reaction the conversion of phenol did not proceed and remained almost constant. This implies that during the reaction there might have occurred catalyst deactivation whose extent is highly dependent on the phenol initial concentration.

When the 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 phenol initial concentration 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 the used catalyst might be due to either the leaching of the active component (Pt) of the catalyst during the reaction and/or accumulation of carbonaceous materials deposited on the catalyst.

To investigate the stability of the Pt/Al_2O_3 catalyst with respect to metal leaching, catalyst samples were taken after the reaction at various temperatures. The concentrations of dissolved Pt and Al metals were analyzed using ICP, but no detectable amount of dissolved Pt and Al metals could be measured. Accordingly at the reaction conditions employed in this research no leaching can be said to occur.

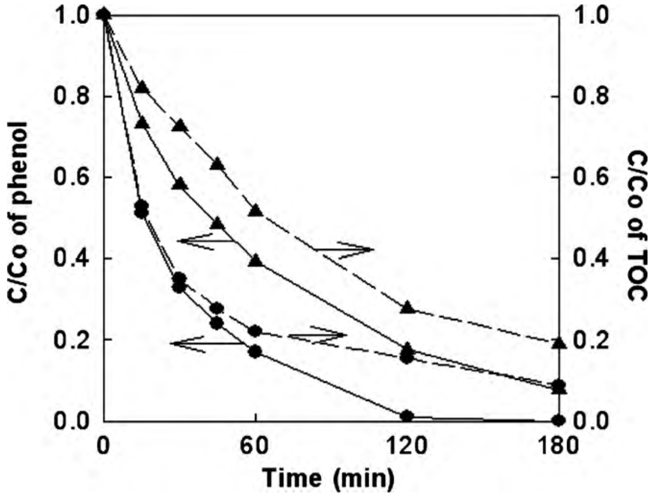

Fig. 5. Time dependence of relative phenol and TOC concentrations during CWAO of phenol at 423 K and 1.4 MPa with 2 g fresh Pt/Al_2O_3 catalyst (●) and 2 g used Pt/Al_2O_3 catalyst (▲).

In the case of reaction with Pt/CeO_2 catalyst (Fig. 6), however, the dependence of conversion on phenol initial concentration appears in somewhat different patterns. When compared with the results from Pt/Al_2O_3, much higher conversions were obtained with Pt/CeO_2 at the corresponding phenol initial concentrations. While the oxidation reaction stopped after 1 h operation with initial phenol concentrations of 5000 mg/L and 10,000 mg/L in the presence of Pt/Al_2O_3 catalyst (Fig. 4), the oxidation reaction continues to proceed up to 3 h operation on Pt/CeO_2 catalyst with initial phenol concentrations of 5000 mg/L and 10,000 mg/L. Therefore catalyst deactivation of Pt/CeO_2, if any, seems to be not so strong as that of Pt/Al_2O_3 during the wet oxidation of phenol.

3.2. Analysis of the deactivated catalysts

Fig. 7 shows TEM images of the Pt/Al_2O_3 and Pt/CeO_2 catalysts which underwent wet oxidation of phenol for 3 h with phenol initial concentration 5000 mg/L. While the fresh Pt/Al_2O_3 and Pt/CeO_2 catalysts were kept clean and free of any deposited materials as previously shown in Fig. 1, huge amount of a certain material was deposited especially on the surface of the used Pt/Al_2O_3 catalyst. In the case of the used Pt/CeO_2 catalyst, however, accumulation of the deposited material is not so outstanding and the deposited material acts as a bridge linking each Pt particles. When looking the deactivated Pt/Al_2O_3 catalyst over in more detail (Fig. 8), the formation of filamentous materials, which link Pt particles, can be clearly seen (Fig. 8A). In addition some of Pt particles are completely encapsulated by deposited material (Fig. 8B). In the deactivated Pt/CeO_2 catalyst, however, both the formation of filamentous material and the Pt encapsulation were not so outstanding as those of the Pt/Al_2O_3 catalyst.

EDX analysis of the used catalysts had demonstrated that the dominant component of the deposited material was carbon. In addition XPS spectra of the used catalysts after reaction with different phenol initial concentrations and reaction times indicated the emergence of a strong C1s peak, confirming the presence of carbonaceous deposits on the catalyst surface. Fig. 9 shows the representative XPS C1s spectra of the Pt/Al_2O_3 catalyst after reaction

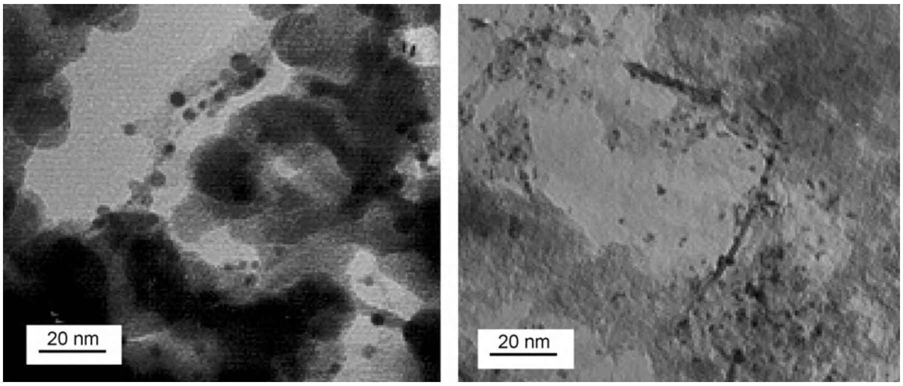

Fig. 7. TEM micrographs of the Pt/Al_2O_3 (left) and Pt/CeO_2 (right) catalysts after 3 h reaction with phenol initial concentration 5000 mg/L.

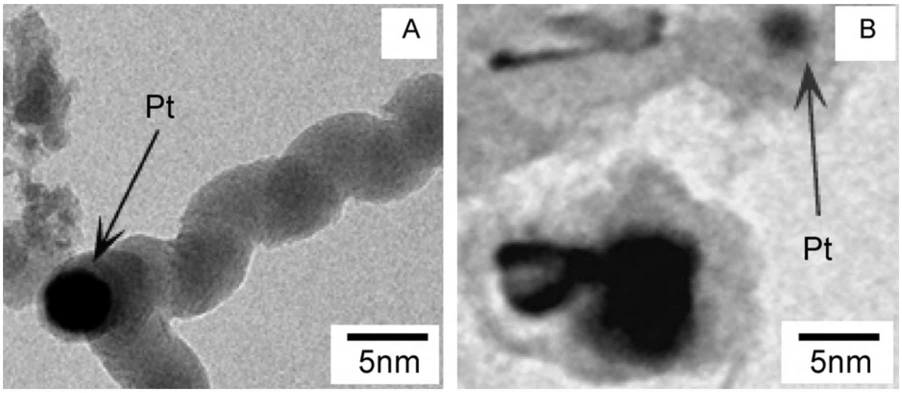

Fig. 8. Detailed TEM micrographs of the Pt/Al_2O_3 catalysts after 3 h reaction with phenol initial concentration 5000 mg/L.

for 1 h (A) and 4 h (B) with phenol initial concentration 1000 mg/L. The maximum intensity of C1s peak appears at binding energy of 286.3 eV. Although the peak intensity of C1s in Pt/Al_2O_3 catalysts increased with increasing phenol initial concentration, both the shape and the binding energy of the peak were almost unchanged. When deconvoluting the XPS spectrum obtained after 1 h reaction (A), C1s peak is known to be composed of three C_1 (286.4 eV), C_2 (288.2 eV) and C_3 (292.9 eV) peaks. As the reaction was proceeded for another 3 h (B), new peak of C_4 appears at the binding energy 289.3 eV. The different binding energies observed for the 4 types of carbon deposits should correspond to 4 different chemical environments.

In Fig. 10 are plotted the changes in the intensities of four representative peaks of C1s spectra with reaction time. C_1 peak increases with reaction time gradually, while peaks of C_2 and C_3 go through maxima. At around the maximum concentrations of C_2 and C_3 peak, C_4 peak begins to appear and increases continuously up to 10 h reaction. This result indicates that at least two carbona-

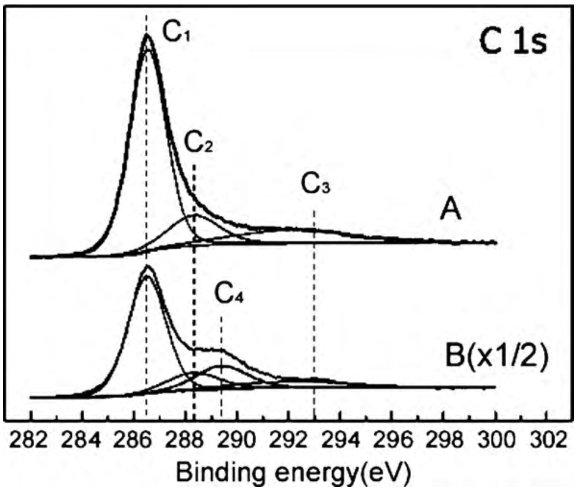

Fig. 9. XPS Cls spectra of Pt/Al_2O_3 after reaction for 1 h (A) and 4 h (B) with phenol initial concentration 1000 mg/L.

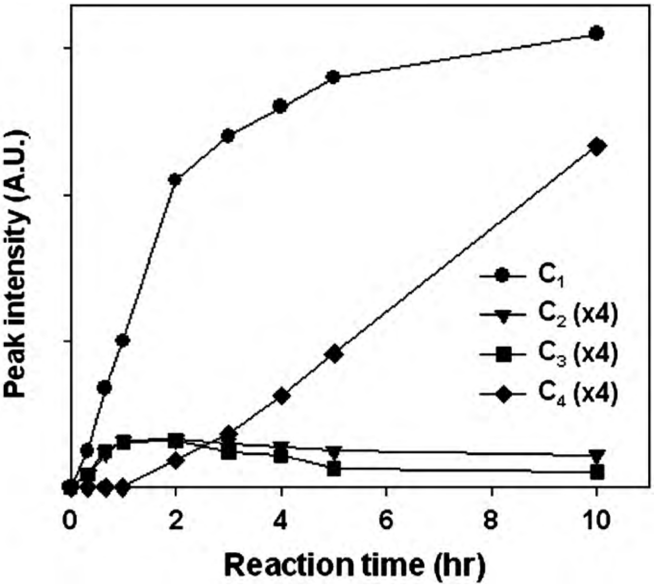

Fig. 10. Changes in the XPS peak intensities with reaction time for Pt/Al_2O_3 catalyst.

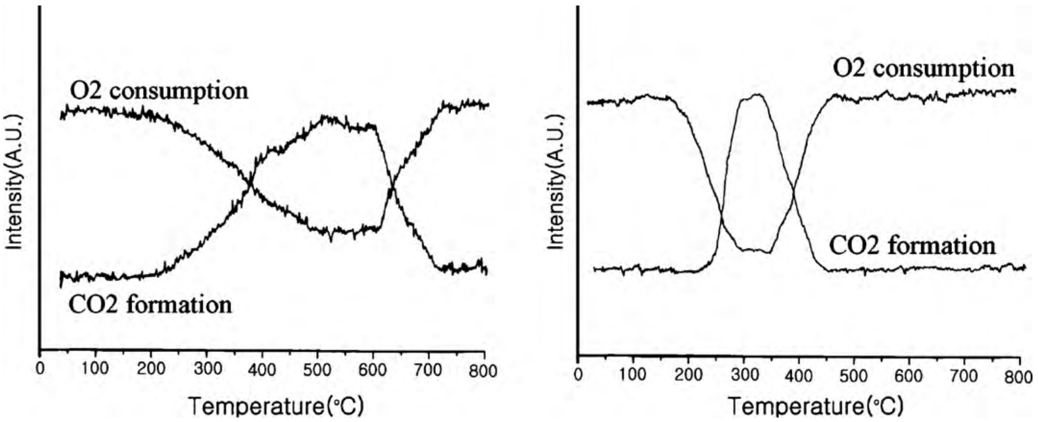

Fig. 11. Profiles of O_2 consumption and CO_2 formation during TPO experiments with Pt/Al_2O_3 (left) and Pt/CeO_2 (right) after reaction for 3 h with phenol initial concentration 5000 mg/L.

ceous materials of C_2 and C_3 transformed morphologically into C_4 material.

In the case of Pt/CeO_2 catalyst, the shape of C1s spectrum was nearly the same as that of Pt/Al_2O_3 after 1 h reaction, but its intensity was more than 10 times lower than that of the corresponding Pt/Al_2O_3 catalyst. Another outstanding difference was that the formation of C_4 peak had never been observed during the reaction up to 10 h and with phenol initial concentration up to 5000 mg/L.

XPS C1s spectra of support-free Pt powder showed the presence of sharp peak appearing at the binding energy of 286.3 eV. C_1 peak is believed to be due to the carbon deposits on the surface of Pt. C_2 peak seems to be assigned to the carbon deposits near Pt particles and the carbon deposits on the support is suggested to be C_4 carbon. The broad peak of C_3 carbon at the binding energy of 293 eV is not clear, and it might be formed through charge neutralization during XPS measurements.

Carbonaceous deposits on the catalysts were analyzed with TPO. Burn-off profiles of carbonaceous deposits on the catalysts after reaction for 3 h with initial phenol concentration 5000 mg/L are shown in Fig. 11. As seen, in accordance with the consumption of oxygen formation of CO_2 occurs at a broad temperature range from 250 °C to 700 °C for Pt/Al_2O_3 and at a temperature range from 250 °C to 450 °C for Pt/CeO_2. This result provides a further evidence that carbonaceous materials must have been deposited on the catalyst during wet oxidation of phenol, and the catalyst deactivation during wet oxidation of phenol must be due to the deposits of carbonaceous materials.

When assuming that the carbonaceous deposits on Pt/Al_2O_3 and Pt/CeO_2 have the same chemical composition and configuration, carbonaceous deposits on both the catalysts are expected to be burned off at the same and narrow temperature range during TPO experiment. Diffusional limitations during carbon combustion might have played a role on modifying the TPO signal. As previously mentioned in Section 2, Pt particles were impregnated on the exterior surface, instead of internal pores, of the Al_2O_3 and CeO_2. Since TPO profiles at low phenol initial concentrations showed two distinct CO_2 peaks, diffusional limitation is, if any, not the main role on the formation of the broad CO_2 peaks. An interesting feature is, however, observed that the carbonaceous deposits on Pt/Al_2O_3 are less reactive toward oxygen (or more difficult to burn) than those on Pt/CeO_2. Carbon deposits on alumina support were reported to be oxidized at temperatures higher than 440 °C [14]. On the other hand participation of Pt metal could catalyze oxidation of carbon deposits, and Pt-catalyzed oxidation of carbon is known to occur generally at temperatures around 280 °C [15,16]. A separate TPO analysis was carried out with Pt powder alone after reaction for 3 h with initial phenol concentration 5000 mg/L, and the result is shown in Fig. 12. The carbonaceous deposit on Pt powder was burned off at narrow temperature range around 250 °C and was completely removed below 300 °C.

The broad profiles of CO_2 formation in Pt/Al_2O_3 and Pt/CeO_2 imply that there are at least two types of carbon deposits burning at different temperatures. One type of deposits, locating on the surface of Pt particles, will burn at around 250 °C, and the other type on Al_2O_3 or CeO_2 will burn at much higher temperatures. The presence of filamentous carbons linking Pt particles on Al_2O_3 and CeO_2 could be confirmed from the TEM micrographs in Figs. 7 and 8.

CeO_2 has received much attention because it acts as an oxygen storage in three-way catalysts to maintain and enhance the activity of oxidation of hydrocarbons and carbon monoxide [17–19]. Although the reason why the carbonaceous deposit on CeO_2 rather than Al_2O_3 was burned off at lower and narrower temperatures cannot clearly be answered at present, CeO_2 might have promoted the oxidation of the deposit on it.

3.3. Migration of carbonaceous deposits

Since the conversion of phenol on Pt-free Al_2O_3 support was almost negligible as shown in Fig. 2, not only wet oxidation of phenol but also initial formation of carbonaceous deposits can be

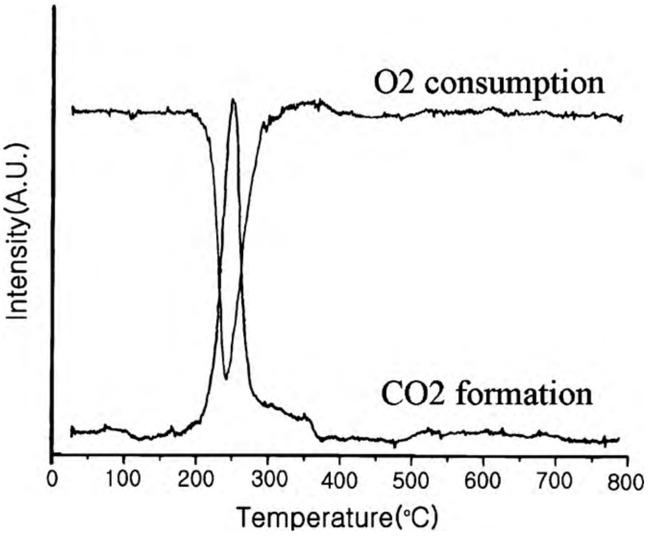

Fig. 12. Profiles of O_2 consumption and CO_2 formation on Pt powder after reaction for 3 h with phenol initial concentration 5000 mg/L.

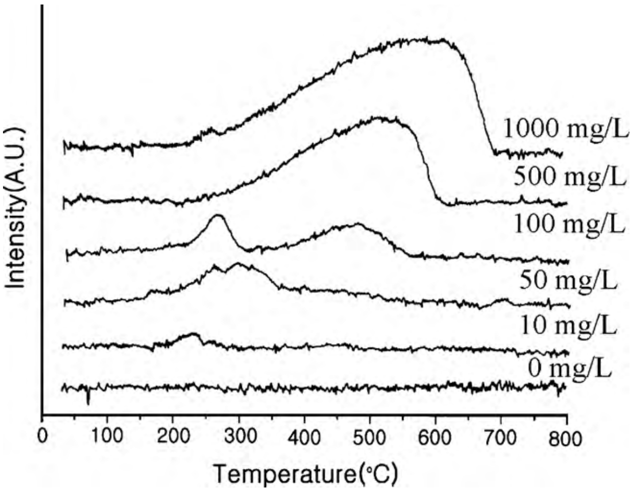

Fig. 13. Effect of phenol initial concentration on CO_2 formation profiles of Pt/Al_2O_3.

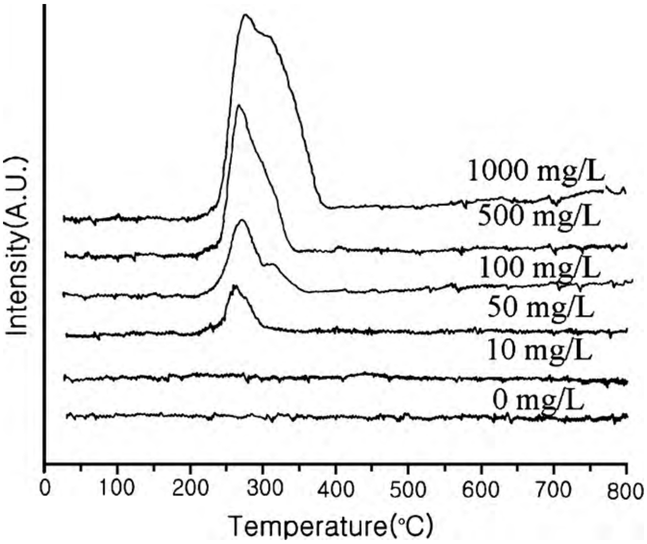

Fig. 14. Effect of phenol initial concentration on CO_2 formation profiles of Pt/CeO_2.

said to occur predominantly on the surface of Pt particles. The carbon deposits, primarily formed on the surface of Pt particles, will then migrate onto the surface of Al_2O_3 and CeO_2 in the vicinity of Pt particles. In order to investigate the migration of carbonaceous deposits, TPO experiments were employed for Pt/Al_2O_3 and Pt/CeO_2 which underwent oxidation of phenol for 3 h with phenol initial concentrations 10 mg/L, 50 mg/L, 100 mg/L, 500 mg/L and 1000 mg/L. The obtained profiles of CO_2 formation for Pt/Al_2O_3 and Pt/CeO_2 are shown in Figs. 13 and 14, respectively. When phenol initial concentration was 50 mg/L or less, most CO_2 was produced at temperatures below 300 °C. These CO_2 peaks are nearly the same as the CO_2 peak from Pt powder (Fig. 12), indicating that carbonaceous deposits are primarily formed on the surface of Pt particles. At the phenol initial concentration 100 mg/L are found new higher temperature peaks which grow further with increasing phenol initial concentration. From the changes in the profiles of CO_2 formation with phenol initial concentration the primarily formed carbonaceous deposits on Pt particles are suggested to migrate onto the surface of Al_2O_3 and CeO_2. Furthermore, when looking carefully over the TEM micrographs of Pt/Al_2O_3 and Pt/CeO_2 (Figs 7 and 8) carbonaceous materials on the supports were known to act as bridges connecting Pt particle islands.

4. Conclusions

Catalytic wet oxidation of phenol was carried out with 1 wt.% Pt/Al_2O_3 and 1 wt.% Pt/CeO_2 in a batch reactor operated at 423 K and 1.4 MPa.

During the wet oxidation reaction catalyst deactivation was observed especially on Pt/Al_2O_3. From the TEM, EDX, XPS and TPO analyses the deactivation was proved to be due to the formation and deposition of carbonaceous materials on the catalyst surface. The formation of carbonaceous deposits on Pt/Al_2O_3 and Pt/CeO_2 were known to be greatly different from XPS analysis, and the profiles of CO_2 formation in TPO experiments were also different to each other.

Carbonaceous deposits were located on the surface of Pt particles as well as supports. The deposit on Pt particles rather than the deposit on the support was much more reactive toward oxygen. The different reactivities of these deposits toward oxygen resulted in the appearance of broad CO_2 formation profiles at temperature range 250–700 °C for Pt/Al_2O_3 and 250–450 °C for Pt/CeO_2. The reason why the deposit on CeO_2 was burned off at lower and narrower temperatures was not clear, but CeO_2 was thought to have promoted the oxidation of the deposit on it.

From the sequential CO_2 formation profiles carbonaceous deposits were suggested to be primarily formed on the surface of Pt particles and then to migrate continuously onto the surface of Al_2O_3 and CeO_2 in the vicinity of the Pt particles.

Acknowledgements

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References

[1] J. Levec, Appl. Catal. 63 (1990) L1.
[2] J. Levec, A. Pintar, Catal. Today 24 (1995) 51.
[3] T.L. Randall, P.V.J. Knopp, Water Pollut. Control Fed. 52 (1980) 2117.
[4] D. Mantzavinos, R. Hellenbrand, A.G. Livingston, I.S. Metcalfe, Appl. Catal. B 11 (1996) 99.
[5] C.J. Chang, J.C. Lin, J. Chem. Tech. Biotechnol. 57 (1993) 355.
[6] A. Pintar, J. Levec, Chem. Eng. Sci. 47 (1992) 2395.
[7] M.J. Dietrich, T.L. Randall, D. Channey, J. Environ. Prog. 4 (1985) 171.
[8] S.H. Lin, S. Ho, Appl. Catal. B: Environ. 9 (1996) 133.
[9] J.E. Atwater, J.R. Akse, J.A. Mckinnis, J.O. Thompson, Appl. Catal. B: Environ. 11 (1996) L11.
[10] T. Hogan, R. Simpson, M. Kin, A. Sen, Catal. Lett. 40 (1996) 95.
[11] E. Zimmerman, J. Chem. Eng. 56 (1958) 117.
[12] F. Luck, Catal. Today 27 (1996) 195.
[13] D.-K. Lee, D.-S. Kim, Catal. Today 63 (2001) 249.
[14] S.M. Augustime, G.N. Alameddin, W.M.H. Sachtler, J. Catal. 115 (1989) 217.
[15] S. Hamoudi, F. Larachi, A. Sayari, J. Catal. 177 (1998) 247.
[16] C.L. Pieck, R.J. Verderone, E.L. Jablonski, J.M. Parera, Appl. Catal. 55 (1989) 1.
[17] D. Kalakkad, A.V. Dayte, Appl. Catal. B: Environ. 1 (1992) 191.
[18] J.G. Hunam, H.R. Robota, M.J. Cohn, S.A. Bradley, J. Catal. 133 (1992) 309.
[19] P. Marecot, L. Pirault, G. Mabilon, M. Prigent, J. Barbier, Appl. Catal. B: Environ. 5 (1994) 57.