



# Effective Pd/C catalyst for chlorobenzene and hexachlorobenzene hydrodechlorination by direct pyrolysis of sawdust impregnated with palladium nitrate

S.V. Klokov<sup>a,b</sup>, E.S. Lokteva<sup>a,b,\*</sup>, E.V. Golubina<sup>a,b</sup>, K.I. Maslakov<sup>a,b</sup>, A.V. Levanov<sup>a</sup>, S.A. Chernyak<sup>a</sup>, V.A. Likholobov<sup>b</sup>

<sup>a</sup> Lomonosov Moscow State University, Chemistry Department, 1–3, Leninskie Gory, Moscow 119991, Russia

<sup>b</sup> Institute of Hydrocarbons Processing of the Siberian Branch of the RAS, 54, Neftezhavodskaya str., Omsk 644040, Russia,

## ARTICLE INFO

### Article history:

Received 8 October 2015

Received in revised form 30 December 2015

Accepted 15 January 2016

Available online 16 January 2016

### Keywords:

Pd catalyst

Sawdust

Hydrodechlorination

Hexachlorobenzene

Chlorobenzene

Pyrolysis

## ABSTRACT

Two Pd/C catalysts were prepared by pyrolysis of Pd(NO<sub>3</sub>)<sub>2</sub> impregnated sawdust. At equal pyrolysis time slow ramping with shorter isothermal heating resulted in 0.9 wt.% Pd/C-S1 sample comprising carbon support with some oxygen-containing moieties and Pd<sup>0</sup> with 2.6 nm average particle size (APS) partially decorated with carbon shell, whereas fast temperature ramping and long isothermal heating provided 0.6 wt.% Pd/C-S2 containing Pd<sup>0</sup> with 3.7 nm APS, with larger fraction of carbon decorated particles. Pd/C-S1 is slightly more efficient than Pd/C-S2 in gas phase chlorobenzene hydrodechlorination to benzene at 100–250 °C. Only Pd/C-S1 provides hexachlorobenzene hydrodechlorination in liquid phase due to lower APS and probably smaller PdC<sub>x</sub> content.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrodechlorination (HDC) is a very promising method of polychlorinated wastes disposal due to the intrinsic absence of polychlorinated dioxins in products, reduced energy demands and the possibility to reuse the hydrocarbon moiety of chlorinated compounds being disposed. Pd/C catalysts are between the most effective systems for HDC both in gas and liquid phases [1]. The process of Pd/C catalyst preparation by wet impregnation according to the “cradle-to-gates” Life Cycle Assessment based on the principles of Green Chemistry includes approximately six stages: pyrolysis of biomass to produce carbon material, its activation, impregnation with a palladium salt, drying, calcination and reduction. At least four stages (pyrolysis, physical activation, calcination and reduction) are energy demanding. Pd/C catalysts comprising carbonaceous support and nanoparticles of Pd<sup>0</sup> but with low S<sub>BET</sub> demonstrated good efficiency in chlorobenzene HDC [2]. These catalysts were prepared by thermal pyrolysis of sawdust impregnated with Pd(NO<sub>3</sub>)<sub>2</sub> to combine pyrolysis, calcination and reduction stages into one. In this work prolonged impregnation of sawdust with Pd(NO<sub>3</sub>)<sub>2</sub> water solution was used to increase S<sub>BET</sub> of resulting material.

Catalytic tests were performed in the gas phase HDC of chlorobenzene (CB) as a convenient model substrate, and in the liquid phase HDC of solid hexachlorobenzene (HCB) as an important environmental pollutant.

## 2. Experimental

Weighted amounts of birch (*Betula pendula*) sawdust sieved fraction (0.25–0.5 mm) were soaked for 3 days in Pd(NO<sub>3</sub>)<sub>2</sub> (JSC “Aurat”, Russia, C<sub>Pd</sub> = 464.6 g/l) acidic (pH = 3) water solution. The concentration and volume of solution was chosen to have no free water in wet sawdust after soaking, and to produce approx. 1 wt.% Pd loading in final catalysts after pyrolysis, using data from [2]. Then the wet samples were pyrolyzed in N<sub>2</sub> flow (15 ml/min) at 430 °C in the oven heated tubular quartz reactor. Two samples were prepared using the same overall pyrolysis duration (5.5 h) but different ramping time and isothermal stage duration: 2.5 h and 3 h for Pd/C-S1, 1.5 h and 4 h for Pd/C-S2.

Specific surface area, pore volume and average pore diameter were calculated from N<sub>2</sub> adsorption/desorption isotherms recorded on Autosorb-1 (Quantachrome Instruments, USA) analyzer. Scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDX) was performed on JEOL JSM-6390LA (JEOL Ltd., Japan).

Raman spectra were recorded by a Horiba Jobin Yvon LabRam HR 800 UV spectrometer (diffraction grating 300 l/mm) coupled to a light

\* Corresponding author at: Lomonosov Moscow State University, Chemistry Department, 1–3, Leninskie Gory, Moscow 119991, Russia.

E-mail address: [les@kge.msu.ru](mailto:les@kge.msu.ru) (E.S. Lokteva).

microscope Olympus BX41 using green radiation (514.532 nm) 50× objective, 10 mW laser source power, exposition time 50 s, and spectral resolution  $3.5 \text{ cm}^{-1}$ . Activated carbon BAU-A (Labtech, Russia) and graphite GL-1 (GraphitService, Russia) were used as comparative samples.

High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analysis are described in [3].

Pd content was found by atomic absorption spectroscopy (AAS) on iCE 3000 Series AA (Thermo Scientific, USA) spectrometer (acetylene flame) with SOLAAR software. Pd/C samples were solubilized by heating for 1 h in a mixture of  $\text{HNO}_3$  and HCl (1:3 vol.). The solution was filtered; filter cake was thoroughly rinsed by  $\text{HNO}_3$ , and the final solution was diluted to Pd concentration of  $\sim 0.1 \text{ mg/l}$ .

The gas phase hydrodechlorination (HDC) of chlorobenzene was performed in a fixed bed flow reactor as described in [2] with 8 mg catalyst loading. Stable-state CB conversions values were used to determine conversion vs. temperature dependence, so the duration of steady-state operation at each temperature was at least 90 min. The products were analyzed by GC on Agilent 6890 N (DBWAX, 30 m). The HDC of hexachlorobenzene was performed under multiphase conditions [4] at  $50^\circ\text{C}$ . Hydrogen (5 ml/min) was passed through the reaction mixture: 0.35 mmol of hexachlorobenzene in toluene, 0.26 mmol of Aliquat 336 (tricaprylmethylammonium chloride), 5% KOH aq. solution, 100 mg of a catalyst. During the reaction samples were taken from the organic phase at fixed intervals and analyzed by GC–MS on Trace DSQ II device (80 eV, DB-5 15 m column). Quantitative composition of the reaction mixture was determined by internal standard (undecane) technique. Selectivity of benzene formation ( $S_B$ ) was calculated as  $S_B = \frac{\nu_B}{\sum_{i=1}^6 i\nu_i}$ , where  $\nu_B$  and  $\nu_i$  are mole fractions of benzene and

product containing  $i$  chlorine atoms.

TOF value was calculated according to formula [5].

$$\text{TOF} = \frac{6 \cdot n_{\text{HCB}}}{t \cdot n_{\text{Pd}}} \left( 1 - \frac{\sum_{i=0}^6 iC_i}{6} \right),$$

where  $n_{\text{HCB}}$  and  $n_{\text{Pd}}$  are the initial amounts of HCB and Pd in the reaction mixture, mol;

$C_i$  is the molar amount of a product containing  $i$  chlorine atoms, mol;  
 $t$  is the reaction time, h.

The fraction of surface Pd atoms was assumed to be 69.4%, on the base of 2.6 nm APS in Pd/C-S1.

### 3. Results and discussion

Pd content, APS and porosity for Pd/C-S1 and Pd/C-S2 samples are presented in Table 1.

$S_{\text{BET}}$  values for both samples are about  $140 \text{ m}^2/\text{g}$ , which is significantly higher than those values ( $6.3 \text{ m}^2/\text{g}$ ) for samples prepared by the same technique using pyrolysis at  $400^\circ\text{C}$  but after short-time sawdust soaking by  $\text{Pd}(\text{NO}_3)_2$  solution [2]. Prolonged water treatment promotes the increase of pore size of wood material due to walls swelling, consequent disruption of the crosslinks between hemicelluloses and the

other components, and depolymerization of polysaccharides (predominantly hemicellulose) at low pH with further dissolution of fragments in water [6]. As the carbonaceous material produced by mild pyrolysis reproduces the texture of original wood [7], preliminary water treatment, especially at low pH values, can lead to an increase of its specific surface area.

Pyrolysis at  $300\text{--}450^\circ\text{C}$  provides carbon–carbon bond cleavage between lignin structural units [8]. At higher temperatures the remaining char undergoes further degradation. The yield of solid pyrolysis product in this work was about 30% at  $430^\circ\text{C}$ . SEM images (not presented) demonstrated that the carbon material formed during pyrolysis reproduced the texture of the original sawdust spreading in the direction of original tree growth and containing large pores. Uniform Pd distribution was found by SEM/EDX. Pd loading found by AAS (Table 1) is lower for Pd/C-S2 due to difference in pyrolysis conditions resulting in variation of carbon yield, but still close to desired value (1 wt.%).

Raman spectra of both samples (Fig. 1) contain G and D lines at  $1570\text{--}1585$  and  $1345\text{--}1350 \text{ cm}^{-1}$ , ascribed to the stretching of C–C bonds in the hexagonal rings [9] and the presence of defects in graphite structure respectively; and no  $G'$  band at  $2500\text{--}2800 \text{ cm}^{-1}$  caused by two-phonon scattering processes [10]. The presence of D line and the absence of  $G'$  line confirms that Pd/C-S1 and Pd/C-S2 contain amorphous carbon and no graphite [11]. This is corroborated by the value of intensity ratio ( $I_D/I_G$ ) that is about 0.5 for both samples, which is typical for activated carbons [12].

Unlike Pd/C-S2, Raman spectrum of Pd/C-S1 (Fig. 1) contains additional peaks at  $550\text{--}750$  and  $3250 \text{ cm}^{-1}$ , which may indicate the presence of incompletely pyrolyzed wood components.

The increase of background intensity at wavenumbers  $> 1000 \text{ cm}^{-1}$  was due to the fluorescence points to high H/C ratio [13–14]. Reduced ratio between background slope and  $I_G$  for Pd/C-S1 indicates the higher H content in comparison with Pd/C-S2. So, we believe that pyrolysis of Pd/C-S1 was incomplete, in contrast with totally pyrolyzed Pd/C-S2.

High resolution C1s and Pd3d XPS spectra for samples are presented in Fig. 2. Deconvolution of Pd/C-S2 C1s spectrum resulted in the main asymmetric peak at  $E_B = 284.5 \text{ eV}$  that is characteristic for  $\text{sp}^2$  carbon [15] with the small contribution from oxygen-containing functional groups. The presence of these groups is more pronounced in the spectra of Pd/C-S1 sample and sawdust impregnated with  $\text{Pd}(\text{NO}_3)_2$ . XPS showed higher O content in Pd/C-S1 (19.8%) in comparison with Pd/C-S2 (12.2%). Therefore XPS results are in good agreement with Raman study and confirm incomplete pyrolysis of Pd/C-S1 and nearly complete pyrolysis of Pd/C-S2.

Pd3d XPS spectrum of comparative  $\text{Pd}(\text{NO}_3)_2/\text{Sawdust}$  sample (Fig. 2b) contains a main doublet with the binding energy of  $\text{Pd}3d_{5/2}$  line at  $337.4 \text{ eV}$ , which is typical for  $\text{Pd}^{2+}$  species in  $\text{Pd}(\text{NO}_3)_2$ . Besides the main components in the spectrum the additional smaller doublet with the binding energy of  $\text{Pd}3d_{5/2}$  line at about  $335.3 \text{ eV}$  is clearly seen. Such binding energy is typical for  $\text{Pd}^0$  species [16]. The presence of a small amount of metal Pd in  $\text{Pd}(\text{NO}_3)_2/\text{Sawdust}$  sample may have resulted from  $\text{Pd}(\text{NO}_3)_2$  decomposition during XPS measurement. In contrast, deconvolution of Pd3d XPS spectrum for Pd/C-S1 sample shows only a doublet of narrow asymmetric lines corresponding to metal Pd. For Pd/C-S1 sample in addition to main lines of  $\text{Pd}^0$  the small contribution from PdO at  $336.3 \text{ eV}$  is observed. Thus both pyrolysis conditions provided very high degrees of Pd reduction on the surface of catalysts. The reduction of  $\text{Pd}^{2+}$  to  $\text{Pd}^0$  is not surprising since carbon

**Table 1**  
Pd content, APS found from TEM, and porosity of Pd/C samples.

Sample designation	Pd, wt.%	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$	Pore volume, $\text{cm}^3/\text{g}$	Average pore diameter, Å	Average Pd particle size (APS), nm
Pd/C-S1	0.9	135	0.092	18.3	2.6 <sup>1</sup>
Pd/C-S2	0.6	148	0.121	16.4	3.7 <sup>2</sup>

<sup>1</sup> based on 780 individual particles.

<sup>2</sup> based on 350 individual particles.

# دانلود مقاله



<http://daneshyari.com/article/49319>



- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات