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$Pd–Pt/Al_2O_3$ bimetallic catalysts for the advanced oxidation of reactive dye solutions

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Abstract

The $Pd–Pt/Al_2O_3$ bimetallic catalysts showed high activities toward the wet oxidation of the reactive dyes in the presence of 1% H_2 together with excess oxygen. Palladium was believed to act as a co-catalyst to spillover the adsorbed H_2 onto the surface of the oxidized Pt surface, and thereby the reducibility of the Pt increased greatly. The organic dye molecule adsorbed on the reduced Pt surface more easily than the oxidized Pt surface under the competition with excess oxygen, which is an essential step for the catalytic wet oxidation (CWO). The $Pd–Pt/Al_2O_3$ catalysts also produced H_2O_2 from H_2/O_2 mixture, and the hydroxyl radical was formed through the subsequent decomposition of H_2O_2. Additional oxidation of the reactive dyes was obtained with hydroxyl radical. The high activities of the $Pd–Pt/Al_2O_3$ catalysts were believed to be due to the combined effects of the faster redox cycle resulting from the increased reducibility of Pt surface and the additional oxidation of the reactive dyes with hydroxyl radical.

Keywords: Catalytic wet oxidation; $Pd–Pt/Al_2O_3$ bimetallic catalysts; Reactive dye solutions; Hydrogen peroxide; Reducibility

1. Introduction

Effluents from textile dyehouses impose environmental problems because of their high chemical oxygen demand (COD) and color [1]. Dyehouse effluent can change color from day to day or even several times a day because the dyestuff used in the dyeing process changes frequently due to customers requirements. The concentration of dye may be much less than 1 ppm, but the dye is visible even at such small concentrations. Such a strong color, if unreacted, would have a masked negative impact on the environment of the receiving water body.

Although there were several other technologies available for the removal of color and COD such as biodegradation [2], sorption [3–5], electrochemical and oxidative degradation [6–12], wet air oxidation is a very attractive and useful technique for treatment of dyehouse effluents [1,13–17]. However, these wet oxidation processes had a detrimental shortcoming that they should be operated under severe conditions of high pressure (6–17 MPa) and high temperature (150–350 °C). Therefore, the development of catalytic wet oxidation (CWO) 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 [15,18–20].

Homogeneous catalysts are in general more effective than heterogeneous oxidation catalysts [21], but

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their use requires a separation step such as precipitation or membrane separation to remove toxic catalyst ions from the final effluent. This drawback can be overcome by using heterogeneous catalysts which are easily recoverable and reused. Many of the investigators have been dealing with heterogeneously catalyzed wet oxidation in the literature. Sadana and Katzer [22,23] studied the CWO of phenol solutions using 10% CuO/Al_2O_3 catalyst. Chowdhury and Ross [24] investigated CWO of wastewaters on various metal oxides and found platinum oxide to be very effective. Imamura et al. [25] developed several heterogeneous catalysts to improve liquid phase oxidation and found that Co/Bi composite oxides were remarkably active for the oxidation of many low molecular weight carboxylic acids. Noble metal catalysts such as Ru, Pt and Rh were also proved to be active toward the wet oxidation of phenols and other model compounds [26]. Mixed copper, zinc and cobalt oxide catalysts were used for the catalytic oxidation of phenol and substituted phenols, and the $CuO/ZnO/Al_2O_3$ catalyst was proved to be effective for the oxidation [27,28].

In this paper, the CWO of the reactive dyes has been investigated using $Pd–Pt/Al_2O_3$ catalysts in the presence of H_2/O_2 gas mixture and the catalytic performance of the $Pd–Pt/Al_2O_3$ bimetallic catalysts was investigated. Reactive black 5, reactive blue 19 and reactive red 198 were used as the model compounds of the reactive dyes.

2. Experimental

2.1. Materials

High purity reactive black 5, reactive blue 19 and reactive red 198 were obtained from Aldrich Co. $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$, supplied from Aldrich Co., were used as the precursors of the $Pd–Pt/Al_2O_3$ catalysts. $Pd–Pt/Al_2O_3$ catalysts were prepared by incipient wetness method. After filling the pores of γ-Al_2O_3 (Strem Chemicals) with an aqueous solution of the $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$ mixture to have 0–1.0 wt.% Pd loading and 1.0 wt.% Pt loading, the samples were dried overnight in air at 90 °C. Although the drying at 90 °C is not sufficient for the complete removal of impurities and thus calcination step is necessary. According to preliminary study the small metal particles showed higher activity. The calcination at high temperatures, however, increased metal particle size due to the agglomeration at high temperatures. In order to make the metal particles as small as possible, the dried samples were just reduced at room temperature with flowing hydrogen atom beams activated by a microwave power generator (Hitachi, 600 W). Pt and Pd particles in the reduced samples were highly dispersed, and their average particle diameter was proved to be less than 2.0 nm from transmission electron microscopy.

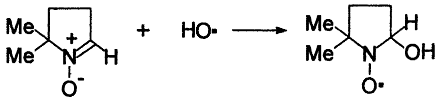
2.2. Catalytic wet oxidation

Oxidation of the reactive dyes was performed isothermally in a 1 L SS 316 autoclave (Parr Instrument Co.) equipped with a Teflon liner and a gas entrainment impeller and in a continuous flow tubular reactor. The operating pressure and temperature was kept to be 2.3 MPa and 200 °C, respectively. The initial concentration of the aqueous solution of the reactive dyes was 1000 mg/l. In the batch reactor experiment, 300 ml of the suspension of pure water and catalyst was introduced into the reactor. After heating up the aqueous solution to 200 °C under nitrogen atmosphere at 1.7 MPa, oxygen and H_2/N_2 were fed to the reactor up to the final pressure of 2.3 MPa. The initial composition of the gas mixture introduced into the reactor was 1% H_2, 25% O_2 and balance N_2. The aqueous solutions of the reactive dyes were then injected into the reactor to have 1000 mg/l concentration under vigorous stirring with 1000 rpm which was sufficient for the oxidation rate not to be controlled by mass transfer. In the continuous flow reactor experiment, the aqueous solutions of the reactive dyes were compressed to 2.4 MPa and fed to the system by a high pressure metering pump (Bran + Lubbe Co.). 1% H_2/N_2, N_2 and oxygen were supplied to the reactor continuously. The constant pressure (2.3 MPa) in the system was maintained by a back pressure regulator. The inside diameter and the length of the reactor were 30 cm and 2.0 nm, respectively. The amount of catalyst in the reactor was 250 g.

Liquid samples were immediately analyzed for total organic carbon (TOC). TOC was measured with a Shimadzu 5000A TOC analyzer whose operation is based on the combustion/non-dispersive infrared (NDIR) gas analysis. Color unit of the sample was measured by following ADMI (American Dye Manufacture Institute) tri-stimulus filter method.

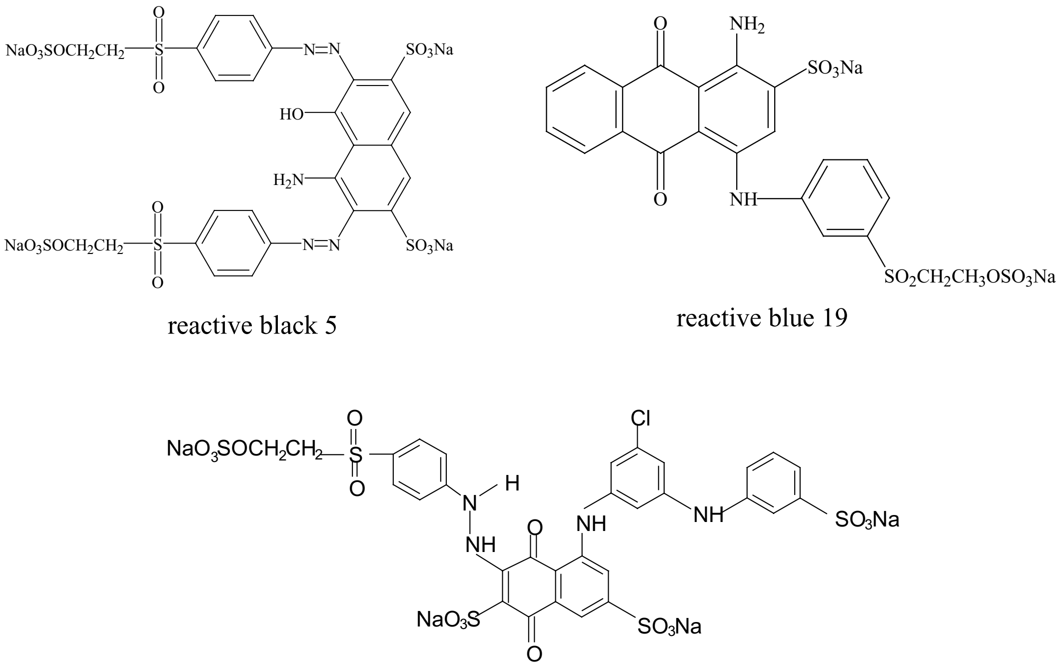
Temperature-programmed reduction (TPR) of the Pd–Pt/Al_2O_3 catalysts was performed in a tubular reactor where 0.5 g catalysts were loaded. The catalysts were oxidized with 20% O_2/N_2 gas mixtures at 200 °C for 4 h, and Ar gas (30 cm^3/min) was flowed over the catalyst for 30 min at 200 °C. The catalysts were then cooled to 25 °C under the flow of Ar. The catalysts were heated from room temperature up to 520 °C at a linear heating rate of 10 °C/min while flowing a mixture of 1.0% H_2 in Ar. The H_2O concentration produced during the TPR experiments was monitored continuously with a quadrapole mass spectrometer.

H_2O_2 concentration was measured by a colorimetric method using a UV/Visible DMS 90 Varian spectrophotometer [29]. Electron paramagnetic resonance (EPR) spin trapping of the hydroxyl radical ($HO^{\bullet}$) occurring during the wet oxidation was performed using a Varian E-4 spectrometer. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was used as a trapping agent because it efficiently scavenges $HO^{\bullet}$ through the following reaction to produce the DMPO/$HO^{\bullet}$ adduct, which has a characteristic EPR spectrum [29,30].



3. Results and discussion

The reactive dyes employed in this work as the model pollutants are reactive black 5, reactive blue 19 and reactive red 198 whose chemical structures are shown in Fig. 1. As expected from complex chemical structure, these compounds are known to be highly refractory. CWO of these refractory reactive dyes was carried out with Pd-free 1 wt.% Pt/Al_2O_3 catalyst in the absence and presence of H_2. As can be seen in Fig. 2, less than 60% of the initial TOC could be removed regardless of the species of reactive dyes in the absence of H_2. When 1% H_2 was fed into the batch reactor together with O_2, the TOC removal



reactive black 5

reactive blue 19

reactive red 198

Fig. 1. Chemical structures of reactive black 5, reactive blue 19 and reactive red 198.

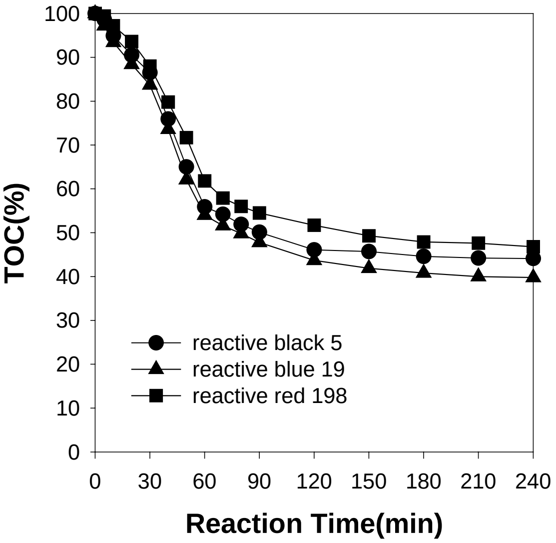


Fig. 2. Time dependences of TOC conversion during the CWO of reactive black 5 (●), reactive blue 19 (▲) and reactive red 198 (■) with 1 wt.% Pt/Al_2O_3 catalyst in the absence of H_2.

efficiencies increased significantly. More than 80% of the initial TOC could be removed within 240 min (Fig. 3). From the results in Figs. 2 and 3, it is evident that small amount of H_2 must have played an important role on accelerating the wet oxidation rate.

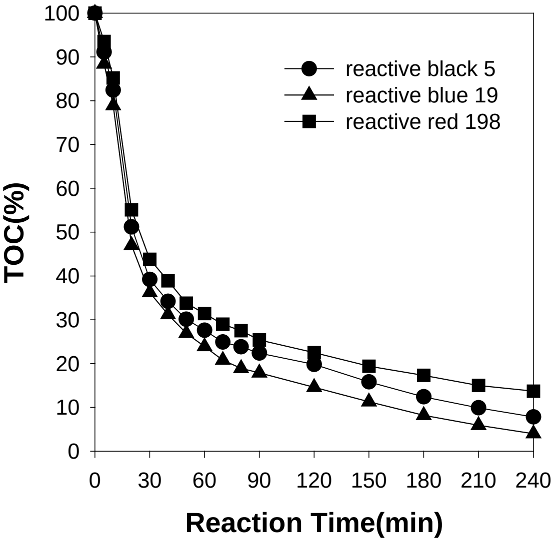


Fig. 3. Time dependences of TOC conversion during the CWO of reactive black 5 (●), reactive blue 19 (▲) and reactive red 198 (■) with 1 wt.% Pt/Al_2O_3 catalyst in the presence of H_2.

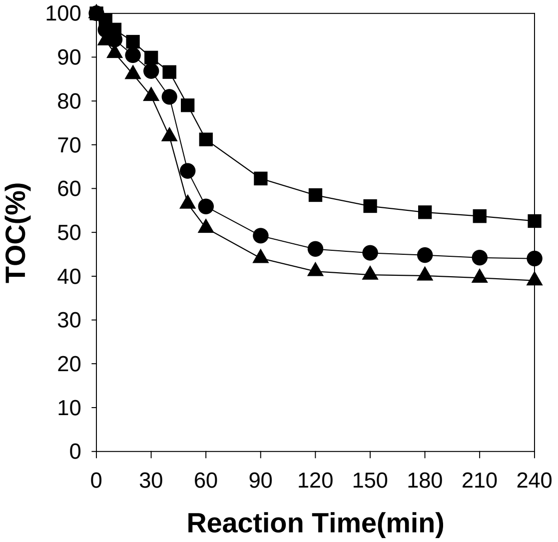


Fig. 4. Changes in TOC removal from reactive black 5 (●), reactive blue 19 (▲) and reactive red 198 (■) aqueous solutions during the CWO with 0.5 g 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst in the absence of H_2.

The effects of H_2 addition become more outstanding when the reaction was carried out with the 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst. In the absence of H_2 there existed slight differences in the TOC removal efficiencies obtained from the Pd-free 1 wt.% Pt/Al_2O_3 and 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst (Figs. 2 and 4). In the presence of H_2 (Fig. 5), however, remarkable enhancement of TOC removal efficiencies was observed. Complete removal of TOC from the reactive black 5 aqueous solution could be achieved in 60 min. Even in the case of the reactive red 198 which was the most difficult to be oxidized, it took 70 min for the complete removal of TOC.

The time required for the complete removal of TOC in the presence of H_2 was influenced significantly by the composition of catalyst (the weight fraction of Pd in the 1 wt.% Pt/Al_2O_3). As summarized in Table 1, while complete removal of TOC could not be achieved up to 240 min with the Pd-free Pt/Al_2O_3 catalyst, drastic TOC decreases were observed during the first 60 min with the 0.2–0.4 wt.% Pd containing 1 wt.% Pt/Al_2O_3 catalysts, implying that fast complete oxidation to CO_2 occurs. When the Pd loadings were higher than 0.4 wt.%, much longer times were required for the complete removal of TOC. Accordingly, 0.2 wt.%

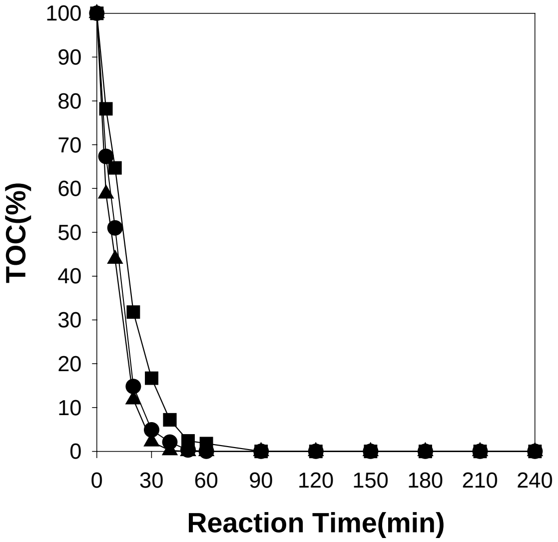


Fig. 5. Changes in TOC removal from reactive black 5 (●), reactive blue 19 (▲) and reactive red 198 (■) aqueous solutions during the CWO with 0.5 g 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst in the presence of H_2.

Pd loading together with 1.0 wt.% Pt seems to be the most effective for the oxidation of the reactive dyes. The faster oxidation rate on the 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 rather than 1.0 wt.% Pd–1.0 wt.% Pt/Al_2O_3 indicates that the oxidation occurs mainly on the surface of Pt, and Pd acts as a co-catalyst. Actually, the activity of the 1.0 wt.% Pd/Al_2O_3 was much lower than that of the 1 wt.% Pt/Al_2O_3. The final TOC values after 240 min reaction with the 1% Pd/Al_2O_3 catalyst in the absence of H_2 were 44.1, 39.8 and 46.8% in the reactive black 5, reactive blue 19 and reactive red 198 solution, respectively. These values are much lower than the corresponding values of 69.5, 64.7 and 74.3% obtained with the 1 wt.% Pt/Al_2O_3 catalyst.

Table 1
The time required for the complete removal of TOC with the Pd containing 1 wt.% Pt/Al_2O_3 catalysts in the presence of H_2

Weight % of Pd	Time (min)		
	Reactive black 5	Reactive blue 19	Reactive red 198
0.0	>240	>240	>240
0.1	70	60	80
0.2	60	50	70
0.3	60	50	70
0.4	60	50	70
0.5	70	60	80
0.6	70	60	80
0.7	80	70	90
0.8	90	80	120
0.9	120	90	150
1.0	120	90	150

The enhancing role of H_2 might be explained by the fast redox cycle during the CWO. CWO reaction occurring on the surface of the active component (in this case Pt) of the catalyst proceeds through the well-known redox mechanism: Organic reactive dye molecule adsorbs on the reduced surface of Pt, and the adsorbed organic reactant will then react with the adsorbed oxygen to produce CO_2 and H_2O. For the wet oxidation reaction reactive dye molecule should compete with excess oxygen for the adsorption sites. As shown below small amount of H_2 might provide the reactive dyes with the higher chance of adsorption by generating vacant sites through the reaction with the predominant surface oxygen, thereby increasing the rate of wet oxidation remarkably.

$$\text{Pt–O} + \text{Pt–H} \leftrightarrow \text{Pt–OH} + \text{Pt}$$

$$2\text{Pt–OH} \leftrightarrow \text{Pt–O} + \text{Pt} + H_2O$$

In order to investigate the high oxidation rate on the 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst, TPR experiments were performed, and the TPR profiles for the Pd–Pt/Al_2O_3 catalysts are shown in Fig. 6. 1.0 wt.% Pt/Al_2O_3 catalyst showed two main reduction peaks in the low temperature range at around 105 and 140 °C,

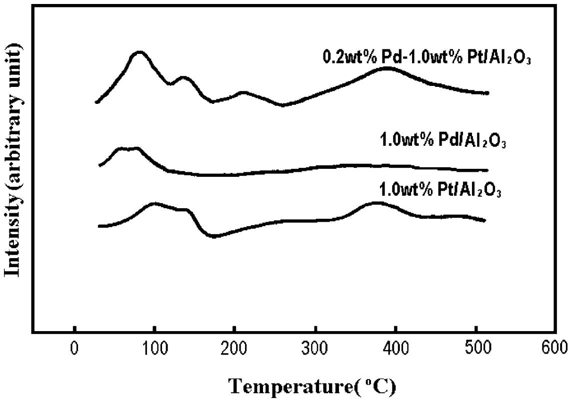


Fig. 6. TPR profiles of the 1 wt.% Pt/Al_2O_3, 1.0 wt.% Pd/Al_2O_3 and 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalysts.

and a small peak at about 380 °C. 1.0 wt.% Pd/Al_2O_3 catalyst was reduced at very low temperature with a maximum signal at about 70–80 °C. TPR profile of the 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst could not be explained by the simple addition of the individual contribution of the two metals, implying some kind of interaction between the metallic particles. The addition of 0.2 wt.% Pd into 1.0 wt.% Pt increased the intensity of TPR signal significantly. That is, Pd increased the reducibility of the Pt particles, which might be due to the spiltover H_2 from Pd particles to Pt particles. The highest oxidation rate observed on the 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 seems to be due to the enhanced reducibility of Pt by the spiltover H_2 from Pd.

Another possible explanation for the highly active 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst in the presence of H_2 might be the production of H_2O_2. Pd–Pt bimetallic catalyst is known to produce H_2O_2 from a mixture of oxygen and hydrogen [31,32]. Hydrogen peroxide is a powerful oxidant that has been used to degrade harmful contaminants in wastewater, drinking water and soil. The decomposition of H_2O_2 under our reaction condition produces free radical intermediates, especially hydroxyl radical. This radical would be capable for reacting with a variety of organic compounds leading to either partial or complete degradation.

In order to observe the formation of hydroxyl radical a separate experiment in the absence of any reactive dye was carried out at the same reaction condition. Fig. 7 demonstrates the plots of the $HO^\bullet$ EPR signal intensity versus reaction time in the absence of H_2. The intensities of $HO^\bullet$ signal were nearly the same irrespective of the kinds of catalyst. The observed hydroxyl radical seems to be mainly formed through thermal activation of H_2O and O_2. Under the presence of H_2 (Fig. 8), however, remarkable increases of $HO^\bullet$ signal intensity were observed with the Pd–Pt/Al_2O_3 bimetallic catalysts. The $HO^\bullet$ intensity increased with increasing fraction of Pd in the Pd–Pt catalysts. These huge amounts of $HO^\bullet$ are believed to be formed from the decomposition of H_2O_2 which had been primarily produced from the reaction of H_2 and O_2 on the Pd–Pt/Al_2O_3 catalysts. Since the intensity of $HO^\bullet$ of the Pd-free Pt/Al_2O_3 catalyst was almost the same as that in the thermal reaction, Pd is essentially necessary for the formation of H_2O_2. The hydroxyl radical, which was produced through the decomposition of the primarily formed H_2O_2 on the Pd–Pt/Al_2O_3 catalysts, must have accelerated the oxidation rate significantly. Additional oxidation of the reactive dyes might be accomplished with hydroxyl radical. However, the role of hydroxyl radical is not predominant, because less amount of hydroxyl radical was formed on the most active 0.2 wt.% Pd–1.0 wt.%

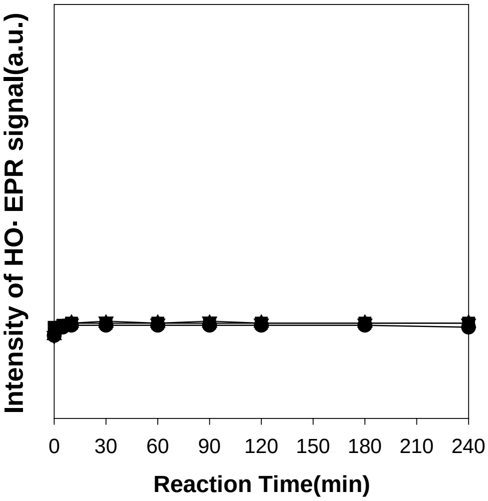


Fig. 7. Time dependence of $HO^\bullet$ formation during the reaction in the absence of H_2 with 1.0 wt.% Pt/Al_2O_3 (●), 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 (▲), 0.5 wt.% Pd–1.0 wt.% Pt/Al_2O_3 (▼), 1.0 wt.% Pd–1.0 wt.% Pt/Al_2O_3 (■) catalyst.

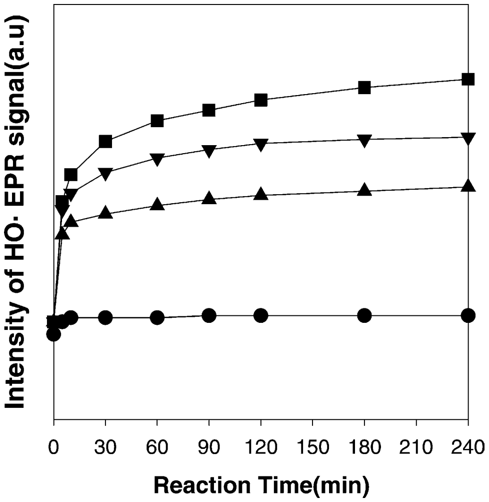


Fig. 8. Time dependence of $HO^\bullet$ formation during the reaction in the presence of H_2 with 1.0 wt.% Pt/Al_2O_3 (●), 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 (▲), 0.5 wt.% Pd–1.0 wt.% Pt/Al_2O_3 (▼), 1.0 wt.% Pd–1.0 wt.% Pt/Al_2O_3 (■) catalyst.

Pt/Al_2O_3 catalyst. Although quantitative discrimination between the roles of faster redox cycle and H_2O_2 is not clear at present, the observed extremely high wet oxidation activities of the Pd–Pt/Al_2O_3 bimetallic catalysts must be due to the combined roles of the faster redox cycle and H_2O_2 formation.

A continuous flow tubular reactor was employed for the treatment of a real effluent produced from the washing process of a certain dyeing industry. In order for dyeing textile substrate the industry had used the aqueous solution of the mixture of reactive black 5, reactive blue 19 and reactive red 198. In addition small amount of some penetrating agents together with NaOH were contained in the effluent. The dark black reddish effluent had TOC value of 7300 mg/l and its color unit was 4900. 100 g of the 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst was loaded inside the reactor, and the liquid hourly space velocities of the effluent were 3600, 4800 and 9600 h^{-1}. 92% of TOC and 95% of color were removed at the 9600 h^{-1} space velocity. At the velocity of 3600 and 4800 h^{-1} complete removal of both TOC and color was achieved.

4. Conclusion

Addition of small amount of H_2 together with oxygen could increase the wet oxidation activity of the bimetallic catalyst, especially 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst, significantly. Palladium in the Pd–Pt/Al_2O_3 catalysts provided Pt with the spiltover H_2, thereby increasing the reducibility of Pt. The reduced Pt surface gave organic reactive dye molecule higher chance of adsorption under the competition with the excess oxygen. In addition the Pd–Pt/Al_2O_3 catalysts produced H_2O_2 from the H_2/O_2 mixture, and hydroxyl radical was formed through the subsequent decomposition of H_2O_2. The extremely high oxidation activities of the Pd–Pt/Al_2O_3 catalysts was believed to be due to the combined roles of the faster reduction of the catalyst surface and the production of hydroxyl radical from the decomposition of the primarily formed H_2O_2. A real effluent from a dyeing industry could successfully be treated in a continuous flow reactor through the CWO on the 0.2 wt.% Pd–1.0 wt.% Pt/Al_2O_3 catalyst with H_2/O_2 mixture. Complete removal of both TOC and color was achieved at the space velocities lower than 4800 h^{-1}.

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