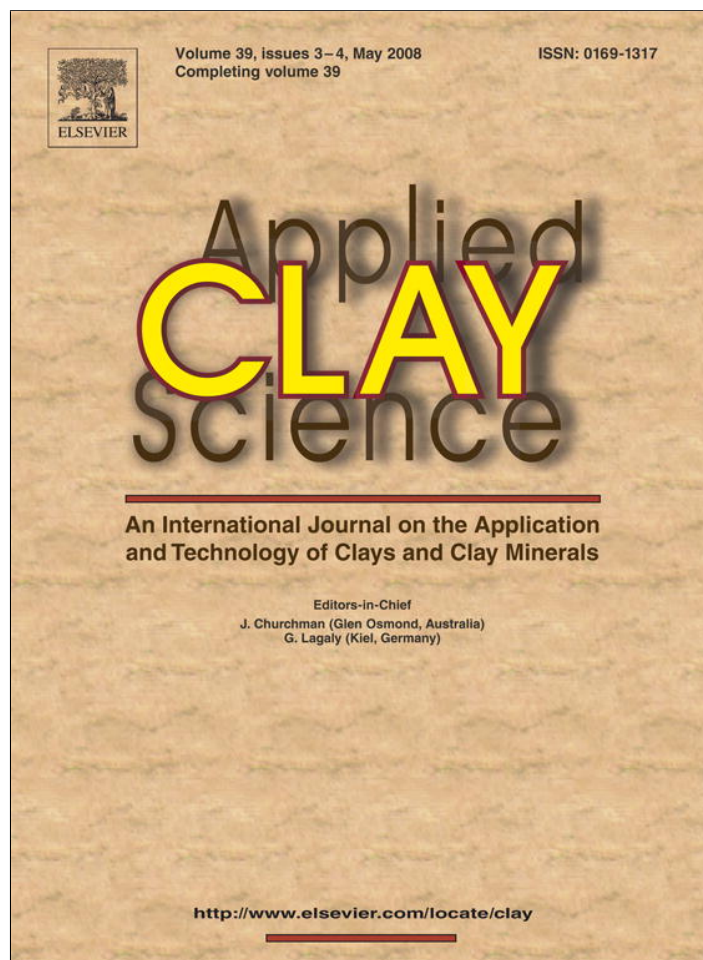


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# Catalytic oxidation of aromatic VOCs with Cr or Pd-impregnated Al-pillared bentonite: Byproduct formation and deactivation studies

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## Abstract

The catalytic behavior of chromium and palladium-impregnated Al-pillared bentonite for the oxidation of aromatic VOCs, i.e. chlorobenzene or xylene, was investigated. The Cr-impregnated bentonite showed high activity for the total oxidation of chlorobenzene and xylene but the materials were completely deactivated during the reaction at 600 °C. Atomic absorption, XPS, XRD and TG analyses suggested three main causes for the deactivation, i.e. the loss of Cr due to the formation of volatile  $\text{CrO}_2\text{Cl}_2$ , a strong decrease on the surface area due to the collapse of the pillars and the formation of coke. For the Pd supported pillared bentonite, the impregnation procedure completely destroyed the Al-pillars but produced a very active and stable catalyst to oxidize aromatic contaminants. However, in the case of chlorobenzene almost 20% yield of the hazardous hexachlorobenzene was obtained likely by an oxychlorination process.

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**Keywords:** Pillared clay; Bentonite; VOC oxidation

## 1. Introduction

Many volatile organic compounds (VOC), particularly chlorinated hydrocarbons, widely used in the chemical industry as organic solvent, in dry cleaning and degreasing processes, very often represent serious environmental hazards (Yim et al., 2000). The current technology for the destruction of chlorinated hydrocarbons is the complete oxidation by thermal incineration. However, the incineration process shows several drawbacks such as the need of high temperatures, ca. 1000 °C, high consumption of fuel, high operational

costs, the need of special incinerators resistant to oxidizing chlorine species formed in the combustion and the formation of highly harmful by-products including nitrogen oxides, phosgene, chlorodioxins and chlorodibenzofurans produced by incomplete combustion.

Several studies have investigated the catalytic oxidation as an alternative to the incineration process for the destruction of VOC, specially chlorinated hydrocarbons. The catalytic oxidation can be highly efficient for the total oxidation avoiding the formation of harmful byproducts. The catalytic reaction is an energy-efficient low cost process and can be carried out at much lower temperatures avoiding the formation of  $\text{NO}_x$ . There have been numerous studies on the catalytic oxidation of several organic compounds using different materials based on noble metals and transition metal oxides, bulky

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and supported, as catalysts (Spivey, 2005; Auer and Hofmann, 1993).

Chromium oxides supported on different materials such as  $\text{Al}_2\text{O}_3$  (Sainio et al., 2005, Feijen-Jeurissen et al. 1999), zeolites (Kawi and Te, 1998) and  $\text{SnO}_2$  (Solymosi et al., 1995) were reported to be effective for the removal of chlorinated hydrocarbons (Padilla et al., 1999). Chromium oxide supported over pillared bentonite was also investigated as support for oxidation catalysts due to their high surface area, porous structure and acidity (Sterte, 1988; Jagtap and Ramaswamy, 2006; Bradley and Kydd, 1993, Oliveira et al., 2003).

We focused on Cr and Pd supported Al-pillared bentonites (where Al means Al oxy-hydroxy oligomers) comparing three important aspects: (i) the oxidation of aromatic contaminants, with and without chlorine, (ii) the formation of harmful chloro-containing byproducts and (iii) the deactivation process.

## 2. Experimental

### 2.1. Methods and techniques

X-ray powder diffraction (XRD) patterns of the catalysts were obtained in a Rigaku Geigerflex,  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) with 40 kV and 35 mA in an angle interval of  $2 < 2\theta < 60$ . Nitrogen adsorption isotherms were obtained with a nitrogen sorptometer Micromeritics ASAP-2000. The microporous region data were calculated with the equation of Harkins and Jura, and the total pore volume was determined with the Gursvitch rule (applied at  $p/p^0 = 0.98$ ). The samples (0.3–0.8 g) were previously degassed at 300 °C during approximately 18 h and then studied at  $-196 \text{ }^\circ\text{C}$ . The TPR analysis was made with a Quantacrome equipment model CHEMBET 3000, with a gas total flow of  $40 \text{ mL min}^{-1}$  (5%  $\text{H}_2/\text{N}_2$ ). XPS data were obtained by KRATOS Analytical XSAM 800 cpi ESCA equipped with a Mg anode (Mg  $\text{K}\alpha$  radiation, 1253.6 eV) and spherical analyzer operating at 15 kV and 15 mA. The oxidation of organic compounds was carried out in a fixed-bed continuous-flow reactor system (Fig. 1). The reactor was a quartz tube operated in the down-flow mode. The sample (30 mg) placed in a quartz tube was exposed to a flow of synthetic air ( $30 \text{ mL min}^{-1}$ ) in a saturator containing the organic compound. The temperature in the

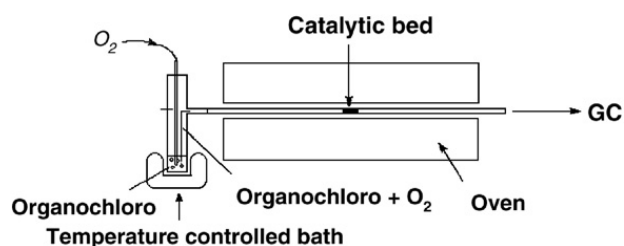


Fig. 1. Experimental set-up for the oxidation of the organic compounds.

Table 1  
XRD  $d_{001}$  values, specific surface area ( $S_{\text{BET}}$ ) and micro-pore volume ( $V_{\text{micro}}$ ) for the catalysts

Sample	$d_{001}/\text{\AA}$	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$V_{\text{micro}}/\text{cm}^3 \text{ g}^{-1}$
Original bentonite	13.1	22	0.004
Pilc	18.2	217	0.073
Cr-imp	17.1	156	0.050
Pd-imp	–	83	0.035

saturator was kept at 0 °C to produce a pressure of 4 mm Hg (or 0.57% of organic compound in volume). The products were analyzed on line in a chromatographic system (Shimadzu GC 17A) with capillary column Alltech Econo-Cap SE ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ ) and detector FID. The reactor effluent was passed through a fine-grained metallic iron to trap corrosive chlorine components, such as HCl and  $\text{Cl}_2$ .

### 2.2. Synthesis of the support

A natural bentonite ( $22 \text{ m}^2 \text{ g}^{-1}$ ; microporous volume =  $0.078 \text{ cm}^3 \text{ g}^{-1}$ ) from San Juan, Argentina, labeled “Original Bentonite”, was used as the starting materials. Mineralogical composition obtained by XRD showed the presence of 91 wt.% of montmorillonite, quartz (1 wt.%) and feldspar (5 wt.%).

The Al-oligocation prepared from  $0.2 \text{ mol L}^{-1}$  of  $\text{AlCl}_3 \cdot 6\text{-H}_2\text{O}$  solution and  $0.5 \text{ mol L}^{-1}$  of NaOH solution, with a molar relationship OH/Al = 2. The sodium hydroxide solution was added into the aluminum chloride solution, which was maintained under stirring at 40 °C. The resultant solution was aged at room temperature for 12 h. This solution was added by dropping into a suspension (15 g bentonite/400 mL de-ionized water). The sample was then washed in a dialysis membrane, dried at 60 °C and calcinated at 600 °C for 2 h. The resulting material was labeled PILC.

### 2.3. Catalyst preparation

The catalysts were prepared by impregnation of the pillared bentonite (1.0 g) with aqueous  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (10 mL; 0.13 mmol) or  $\text{PdCl}_2$  solution (10 mL, 0.21 mmol). After the impregnation the samples were dried for 24 h (110 °C) and calcined at 500 °C for 3 h. The Cr or Pd content was 5 wt.% and the catalysts were labeled as Cr-imp and Pd-imp, respectively.

## 3. Results and discussion

### 3.1. Catalyst characterization

XRD analyses (Table 1) showed that the  $d_{001}$  of 13 Å for the original bentonite increased to 19 Å after pillarization and decreased to 18 Å upon calcination at 600 °C (Fig. 2). This pillar process produced a

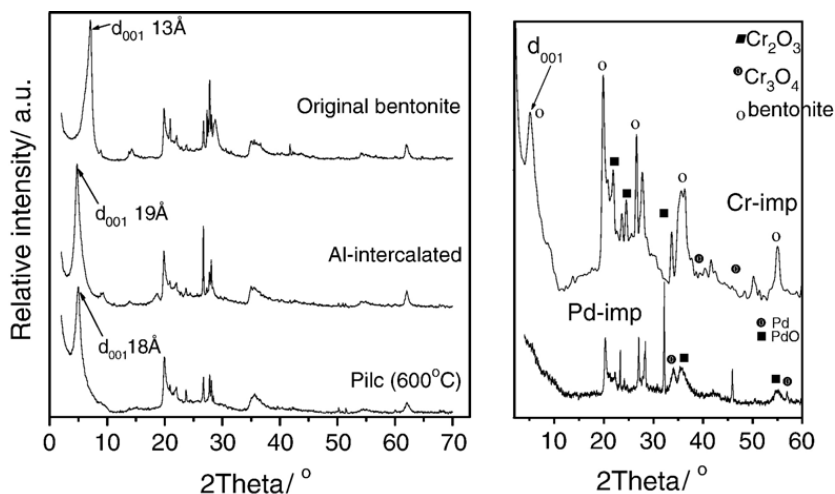


Fig. 2. XRD of the original bentonite, the bentonite intercalated with aluminum oligomer before calcination (Alsc) and after calcination at 500 °C (pilc).

remarkable increase in the surface area from  $22 \text{ m}^2 \text{ g}^{-1}$  to  $217 \text{ m}^2 \text{ g}^{-1}$ , with pore size distribution centered at about  $7 \text{ \AA}$  (Fig. 3a).

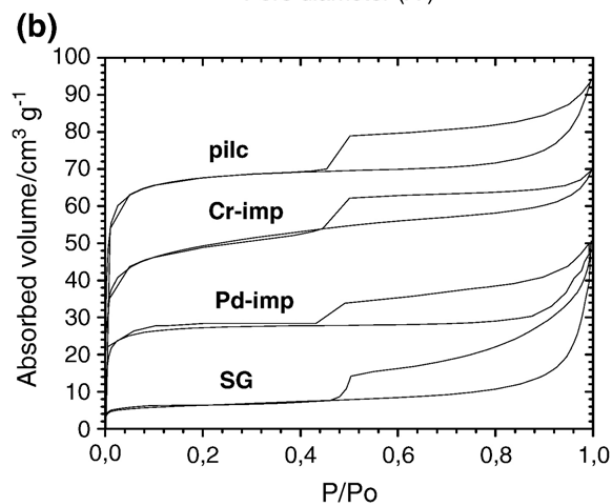
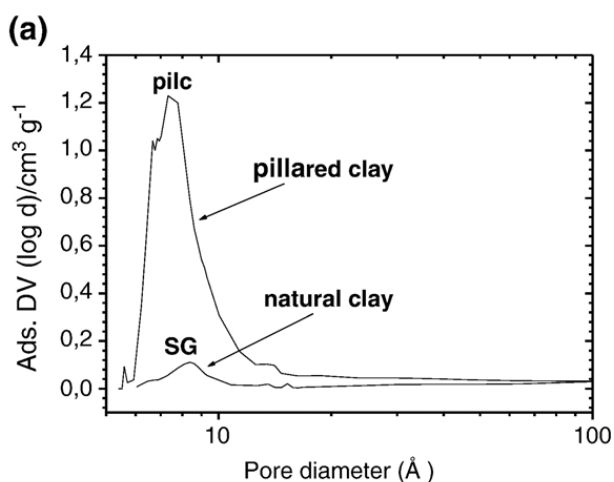


Fig. 3. Pore size distribution of pilc and SG (3a) and  $\text{N}_2$  adsorption/desorption isotherms of SG, pilc and catalysts (3b).

The XRD pattern showed that the impregnation does not affect significantly the pillared structure and low intensity Cr oxides phases ( $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_3\text{O}_4$ ) with  $d$  values of 3.62, 2.66, 1.67, 2.58 and 2.16 Å were observed.

The XRD for the palladium-impregnated bentonite clearly showed the collapse of the pillars. This is probably due to the strong acidity of the  $\text{PdCl}_2$  solution used in the impregnation. Similar results were obtained with  $\text{H}_2\text{PdCl}_4$ . XRD suggested the presence of  $\text{Pd}^0$  (2.98, 2.64 and 1.65 Å) and  $\text{PdO}$  (1.67 and 2.63 Å).

$\text{N}_2$  adsorption-desorption isotherms (Fig. 3b) showed that the incorporation of the Cr and Pd phases led to a decrease of the adsorbed volume in the microporous zone, especially for Pd-imp also suggesting the collapse of the pillars.

### 3.2. Catalytic studies

The catalytic oxidation studies were carried out using chlorobenzene as a probe molecule. The PILC (Al-pillared clay) and the original bentonite alone did not present any catalytic activity for the oxidation of chlorobenzene up to 600 °C (Fig. 4). The Cr or Pd-imp bentonites showed catalytic activity from 300 °C reaching more than 90% oxidation at 600 °C. If Cr or Pd were impregnated directly on the original bentonite without pillar a much lower activity was observed for both metals.

Based on GC analyses of the reaction products, organic by-products were not observed for the chromium catalyst, suggesting a complete oxidation to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$  and/or  $\text{Cl}_2$ . The reaction in the presence of Pd-imp resulted in a new GC peak and a white crystalline solid crystallized in the cold reactor exit. This white solid

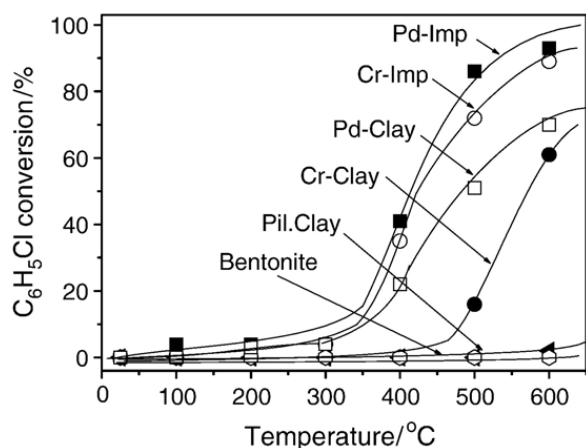


Fig. 4. Conversion of chlorobenzene in the presence of Cr-imp, Pd-imp, pilc and the original bentonite.

showed a melting point of 228–237 °C. <sup>1</sup>H RMN suggested the absence of protons whereas <sup>13</sup>C showed chemical shifts of 132 ppm suggesting only carbons bond

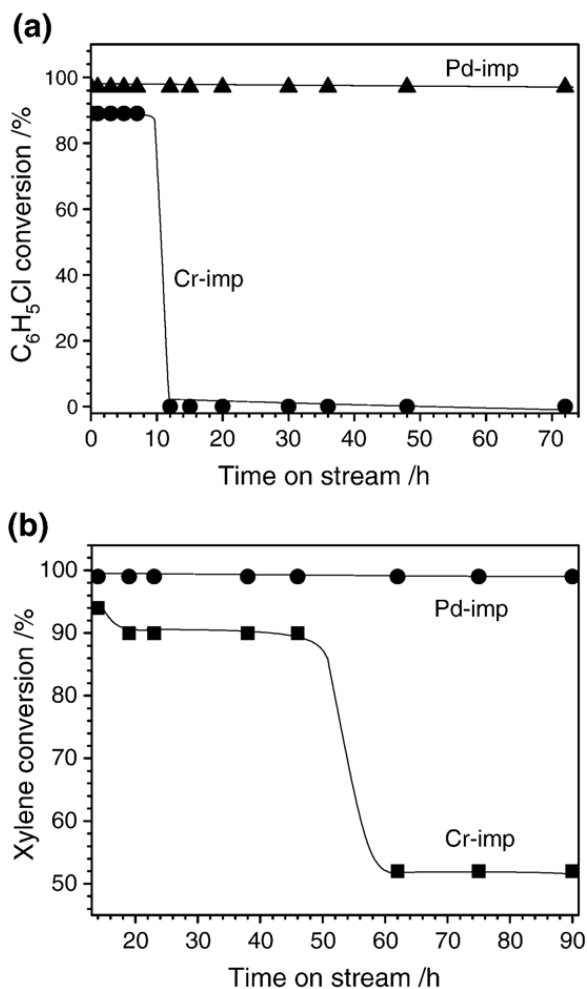


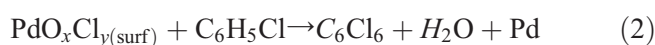
Fig. 5. Life time of the catalysts in the reaction with chlorobenzene (a) and xylene (b).

to chlorine. Elemental analysis showed approximately 25.8% of C with H of 0.1%. These results showed the formation of hexachloro benzene C<sub>6</sub>Cl<sub>6</sub>, which was also confirmed by FT-IR by the absorptions at 1350, 1300 and 700 cm<sup>-1</sup>.

Although the mechanism for the formation of the polychlorinated aromatic compound is not clear, the oxidation of chlorobenzene to CO<sub>2</sub>, H<sub>2</sub>O and HCl/Cl<sub>2</sub> can produce a palladium oxychloro surface species:



This Pd oxychloro species can then chlorinate chlorobenzene to hexachlorobenzene and water.



### 3.3. Deactivation of the catalysts

The catalytic activity of Pd-imp was maintained for more than 70 h during reaction with chlorobenzene or xylene. The Cr-imp catalyst was completely deactivated after 10 h reaction with chlorobenzene at 600 °C (Fig. 5).

Chromium catalyst before and after reaction showed a Cr 2p3/2 spectrum with two peaks, at ca. 579 eV for Cr(VI) and at 577 eV for Cr(III). After reaction with chlorobenzene the relative intensity of the signal 579 eV decreased suggesting that Cr(VI) species were consumed during reaction (Fig. 6). It has been suggested that Cr(VI) is the active catalytic species for the

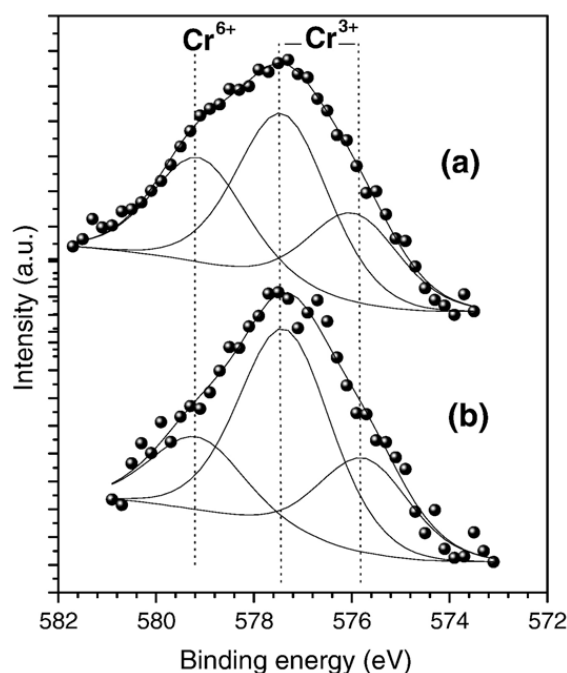


Fig. 6. XPS spectra of Cr-imp before (a) and after (b) reaction with chlorobenzene.

complete oxidation of chlorinated hydrocarbons (Storaro et al., 1997). The signals for Cr, Si and Al before and after reaction with chlorobenzene clearly showed that the ratio Cr/Si of 0.058 and Cr/Al of 0.084 decreased to 0.032 and 0.059, respectively. These results suggest that Cr surface concentration after reaction decreased to half of its initial concentration. In fact, Cr analyses by atomic absorption in the catalyst before reaction showed the presence of ca. 0.7% Cr that decreased to 0.5% after reaction.

The deactivation of the Cr-imp catalyst is at least partly due to the loss of the Cr(VI) active species from the surface. The HCl and Cl<sub>2</sub> formed can react with surface Cr species to produce the volatile compound CrO<sub>2</sub>Cl<sub>2</sub>.

To investigate the role of the chlorine on the catalyst deactivation a reaction with xylene was carried out. The catalyst Cr-imp was more stable during the reaction with xylene. However, after 46 h the catalyst deactivated rapidly suggesting that other deactivation processes not related to chlorine were present in the reaction. The dark color of the catalyst after reaction suggests the deposition of coke on the surface. In fact TG analysis of the catalyst after reaction showed a weight loss of approximately 0.3% between 350–450 °C likely related to carbonaceous deposits. Powder XRD analyses showed the complete disappearance of the *d*<sub>001</sub> reflection suggesting the collapse of the pillars. Although, the reasons for this collapse are not clear, the presence of water and the acidic species HCl at 600 °C should cause severe damage to the Al pillars. This collapse should be responsible for the strong decrease on the specific BET surface area of the catalyst to 30 m<sup>2</sup> g<sup>-1</sup>.

#### 4. Conclusion

The pillared montmorillonite with high specific surface of 217 m<sup>2</sup>g<sup>-1</sup> (pilc) produced an effective support to disperse catalytic active phases Cr and Pd by impregnation.

Chromium impregnated pillared bentonite showed high catalytic activity for the total oxidation. However, strong deactivation took place after several hours at 600 °C, due to: (i) loss of Cr from the catalyst surface, likely related to the formation of the volatile CrO<sub>2</sub>Cl<sub>2</sub>, (ii) coke formation, (iii) collapse of the pillars.

The Pd-imp catalyst showed a stable high catalytic activity for the conversion of chlorobenzene at 600 °C. However, the chlorobenzene was partially converted to hexachlorobenzene.

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