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Palladium loaded BEA zeolites as efficient catalysts for aqueous-phase diclofenac hydrodechlorination

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Abstract

Herein the catalytic performance of two 1 wt % Pd loaded BEA zeolites with Si/Al ratio of 19 and 1300 were investigated for the aqueous phase hydrodechlorination (HDC) of diclofenac, the latter compound a prevalent nonsteroidal anti-inflammatory drug. 1 wt %Pd/SiO₂ and 1 wt %Pd/Al₂O₃ being commonly used HDC catalysts were also studied for comparison purposes. Independently of the Si/Al ratio, palladium loaded BEA catalysts show over 6 times higher activity than conventional Pd/support catalytic systems. This remarkable behavior is largely due to the effect of the three-dimensional structure of zeolite material and the broad range of Pd NPs size obtained.

Keywords: palladium, BEA zeolite, batch hydrotreatment, pharmaceutical micropollutants, diclofenac.

1. Introduction

When we reach for another sip of water, we usually do not think about its composition or the importance of water quality for our health. However, we must be aware that the water flowing out of the treatment plants (WWTPs) still contains micropollutants in the form of medicines or personal care products. This group of pollutants includes diclofenac (DCF), an anti-inflammatory drug, resistant to natural biological degradation and conventional water treatment [1]. Diclofenac present in wastewater from sewage treatment plants and surface waters is becoming a threat to the ecosystem and human health, where in extreme cases leading to damage to the liver, kidneys, as well as anemia and drug resistance [2]. Accordingly, a great deal of effort is being made to find out ways to deactivate or eliminate diclofenac present in surface water and/or wastewater.

Different advanced water treatment technologies have been tested for chlorine-containing pharmaceuticals removal. Among them, the adsorption on activated carbons and advanced oxidation processes (AOP) have received significant attention. Although adsorption is somewhat effective in water purification, it is not selective, and it only allows the separation of the pollutant from the water phase, requiring further management of the saturated adsorbent [3]. On the other hand, the application of AOP methods is still not efficient enough [4], or can lead to a wide variety of more toxic byproducts [5]. Furthermore, diclofenac is particularly refractory to oxidation, requiring longer reaction times than other pharmaceutical compounds [6]. Application of microorganisms or enzymes for water purification from chlorine-containing pharmaceuticals gave promising results, but this process is slow and still a long way from the real use [7].

Similarly, the microwave radiation method - although it gives promising results, high radiation power makes it impossible to be used in real applications [8]. Reductive techniques

could be an attractive alternative for these methods [9,10]. Among them, catalytic hydrodechlorination (HDC) seems to be a promising technology for the elimination of chlorinated pharmaceutical compounds [11]. In this process, hydrogen reacts with the pollutant to produce the corresponding hydrogenated chlorine-free product(s) and hydrochloric acid. Therefore, HDC is an environmentally friendly process, which allows to reduce the ecotoxicity of the effluent significantly and avoid the formation of more harmful intermediates [12] under ambient temperature and pressure [13]. Despite the considerable potential of hydrodechlorination for the removal of diclofenac, it has been scarcely investigated towards this goal so far [14]. Catalytic hydrodechlorination (HDC) includes the transfer of hydrogen into the target molecule. Since hydrogen chemisorption is excellent on Pd [15], this noble metal is chosen as a catalyst for the HDC reaction.

Regarding the support, activated carbon and alumina have received significant attention [16,17]. Among them, the latter is particularly interesting due to its higher mechanical resistance as well as to its strong interaction with the supported metal nanoparticles, enhancing their dispersion. However, Wu et al. [15] investigated the effect of support (Al_2O_3 , activated carbon (AC), SiO_2 , and CeO_2) on the catalytic performance of supported palladium catalysts in diclofenac HDC reaction in water. They showed that Pd/ SiO_2 exhibits a nearly negligible catalytic activity, whereas diclofenac concentration decreases by 100, 86, and 29% within 50 min of reaction on the Pd/ CeO_2 , Pd/ Al_2O_3 , and Pd/AC, respectively. Consequently, Pd/ CeO_2 was selected as the best catalyst that allowed the relatively fast removal of DCF (50 min) under ambient conditions [15]. On the other hand, the complete removal of the diclofenac was achieved in short reaction time (20 min) at ambient conditions using the commercial Pd/ Al_2O_3 catalyst

[14]. Additionally, this catalytic system showed a reasonable stability and an acceptable versatility in real environmental conditions relevant with water matrices.

Application of biogenic Pd-catalyst, using bacteria as the support of metal, reduced process cost [18]. However, exceptionally long reaction times were required to achieve significant removals of DCF (up to 44% in 24 h) even using relatively high concentrations of catalyst (50 mg Pd L⁻¹). Modification of biogenic Pd-catalyst by addition of Au improved hydrodechlorination of diclofenac at environmentally relevant pH in comparison to Pd-only catalyst. The beneficial role of Au had also been confirmed for Amberlite 717 resin supported Pd-Au nanoparticles with a core-shell structure for the degradation of diclofenac [19] and chloramphenicol [20].

Our study aimed to investigate the effect of preparation procedure on the catalytic performance of Pd-loaded BEA zeolites for water purification from diclofenac. To the best of our knowledge, such studies have not yet been reported. Our results showed that the combination of 1 wt % Pd with BEA zeolite indicate the highest efficiency for the aqueous phase diclofenac hydrodechlorination, in comparison to Pd/SiO₂ and Pd/ γ -Al₂O₃ of the same metal loading. The results were rationalized using physicochemical characterizations by physisorption, chemisorption and TEM measurements.

2. Experimental

2.1. Catalysts synthesis

In accordance with literature [21,22], the palladium precursors were selected based on the zeta-potential (and the isoelectric point) of the support's surface. SiO₂ has a low isoelectric point (2.0) and high acidity in aqueous suspensions, and siliceous dealuminated BEA zeolite has also

low isoelectric point, ca. ~ 2.0 , in contrast to $\gamma\text{-Al}_2\text{O}_3$ with lower charge and a higher isoelectric point, ca. ~ 6.0 . Therefore, different palladium precursors were used for the synthesis of these catalysts. However, independently of the synthesis method, each catalyst contained 1 wt % Pd. Palladium loaded BEA zeolites were synthesized by a two-step post-synthesis method (PdSiBEA) and the conventional wet impregnation (PdHAlBEA) method, according to the procedures described earlier by Kamińska et al. [23].

$\text{Pd/SiO}_2(\text{s})$ was synthesized by ion exchange between the hydroxyl group of silica and $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$, which was preceded by the pre-calcination of Davison 62 SiO_2 support material (75 – 210 mesh) in air at 723 K for 4 h. $\text{Pd/Al}_2\text{O}_3$ was synthesized by typical incipient wetness impregnation of chlorine-free γ -alumina, Puralox SCCa series (supplied by Sasol) by an aqueous solution of $\text{Pd}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$. Each 1 wt % Pd containing catalyst was calcined in air flow at 773 K for 3 h and then reduced in 10 % H_2/Ar gas flow for 3 h at 673 K.

2.2. Catalysts characterization

Four palladium catalysts were characterized by physisorption, chemisorption, and electron microscopic measurements. Surface areas and porosities of the samples after reduction in 10 % H_2/Ar mixture were measured with an ASAP 2020 instrument (Micromeritics) using the BET (Brunauer-Emmett-Teller) and HK (Horwath-Kawazoe) methods and nitrogen as the adsorbate gas. Before measuring the adsorption isotherm at 77 K, the samples were kept at 473 K for 4 h in vacuum to remove mainly adsorbed water and other gases. CO chemisorption measurements were carried out using the static method according to the procedure described previously [24] and an ASAP 2020 Chem. Instrument.

Transmission Electron Microscopy (TEM) studies after reduction of the catalysts were carried out using the JEOL JEM-100CXII electron microscope and 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 voltage of the electron beam 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.

2.3. Catalysts activity evaluation

The aqueous phase hydrodechlorination of diclofenac was performed in a batch reactor at mild conditions (atmospheric pressure, 303 K). For every run, the initial reaction mixture contained $\sim 75 \text{ mg L}^{-1}$ DCF and 350 mL of MiliPore Water (30 min. saturated with hydrogen before DCF addition). The samples were analyzed using the Waters Acquity UPLC system equipped with a PDA e λ detector on a C18 column (3 μm , 120 \AA ; 2.1x50 mm) (Lumiseq, Poland). The isocratic method of analysis with mobile phase (0.1 % formic acid: acetonitrile 1:1 v/v) at the flow rate of 0.3 ml/min was used.

3. Results and discussion

3.1. Structural characterization of catalysts

A comparison of the physicochemical properties of palladium loaded BEA with two Pd/support systems (PdSiO₂ and PdAl₂O₃) clearly indicate that zeolite materials have much higher specific surface area and typical for zeolites - microporous structure. On the other hand,

Pd/SiO₂ and Pd/ γ -Al₂O₃ do not have micropores in their structure (Table 1). The slight difference between the BET specific surface area of PdSiBEA and PdHAIBEa could be due to some differences between the pretreatment methods of the parent TEABEA zeolite (Si/Al=19). Calcination and ion-exchange of zeolite BEA catalysts did not affect the Si/Al ratio. However, the dealumination resulted in the formation of SiBEA with Si/Al ratio of 1300.

Table 1. Textural properties and Pd particles size of the various Pd loaded catalysts.

Sample	BET specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)	Palladium particle size (nm) estimated from	
					CO chemisorption	TEM
PdSiBEA	393 ± 39	0.16	0.13	0.03	11	8
PdHAIBEa	377±37	0.14	0.10	0.04	14	9
Pd/SiO ₂	240 ± 24	1.0	-	1.0	1.3	2
Pd/Al ₂ O ₃	213 ± 21	0.56	-	0.56	15	6

Despite the differences between HAIBEa and SiBEA, the impregnation of the zeolite materials by an aqueous solution of Pd(NO₃)₂ · 2 H₂ O and their pretreatment under identical conditions led to the formation of Pd particles with similar average size (Table 1). Due to the structure sensitivity of the hydrodechlorination catalytic reaction [25], it seems rather evident that PdSiBEA and PdHAIBEa are characterized by similar catalytic activity for the diclofenac hydrodechlorination.

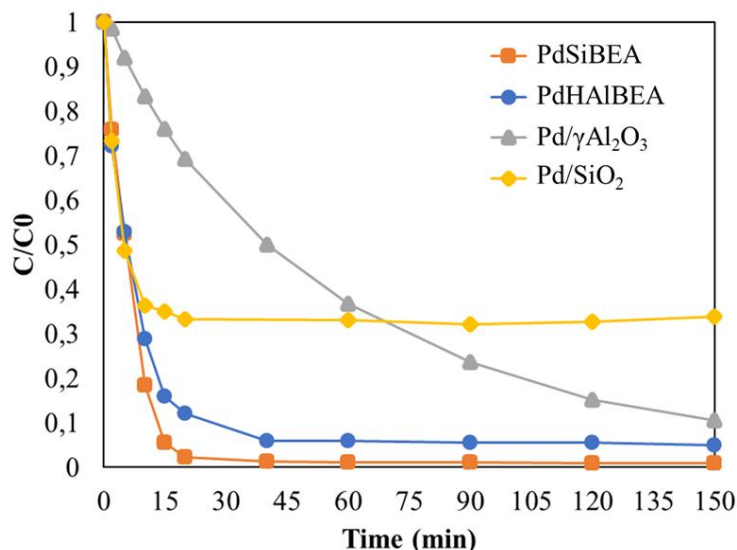


Fig. 1. Kinetic studies of diclofenac hydrodechlorination reaction in the presence of Pd catalysts (303 K, atmospheric pressure, 240 μ M DCF).

Fig. 1 shows the evolution of the diclofenac conversion in terms of C/C_0 versus time of reaction carried out in the presence of palladium loaded BEA zeolites and Pd/SiO₂ and Pd/Al₂O₃ for comparison purpose. In all catalytic systems, 2-anilinophenylacetic acid was the only organic product as confirmed by HPLC-MS analysis. Independent sorption experiments for all supported Pd catalysts did not show any sorption ability (results not shown). PdSiBEA and PdHAIBEA zeolite catalysts indicated remarkable activity for the aqueous phase hydrodechlorination of diclofenac in batch conditions (Fig. 1, Table 2). The comparative study between the two zeolite catalysts shows slight differences in C/C_0 profiles. After 20 min of reaction, almost all diclofenac (99%) was removed from water when a palladium catalyst synthesized by the two-step postsynthesis method was used (PdSiBEA), whereas 88% removal of diclofenac with PdHAIBEA catalyst having slightly larger average palladium particles size was obtained (Table 1).

Nevertheless, both Pd-loaded BEA zeolites show much higher activity than Pd/ γ -Al₂O₃ with similar average palladium particles size (Fig. 1, Tables 1 and 2). On the other hand, Pd/SiO₂ with 2 nm Pd NPs, shows almost identical activity like the zeolite materials during the first 10 min of diclofenac hydrodechlorination. After this time, deactivation of the silica Davison 62 supported Pd catalyst is observed (Fig. 1), in contrast to PdSiBEA and PdHAIBEa. For these two latter materials, deactivation was not observed. This could be explained by the higher affinity of small palladium nanoparticles present in both materials to chloroorganic molecules activation than to hydrogen activation on larger palladium nanoparticles [15,26]. Therefore, without the sufficient amount of activated hydrogen, palladium active species in Pd/SiO₂ deactivated due to chlorine deposits under HDC conditions [27,28], in contrast to PdSiBEA and PdHAIBEa zeolites, where chlorine deposits are not formed. However, deactivation of Pd/SiO₂ due to organic species formation could not be excluded. For example, Diaz et al. [29] postulated that deactivation of palladium supported on activated carbon used for the aqueous-phase hydrodechlorination (HDC) of 4-chloro-2-methylphenoxyacetic acid under ambient-like conditions was attributed to the accumulation on the catalyst surface of organic (in particular, organochlorinated) species involved in the reaction. While everything seems clear in the case of Pd/SiO₂, the catalytic results obtained for Pd/ γ -Al₂O₃ seem rather unexpected (Fig. 1, Tables 1 and 2).

Table 2. The reaction rate constant k , coefficient of determination R^2 , initial reaction rate r_{600} and TOF values for the hydrodechlorination of diclofenac on 1 wt % Pd catalysts.

Sample	k (min ⁻¹) ^a	R^2	r_{600} ^b (mol L ⁻¹ s ⁻¹ g _{Pd} ⁻¹) x 10 ⁻⁴	TOF ^c (s ⁻¹) x 10 ⁻²
red-C-PdSiBEA	0.19	0.9929	3.43	26.1

red-C-PdHAlBEA	0.11	0.9865	2.67	23.7
red-C-PdSiO ₂	0.02	0.9482	2.37	4.50
red-C-PdAl ₂ O ₃	0.09	0.9972	0.72	4.1

^aThe reaction rate constant k calculated from the equation $\ln(C/C_0) = -kt$, where k is the first-order rate constant (min^{-1}) and t is the reaction time (min).

^b The initial reaction rate calculated from the equation: $r_{600s} (\text{mol s}^{-1} \text{gPd}^{-1}) = (n_{t=0} - n_{t=600s})/(\Delta t \cdot \text{mPd})$, where $n_{t=0}$ (mol) - the initial amount of DCF moles, $n_{t=600s}$ (mol) - amount of DCF moles after 600 s of reaction, Δt (s) = 600 - initial reaction time, mPd (g) - mass of Pd in the catalyst.

^c TOF calculated from the equation: $\text{TOF} (\text{s}^{-1}) = (r_{600} \cdot M \cdot 100)/D$, where r_{600} ($\text{mol s}^{-1} \text{gPd}^{-1}$) - the initial reaction rate, M (g mol^{-1}) - atomic mass of Pd, D (%) - metal dispersion estimated from TEM results.

The catalytic results obtained for both palladium loaded zeolites are in agreement with earlier data [25] and indicate the Pd particles size dependent activity. However, it seems that this is not the only factor explaining the very high activity of PdSiBEA (99% DCF removal after 20 min of reaction) and PdHAlBEA (with 88% of DCF removal) as opposed to 33 % at the same time for Pd/ γ -Al₂O₃ with similar average Pd NPs size (Fig.1, Table 1). A careful analysis of TEM results has been helpful in this regard (Fig. 2). Although the average palladium particles size seems similar for PdSiBEA, PdHAlBEA and Pd/ γ -Al₂O₃ catalysts (Table 1), their distributions differ significantly (Fig. 2). For both Pd loaded BEA zeolites a broad range of particle sizes is observed (from 1 to 20 nm). It is essential to mention here that the dominant frequency of occurrence of given particle size is not larger than 15% for PdSiBEA and 11% for PdHAlBEA. In the case of Pd/ γ -Al₂O₃, small and large Pd particles are also observed, with evident domination of smaller (1-5 nm) Pd particles (60 % of frequency). Therefore, the activity of PdSiBEA and PdHAlBEA expressed in terms of TOF (s^{-1}) is, respectively, ~ 6 times higher than that of Pd/ γ -Al₂O₃ and Pd/SiO₂ (Table 2). This behavior could suggest that the catalytic activity of PdSiBEA and PdHAlBEA catalysts strongly depends on two factors, namely, the palladium particles size and their distribution (Table 2, Figs 1 and 2). Moreover, it should be

stressed here that such a high catalytic activity for the diclofenac hydrodechlorination has not yet been reported in the literature [5,14,18,30].

The obtained results are in accordance with earlier studies, which indicate that the bimodality of the Pd catalyst could be beneficial for the diclofenac hydrodechlorination [31]. Kowalewski et al. [31] came to important conclusions during comparative studies of the catalytic activity of unimodal and bimodal Pd nanoparticles in diclofenac hydrodechlorination. The outstanding efficiency of the bimodal catalyst was the effect of the close coexistence of small and large metal nanoparticles with different affinity to hydrogen and the chloroorganic compound. The larger Pd nanoparticles (> 5 nm) characterized by a higher affinity for hydrogen are the source of H atoms formation necessary for the HDC process. On the other hand, the presence of smaller (1-5 nm) Pd NPs significantly improve the C-Cl bond activation to a larger extent than the larger nanoparticles. The present work shows that, not only the close coexistence of large and small Pd NPs but also the specific ratio between the amounts of small and large Pd NPs guarantees the high efficiency of the catalyst for the aqueous-phase hydrodechlorination of diclofenac reaction.

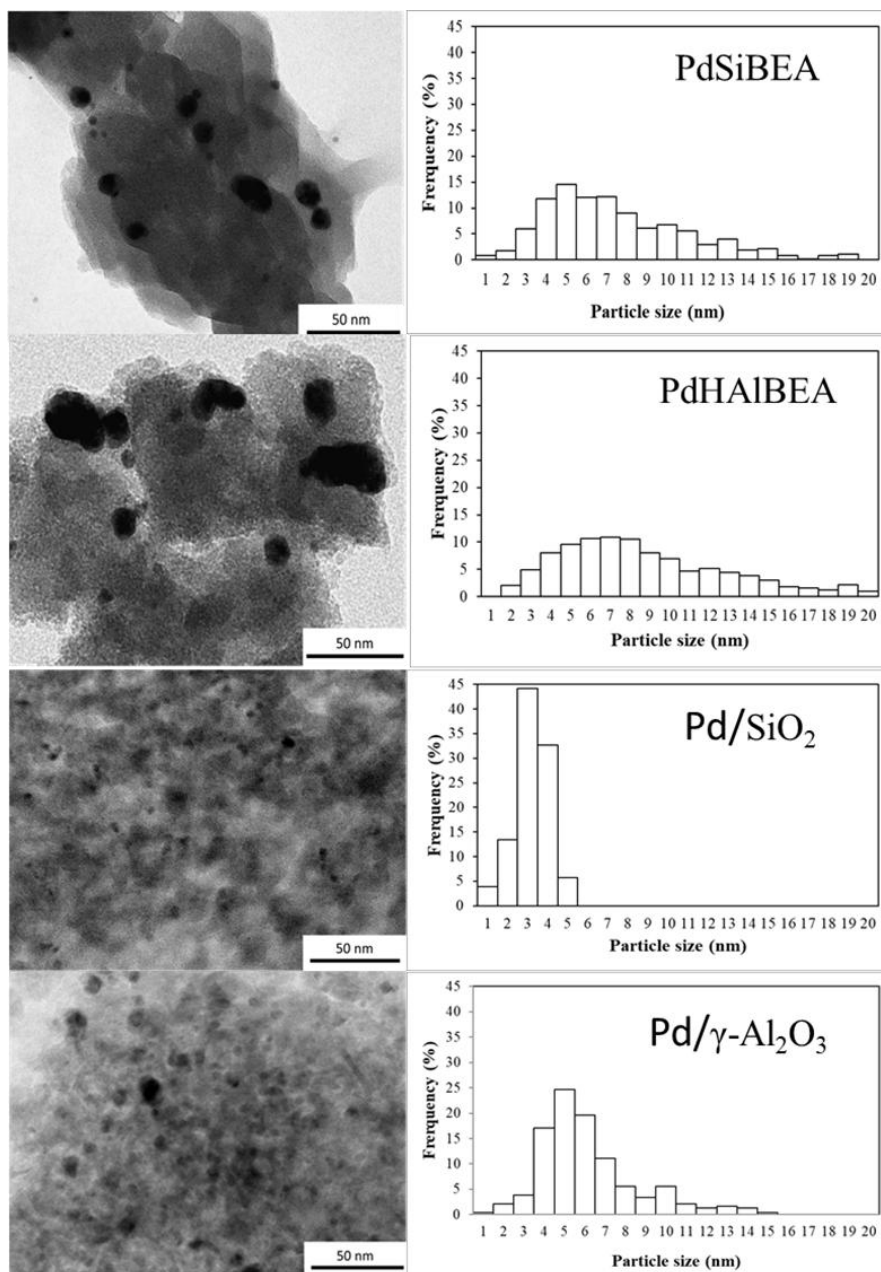


Fig. 2. TEM images and Pd particles size distribution of the various supported Pd catalysts investigated.

4. Conclusions

In the present work, we have demonstrated the large potential of Pd-loaded BEA zeolites towards the aqueous-phase hydrodechlorination of diclofenac. The observed unique activity is

the effect of the three-dimensional structure of zeolite material which allows the coexistence of a suitable amount of large and small Pd nanoparticles of different affinity to H₂ and C-Cl bond activation, respectively.

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