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WET OXIDATION OF WASTEWATER CONTAINING HYDROCARBONS BY NOVEL SUPPORTED Pd CATALYSTS

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Abstract – Pd catalysts supported on TiO_2, ZrO_2, ZSM-5, MCM-41 and activated carbon were used in catalytic wet oxidation of hydrocarbons such as phenol, m-cresol and m-xylene. It was found that the Pd/TiO_2 catalyst was highly effective in the wet oxidation of hydrocarbon. The activities of catalysts with various hydrocarbon species, catalyst support, oxidation state of catalyst performed in a 3-phase slurry reactor show that reaction on Pd surface is more favorable than that in aqueous phase and that the active site is oxidized Pd in catalytic wet air oxidation of hydrocarbons. Based on the experimental results, a plausible reaction mechanism of wet oxidation of hydrocarbons catalyzed over Pd/TiO_2 catalyst was proposed. This catalyst is superior to other oxide catalysts because it suppressed the formation of hardly-degradable organic intermediates and polymer.

Key words: Pd Catalyst, Wet Air Oxidation, Hydrocarbons, Wastewater, Mechanism

INTRODUCTION

Until now, various methods for wastewater treatment have been developed. Among them, mainly three treatment methods and their modified versions have been used for industrial wastewater. The first method is a biological treatment. It is a well-known method for municipal wastewater treatment. The cost of this method is cheaper than the other methods. However, it needs a long treatment time and cannot treat concentrated wastewater. Moreover, if aldehyde compounds are present in wastewater, biomass can not survive [Nemerow and Dasgupta, 1991]. When the solid waste content is high enough to sustain combustion, incineration method is used. Sometimes, combustion additive is required to burn organic compound of low concentration in wastewater. Additives for incineration can raise its treatment cost. The third method is wet air oxidation (WAO) [Mishra et al., 1995; Kim et al., 1995].

Wet air oxidation is a modified form of Zimpro process. Zimpro process requires high pressure (16-200 atm) and temperature (200-370 °C) [Zimmermann and Diddams, 1960]. It needs high equipment cost and cannot remove COD (Chemical Oxygen Demand) in wastewater efficiently (40-80 % removal). Furthermore, because of high reaction temperature, ammonia compounds can be produced during process. Wet air oxidation can be performed under relatively low temperature and pressure with adequate catalysts. Three main methods using catalyst have been developed. Photocatalytic wet air oxidation has advantages in its low energy cost and effectiveness. However, there is a problem for light to penetrate wastewater in full depth. Hence, it is impossible to treat relatively large amount of wastewater [Bouquet-Somrani et al., 1996]. Supercritical wet air oxidation adopted supercritical condition in wastewater treatment. The solubility of hydrocarbon increases under supercritical condition, which helps hydrocarbons to contact easily with catalyst in wastewater. However, this method is not economical because of cost [Gloyna and Li, 1995]. Catalytic wet air oxidation is operated at relatively mild temperature (100-250 °C) and pressure (10-100 atm). This method takes advantages in treating concentrated wastewater and industrial wastewater containing hydrocarbons which cannot be treated easily by biological and incineration method [Kim et al., 1995].

In wet air oxidation, hydrocarbons and unstable intermediates can be oxidized directly to CO_2 and H_2O. In the other way, carboxyl acids, aldehydes and lower-molecular weight compounds produced during oxidation procedure, are oxidized to CO_2 and H_2O [Li et al., 1991; Grover and Chaudhari, 1989]. Hydrogen abstraction from hydrocarbon produce alkyl radical which is easily oxidized to CO_2 and H_2O and the site of hydrogen abstraction is the carbon bonded with OH or NH_2. Aldehydes are further reacted to alkyl radical, carboxylic acids and CO_2. Hydrogen abstraction in carboxyl acids happens at α carbon.

The catalytic properties and characterization of novel Pd catalyst supported on TiO_2 of various crystalline structures, ZrO_2, ZSM-5, MCM-41 and activated carbon in wet oxidation are reported in this paper. Based on these results, a reaction mechanism in WAO of hydrocarbons on Pd catalyst is also suggested.

EXPERIMENTAL

1. Catalyst Preparation

The catalysts used in this reaction were prepared by incipient wetness method. $PdCl_2$ was used as a Pd precursor. After

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impregnation of $PdCl_2$ onto suitable support, it was dried at 80 °C for 8 hr, calcined at 400 °C for 5 hr and then reduced at 310 °C with H_2 for 2 hr. TiO_2 having rutile or anatase crystalline structure, ZrO_2, ZSM-5, MCM-41 and activated carbons were adopted as a support.

Sol-gel method was adopted to prepare Pd catalysts supported on a hydrophobic support. Silica source such as methyl triethoxy silane (MTEOS) or tetraethoxy silane (TEOS) was mixed with titanium isopropoxide in isopropyl alcohol at the ratio of Ti to Si of 4. The mole ratio of source and solvent was 1 : 10. The resulting solution refluxed at 80 °C under N_2 for 4 hr, and then dried in rotary evaporator at 100 °C for 2 hr. After drying, incipient wetness method was used. Calcination and reduction condition was performed at 400 °C with O_2 for 5 hr and at 310 °C with H_2 for 2 hr respectively. BET surface area of (TiO_2+SiO_2) [MTEOS+TEOS] and (TiO_2+SiO_2) [MTEOS] were 19 and 22 m^2/g, respectively.

2. Reaction

The reaction was performed in a high-pressure 3-phase slurry reactor (1.8 L high pressure Parr reactor). Catalyst and 1 L of wastewater containing hydrocarbons was introduced to the reactor. Reactor was pressurized with O_2 (99 % pure) to 10 atm at room temperature, and then heated to reaction temperature. Reaction time was started to count after reaction temperature was reached. Sampling of reaction products was regularly taken.

3. Analysis

The sample was analyzed with HP5890 gas chromatography equipped with FID detector. Vocol capillary column (#4879-02B, 30 M × 0.53 mm) was used. The crystalline structure of supports was analyzed with XRD (X-ray Diffraction; Rigaku D/MAX-IIIC). The intermediate species was investigated by GC-MS (Gas Chromatography-Mass Spectroscopy; Trio1000, Fisons).

BET surface area of TiO_2 support were measured with automatic volumetric sorption analyzer (Micromeritics: ASAP 2000) and H_2 chemisorption measurement after reduction with H_2 at 310 °C for 2 hr were performed with automatic volumetric sorption analyzer (Micromeritics: ASAP 2010C). H_2 chemisorption procedure is as follows;

(1) Evacuation at 350 °C for 30 min after He purge
(2) Evacuation at 100 °C for 30 min
(3) H_2 adsorption at 100 °C
(4) H_2 adsorption at 100 °C after evacuation at 100 °C for 1 hr to remove physically adsorbed H_2

RESULTS AND DISCUSSION

1. Wet Oxidation over Pd Catalyst Supported on TiO_2

1-1. Effect of Hydrocarbon Species on Wet Oxidation Rate

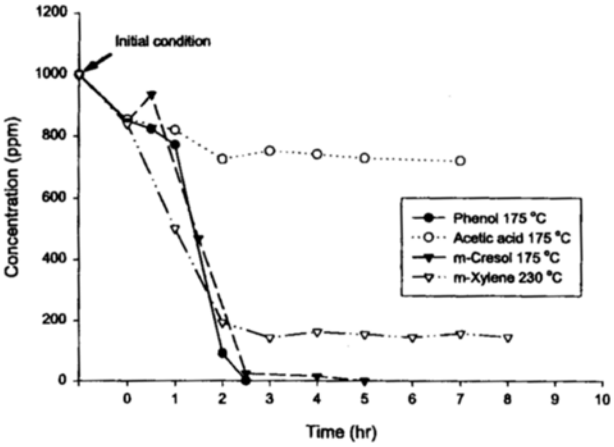

Fig. 1. Wet oxidation of various hydrocarbons over 2 wt% Pd/TiO_2 (Alfa).
(175 °C, initial oxygen pressure 10 atm, 1 g catalyst).

Fig. 1 shows the rate of wet air oxidation of different hydrocarbons catalyzed over 2 wt% Pd/TiO_2 (rutile: Alfa). Phenol and m-cresol were decomposed into mostly H_2O and CO_2 at 175 °C. The wet oxidation rate is 683 ppm-phenol/(hr × g-catalyst) and 456 ppm-m-cresol/(hr × g-catalyst) respectively. Acetic acid was not removed easily with Pd/TiO_2. The wet oxidation rate is 65 ppm/(hr × g-catalyst). 100 % of TOC (total organic carbon) was removed in wet air oxidation of 5000 ppm of acetic acid at 248 °C for 1 hr over Cu/Co/Bi oxide catalyst (catalyst concentration is 20 mM). Apparent activation energy was 105.9 kJ/mol [Imamura et al., 1982]. The removal rate at 175 °C was calculated to be 416 ppm/(hr × g-catalyst). Cu/Co/Bi oxide catalyst is more active by 7 times than Pd/TiO_2. The reason why acetic acid was not removed easily can be explained according to the decomposition reaction mechanism of acetic acid suggested by Levec and Smith [1976]. Acetic acid adsorbed on vacant site of FeO reacted with oxidized site of catalyst to produce HCHO and CO. HCHO was further oxidized to HCOOH. Reaction determining step of this mechanism seems to be an adsorption step of acetic acid, because HCHO, HCOOH and CO was easily converted to CO_2 and H_2O [Levec and Smith, 1976]. The more hydrophobic nature of Pd surface of Pd/TiO_2 will suppress the adsorption of hydrophilic CH_3COOH in the wet oxidation of acetic acid catalyzed over Pd/TiO_2.

m-Xylene was hardly decomposed at 175 °C. However, wet oxidation rate of m-xylene over Pd/TiO_2 was 323 ppm-m-xylene/(hr × g-catalyst) at 230 °C and about 150 ppm of m-xylene was not removed anymore. m-Xylene was not decomposed without catalyst at 230 °C. This result indicates that Pd/TiO_2 was completely deactivated after reaction of 3 hr with m-xylene. The ESCA analysis of this deactivated catalyst shows the complete blocking of Pd surface with carboneous species [Cho et al., 1997]. The formation of carboneous species were facilitated at high temperature.

In case of Pd/TiO_2, wet oxidation rate of phenol is much higher than m-xylene indicating that hydrocarbons having OH group are more easily oxidized than those having methyl group. Phenoxy radical seems to be an initial radical and to play an important role for complete wet oxidation of phenol.

1-2. Effect of Phenol Concentration

Wet oxidation rate of phenol of different concentration over 2 wt% Pd/TiO_2 (Strem) are shown in Fig. 2. In wet oxidation of 500 ppm and 1,000 ppm of phenol, the reaction rate was 462 ppm-phenol/(hr × g-catalyst) and 955 ppm-phenol/(hr × g-catalyst), respectively. When phenol concentration was

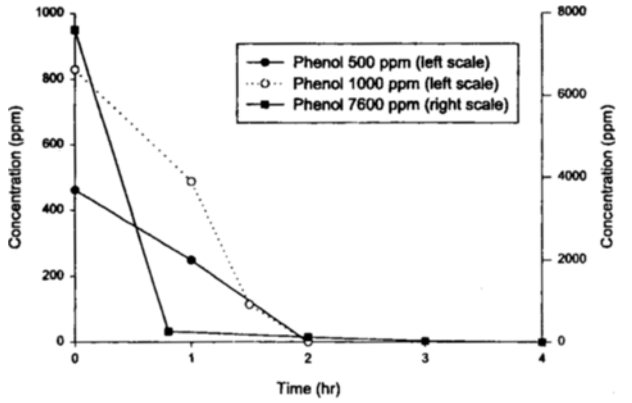

Fig. 2. Wet oxidation of phenol with different concentration over 2 wt% Pd/TiO_2 (Strem); phenol 500 ppm, 1,000 ppm and 7,600 ppm.
(170 °C, initial oxygen pressure 10 atm, 0.5 g catalyst for 500 and 1,000 ppm, and 1 g catalyst for 7,600 ppm).

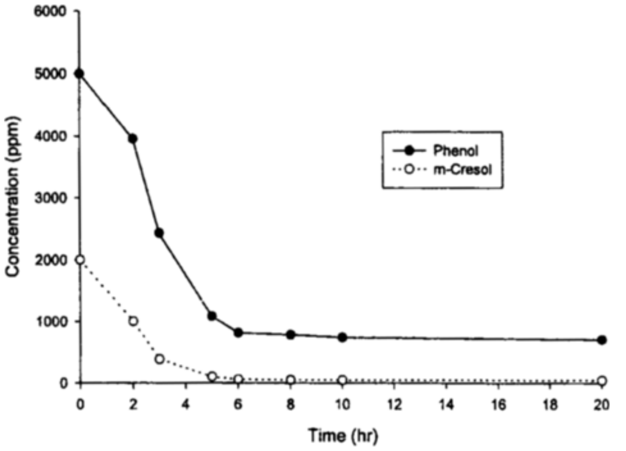

Fig. 3. Wet oxidation of the mixture of phenol and m-cresol over 2 wt% Pd/TiO_2 (Strem).
(175 °C, initial oxygen pressure 10 atm, 1 g catalyst).

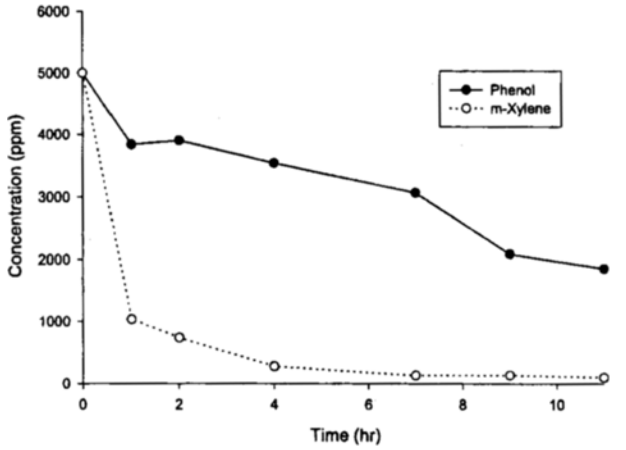

Fig. 4. Wet oxidation of the mixture of phenol and m-xylene over 2 wt% Pd/TiO_2 (Strem).
(170 °C, initial oxygen pressure 10 atm, 1 g catalyst).

7,600 ppm, reaction rate was about 9,000 ppm-phenol/hr·g-catalyst as shown in Fig. 2b. These results indicate that the apparent reaction order of wet oxidation of phenol in 3-phase slurry reactor is first-order which is in agreement with the result of Sanada and Katzer [1974]. The reaction rate during induction period at 145 °C over 10 % CuO on γ-alumina (Harshaw Cu-0803T 1/8) was 108 ppm-phenol/(hr × g-catalyst) and steady state reaction rate was 206 ppm-phenol/(hr × g-catalyst) in WAO of 4,600 ppm of phenol. In two regions, the reaction orders of phenol are first-order [Sanada and Katzer, 1974]. However, Ohta et al. [1980] reported that the reaction order of phenol is 0.44 and that of oxygen is 0.55 in a rotating basket reactor over the same catalyst with Sanada and Katzer's. The catalytic activity of Pd/TiO_2 is much higher than CuO/γ-alumina.

When the reaction rate determining step is an adsorption of phenol in aqueous phase on catalyst surface and the concentration of phenol is very low, the reaction rate is proportional to the concentration of phenol. The second possible mechanism is that phenol in aqueous phase can react with oxygen adsorbed on catalyst surface like Eley-Rideal mechanism. The third is that surface oxygen on catalyst can react with phenol in aqueous phase to form peroxo or phenoxy radicals that contribute wet oxidation of phenol. The reaction order will be first-order in these cases.

1-3. Effect of Combination of Hydrocarbon

Wet oxidation of 5,000 ppm of phenol and 5,000 ppm of m-cresol ppm was performed at 170 °C over 2 wt% Pd/TiO_2 (Strem) catalyst as shown in Fig. 3. The reaction rate was 930 ppm-phenol/(hr × g-catalyst) and 270 ppm-m-cresol/(hr × g-catalyst), respectively. Catalyst was deactivated after the reaction of 6 hr. Because 7,600 ppm of phenol in absence of m-cresol was completely decomposed over Pd/TiO_2, it can be suggested that hardly-degradable intermediates or polymers seems to be more easily produced in the presence of m-cresol having methyl group, and deposited on the surface of catalyst. The wet oxidation with both 5,000 ppm of m-xylene and phenol gave a similar result as shown in Fig. 4. m-Xylene was not decomposed in the absence of phenol at 175 °C. This result indicates that phenol was converted to a radical which initiates the decomposition of xylene at 175 °C. Because TiO_2 is known as a hydrophobic support, m-cresol and m-xylene could be adsorbed on catalyst surface better than phenol. The faster wet oxidation rate of m-xylene and m-cresol might be explained by the assumption that the reaction pathway on the surface of catalyst is dominated over the reaction pathway in aqueous phase.

1-4. Wet Oxidation Without Catalyst and With TiO_2 Only

Wet oxidation of 5,000 ppm of phenol and 5,000 ppm of m-xylene without catalyst are shown in Fig. 5. Phenol decompostion rate was 475 ppm-phenol/hr in steady state and m-xylene was almost not decomposed. Phenol could be removed even without catalyst in a homogeneous aqueous phase reaction. Removal rates of phenol without catalyst reported by Baillod are 1,410 ppm-phenol/hr at 204 °C, 2,369 ppm-phenol/hr at 232 °C, and 3,328 ppm-phenol/hr at 260 °C [Baillod et al., 1982]. However, formic acid, acetic acid, succinic acid, acetone and acetaldehyde were produced and not decompos-

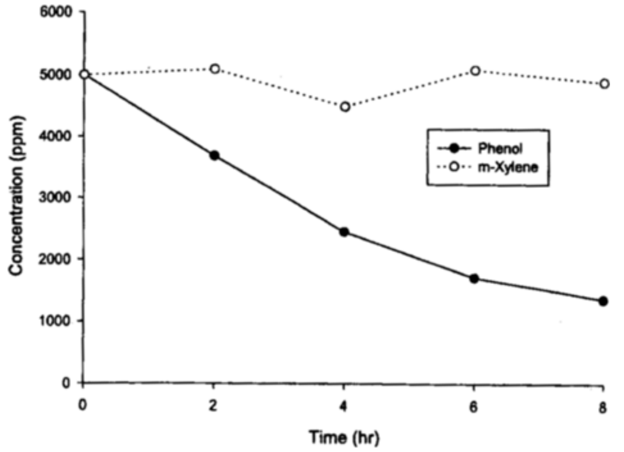

Fig. 5. Wet oxidation of phenol and m-xylene without catalyst.
(170 °C, initial oxygen pressure 10 atm).

ed further easily. Acrolein, phenol, formic acid, chloroform and toluene are decomposed easily at 275 °C in wet air oxidation without catalyst [Dietrich et al., 1985].

As shown in Fig. 5, m-xylene was not decomposed at all in the absence of catalyst, indicating that surface reaction plays an important role in dissociation of m-xylene. Phenol could produce radicals in aqueous phase without catalyst. However, the decomposition of phenol without catalyst is quite low and produces a large amount of hardly-degradable organic compounds.

In wet oxidation of 1,000 ppm of phenol over TiO_2 (Strem), the reaction rate was 204 ppm-phenol/(hr × g-catalyst) as shown in Fig. 6. Even without Pd, phenol was completely removed in 4 hr. TiO_2 might play some role as a catalyst. However, it was known that phenol can be removed easily without catalyst. The reaction order of phenol without catalyst is one, and the reaction rate of phenol without catalyst was 95 ppm-phenol/hr. In comparison with Fig. 2, the ratio of the extent in heterogeneous reaction to homegeneous reaction was 9 : 1 in wet oxidation of 1,000 ppm of phenol over 2 wt% Pd/TiO_2. The ratio of phenol decomposition reaction rate on Pd, TiO_2 and in aqueous phase was about 7.9 : 1.1 : 1. As reported by Levec and Pintar [1994], when the portion of heterogeneous reaction was large, the production of hardly-degradable organic compounds and polymers was decreased. The production of hardly-degradable organic intermediates was not observed in the wet oxidation of phenol catalyzed over 2 wt% Pd/TiO_2 (Strem). Other oxide catalysts produced hardly-degradable organic intermediates resulting in the incomplete oxidation of hydrocarbons [Mishra et al., 1995].

1-5. Effect of Oxidation State of Pd

Wet oxidation rates catalyzed over Pd/TiO_2 (Strem) in reduced and calcined states are shown in Fig. 7. In the reaction over reduced catalyst, induction period was observed. Reaction rates were 958 ppm-phenol/(hr × g-catalyst) and 801 ppm-phenol/(hr × g-catalyst) respectively in rapid reaction region. Pd in reduced state needs an induction time to generate an oxidized Pd species.

Sanada and Katzer [1974] first reported that free radicals were involved in wet oxidation mechanism of phenol with 10 % CuO/γ-alumina commercial catalyst (Harshaw Cu-0803T 1/8). Induction periods were frequently observed in homogeneous oxidation which was explained by a free-radical mechanism. It was suggested that these radicals produced on catalyst surface would react with hydrocarbons in aqueous phase, and were finally terminated in aqueous phase or on catalyst surface. Free radicals were initiated with dissociative adsorption of phenol or decomposition of hydrogen peroxide on catalyst surface [Sanada and Katzer, 1974]. However, the time to produce radicals is relatively short in wet oxidation over calcined 2 wt% Pd/TiO_2 as shown in Fig. 7. Hence, induction period in reduced catalyst is the time needed to produce PdO, the active site of wet oxidation of phenol.

1-6. Effect of Crystalline Structure of Support

2 wt% Pd catalysts supported on TiO_2 which have two different crystalline structures, rutile and anatase were used in wet oxidation of 1,000 ppm of phenol. The support from Strem (surface areas of Strem is 2-3 m^2/g) has a rutile crystalline structure. The supports from Alfa and Degussa (surface area 10 and 13 m^2/g, respectively) have an anatase crystalline struc-

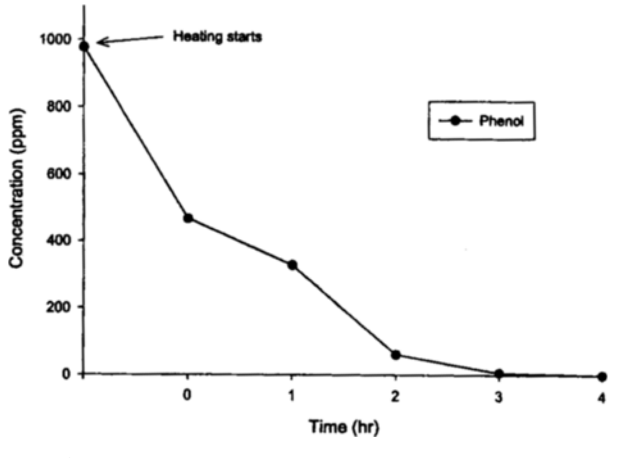

Fig. 6. Wet oxidation of phenol over TiO_2 (Strem).
(170 °C, initial oxygen pressure 10 atm, 1 g catalyst).

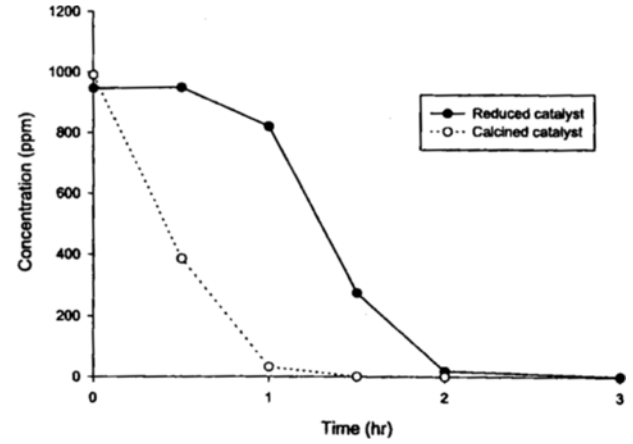

Fig. 7. Presence of induction period in reduced catalyst.
(170 °C, initial oxygen pressure 10 atm, 2 wt% Pd/TiO_2 (Strem) 1 g).

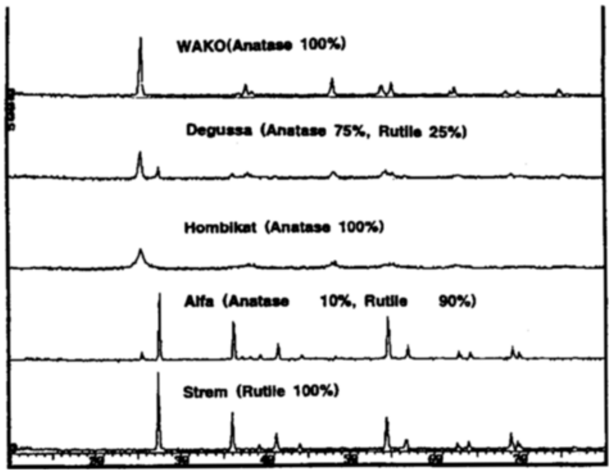

Fig. 8. XRD patterns of various TiO_2 supports.

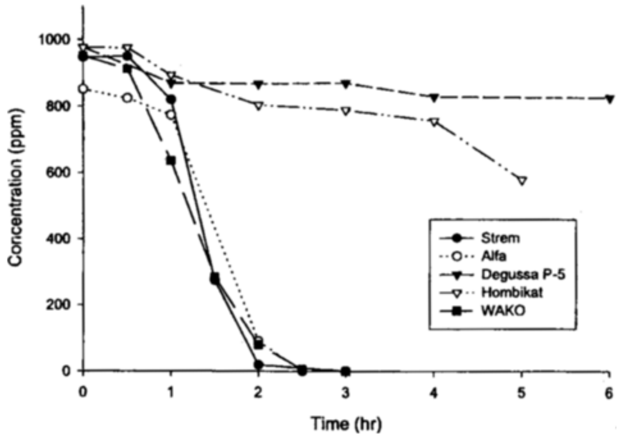

Fig. 9. Effect of TiO_2 supports on the activity of reduced 2 wt% Pd/TiO_2 in WAO of phenol.
(175 °C, initial oxygen pressure 10 atm, 2 wt% Pd catalyst 1 g).

ture mixed with a rutile structure. The supports from Hombikat and WAKO (surface area 50 and 13 m^2/g, relatively) have a pure anatase structure. XRD patterns of crystalline structure of TiO_2 are shown in Fig. 8. As shown in Fig. 9, the catalyst supported on rutile TiO_2 showed a higher activity. The metal dispersion of catalysts supported on Strem and Alfa were lower (3 % and 7 % respectively) than that of WAKO (22 %) or that of Degussa (52 %) or Hombikat (57 %). This result indicates that larger particles of Pd on catalyst surface are superior to smaller ones in the formation of active phase. The larger Pd particles have an advantage in the formation of PdO and in maintaining PdO phase. It can be speculated that smaller particle size of Pd might be converted easily to Pd $(OH)_x$ species during the reaction.

2. Pd Catalysts Supported on Hydrophobic Supports

Pd catalyst supported on ZSM-5 was used to decompose phenol and m-xylene as shown in Table 1. Incipient wetness method was used to prepare catalyst. In decomposition reaction of 5,000 ppm of phenol and 2,000 ppm of m-xylene, the reaction rate of phenol was 417 ppm-phenol/(hr × g-catalyst) and that of m-xylene was 94 ppm-m-xylene/(hr × g-catalyst). This result indicates that hydrophobic m-xylene selectively absorbed on catalyst surface prevents phenol from adsorbing on catalyst surface and from producing radicals for wet oxidation.

The wet oxidation of 5,000 ppm of phenol and 5,000 ppm of m-xylene over 2 wt% Pd catalyst supported on support prepared by sol-gel method are shown in Table 1. MTEOS (methyl triethoxy silane) and TEOS (tetraethoxy silane) were used as a Si precursor for support to prepare 2 wt% Pd/(TiO_2+SiO_2/MTEOS+TEOS). The mixing ratio was 1 : 1. 77 % of phenol and 7 % of m-xylene were decomposed within 9 hr. When methyl triethoxy silane was used as a Si source for support to prepare 2 wt% Pd/(TiO_2+SiO_2/MTEOS), 5 % of phenol and 38 % of m-xylene were decomposed within 6 hr. These results indicate that the adsorption of hydrocarbons on hydrophobic support is not the most important step in wet oxidation of hydrocarbons.

3. Pd Catalysts Supported on Various Supports

2 wt% Pd catalyst supported on ZrO_2 (MEL chemical, 10 nm diameter) were used to decompose 1,000 ppm of phenol. The reaction rate [111 ppm-phenol/(hr × g-catalyst)] is much smaller than that [955 ppm-phenol/(hr × g-catalyst)] of 2 wt% Pd/TiO_2 (Strem) as shown in Table 1. The Pd dispersion of 2 wt% Pd/ZrO_2 was 65 %. This high dispersion of Pd might be the reason why Pd/ZrO_2 has smaller catalytic activity.

2 wt% Pd catalyst supported on mesoporous MCM-41 were used in wet oxidation of 5,000 ppm of phenol and 5,000 ppm of m-xylene. The reaction rate of phenol was 304 ppm-phenol/(hr × g-catalyst) and that of m-xylene was 130 ppm-phenol/(hr × g-catalyst) as shown in Table 1. The removal rate

Table 1. Activities of Pd catalysts supported on hydrophobic supports, ZrO_2, MCM-41 and activated carbon
(170 °C, initial oxygen pressure 10 atm, 1 g catalyst)

Catalyst	Initial concentration	Reaction rate at steady state
2 wt% Pd/ZSM-5	Phenol 5,000 ppm	417 ppm-phenol/hr · g-catalyst
	m-Xylene 2,000 ppm	94 ppm-m-xylene/hr · g-catalyst
2 wt% Pd/(TiO_2+SiO_2)	Phenol 5,000 ppm	500 ppm-phenol/hr · g-catalyst
[MTEOS+TEOS]	m-Xylene 5,000 ppm	360 ppm-m-xylene/hr · g-catalyst
2 wt% Pd/(TiO_2+SiO_2)	Phenol 5,000 ppm	292 ppm-phenol/hr · g-catalyst
[MTEOS]	m-Xylene 5,000 ppm	500 ppm-m-xylene/hr · g-catalyst
2 wt% Pd/ZrO_2	Phenol 1,000 ppm	111 ppm-phenol/hr · g-catalyst
2 wt% Pd/MCM-41	Phenol 5,000 ppm	304 ppm-phenol/hr · g-catalyst
	m-Xylene 5,000 ppm	130 ppm-m-xylene/hr · g-catalyst
2 wt% Pd/activated carbon	Phenol 500 ppm	85 ppm-phenol/hr · g-catalyst

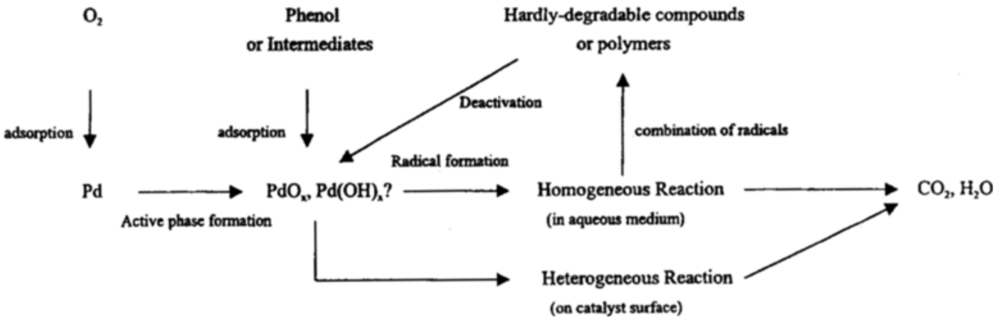

Fig. 10. Plausible wet oxidation mechanism of phenol.

of phenol was one third and that of m-xylene was a half in comparison with reaction rate over 2 wt% Pd/TiO_2 (Strem).

2 wt% Pd catalyst supported on activated carbon was used in wet oxidation of phenol 500 ppm. Reaction rate in steady state period was 85 ppm-phenol/hr·g-catalyst as shown in Table 1. However, most of phenol seems to be adsorbed on activated carbon. Adsorption of hydrocarbons on activated carbon did not increase wet oxidation rate of phenol.

4. Detection of Intermediates during Wet Oxidation

In wet oxidation of phenol, m-cresol and m-xylene over 2 wt% Pd/TiO_2 (Strem), the amount of intermediates species was much smaller than in wet oxidation over other catalysts. After extended period of wet oxidation of phenol, not any intermediates were detected. Acetic acid was reported as an intermediate in wet oxidation of phenol over CuO/ZnO catalyst by Levec and Pintar [1995]. However, acetic acid was not detected in wet oxidation of phenol, m-cresol and m-xylene over Pd/TiO_2. When Pd/ZSM-5 was used as a catalyst, acetic acid was detected in wet oxidation of phenol and m-xylene. This result indicates that intermediate species and reaction pathway in catalytic wet oxidation must be varied with catalysts. Pd/TiO_2 has an advantage in not producing acetic acid as an intermediate and can remove TOC more efficiently.

The stable intermediate species during wet air oxidation of 1,000 ppm of phenol and xylene over 1 wt% Pd/TiO_2 catalyst (Strem) at 170 °C for 8 hr were analyzed with GC-MS. The species having lower molecular weight than those of phenol and m-xylene are acrylic acid, acrylic aldehyde, formaldehyde as well as some other species. Compounds having molecular weight higher than that of phenol and m-xylene are 2-methyl-benzaldehyde, 4-methyl benzaldehyde, 3-(2-hydroxyphenyl)-2-propenoic acid, dihydrobenzofuran and (E)-2-propenoic acid. Hydrocarbons of higher molecular weight higher than 250 can not be detected with GC-MS.

It can be suggested that from this intermediate analysis, phenoxy, peroxo and propenoic radicals are produced. Polymerization, combination, and the reaction of these radicals with other radicals or stable intermediates in aqueous phase can produce hardly-degradable hydrocarbons with high molecular weight and reduce the efficiency of catalytic wet oxidation.

5. Reaction Mechanism

The reaction mechanism was proposed based on our results as shown in Fig. 10. O_2 or H_2O was adsorbed on catalyst surface and generated Pd-O species. Phenol was adsorbed on oxidized catalyst surface and reacted with oxygen in PdO to form phenoxy or peroxo radicals on catalyst surface and in aqueous phase. Reduced Pd was reoxidized by O_2. If this redox cycle on the catalyst surface is fast, the possibility to produce hardly-degradable intermediates or polymers in aqueous phase can be suppressed. These hardly-degradable intermediates and polymers can be adsorbed on catalyst surface to block active sites. Hydrocarbons with lower molecular weight can be easily converted to CO_2 and H_2O except for acetic acid. However, hydrocarbons of low molecular weight can produce hydrocarbons of high molecular weight in the reaction with other radicals in aqueous phase. The wet oxidation reaction on the surface of Pd/TiO_2 catalyst is more effective than wet oxidation in aqueous phase.

CONCLUSIONS

Novel Pd catalysts supported on TiO_2 show a good activity in wet oxidation of phenol. Large particles of Pd on TiO_2 support show a higher activity in WAO of phenol. It was suggested that smaller Pd cluster was deactivated more rapidly via the formation of $Pd(OH)_x$.

The active site of Pd/TiO_2 catalyst in WAO of phenol is oxidized Pd phase, mainly PdO. PdO is reduced by the reaction with hydrocarbons adsorbed on catalyst surface or those in aqueous phase to produce oxygenated radicals. Pd is reoxidized by the reaction with oxygen supplied from aqueous phase.

In catalytic wet air oxidation over Pd/TiO_2 catalyst, the aromatic compounds having OH group are dissociated more easily than those with alkyl functional group. Phenol and m-cresol can produce radicals for wet oxidation at 175 °C without catalyst. However, m-xylene cannot generate radicals without catalyst even at 230 °C. m-Xylene was not wet oxidized at 175 °C with Pd/TiO_2 catalyst. However, the presence of phenol at 175 °C initiated the wet oxidation of m-xylene via the attack of phenoxy radical on m-xylene.

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