



Multiphase hydrodechlorination of polychlorinated aromatics – Towards scale-up



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HIGHLIGHTS

- Dichlorobenzene is quantitatively converted into benzene.
- No solvent.
- Product physically separates from the catalyst and by-products.
- Catalyst system can be fully recycled.
- Calculation of material costs gives an estimate of the cost-efficiency.

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ABSTRACT

We describe a chemical technology for the reductive catalytic multiphase hydrodechlorination (HDC) of chlorinated aromatics to greatly reduce their toxicity and aid the disposal of such species. The system requires no solvent and the catalyst displays a high recycling efficiency. In the present case, 1,3-dichlorobenzene (1,3-DCB) was used as a model compound, and was quantitatively hydrodechlorinated to benzene with hydrogen, in a tri-phasic liquid system consisting of the chlorinated aromatic itself as the top organic phase, an aqueous sodium hydroxide bottom phase (that neutralises acids formed), and an Aliquat[®]336 (A336) intermediate phase containing a Pd/C catalyst.

Once the reaction was complete the top phase (now just benzene) and the bottom phase (now principally aqueous NaCl) were removed and the remaining catalytic A336/(Pd/C) phase recycled.

This model study was conducted on a multi-gram scale with a view of demonstrating its applicability to the detoxification of PCBs. Comparison of the Mass Intensity (MI) and turnover frequency (TOF) of our model reaction with three examples of published procedures for the HDC of DCB, indicated that the MI for our system (MI = 6.33) was lower by an order of magnitude or more than that of the others (MI = 27.9, 64.6, 96016), and that TOFs were comparable.

A preliminary cost analysis indicates approximately 2000 €/tonne to treat tonne-scale amounts of chlorinated aromatics, making the system in principle useful for industrial implementation.

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1. Introduction

The responsible chemical disposal of dangerous polychlorobiphenyls (PCBs), is a continuing environmental issue due to constantly updated legislation, as well as due to the emergence of new markets in need of reliable, safe and efficient technologies for the detoxification of persistent chlorinated pollutants.

A variety of methods are already available for the chemical degradation of PCBs and additional details can be obtained from the documents and reports available from the United Nations Industrial Development Organization ([The Stockholm Convention](#)), the United Nations Environment Program ([Persistent Organic Pollutants](#)) and the United States Environmental Protection Agency ([Reference Guide to non-Combustion Technologies for the Remediation of Persistent Organic Pollutants in Stockpiles and Soil](#)). Among the reported technologies for the chemical degradation of PCBs many are oxidative ([Salen et al., 2000](#); [Surma et al., 1998](#); [Carson and Bremer, 2003](#); [Brouns et al., 1983](#); [Lampson et al.,](#)

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2001; Deam et al., 1993; Takahashi et al., 2005; Sako et al., 2000; Rogers et al., 1991), and may in principle generate polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/DFs) during the degradation process. Others are reductive (Kawahara and Michalakos, 1997; Birke, 2002; Birke et al., 2004; Arizumi et al., 1997; Getman et al., 2000; Hellet, 1989; SPHTD; Hydrodec; Tumiatti, 1997; Sea Marconi; Japan Environmental Safety Corporation, 2005) and are intrinsically free from dioxin production. The various technologies allow treatment of a wide range of contaminated matrices starting from different PCB concentrations. It is beyond the scope of this introduction to review and discuss each existing technology, or to indicate which is best for a given matrix and concentration. However, the HydroDec technology (Hydrodec), the Chemical Decomposition Process patented by Sea Marconi (Tumiatti, 1997; Sea Marconi) and the Japan Environmental Safety Corporation (JESCO) Catalytic Hydro-Dechlorination Method (Japan Environmental Safety Corporation, 2005) are noteworthy in the present context as they are based on reductive dehalogenation. In particular, the HydroDec (Hydrodec) process involves mechanochemical dehalogenation of halo-organic compounds in the presence of reducing agents such as Mg, Al or Fe and of a source of hydrogen; the Sea Marconi process (Tumiatti, 1997; Sea Marconi) involves decomposition of halogenated contaminants with reducing metals, a polyethyleneglycol and alcoholates while the JESCO process (Japan Environmental Safety Corporation, 2005) involves hydrogenation of PCBs on Pd/C at 533 K. Nonetheless, a variety of PCB dechlorination methods continue to be studied (Ido et al., 2015; Ma et al., 2014), implying that an exhaustive technology has yet to be developed.

We reported previously the development of a laboratory reaction system for the catalytic hydrodehalogenation of chlorinated aromatics and pollutants using hydrogen at atmospheric pressure, a heterogeneous catalyst (supported Pd, Pt, Ni), and a quaternary ammonium salt, such as A336 (trioctylmethylammonium chloride: A336), which is liquid at ambient conditions and which can be synthesized by a completely green (in terms of using green reagents, being solventless and being 100% atom efficient) procedure (Fabris et al., 2009; Tundo and Perosa, 2007). By coupling an aqueous alkaline solution, an organic (hydrocarbon) solvent, and A336, one obtains a triphasic liquid system (Zinovyev et al., 2004a). The chlorinated reagent and the reduced hydrocarbons reside in the top organic phase, the hydrochloric acid is neutralized and captured by the aqueous alkaline phase as a salt, while the supported metal catalyst is immobilized in the intermediate third

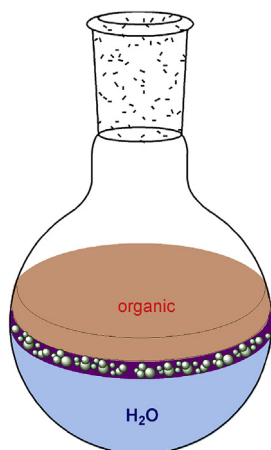


Fig. 1. Triphase liquid-liquid-liquid system: the intermediate layer is constituted by A336 that incorporates the supported metal catalyst.

phase of A336 (Fig. 1) (Tundo and Perosa, 2007). The hydrodehalogenation of chlorinated aromatics takes place by bubbling hydrogen at atmospheric pressure at $T < 323$ K and goes rapidly to completion (Marques et al., 1994). For example, with Pd/C and H_2 it was possible to detoxify PCDD/F mixtures (Perosa et al., 2001), as well as other chlorinated pollutants such as: lindane (Zinovyev et al., 2004b), dieldrin (Zinovyev et al., 2005a), DDT (Zinovyev et al., 2005a), chlorophenoxy-pesticides (Zinovyev et al., 2005b), and PCBs (Marques et al., 1994). Based on this long-standing experience in the study of the catalytic hydrodehalogenation of chlorinated pollutants described above, we asked ourselves whether this kind of approach could be applied to the detoxification of sizeable batches of pure chlorinated organics such as PCBs, or mixtures of PCBs and hexachlorobenzene, as found for example in electrical transformers. Also, we wanted to evaluate in a preliminary way the mass efficiency of this technology and whether it might be economically viable.

Thus, here we illustrate a catalytic hydrodehalogenation methodology using a multiphase system, that allows to convert gram-scale quantities of the neat chlorinated aromatic model compound 1,3-dichlorobenzene to the corresponding hydrocarbon, *i.e.* benzene, using Pd/C and hydrogen. The main positive features of this system are four: (a) the built-in separation of the products and by-products that can be achieved by liquid-liquid-liquid phase separation, (b) the recovery and re-use of the solid catalyst that is dispersed in an inexpensive ionic liquid phase, both of which are available in commercial quantities, (c) the absence of added organic solvents, and (d) the very mild reaction conditions ($P = 1$ atm, $T = 323$ K). Once established that the reaction could be scaled-up from milligrams to grams (Zinovyev et al., 2004a; Paganelli et al., 2007), we further decided to assess its chemical efficiency compared to similar systems, through a calculation of its mass intensity (MI). We finally also carried out an evaluation of the projected cost for removal of each atom of chlorine from DCB.

The choice of 1,3-DCB as a model substrate representative of PCBs is justified by the fact that both PCBs and 1,3-DCB are liquids at ambient conditions, by the fact that 1,3-DCB is much safer than PCBs, and by our previous experience that indicates similar chemical behaviour under the conditions employed (Marques et al., 1994). Finally, the reaction can be easily monitored by GC.

2. Materials and methods

The reactions were conducted based on the conditions previously reported by us using a triphase system such as the one schematized in Fig. 1 (Perosa et al., 2001; Paganelli et al., 2007).

The chemicals used in the study: 1,3-dichlorobenzene (Sigma-Aldrich product no. 11308, 98%), A336 (Sigma-Aldrich product no. 205613), Pd/C (Sigma-Aldrich product no. 75992, 5% Pd) and NaOH were purchased from Sigma-Aldrich and used without further purification. Hydrogen (99.995%) was obtained from Società Italiana Acetilene e Derivati (SIAD). Gas chromatographic (GC) analyses were performed on an HP5970 GC equipped with an HP-5 a fused silica capillary column (30 m \times 0.25 mm) using nitrogen as carrier gas, operating in split-splitless mode and with a FID detector. The sample for GC analysis was prepared by collecting an aliquot (0.5 mL) of the organic phase with a syringe, diluting it with 5 mL ethyl ether and treating with 0.5 g of silica to ensure removal of ionic impurities. After injection of the sample (1.0 μ L) the GC oven was ramped from 50 to 250 $^{\circ}$ C at 10 $^{\circ}$ C/min.

2.1. Procedure for the scaled-up hydrodechlorination of 1,3-dichlorobenzene

Based on the optimized experimental procedure described

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