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# Pd-based catalysts for catalytic wet oxidation of combined Kraft pulp mill effluents in a trickle bed reactor

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## Abstract

Catalytic wet oxidation of combined pulp mill effluents was studied in a trickle bed reactor. Two types of supported Pd-based catalysts, eggshell and uniform catalysts, and a supported Pd–Pt uniform catalyst were employed. Supported Pd catalysts showed high activity for total organic carbon (TOC) and color removal at temperatures of 353–448 K and 1.84 MPa. Compared to uniform catalysts, the eggshell catalysts with a 0.2 wt.% Pd loading show promise for treatment of combined pulp mill effluents. High activity for TOC and color removal can be attributed to the high density of active Pd sites in the shell area and to the decrease of diffusion path for reactants and intermediates. No apparent deactivation of eggshell catalysts was observed after 40 h on stream. Potential application of the supported Pd catalysts for treatment of combined pulp mill effluents is discussed. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Catalytic wet oxidation; Pd catalysts; Trickle bed reactor; Pulp and paper effluents; Wastewater treatment

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## 1. Introduction

Effluents from pulp and paper industries impose coloration and toxicity problem in the receiving waters, causing serious environmental hazards. The toxicity of the pulp mill effluents is mainly due to the phenolic nature of organic components contained in the effluent streams, such as chloro-, thio-, and alkali-lignin [1], various resin acids [2], these compounds are considered to be extremely toxic to aquatic life and generally resistant to biological degradation treatment. It has been shown that more than half of the COD in the pulp and paper effluents is likely to be of non-biodegradable [3]. The dark brown color associated with the effluents is primarily due to the chromophores existing in lignin and its various derivative structures [1,4]. The problem of color removal from pulp mill effluents has been a subject of research for the last few decades. Chemical oxygen demand (COD), absorbable organic halides (AOX) and color of the pulp and paper effluents are major parameters to be controlled in order to meet the increasingly stringent discharge regulation [5]. Conventional technologies, such as incineration, biological treatment (activated sludge), coagulation and flocculation treatment are not satisfactory for effectively removing both toxic organic compounds and color from the pulp and paper effluents either due to the economic reason or the limitation of the technologies [3,6–8]. Wet air oxidation (WAO) process has been used as an alternative technology for treatment of pulp mill effluents [7,8]. In WAO process, the organic pollutants in pulp mill effluents are converted into carbon dioxide and low molecular weight carboxylic acid, mainly acetic acid. However, high capital costs and safety implications resulting from the high operating temperatures (400–573 K) and

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pressures (0.5–20 MPa) greatly limited the application of WAO technology. Catalytic wet oxidation (CWO) technology is an upgraded WAO, with the incorporation of the suitable catalysts, the CWO process can be carried out at much milder temperature and pressure conditions, thus reducing the capital costs and corrosion. Many heterogeneous metal oxide catalysts, such as alumina supported CuO, $Fe_2O_3$, MnO, ZnO, NiO, and $TiO_2$ supported Ru, etc. have been studied for oxidation of model organic compounds, such as phenol, chlorophenol, carboxylic acids [9–15]. It was reported that metal oxide catalysts (CuO, $MnO_2$, ZnO) were only nominally effective for WAO of black liquors from pulp and paper mills [8]. Our previous studies in a laboratory slurry reactor have shown that supported Pd-based catalysts are very effective for removing both TOC and color in the effluent streams from Kraft pulp mills [16–18,20]. It is evident that the development of active, cheap and stable catalysts is crucial to the commercialization of CWO technology. This study was aimed to optimize supported Pd catalyst and test the activity for TOC and color removal of the combined effluent streams from a Kraft pulp mill in a continuous trickle bed reactor. Combined effluent stream was used since our previous study has shown advantages of use of combined streams in reduction of corrosion, and metal leaching from the catalyst. In this study, stability of supported Pd catalysts were also tested at 435 K and 1.84 MPa in a trickle bed reactor. Potential application of supported Pd catalysts for the treatment of combined pulp mill effluents is discussed.

## 2. Experimental

### 2.1. Catalyst preparation

Two types of alumina supported-Pd catalysts (uniform and eggshell) were prepared and used in this study. Activated $\gamma$-$Al_2O_3$ (BET surface area of 336 $m^2$/g, pore volume of 0.4078 ml/g, received as pellets) and ALON$^{TM}$ (BET surface area of 102 $m^2$/g, pore volume of 0.765 ml/g, received as fine powder, Cabot Corporation) were used as supports. To make the catalysts suitable for use in the trickle bed reactor, the activated $\gamma$-$Al_2O_3$ pellets were crushed to 20–35 mesh and ALON powder was mixed with hydrochloric acid aqueous solution (ca. 1.2 N) to form paste followed by drying and calcination at 773 K for 5 h. The calcined ALON was then crushed and screened to 20–35 mesh for use as support. It is shown that the mechanic strength of the ALON support can be improved by HCl treatment followed by higher temperature calcination. The uniform catalysts (1 wt.% Pd/$\gamma$-$Al_2O_3$ and 1 wt.% Pd/ALON) were prepared by incipient wetness impregnation of the supports with palladium chloride (Colonial Metals) aqueous solution. The supports were dried in a rotary evaporator at ambient atmosphere under an infrared light for 8 h followed by calcination in an oven at 623 K for 6 h. To prepare the supported bimetallic catalyst, Pt metal was introduced by impregnation of the calcined Pd-catalyst with a tetraammine platinum (II) nitrate solution (Pt 5.5 wt.%, Colonial Metals) followed by the same drying and calcination procedures. Our previous study showed that a small amount of Pt presented in the supported Pd catalysts has a positive effect on stability of the supported Pd catalysts for the oxidation of effluent from a Kraft pulp mill [18].

Two eggshell catalysts, 0.2 wt.% Pd/ALON and 0.2 wt.% Pd/$\gamma$-$Al_2O_3$, were prepared by a method developed by Lin and Chou [19]. Alumina supports were impregnated with a toluene solution of $Pd(CH_3COO)_2$. The obtained samples were then treated by the same procedures as described in the preparation of uniform catalysts. The eggshell configuration of the catalysts was confirmed with an optical microscopy. The average thickness of the outer shell was determined to be about 10 μm.

### 2.2. Combined effluents from a Kraft pulp mill

The feed wastewater used in this study was the combined effluents from DO and EOP stages in a Kraft pulp mill. Typical properties of these effluents are listed in Table 1. Precipitation occurred after the combination of EOP and DO effluents, thus the combined effluent was filtrated before fed into the liquid pump to avoid clogging.

### 2.3. Experimental procedures

The experimental setup is shown in Fig. 1. The trickle bed reactor consists of a stainless steel tube

Table 1
Properties of the effluents from DO and EOP stages of a Kraft pulp mill

| Samples | pH | Color units[a] | TOC (ppm) |
|---|---|---|---|
| DO | 1.85 | 3469 | ~800 |
| EOP | 11.12 | 2475 | 1300–1500 |
| Combined (DO:EOP = 1:1.10) | 7.0–8.2 | 3469 | 1000–1100 |

[a] Color measured at pH 7.6 ± 0.1.

(length 413 mm, ID 10.6 mm) with a thermocouple well in the center of the reactor. The reactor was packed in three layers: ceramic particles, catalysts and ceramic particles. Catalysts of particle size of 20–35 mesh were loaded in the constant temperature zone of the reactor (about 15 cm from the top of the reactor). Pure oxygen and the combined effluents flow concurrently downwards through the reactor. The effluent from reactor was condensed in a condenser and separated in a gas–liquid separator. The pressure was controlled by a back-pressure controller. Liquid samples were taken periodically from the separator after reaction system reached steady state.

### 2.4. Analysis

Total organic carbon (TOC) was analyzed with a TOC analyzer (Shimadzu 5050). Color of the liquid samples was measured according to the standard method based on the color match between the Kraft pulp mill effluents and the standard platinum–cobalt solution [21]. In the present work, the absorbances of the samples were measured using a Colorimeter (Cole & Parmer) at the wavelength of 460 nm, 1 color unit (CU) is equivalent to the absorption of light at the wavelength of 460 nm by 1 mg/l platinum in the platinum–cobalt standard solution. Before the measurement, the pH of the samples were adjusted with HCl or NaOH solution to 7.6 ± 0.1.

TOC conversion, $X_{\mathrm{TOC}}$ and color removal are, respectively, defined as

$$X_{\mathrm{TOC}} = [(\mathrm{TOC})_{\mathrm{in}} - (\mathrm{TOC})_{\mathrm{out}}]\frac{100}{(\mathrm{TOC})_{\mathrm{in}}},$$

$$\text{color removal} = [(\mathrm{CU})_{\mathrm{in}} - (\mathrm{CU})_{\mathrm{out}}]\frac{100}{(\mathrm{CU})_{\mathrm{in}}}$$

BET surface areas and the total pore volume of the catalysts were measured using Omnisorp 360 analyzer based on nitrogen adsorption.

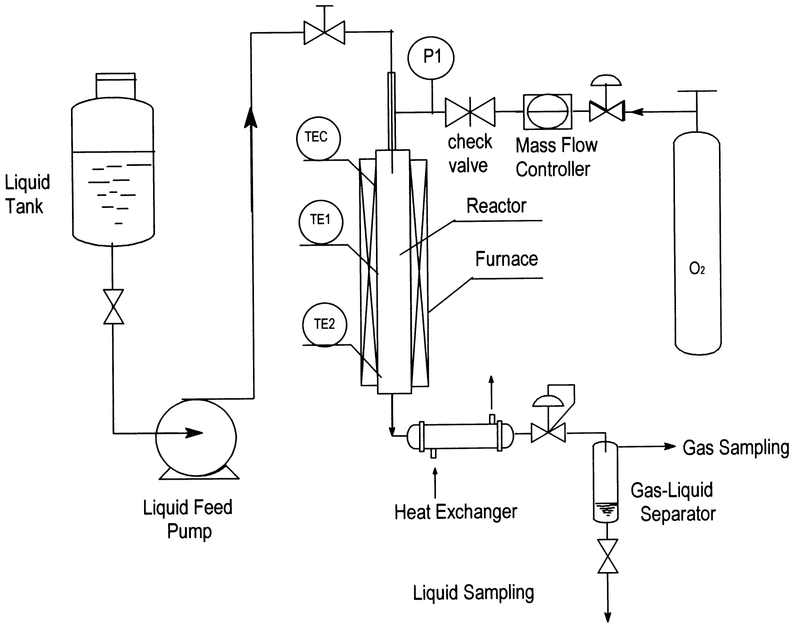

Fig. 1. Schematic diagram of experiment equipment.

## 3. Results and discussion

### 3.1. TOC conversion over supported Pd catalysts

The influences of Pd metal loading and supports on TOC conversion of the combined effluents are shown in Fig. 2. All Pd catalysts showed much higher activity than non-catalytic ceramic particles. Without a catalyst, the TOC conversion is only 8.85% at 432 K and 1.84 MPa, which indicates that non-catalytic oxidation has a very limited contribution to the total TOC removal. At lower temperatures eggshell catalysts with only 0.2 wt.% Pd loading exhibited same level of TOC conversion as that of uniform catalysts, as the temperature increase the difference of TOC conversion among these catalysts becomes increasingly evident, catalysts with higher Pd loading showed higher TOC conversion.

Combined Kraft pulp mill effluents is a very complex system which contains pulp chemicals and substituted lignin-related organic polymeric compounds. Catalytic oxidation of organic components in such a complicated mixture is a multistep reaction involving various reactants and intermediates. It is generally accepted that larger organic molecules will be oxidized in a CWO process to smaller intermediates and followed by the further oxidation of the intermediates to end products, usually acetic acid, $CO_2$ and water. At low temperatures, the overall oxidation rate was lower and oxidation of larger organic compounds to smaller intermediates might dominate in the process. It is reasonable to speculate that oxidation of larger organic compounds mainly took place on those active Pd sites located on the outer surface area of the catalyst particles. For 0.2 wt.% Pd eggshell catalysts with a shell thickness of about 10 μm, the average local Pd content in the shell area is 2.2 wt.% and over 90% of the particle volume contains no Pd metal. The higher density of Pd active sites and shorter diffusion path in the thin shell area appeared to favor oxidation of larger organic compounds. Hence the observed TOC conversion was higher with uniform catalysts at higher temperatures. The dependence of TOC conversion on temperature suggested that the active Pd sites on outer surface or large pores of the catalysts and the active sites in the internal pores of the catalysts might play

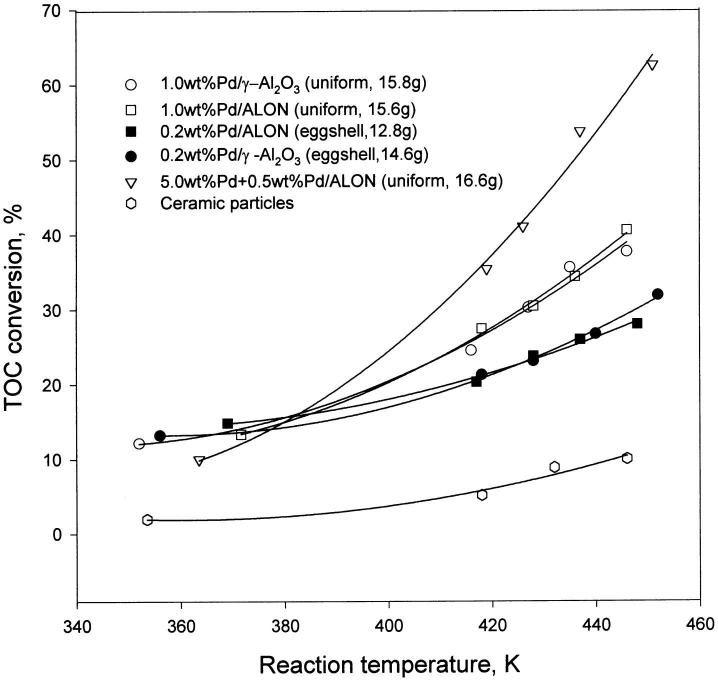

Fig. 2. TOC conversion over different supported Pd catalysts at 1.84 MPa and LHSV of 12.3 $h^{-1}$.

different roles in the oxidation of organic compounds in the pulp mill effluents. The Pd in the shell might be responsible for the conversion of large organic compounds and the Pd in the internal pores might be useful for the further oxidation of smaller organic compounds or intermediates. It is known that larger organic compounds in pulp mill effluents mainly consist of lignin-related polymeric compounds that contribute to color of the effluents. It is expected that eggshell catalysts with high concentration of Pd on the outer layer of the catalyst particles should be more effective for the color removal, which was confirmed by the color removal results discussed below.

### 3.2. Color removal over supported Pd catalysts

Fig. 3 presents color removal results over different supported Pd catalysts. Over 60% of color removal was obtained with all Pd catalysts at 435–440 K. The color removal efficiency of eggshell catalysts is superior to other supported Pd catalysts. Although the exact nature of the color-causing structures of Kraft lignin is still uncertain, it is believed that the chromophoric structures, such as CH=CH double bonds conjugated with the aromatic ring and quionemethids and quinones are responsible for the color of the Kraft lignin [1,4]. Hence, color removal is closely related to the destruction of these larger chromophoric organic components. Eggshell catalysts with active metal concentrated in the thin shell area provided more accessible oxidation sites for these larger molecule than that of uniform catalysts, therefore demonstrated the highest color removal efficiency among the tested Pd catalysts in oxidation of the combined pulp effluents. At higher temperatures (above 373 K), further oxidation of intermediates to mineralized end products may be favorable over the uniform catalysts. However further oxidation of intermediates contributes only to the TOC conversion not color removal, since the latter is only related to conversion of large lignin type molecules. To further illustrate the effect of Pd distribution on the oxidation of combined effluents over uniform and eggshell Pd catalysts, overall TOC and color removal rates based on per gram Pd were given in Fig. 4. Eggshell catalysts showed the highest activity among the tested Pd catalysts based on TOC and color removal rates per gram Pd. At 440 K and 1.84 MPa, TOC removal rate over eggshell catalysts

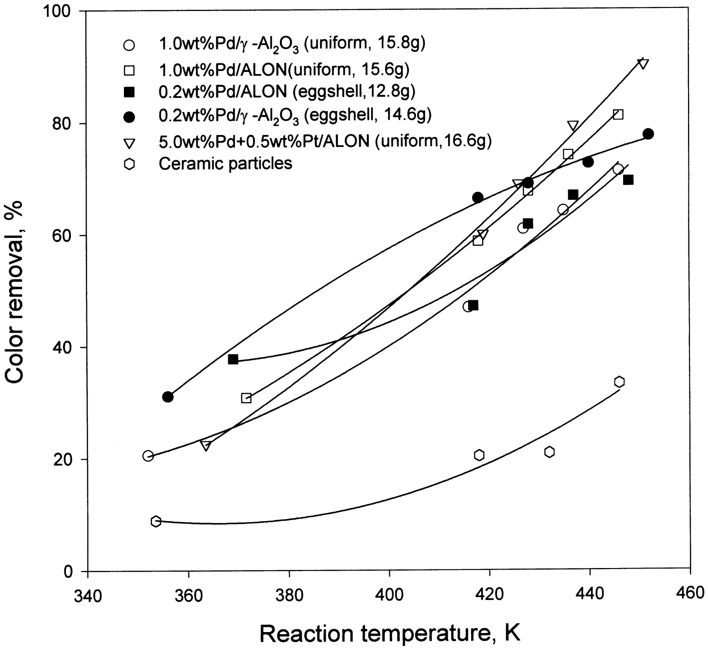

Fig. 3. Color removal over supported Pd catalysts at 1.84 MPa and LHSV of 12.3 $h^{-1}$.

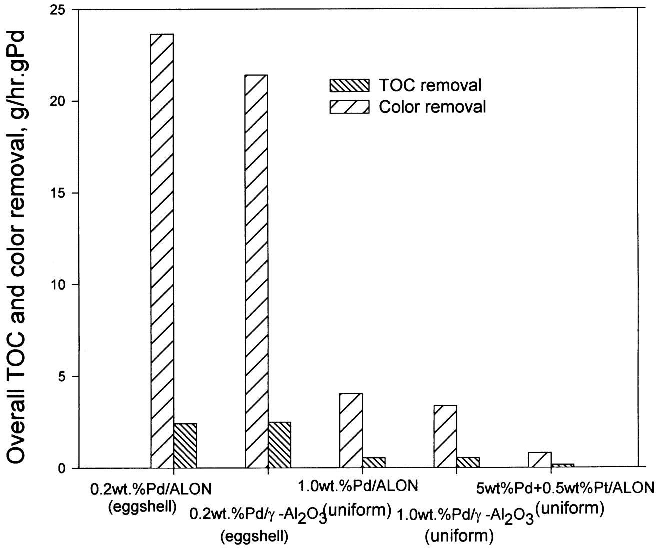

Fig. 4. Overall TOC and color removal at 440 K and 1.84 MPa. LHSV: 12.3 $h^{-1}$, $O_2$ flowrate: 1.13 $dm^3$/min (STP).

is about 4.5 times that of 1 wt.% Pd uniform catalysts and 15 times that of 5 wt.% Pd uniform catalysts. The color removal rate over eggshell catalyst is about five times that of 1 wt.% Pd uniform catalysts and 25 times that of 5 wt.% Pd uniform catalyst, respectively. These results clearly show that eggshell catalysts are very effective in oxidative destruction of color related large organic compounds in the combined pulp mill effluents, since color related organic compounds in the pulp mill effluents are often known as non-biodegradable. CWO process with eggshell catalysts provides an effective means for pretreatment of pulp mill effluents. It is expected that CWO pretreatment will significantly improve the biodegradability of the effluents.

### 3.3. Stability of the catalysts

No significant decreases in TOC conversion and color removal were observed over 0.2 wt.% Pd/ALON, 1.0 wt.% Pd/ALON and 1.0 wt.% Pd/$\gamma$-$Al_2O_3$ at 435 K, 1.84 MPa for 20 h (Fig. 5). The 0.2 wt.% Pd/ALON eggshell catalysts exhibited remarkable stability during a 20 h on stream. To further evaluate the stability of this catalyst, additional experiment were carried out under higher LHSV of 30 $h^{-1}$. It is interesting to notice a slight increase in the activity at a high liquid feed flowrate of 11 $cm^3$/min (Fig. 6). No apparent deactivation was observed during the subsequent 20 h testing period. For the uniform catalysts, a slight decrease in TOC conversion was observed (Fig. 5). Less than 7% decrease in color removal was also observed with two uniformly Pd catalysts. It was found that brown polymer-like compounds were formed on surface of the used catalysts. The pH of effluent water resulted from catalyst washing with hot deionized water was much greater than that of the liquid feed indicating the formed polymer like compounds might result from partial decomposition of alkali Kraft lignins. No apparent effect of these intermediates on gaseous end-products ($CO_2$ and $H_2O$) were observed with this catalyst. Compared to the fresh catalysts, slight decrease in BET surface area of two uniform catalysts occurred (Table 2). However, an unexpected slight increase in BET surface area and total pore volume was observed with the used 0.2 wt.% Pd/ALON egg-shell catalyst. It is not clear what caused the increase in the BET surface area. The slight increase of BET-surface area for spent Pd/ALON catalyst has also been observed in our previous studies and XRD results showed that BET surface area increase is related to the change of ALON in the wet oxidation atmosphere [22].

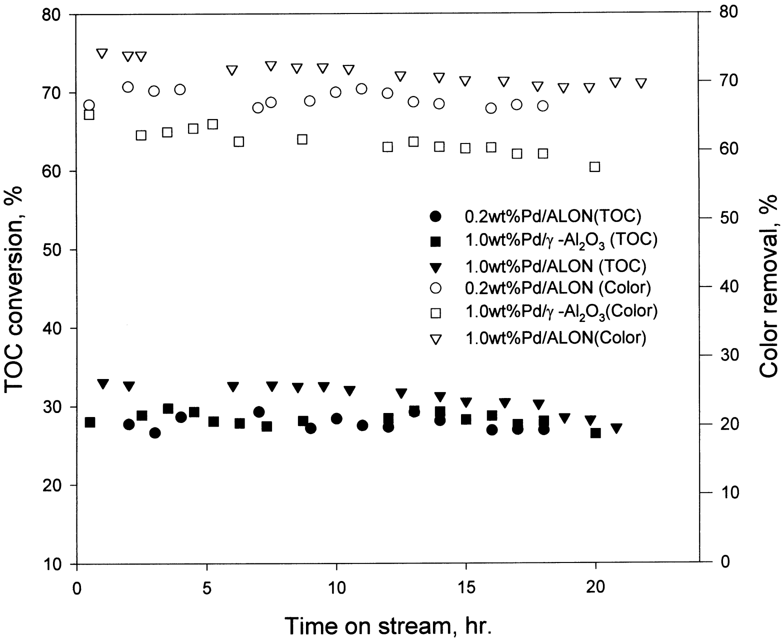

Fig. 5. Stability of supported Pd catalysts at 435 K and 1.84 MPa. LHSV: 12.3 h$^{-1}$, $O_2$ flowrate: 1.13 dm$^3$/min (STP), catalyst loading: 0.2 wt.% Pd/ALON, 12.8 g; 1.0 wt.% Pd//γ-$Al_2O_3$, 16.61 g; 1.0 wt.% Pd/ALON, 15.63 g.

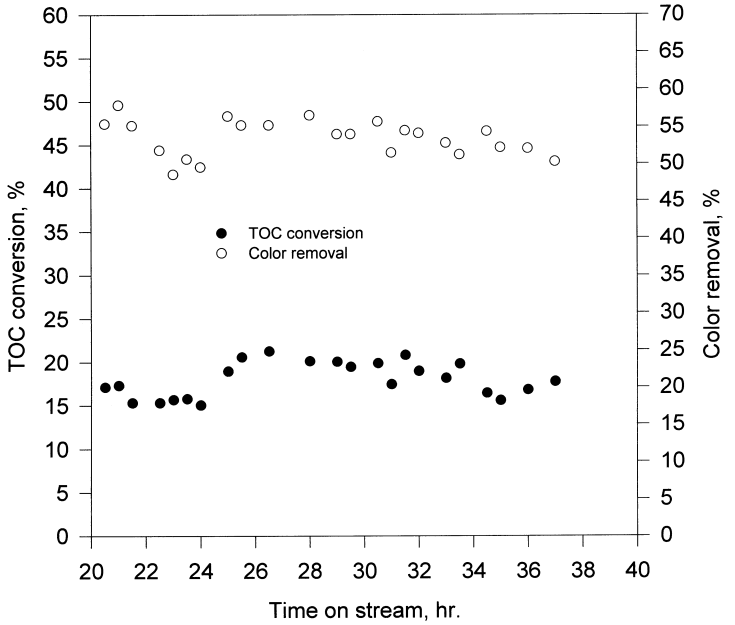

Fig. 6. Further test of 0.2 wt.% Pd/ALON catalyst at 436 K and 1.84 MPa. LHSV: 30 h$^{-1}$, $O_2$ flowrate: 1.13 dm$^3$/min (STP), catalyst loading: 12.8 g. Catalyst was used at 435 K for 20 h.

Table 2
BET surface area of fresh and used catalysts

| Samples | BET (fresh) ($m^2$/g) | BET (used) ($m^2$/g) | Total pore volume (fresh) (ml/g) | Total pore volume (used) (ml/g) |
|---|---|---|---|---|
| 0.2 wt.% Pd/ALON | 95.49 | 121.25 | 0.8816 | 0.9206 |
| 1.0 wt.% Pd/ALON | 94.429 | 78.175 | 0.6022 | 0.4583 |
| 1.0 wt.% Pd/$\gamma$-$Al_2O_3$ | 270.57 | 264.16 | 0.4831 | 0.4402 |

## 4. Conclusions

- Alumina supported Pd catalysts are very active for reduction of TOC and color of the combined pulp mill effluents from Kraft pulp mills.
- Eggshell catalysts with a Pd loading of 0.2 wt.% show promise for treatment of combined pulp mill effluents. High activity for TOC and color removal can be attributed to high density of active Pd sites in shell area and decreased diffusion path for reactants and intermediates to the active sites.
- No apparent deactivation was observed with the supported Pd catalysts after 20 and 40 h lifetime tests in a continuous trickle bed reactor. These results clearly indicate the advantages of the combined treatment of pulp mill effluents.

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