

# Application of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst to remove diclofenac from water

## Zastosowanie katalizatora Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> do usuwania diklofenaku z wody

Bartosz Zawadzki, Monika Asztemborska, Emil Kowalewski, Krzysztof Matus, Anna Śrębowata<sup>\*)</sup>

**Keywords:** hydrodechlorination, diclofenac, palladium catalysts

### Abstract

Herein we investigate alumina-supported palladium catalysts' properties in water purification from diclofenac. Three different pretreatment conditions subjected Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared by incipient wetness impregnation. The resulting materials were characterized by CO chemisorption and TEM. We have shown that catalytic performance of 1 wt. % Pd/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in hydrodechlorination of diclofenac depends on the pretreatment conditions. The highest activity has shown palladium catalyst pretreated under the mildest conditions.

**Słowa kluczowe:** wodoroodchlorowanie, diklofenak, katalizatory palladowe

### Streszczenie

W niniejszej pracy zbadano właściwości katalityczne katalizatorów palladowych, osadzonych na  $\gamma$ -tlenku glinu, w oczyszczaniu wody z diklofenaku. Katalizator Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> przygotowany metodą suchej impregnacji i poddano trzem różnym warunkom obróbki wstępnej. Otrzymane materiały scharakteryzowano za pomocą chemisorpcji CO oraz TEM. Wykazaliśmy, że wydajność katalityczna 1 % wag. Pd/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> w wodoroodchlorowaniu diklofenaku zależy od warunków obróbki wstępnej. Największą aktywność wykazał katalizator palladowy poddany obróbce wstępnej w najłagodniejszych warunkach.

## Introduction

Surface water quality as a drinking water resource is essential to public health. Nowadays, the drinking water of millions of people comes directly or indirectly from rivers and lakes. Although the wastewater treatment plants (WWTPs) usually consist of physical, chemical, and biological processes to eliminate conventional contaminants from the effluents without harming the natural environment, they are not explicitly designed to eliminate micropollutants such as pharmaceuticals and personal care products (PPCPs). Thus, many of them can pass through wastewater treatment processes by persistency or/and continuous introduction, which has been documented and reported as an emerging environmental issue [1]. For example, the frequently detected anti-inflammatory medicine – diclofenac (2-[2-(2,6-dichloroanilino)phenyl] acetic acid is known to be refractory to natural biological degradation and conventional water treatments [2]. Diclofenac (DCF) adsorption onto the primary and secondary sludge accounted only for 5–15% and <5%, respectively. Approximately 95% still remained after 48–55 h of reaction under oxic and anoxic conditions [3]. Diclofenac presented in the water can cause oxidative stress and disturb metabolic processes in different groups of organisms. It can also contribute to DNA damage.

Additionally, it can cause histopathological changes in various organs and accumulate in them [4]. Toxicity tests indicated that diclofenac is harmful to the liver, kidney and gills of rainbow trout [5]. It also contributed to the extinction of vast amounts of wild vultures across the Indian subcontinent [6]. Since it has been shown to interfere

with the biochemical functions of fish and cause tissue damage at environmentally relevant concentrations, diclofenac may be considered one of the most relevant compounds with respect to the persistence of pharmaceuticals in the environment. According to the precautionary principle, the environmental input of such persistent and long-living, mobile compounds should be limited [7]. Therefore, based on the EU's Joint Research Centre Technical Reports, diclofenac is listed as one of the Commission's Priority Substances [8].

Accordingly, a great deal of effort is being made to find ways to deactivate or eliminate diclofenac in surface water and/or wastewater under near-neutral conditions [9]. However, diclofenac, as a chloroorganic compound, is particularly resistant to conventional oxidation, requiring longer reaction times than other pharmaceutical compounds [10]. Application of bioelectrochemical systems for degradation of the pharmaceutical micropollutants containing three different functional groups results in the breaking of the C-Cl bond, but the nitroso – or amine groups were formed [11]. Although applying microorganisms or enzymes for water purification gave promising results, this process is very slow and still a long way from a real application [12]. Similarly, the microwave radiation method: although the results are promising, high radiation power makes it impossible to apply this method on a big scale [13]. An attractive alternative to these methods can be hydrodechlorination (HDC) of diclofenac. In this process, hydrogen reacts with the pollutant to produce the corresponding hydrogenated chlorine-free product(s) and hydrochloric acid [14]. Therefore, HDC is an environmentally-friendly process which significantly reduces effluent ecotoxicity and avoids forming more harmful intermediates

<sup>\*)</sup> Bartosz Zawadzki, Monika Asztemborska, Emil Kowalewski, Anna Śrębowata, Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland, Krzysztof Matus, Materials Research Laboratory, Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland, Corresponding author: asrębowata@ichf.edu.pl

under ambient temperature and pressure [15]. First attempts of hydrodechlorination of chloroorganic pharmaceuticals at different real aqueous matrices (mineral, surface, tap waters and WWTP effluent, hospital wastewater) confirmed the effectiveness of this method in water purification. Application of HDC led to complete degradation of the micropollutants containing chlorine atoms in short reaction times, obtaining chlorine-free products and, thus, non-toxic effluents [16, 17]. However, finding an active, cheap and stable catalyst is essential.

Since hydrogen adsorbs excellently on Pd, this noble metal is the most often chosen as a catalyst for HDC reaction [18]. Regarding the support,  $\gamma$ - $\text{Al}_2\text{O}_3$  is one of the most popular support for palladium catalysts [19]. However, the pretreatment conditions strongly affect the activity of Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  in the hydroconversion of  $\text{C}_6$  alkenes [20].

Inspired by the results obtained for hydrocarbons conversion, we have investigated the effect of the pretreatment conditions on the catalytic performance of alumina-supported palladium in diclofenac hydrodechlorination. For comparison investigations, we used 4 catalytic materials: the catalyst after 3 h reduction at 400°C (red-400-Pd), the catalyst after calcination and reduction at 400°C (calc-red-400-Pd), the catalyst after calcination and 17 h of the reduction at 600°C (cal-red-600-Pd).

## Experimental part

### Synthesis method

1 wt.% Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  was synthesized by incipient wetness impregnation with the usage of  $\gamma$ -alumina, Puralox SCCa as support and an aqueous solution of palladium nitrate (supplied by Chempur, Piekary Śląskie, Poland) as a metal precursor. Incipient wetness impregnation was performed on a rotary beaker with simultaneous heating (with a standard 200 W infrared lamp) for 24 h until complete evaporation of the water. Afterwards, the material was separated into three portions and pretreated by different pathways. One portion was reduced in the flow of 25  $\text{cm}^3/\text{min}$  of 10%  $\text{H}_2/\text{Ar}$  at 400°C for 3 h. The second portion was calcined 3 h in 50  $\text{cm}^3/\text{min}$  of air flowing at 500°C and reduced 3 h at 400°C. The third portion was calcined under the same conditions as the second sample but reduced at 600°C. The obtained catalysts were labelled as red-400-Pd, calc-red-400-Pd and cal-red-600-Pd, respectively.

### Physicochemical characterization

Transmission Electron Microscopy (TEM) studies after the reduction of the catalysts were carried out using the electron microscope Titan G2 60–300 kV (FEI, Japan) equipped with EDAX EDS (energy-dispersive X-ray spectroscopy) detector. Electron microscopic studies were performed at an accelerating electron beam voltage equal to 100 keV or 300 kV, respectively. The samples were prepared by dispersing them in pure alcohol using an ultrasonic cleaner and placing a drop of the suspension on carbon films on copper grids.

CO chemisorption measurements were carried out according to the previously described static method [21] on ASAP 2020 Chem. Instrument.

### Catalytic reaction

Catalytic removal of diclofenac from the water was performed in a batch reactor at 30°C and under atmospheric pressure. The initial reaction mixture contained  $\sim 75 \text{ mg L}^{-1}$  DCF and 350 mL of MiliPore Water. Before adding DCF, water was saturated for 30 min with 60  $\text{cm}^3/\text{min}$  of hydrogen. For every run, the mass of the catalyst was 100 mg.

Every time the reaction progress was analyzed using the Waters Acquity UPLC system equipped with a PDA e $\lambda$  detector on a C18 column (3  $\mu\text{m}$ , 120 Å; 2.1  $\times$  50 mm) (Lumiseq, Poland). The isocratic analysis method with mobile phase (0.1% formic acid: acetonitrile 1:1 v/v) at the flow rate of 0.3 ml/min was used.

## Results and discussion

**Fig. 1** shows the microscopic images for three palladium catalysts. Independently on the pretreatment conditions, Pd nanoparticles of different sizes are well dispersed on the  $\gamma$ - $\text{Al}_2\text{O}_3$  surface. An advantage in the number of small particles shows the Pd catalyst pretreated only by the reduction at 400°C. Calcination at 500°C prior to reduction leads to changes in the Pd particle size distribution. Decreases the amounts of the particle in 2-3 nm in size and increases the amounts of the bigger > 4 nm. Extending the reduction time to 17 h at higher temperature results in the formation of the nanoparticles with an average size of around 9 nm.

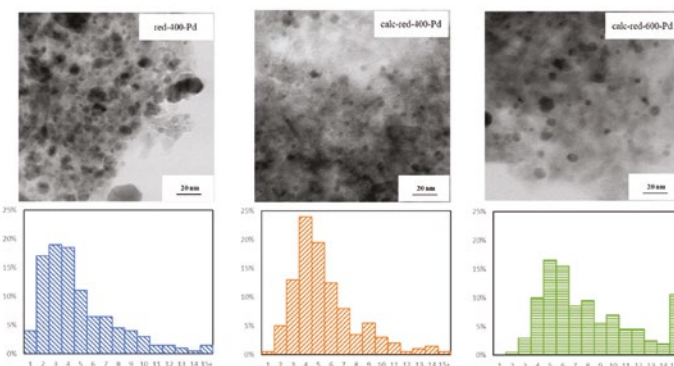


Figure 1. TEM images and palladium particles size distribution for 1 wt.%Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  pretreated under different conditions.

Moreover, **Tab. 1** contains the Pd particle size estimated by TEM and CO chemisorption measurements. Disagreement between values (Tab. 1) emerges from the fact that CO chemisorption determines real amounts of the active sites for reagent sorption, and TEM allows for identifying both accessible and inaccessible particles. However, the trend is maintained regardless of the used method (TEM or CO chemisorption). The particle size increases in order: calc-red-400-Pd < red-400-Pd < calc-red-600-Pd. The application of the long-term reduction at 600°C led to particles sintering.

Table 1. Influence of the pretreatment conditions on Pd particle size.

Sample	Palladium particle size (nm) estimated from	
	CO chemisorption	TEM
red-400-Pd	16.1	4.9
calc-red-400-Pd	15.0	5.5
calc-red-600-Pd	26.9	8.5

**Fig. 2** shows the diclofenac conversion in terms of  $C_{\text{DCF}}/C_{\text{DCF},0}$  versus time of reaction carried out in the presence of three palladium catalysts. Independent sorption experiments for  $\gamma$ - $\text{Al}_2\text{O}_3$  and Pd catalysts did not show sorption ability (results not shown). Independently on the pretreatment conditions, all catalysts based on 1 wt.% Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  show activity in catalytic hydrodechlorination of diclofenac. However, catalytic results reveal differences between the palladium catalysts.

The best results were obtained for the red-400-Pd catalyst. After 150 min of reaction, almost all diclofenac (98%) was removed from the water when a palladium catalyst pretreated under mild conditions. On the other hand, the catalyst calcinated and reduced 17 h at 600°C showed better diclofenac conversion than the analogous catalyst reduced at a lower temperature. This means that not only the average Pd particle size determines these materials' catalytic behaviour. Following earlier studies, the coexistence of smaller and bigger nanoparticles with different affinity to hydrogen and chloroorganic compound and the specific ratio between their distribution results in the high efficiency

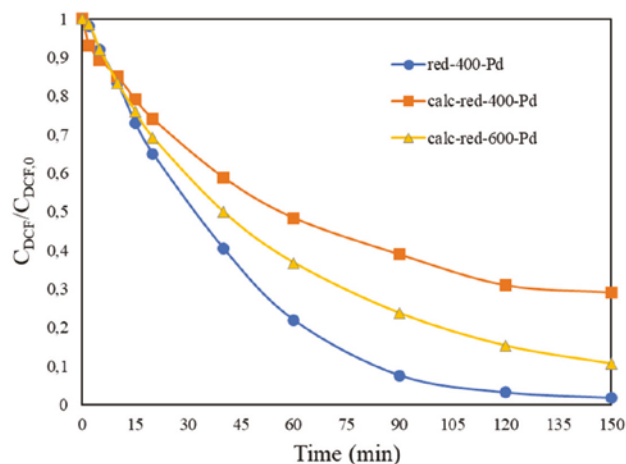


Fig. 2. Kinetic studies of diclofenac hydrodechlorination reaction in the presence of Pd catalysts (30°C, atmospheric pressure, 75 mg L<sup>-1</sup> DCF).

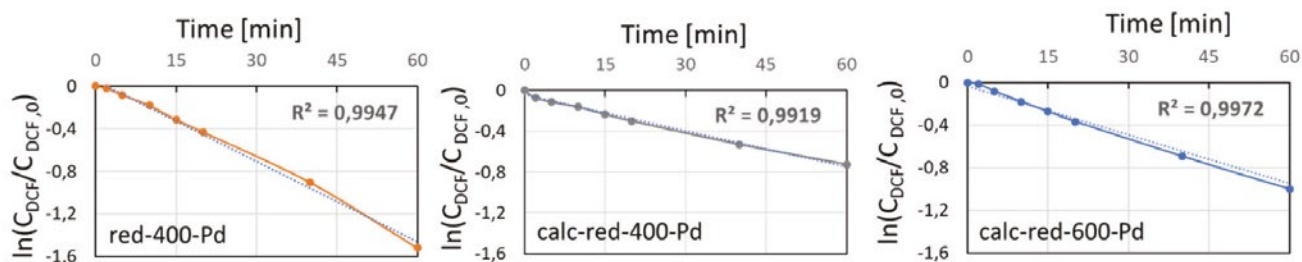


Fig. 3. Plot of  $\ln(C_{DCF}/C_{DCF,0})$  versus time for 1 wt.%Pd/γ-Al<sub>2</sub>O<sub>3</sub> after pretreatment at different conditions.

of the Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for the DCF hydrodechlorination. Moreover, 17 h of the reduction may result in forming Pd-Al species, which reveal unique electronic properties via electron transfer from Pd to Al. Consequently, it could increase Pd-Al affinity to chloroorganic compounds and explains the differences between activities of calc-red-400-Pd and calc-red-600-Pd.

The catalytic removal of diclofenac from water by hydrodechlorination could be assumed as pseudo-first-order due to the predominant amounts of hydrogen compared to DCF. A linear approximation of experimental points (Figure 3) allowed us to calculate the reaction rate constant *k* and the reaction rate after 900s of the reaction for three catalytic materials (Table 2). The highest values of the reaction rate constant and the reaction rate revealed the catalyst after the pretreatment under the mildest conditions.

Table 2. The reaction rate constant *k*, initial reaction rate *r*<sub>1</sub> values for the DCF hydrodechlorination.

Sample	<i>k</i> [s <sup>-1</sup> ] <sup>a</sup>	<i>r</i> <sub>1</sub> [mol s <sup>-1</sup> g <sub>Pd</sub> <sup>-1</sup> ] <sup>b</sup>
red-400-Pd	1.70	2.53E-05
calc-red-400-Pd	0.70	2.19E-05
calc-red-600-Pd	0.91	2.42E-05

<sup>a</sup> The reaction rate constant *k* calculated from the equation  $\ln(C/C_0) = kt$ , where *k* is the first-order rate constant (s<sup>-1</sup>) and *t* is the reaction time (s)

<sup>b</sup> The initial reaction rate calculated from the equation:  $r_1 \text{ (mol s}^{-1}\text{g}_{Pd}^{-1}\text{)} = (n_0 - n_t)/(\Delta t \cdot m_{Pd})$ , where *n*<sub>0</sub> = 0 (mol) – the initial amount of DCF moles, *n*<sub>t</sub> = 900s (mol) – amount of DCF moles after 900 s of reaction, Δ*t* (s) = 900 s – initial reaction time, *m*<sub>Pd</sub> (g) – mass of Pd in the catalyst.

## Conclusions

Aqueous-phase catalytic hydrodechlorination of diclofenac is an efficient way of water purification from chlorine-containing pharmaceuticals like diclofenac. From a perspective, this method could be

implemented with the success of the wastewater treatment plants. 1 wt.% Pd/γ-Al<sub>2</sub>O<sub>3</sub> are active in DCF removal from water. Their effectiveness strongly depends on the catalyst's pretreatment conditions. The highest efficiency (~100% DCF conversion) was obtained for the catalyst prepared in conditions requiring the least energy expenditure (red-400-Pd).

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