MICROWAVE ASSISTED CATALYTIC DECHLORINATION OF PCB

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The purpose of this study is to investigate the catalytic dechlorination of PCB (polychlorinated biphenyls). The process is activated by conventional or microwave heating. Solutions of PCB in 2-propanol with concentrations between 0.01 and 0.1M were used for the catalytic dechlorination. Different heterogeneous catalysts were tested for dechlorination of PCB: Pd/Al\textsubscript{2}O\textsubscript{3}, Pd/aluminosilicate, Pt/Al\textsubscript{2}O\textsubscript{3}, Ni/C, Fe and Ni(50\%)/Al(50\%). The dechlorination proceeds only in the presence of Pd on aluminosilicate (or alumina). The presence of Na is mandatory for the dechlorination to occur. The optimum temperature for the dechlorination process using Pd supported on aluminosilicate is around 130-150°C. The increase of delivered microwave power to the catalytic system has a favorable effect on dechlorination process: it decreases the time necessary to reach total dechlorination of PCB.

Keywords: PCB, dechlorination, Pd catalyst, microwave

1. Introduction

Polychlorinated biphenyls (PCB) were used to produce electric equipment such as transformers and capacitors, but also as additives for lubricants, hydraulic fluids and adhesives, due to their unique combination of properties: chemical inertness, resistance to heat, non-flammability, low vapour pressure and high dielectric constant. The problems with PCBs derive from their toxicity to humans and to the environment. PCB are resistant to biodegradation and have negative

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effects on life forms even at very low concentrations because they bioaccumulate in fatty tissues [1].

The production of PCB has been banned all over the world since 1998. In Romania there are large quantities of transformer oils containing PCB, in storage. For the existent quantities, a friendly environmental process must be developed because year 2028 was set as the time limit for implementing of environmental sound management of all PCB wastes [1, 2].

Nowadays, the destruction and/or treatment methods of PCB include two types of processes. First type of process refers to combustion at high temperatures [3] and is the most used process to destroy PCB. However, evidence of environmental and public health impact of incinerators has created strong public opposition to incineration. The second types of process include all physico-chemical processes, by which PCB are transformed into non-polluting or into reusable products such as biphenyl. The use of these technologies is limited because they imply high costs of investment, consumption of expensive reactive or severe temperature and pressure conditions (wet oxidation in supercritical conditions) [4-13]. All the issues presented above indicate the necessity of searching for alternatives.

Catalytic dechlorination of PCB could be a viable treatment technique. Conventional research into the removal of halogenated aliphatic and aromatic hydrocarbon compounds from fluid waste streams includes reactions catalysed by supported noble metal-based catalysts, typically in gas phase or in organic liquids. Recent studies have focussed on the dechlorination of aromatic compounds in 2-propanol [14]. It has been observed that the dechlorination rates increased with decreasing number of chlorine substituents [15]. In this transformation 2-propanol is the source of hydrogen, including hydrogen transfer from 2-propanol to organic halides [16-18]. A characteristic of this system is that the substitution of halogen by hydrogen occurs selectively without hydrogenation of the aromatic ring.

The transformation of PCB by hydrogen donor process is known to provide biphenyl, acetone and NaCl [19] in accordance with the following equations:

\[ CH_3 - CH(OH) - CH_3 \rightarrow CH_4 - C(O) - CH_3 + 2H^+ \]  \hspace{1cm} (1)
\[ C_{12}H_{10-m}Cl_m + 2H^+ \rightarrow C_{12}H_{10-m+1}Cl_{m-1} + HCl \]  \hspace{1cm} (2)
\[ HCl + NaOH \rightarrow NaCl + H_2O \]  \hspace{1cm} (3)

\[ C_{12}H_{10-m}Cl_m + CH_3 - CH(OH) - CH_3 + NaOH \rightarrow \]
\[ C_{12}H_{10-m+1}Cl_{m-1} + CH_3 - C(O) - CH_3 + NaCl + H_2O \]

where H* indicates the hydrogen-transfer species and m = 1, 2, ..., 10.
Despite the fact that the procedure is recognized to be facile and efficient, the practical application of catalysts to dehalogenation of organic halides is always accompanied by the problem of the catalyst deactivation. Deactivation may occur by adsorption of halogen, halogenation of catalyst [20], and formation of oligomers and coke [21]. In this context, it is important to find a method that maintains a good activity of the catalyst for a prolonged time.

Microwave induced catalytic technology offers a potential solution to these problems [21]. The advantages of microwave-induced catalysis in certain types of reactions derive from its very different way of energy input. Microwave heating is selectively applied to catalyst resulting in rapid heating of the catalysts. Thus, the catalyst serves both as a promoter of the chemical reactions on the surface and as an efficient converter of the incident microwaves to thermal energy necessary for the reaction activation. This way, reactions can be initiated at catalyst surfaces even though the bulk of the reactor and reagents are maintained at a lower temperature.

2. Experimental

The used substances and reactives were: complex mixture of PCB, 2-propanol, catalysts (Pd/PdAl₂O₃, Pd/aluminosilicate, Pt/PdAl₂O₃, Ni/C, Fe and Ni(50%)/Al(50%)), biphenyl, metallic Na, and chromatographic standards of PCB. Pd/aluminosilicate was purchased from Viromet S.A., Romania. The composition of this catalyst is: Na - 7.33%, Al - 18.84%, Si - 68.40%, Pd - 5.16%, Ca - 0.27%. The characteristics of the aluminosilicate support are: specific surface = 400 m²/g, apparent density = 800 g/l; 0.1 μm < diameter of particle < 0.16 μm.

Catalytic dechlorination reactions were carried out in glass thermoresistant vials (2-5 ml) sealed with rubber septa. The mixtures were homogenized by magnetic stirring. The heating of the reaction mixtures was accomplished by conventional (electrically heated oil bath) or microwave source. Microwave heating was carried out by a microwave Initiator apparatus (from Biotage). The Initiator was programmed to keep a constant temperature inside vials by variation of input microwave power. Air cooling of the reaction vial can be provided during microwave heating. In these conditions, the microwave power delivered to the vial is higher (100W) compared to microwave heating without cooling (50W) (see Fig. 1). One of the active Pd catalyst (suported on aluminosilicate) was selected to study the influence of heating type: conventional heating (CONV), microwave heating without cooling (MW) and microwave heating with cooling (MWC).
3. Results and discussion

The mixture of PCB subjected to dechlorination is very complex [22]. Its characteristics were established by comparison with chromatograms of Sigma-Aldrich standard solutions of PCB (PCB MIX 7 and Aroclor 1254). Accordingly, the following characteristics for the mixture of PCB were obtained: average chlorine content in PCB of 39.1%; average number of chlorine atoms for a molecule of PCB of 2.81; average molecular mass of PCB of 251 g/mol.

The experiments were focused on:

- Testing the catalysts (Pd/Al₂O₃, Pd/aluminosilicate, Pt/Al₂O₃, Ni/C, Ni(50%)/Al (50%) and metallic Fe) for dechlorination of PCB solution in 2-propanol, with sodium izopropoxide (molar ratio Na:Cl of 2:1), at a temperature of 150°C by microwave heating. It was noticed that only Pd catalysts are active for PCB dechlorination.

- Studying the catalytic dechlorination process using the selected active catalyst (Pd/aluminosilicate) in the following conditions:
  - at different temperatures: 110°C, 130°C and 150°C;
  - after different reaction time: 1, 3, 5, 8, 10, 15 min;
  - changing the type of heating: conventional, with microwaves without cooling and with microwaves with cooling;
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- at different initial concentrations of PCB: 0.01, 0.05 and 0.1 M;

The dechlorination process was evaluated by computing two parameters:

- Total dechlorination efficiency of PCB to biphenyl (TDE):

\[
\text{TDE} (\%) = \left( \frac{\text{[BF]}_{\text{final}}}{\text{[PCB]}_{\text{initial}}} \right) \times 100 \approx \frac{\text{[BF]}_{\text{final}}}{\text{[PCB]}_{\text{final}} + \text{[BF]}_{\text{final}}} \times 100
\]  

(4)

- Partial dechlorination efficiency (PDE):

\[
\text{PDE} (\%) = \frac{\text{[Chlor]}_{\text{initial}} - \text{[Chlor]}_{\text{final}}}{\text{[Chlor]}_{\text{initial}}} \times 100
\]  

(5)

Where:
- \([\text{BF}]_{\text{final}}\) is the concentration of biphenyl obtained after the catalytic treatment, M;
- \([\text{PCB}]_{\text{initial}}\) is the initial concentration of PCB, M;
- \([\text{PCB}]_{\text{final}}\) is the final concentration of PCB after the catalytic treatment, M;
- \([\text{Chlor}]_{\text{initial}}\) is the average chlorine content of PCB before the catalytic treatment, %gr;
- \([\text{Chlor}]_{\text{final}}\) is the average chlorine content of PCB after the catalytic treatment, %gr;

The gas chromatographic analysis showed that partial dechlorinated products are PCB with lower number of chlorine atoms than initial PCB. No other organic chlorinated compounds were formed. Thus, the approximation from equation (4) is righteous.

3.1 Influence of the type of heating

The dechlorination process is complete at initial concentrations of 0.01 and 0.05M of PCB. (Fig. 2 and Fig. 3). The reaction time needed for complete dechlorination of PCB decreases in the following order: conventional heating > microwave heating without cooling > microwave heating with cooling. This observation indicate the positive effect of microwaves on the catalytic dechlorination of PCB. When the initial concentration of PCB is increased to 0.1M, the efficiencies of dechlorination have low values (<50%) for all types of heating used (Fig. 4).
Fig. 2. Influence of heating type on catalytic dechlorination efficiencies (TDE and PDE) (temperature 130°C; 0.025g Pd/aluminosilicate, [sodium isopropoxide]=0.056 mol/L, [PCB]₀= 0.01 moles/L).

Fig. 3. Influence of heating type on catalytic dechlorination efficiencies (TDE and PDE) (temperature 130°C; 0.025g Pd/aluminosilicate, [sodium isopropoxide]=0.242 mol/L, [PCB]₀= 0.05 moles/L).
3.2 Influence of temperature on the dechlorination catalytic process

The optimum temperature of the Pd catalysed dechlorination reaction (with microwave heating) is in the range of 130-150°C, at low PCB concentrations (Fig. 5). At these temperatures the total dechlorination occurs in 1 minute (at 150°C) and 8 minutes (at 130°C).
3.3 Influence of the initial PCB concentration

![Graph showing the influence of the initial PCB concentration on catalytic dechlorination efficiencies (TDE)].

**Fig. 6.** Influence of the initial concentration of PCB and of heating type on catalytic dechlorination efficiencies (TDE) (temperature 130°C; 0.025g Pd/aluminosilicate, [sodium isopropoxide]=0.056-0.562 moles/L, molar ratio Na:Cl is 2:1).

Complete dechlorination of PCB occurs only at concentrations of PCB lower than 0.05M. When the initial concentration of PCB is increased to 0.1M the dechlorination of PCB is not efficient even if microwaves are used as heating source. For longer reaction time, dechlorination efficiencies have low values. This result can be explained by a possible deactivation of the catalyst (Fig. 6).

3.4 Influence of Na : Cl molar ratio

![Graph showing the influence of Na : Cl molar ratio on catalytic dechlorination efficiencies (TDE and PDE)].

**Fig. 7.** Influence of Na : Cl molar ratio and of the type of heating on catalytic dechlorination efficiencies (TDE and PDE) (microwave heating, temperature 130°C; 0.025g Pd/aluminosilicate, [PCB]₀=0.01 moles/L,).
The presence of a compound able to capture the chlorine ions released into solution by cleavage of C-Cl bonds from PCB is mandatory for the dechlorination to occur. A molar ratio Na:Cl of 2:1 is necessary for an efficient removal and to accomplish total dechlorination of PCB (Fig. 7). This behaviour has been explained by taking into account the increase of the alkaline pH of the reaction medium that solubilises the Pd$^0$ [18].

4. Conclusions

Several types of catalysts (Pd/Al$_2$O$_3$, Pd/aluminosilicate, Pt/Al$_2$O$_3$, Co-Mo/Al$_2$O$_3$, Ni/C, Fe metallic, Ni 50% / Al 50%) were tested for the dechlorination process of PCB. The dechlorination proceeds only in the presence of Pd catalysts.

Sodium ions presence is mandatory for the dechlorination to occur. Furthermore, sodium ions should be in sufficient amount in order to provide the caption of all chlorine atoms released in solution by cleavage of C-Cl bonds from PCB.

The optimum temperature for the catalytic dechlorination of PCB with Pd/aluminosilicate catalyst is between 130 and 150 °C.

The increase of delivered microwave power to the catalytic system has a favorable effect on dechlorination process; it decreases the necessary time to reach total dechlorination of PCB.

REFERENCES