

# Application of catalytic hydrodehalogenation for the removal of brominated flame retardants

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**Abstract** The aim of this work is to evaluate the feasibility of aqueous-phase catalytic hydrodehalogenation (HDH) for the fast and environmentally-friendly degradation of the flame retardant tetrabromobisphenol A (TBBPA). TBBPA is a pollutant of emerging concern characterized by a strong persistence that has been associated with negative effects on both the environment and human health. The complete degradation of TBBPA during the HDH reaction ( $[TBBPA]_0 = 1 \text{ mg L}^{-1}$ ) was achieved in short reaction times (5 min) under ambient conditions using  $1 \text{ g L}^{-1}$  of a commercial Pd/Al<sub>2</sub>O<sub>3</sub> (1% wt.) catalyst. Remarkably, bisphenol A, a known endocrine disruptor, was generated along reaction once TBBPA was completely debrominated. However, its complete removal was achieved by further hydrogenation. Although TBBPA suffered a strong adsorption on the catalyst surface, both adsorbed and free molecules reacted completely, and bromine balance was closed (>95%). HDH of TBBPA followed a pseudo-first order kinetic and a kinetic constant value of  $1.03 \text{ min}^{-1}$  was obtained. Furthermore, the effect of the temperature was evaluated between 15 and 35 °C, obtaining higher degradation rates when the temperature increased. A resulting apparent activation energy of  $36 \text{ kJ mol}^{-1}$  was calculated. Notably, the catalyst showed a notable stability after three consecutive HDH runs.

**Keywords:** catalytic hydrodehalogenation; water treatment; Pd supported catalyst; brominated flame retardant; TBBA

## 1. Introduction

Brominated flame retardants (BFRs) are compounds widely used in the industry for materials protection against ignition. Among them, tetrabromobisphenol A (TBBPA) is one of the most produced and used due to its extraordinary flame resistance. Nevertheless, due to its high persistence, this compound is usually detected in the aquatic environment and represents an issue of increasing concern, being an important threat to the environment as well as to the public health (Covaci *et al.*, 2009). For instance, TBBPA has been detected in breast milk, demonstrating that the compound is absorbed in humans after exposure (Wikoff *et al.*, 2015). Hence, it is necessary to search an effective technology for the treatment of this group of micropollutants prior their introduction in the water environment.

Oxidation processes have been widely investigated for TBBA degradation. Nevertheless, highly toxic brominated compounds can be generated along the treatment (Han *et al.*, 2019). In this sense, aqueous-phase catalytic hydrodehalogenation (HDH) appears as a promising technology for such goal. In this system, the organohalogenated compounds reacts with hydrogen in the presence of a catalyst, leading to halogen-free organic products and the corresponding hydrohalic acids. The process can be operated under ambient conditions and it is characterized by a notable capability of toxicity abatement (Mackenzie *et al.*, 2006). HDH reaction is usually performed using catalysts based on precious metals such as Pd supported onto inert materials like alumina (Urbano and Marinas, 2001).

This work aims at evaluating the feasibility of the HDH technology for the removal of the brominated flame retardant TBBPA. A complete operating conditions study has been carried out considering catalyst concentration, temperature and H<sub>2</sub> flow. Finally, the stability of the catalyst in consecutive runs has been evaluated.

## 2. Materials and methods

### 2.1. Materials

Tetrabromobisphenol A (97%) and Bisphenol A ( $\geq 99\%$ ) were supplied by Sigma-Aldrich. Methanol ( $\geq 99\%$ ) was delivered by Scharlau. Hydrogen (99.999 %) was provided by Praxair. The experiments were carried out using deionized water. A commercial Pd/Al<sub>2</sub>O<sub>3</sub> (1% wt.) catalyst (supplied by Alfa Aesar) was used in this study. Table 1 collects its main characteristics.

**Table 1.** Main characteristics of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

dp (μm)	BET (m <sup>2</sup> g <sup>-1</sup> )	Pd <sup>0</sup> /Pd <sup>n+</sup>	PZC
24	270	1.04	8.7

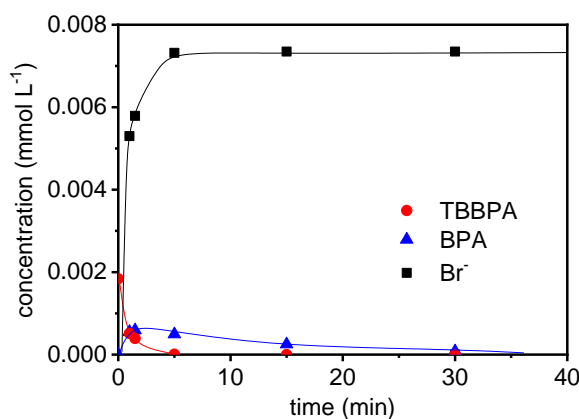
### 2.2. Experimental Procedure

HDH experiments were performed batch-wise in a magnetically stirred glass slurry-type reactor (500 mL) equipped with temperature control. The reactions were carried out under ambient conditions (25 °C, 1 bar) and continuous feeding of H<sub>2</sub>. The reaction volume was fixed

at 450 mL whereas the initial concentration of TBBA was  $1 \text{ mg L}^{-1}$  ( $0.0018 \text{ mmol L}^{-1}$ ). The effect of catalyst concentration ( $0.25 - 1 \text{ g L}^{-1}$ ), temperature ( $15 - 35 \text{ }^\circ\text{C}$ ) and  $\text{H}_2$  flow ( $10 - 50 \text{ N mL min}^{-1}$ ) was evaluated.

Liquid samples were periodically withdrawn from the reactor, separating the catalyst by centrifugation prior analysis. The evolution of TBBPA and the reaction intermediates was followed by HPLC (Prostar, Varian

model 410) using an Eclipse Plus C18 column (15 cm length, 4.6 mm diameter) (Agilent) as stationary phase. The analyses were carried out at 270 nm using a 80/20% (v/v) mixture of methanol and water as the mobile phase. Bromide ions produced along reaction were quantified by ion chromatography (Metrohm 883 Basic IC Plus). A Metrosep A supp 5-250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and a  $3.2 \text{ mM Na}_2\text{CO}_3$  aqueous solution as the mobile phase.



**Figure 1.** HDH of TBBPA with  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst.

( $[\text{TBBPA}]_0 = 0.0018 \text{ mmol L}^{-1}$ ;  $\text{H}_2 = 50 \text{ N mL min}^{-1}$ ;  $[\text{Pd}/\text{Al}_2\text{O}_3]_0 = 1 \text{ g L}^{-1}$ ; 900rpm;  $25 \text{ }^\circ\text{C}$ )

### 3. Results

#### 3.1. Catalytic hydrodehalogenation of TBBPA

A previous experiment was carried out in absence of  $\text{H}_2$  to determine the adsorption of TBBPA ( $1 \text{ mg L}^{-1}$ ) on the  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst ( $1 \text{ g L}^{-1}$ ). Under these operating conditions, 60% of TBBPA was adsorbed onto the catalyst surface in a few minutes. According to these results, an initial adsorption 15 min stage was included in the experimental procedure prior starting the reaction by the feeding of  $\text{H}_2$  gas flow. Figure 1 shows the evolution of TBBPA, BPA and bromine upon HDH reaction at  $25^\circ\text{C}$  using  $1 \text{ g L}^{-1}$  of  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst. As observed, TBBPA concentration decreased during reaction, and it was completely removed in a short reaction time (5 min). TBBPA followed pseudo-first order kinetics, obtaining an apparent rate constant value of  $1.03 \text{ min}^{-1}$ . No TBBPA derivatives ( $\text{B}_3\text{BPA}$ ,  $\text{B}_2\text{BPA}$  and  $\text{BBPA}$ ) were identified, which are characterized by higher toxicity than the parent compound, but the widely used BPA product was formed (Debenest *et al.*, 2010). In fact, TBBPA is generated in the industry by the bromination of BPA. However, BPA has not been identified as a metabolite of TBBPA, so there is no evidence that TBBPA dehalogenation to BPA occurred *in vivo* (Wikoff *et al.*, 2015). Remarkably, BPA, which is a well-known an endocrine disruptor (Yen *et al.*, 2011), was completely hydrogenated along reaction. Despite TBBPA strong adsorption, the brominated flame retardant reacted completely since bromine balance was almost completely closed (>95%). Adsorption of BPA on the

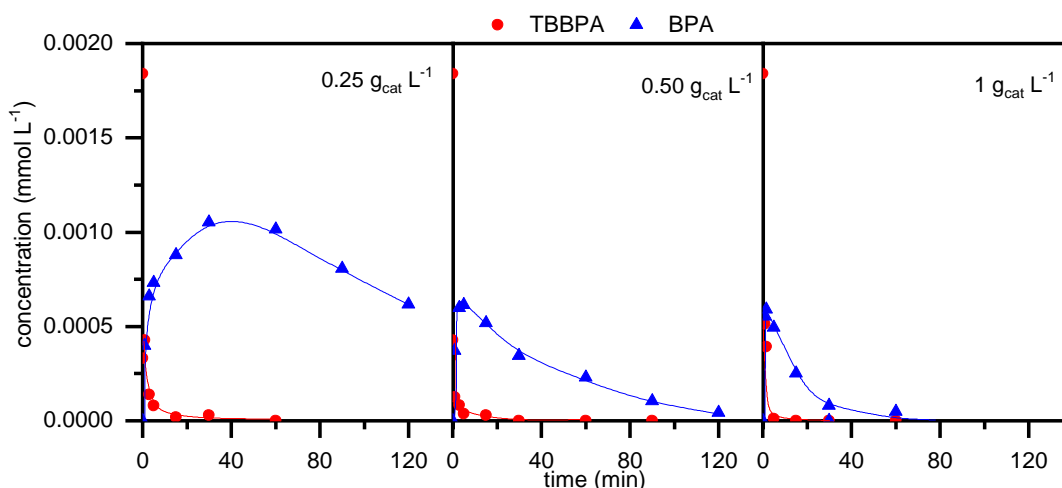
catalyst surface was discarded in an additional experiment carried out in the presence of  $\text{Pd}/\text{Al}_2\text{O}_3$ .

#### 3.2. Operating conditions study

A complete operating conditions study was carried out. The effect of temperature was evaluated in the range of 15 to  $35 \text{ }^\circ\text{C}$ . The temperature increase led to higher degradation rates, and kinetic constants of  $0.84$  and  $2.24 \text{ min}^{-1}$  were obtained for 15 and  $35^\circ\text{C}$ , respectively. The apparent activation energy for the HDH of TBBPA was calculated from the Arrhenius equation, obtaining a value of  $36 \text{ kJ mol}^{-1}$ . This value is close to those previously reported in the literature for the HDH of different organochalogenated compounds using  $\text{Pd}/\text{Al}_2\text{O}_3$  catalysts (Nieto-Sandoval *et al.*, 2019).

Figure 2 shows the evolution of TBBPA at different catalyst concentration ( $0.25$  to  $1 \text{ g L}^{-1}$ ). As expected, higher catalyst load led to an increase in the degradation rates. Also, BPA hydrogenation rate increased at higher catalyst load. Rate constant values of  $0.18$  and  $0.44 \text{ min}^{-1}$  obtained for TBBPA using  $0.25$  and  $0.50 \text{ g L}^{-1}$  catalyst concentrations, respectively. Therefore, TBBPA degradation rate linearly correlated with the catalyst load, which allows to discard external mass transfer limitations under the operating conditions used in this work.

Finally,  $\text{H}_2$  flow was evaluated between at 10, 30 and  $50 \text{ N mL min}^{-1}$ , achieving in all cases similar activities. Thus, it can be assumed that HDH reaction was operated in high excess of  $\text{H}_2$  and there were no limitations related to the availability of hydrogen in the active centers of the catalyst.



**Figure 2.** HDH of TBBPA with Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

([TBBPA]<sub>0</sub> = 1 mg L<sup>-1</sup>; H<sub>2</sub> = 50 N mL min<sup>-1</sup>; 900rpm; 25 °C).

### 3.3 Catalyst stability

One of the main limitations of HDH is the catalyst deactivation due to hydrohalic acids poisoning, metal component leaching or by-products adsorption (Yuan and Keane., 2003). Thus, given the high catalyst cost, ensuring its stability for consecutive application is crucial. In this work, the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst stability was evaluated upon three consecutive runs. Notably, the activity after the third run was close to the fresh catalyst. TBBPA was completely degraded in short reaction times and BPA was completely hydrogenated. Despite the strong adsorption of TBBPA at the beginning of reaction, carbonous deposits did not block the Pd active sites probably due to the complete reaction of the adsorbed TBBPA.

## 4. Conclusions

HDH has proved to be a promising process for the removal of TBBPA, a brominated micropollutant of high environmental concern, from aqueous solutions. The complete disappearance of the chemical was achieved in a short reaction time (< 5 min) under ambient conditions using the commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Although TBBPA suffered a strong adsorption effect on the catalyst surface, the micropollutant reacted completely and bromine balance was closed (> 95%). Remarkably, the bromine-free BPA product was formed but it was further completely hydrogenated along reaction. TBBPA followed pseudo-first order kinetics, and a kinetic constant value of 1.03 min<sup>-1</sup> was obtained. From the operating conditions study it can be evidenced that temperature increase led to higher degradation rates, obtaining an apparent activation energy of 36 kJ mol<sup>-1</sup>. In addition, degradation rates increased linearly at higher catalyst load, allowing to discard mass transfer limitations, and H<sub>2</sub> flow is not a limiting reagent at the operating condition tested in this work. Remarkably, the catalytic system showed a reasonable stability upon three consecutive HDH runs.

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