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Ion-exchange resin-supported palladium catalysts for hydrodehalogenation of aryl halides under batch and continuous flow conditions

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A R T I C L E I N F O

Dedicated to Professor Howard Alper, in recognition of his outstanding contributions to organic chemistry and catalysis, and his tireless work to shape and strengthen science policy

Keywords:
Anion-exchange resin
Flow microreactor
Hydrodehalogenation
Immobilization
Palladium

A B S T R A C T

Anion-exchange resin-supported palladium catalysts for dehalogenation of aromatic halides have been prepared by immobilizing Pd(II) on anion-exchange resins followed by reduction in hydrogen atmosphere. These catalysts showed high catalytic activity and selectivity in the hydrodehalogenation of various aryl halides both by hydrogen transfer from aqueous sodium formate in water–ionic liquid mixtures under batch conditions, and by hydrogenation in ethanol under moderate pressure of H_2 in a continuous flow microreactor.

1. Introduction

Organic halides belong to the most important compounds of our daily life. They are used as pharmaceuticals, herbicides, pesticides, polymers, solvents, and many more [1,2]. However, their extensive use led to serious problems of environmental pollution (such as e.g. the accumulation of chloroethylenes, chloroaromatics, and residues of chlorinated pharmaceuticals in surface and ground waters) [3]. It can be stated that both the introduction and removal of halogen atoms into/from an organic substrate are important and sometimes very challenging synthetic reactions, especially when selective transformations are required [4–7].

Reductive dehalogenation of organic halides with the use of metal-based catalysts is a well-established procedure [6,7] which can be performed with the use of molecular H_2 [8–10], by transfer hydrogenation [8,11] from a suitable hydrogen donor, or by using other reducing agents (hydrazine [12], $NaBH_4$ [13], hydrosiloxanes [14], $Me_2NH{\cdot}BH_3$ [15], etc.). The catalysts may contain various transition metals of which palladium is used most often [6,16]. Suitable hydrogen donors may include alcohols [8], formic acid/formates [11,17–19], and others. The vast field of catalytic dehalogenation was comprehensively reviewed by Alonso, Beletskaya, and Yus [6] therefore only selected examples are treated here which are relevant to the research described in this paper.

A large part of homogeneous catalysts are soluble metal complexes which can lead to high selectivity also in hydrodehalogenation [6,7]. However, practical synthetic procedures favour heterogeneous catalysts especially in large-scale industrial applications. For that reason, methods of heterogenization of intact metal complexes were developed [20–25] in order to achieve easy recovery of metal-complex catalysts. An important method of metal-complex heterogenization is in the application of two immiscible liquid phases (often aqueous-organic biphasic mixtures) one of which contains the catalyst while the other dissolves the substrate and product(s) [26–28]. Another approach is the use of metal catalysts, either as colloids or stabilized metal nanoparticles (NP-s) in liquid phases, or deposited onto a solid support. Such catalysts most often include Pd deposited on various forms of carbon (activated carbon, charcoal [15], nanodiamond [29], carbon nanotube-Ni foam [30], SiO_2 [9,31], Al_2O_3 [3,9,32], etc. However, other platinum metals, including e.g. Pt, Rh, Ir [6] and more abundant transition metals, such as Ni [15], and Mn [33] have been also studied. In biphasic aqueous–organic mixtures, certain additives (onium salts, amines, polyethylene glycol) significantly changed the activity and selectivity of Pd/C and Pt/C catalysts in hydrodehalogenation reactions [34]. Recent developments in the use of ionic liquids (IL-s; often 1,3-disubstituted

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imidazolium salts) as solvents for catalysis [35,36] revealed that metal nanoparticles can be stabilized by formation of *N*-heterocyclic carbene (NHC) complexes on the surface of NP-s [37,38]. The NHC-stabilized NP-s were applied for –among others– catalysis of *C-C* cross couplings [37,38] and in H/D exchange reactions [39,40]. Metal NP-s were often deposited onto synthetic polymers without [41–43] or with various anchor groups. Both neutral substituents (tertiary phosphine, amine, polyamine, polyoxyethylene, NHC, etc.), and ionic functionalities (e.g. $-SO_3^-$, $-COO^-$, $-NR_3^+$) can serve as such anchors [24].

Synthesis and catalytic application of Pd nanoparticles anchored onto ionically substituted polymers (most often commercial cation- or anion-exchangers) is well documented and reviewed [13,44–48]. Such Pd-NP catalysts were easily obtained in suspension by hydrogenation or hydrogen transfer reduction of cationic or anionic Pd-complexes (such as e.g. $[Pd(NH_3)_4]^{2+}$ [12,49], or $[PdCl_4]^{2-}$ [13,46]) sorbed on the ion-exchange resin [50,51]. They were used for catalysis of a variety of reactions, such as, for example, hydrogenation [12,23,47,52,53], *C-C* cross coupling [37,38,48,54], and hydrodehalogenation [55–60]. Important applications of hydrodehalogenation with the use of Pd@resin catalysts included removal of toxic chlorinated pollutants from waters [55–60]. The great number of commercially available ion-exchangers allowed synthesis of a wide array of Pd@resin catalysts [44]. Application of solid supports for metal complexes and nanoparticles made also possible the use of flow (micro)reactors for various reactions [21,23,25,30,48,54,61–66]. The latter, such as e.g. the H-Cube microfluidic hydrogenation reactor proved their operational simplicity and safety in widespread applications, and are now commercially available. Hydrogenation as well as hydrodehalogenation reactions specifically benefit from elimination of the need for bottles of compressed hydrogen.

Although supported metal heterogeneous catalysts (such as e.g. Pd/C) are widely used for hydrodehalogenations, and despite the fact that ion-exchanger-supported metal catalysts proved their usefulness in several important synthetic processes, application of the latter type of catalysts in hydrodehalogenation reactions is still relatively scarce. In the following we describe a simple synthesis of Pd catalysts supported onto commercial anion-exchange resins. The obtained Pd@resin products were used for catalysis of transfer hydrodehalogenation of halobenzenes from aqueous sodium formate in batch reactions with the use of water-ionic liquid mixtures as solvent. Furthermore, the catalytic properties of these supported Pd catalysts were studied and compared to Pd/C in hydrodehalogenation of halobenzenes and haloacetophenones in ethanol, ethanol–water and ethanol-toluene solvents under flow conditions with the use of a H-Cube microreactor.

2. Experimental

2.1. Reagents and materials

All chemicals and reagents used in this work were purchased from Sigma-Aldrich, Molar Chemicals and VWR International and were used as received. Various DIAION resins were purchased from Mitsubishi Chemical Company. All anion-exchange resins were pre-treated before immobilization by three successive washings with 0.1 M aqueous solutions of NaOH and HNO_3, respectively, at room temperature. Then the anionite was collected on a glass filter and was washed several times with deionized water then ethanol, and dried in vacuum.

2.2. Instrumentations

In case of halobenzenes and chloroacetophenones, reaction mixtures were analyzed by gas chromatography on an Agilent Technologies 7890 A instrument (OPTIMA 1 column, 0.25 μm×30 m×0.32 mm, FID 300 °C; carrier gas: nitrogen, 1.9 mL/min). In general, the products were identified by comparison of their retention time with known compounds. However, in case of chloroacetophenones, ethylbenzene was identified by GC–MS with a 5975C inert MSD Triple-Axis detector. Products of acetophenone hydrogenations were separated on a Hewlett-Packard Series II 5890A type gas chromatograph (CYCLODEX B column, 0.25 μm×30 m×0.32 mm, FID 300 °C; carrier gas: argon, 1.9 mL/min). In all experiments, decane was used as an internal standard. Other details of gas chromatographic separations can be found in the Supporting Information (Figures S1- S3, Table S1).

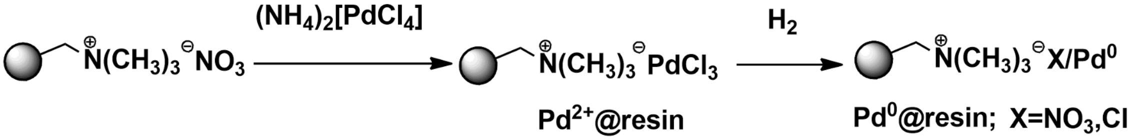
UV–visible spectra were recorded with the use of a Shimadzu UV-1700 spectrophotometer equipment. IR spectra were recorded on Perkin Elmer Spectrum One FT-IR spectrometer equipped with a Universal ATR Sampling Accessory. The palladium content of the resins were determined by ICP-OES using a Thermo IRIS Intrepid II XPS instrument (detection limit 0.9 μg/L, Pd 340.458 nm; n=5) or an Agilent Technologies 5110 VDV spectrometer.

Flow reactions were studied using an H-Cube microfluidic flow reactor (ThalesNano Nanotechnology Inc., Budapest, Hungary). 100 mg of the resin-supported catalysts were packed into commercially available stainless steel CatCart columns (30×4 mm). Commercial 10% Pd/C catalyst (in 30×4 mm CatCart, m = 110±5 mg, 0.103 mmol Pd) was purchased from ThalesNano Nanotechnology Inc.

2.3. Characteristics of the anion-exchange resins used in this study and synthesis of the supported palladium catalysts

Four strongly basic anion-exchange resins with quaternary ammonium functional groups (DOWEX 1x8, **1**; DIAION PA308/L, **2**; DIAION HPA25, **3**; ReliSorb QA405/EB, **4**) and the weakly basic DIAION WA21J resin, **5** (with polyamine functional groups) were used for catalyst preparation. **1** is a gel-type anionite, while **2**–**5** are highly porous resins. Other important properties of these resins are presented in the Supporting Information (Table S2). General scheme of the preparation of the resin supported Pd-catalysts is shown on Scheme 1. Representation of Pd^{2+}@resin products as containing anchored $[PdCl_3]^-$ species is based on the Pd(II)-complex distribution in 0.1 M HNO_3 (Figure S4) [67,68].

For deposition of Pd(II)-chlorocomplexes on the ion-exchange resins, 1.0 g of acid/base pre-treated dried resin was added at room temperature to a solution of $(NH_4)_2[PdCl_4]$ (0.120 g, 0.43 mmol) in 0.1 M HNO_3 (100 mL). In a short time (approx. 20 min) the color of the aqueous phase changed from yellow to colourless with a simultaneous colour change of the initially white resin to yellow. The ion-exchange process was followed by uv–visible spectrophotometry (Figure S5). The suspension was left to stay for an additional 2 h. The supported Pd(II)-complex was collected on a glass filter and washed several times with deionized water then ethanol, and dried in vacuum. Infrared spectra of the anionites did not show changes upon ion-exchange with $[PdCl_4]^{2-}$ (Figure S6). Pd@resin catalysts Pd@**1**–**5**, were obtained by placing a yellow, Pd^{2+}-loaded resin under hydrogen at 5 bar pressure at room temperature, with no added solvent, which resulted in an immediate colour change to black. The Pd-content of the supported catalysts was



Scheme 1. Synthesis of palladium containing resins.

determined by ICP-OES and found as follows (w/w %): Pd@**1** – 2.84; Pd@**2** – 3.46; Pd@**3** – 3.94; Pd@**4** – 3.08, Pd@**5** – 4.48. Variation in the Pd-content of the final catalysts is presumably caused by the different water content of the anionites used as support, although the different particle size of the ion-exchange resins may also influence Pd deposition (Table S2).

2.4. Typical experimental procedure for dehalogenation reactions under batch conditions

In a typical experiment, 60 mg of the yellow Pd^{2+}@resin was placed into a thick-wall reactor tube and pressurized with 5 bar H_2 for in situ generation of the active Pd@resin catalyst. After 5 min the pressure was released and halobenzene (2.5 mmol), 0.5 mL ionic-liquid, and 0.5 mL 5 M aqueous sodium-formate solution (2.5 mmol HCO_2Na) were added yielding a homogeneous liquid phase. The reaction mixture was heated on air to 80 °C with magnetic stirring. In dehalogenations with H_2, 0.5 mL water was added instead of the sodium-formate solution, and the mixture was stirred under H_2 gas of the required pressure. After 2 h, the reaction mixture was cooled in an ice bath and extracted with diethylether (1.5 mL). The organic phase was dried by passing through a $MgSO_4$ column and the reaction products were identified and quantified by gas chromatography.

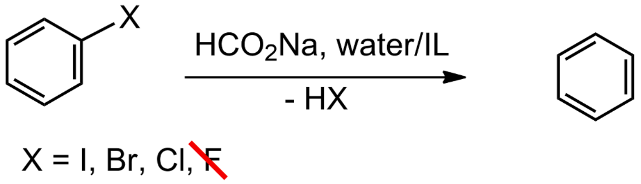
2.5. Typical experimental procedure for dehalogenation reaction in H-Cube flow reactor

In a typical experiment, a solution of halobenzene (0.1 M) in ethanol was pumped through the catalyst-packed cartridge (30 mm×4 mm) with 1 mL/min flow rate, under 10, 20, 40, 60, 80, or 100 bar hydrogen pressure at temperatures of 20, 40, 60, 80, or 100 °C. Catalyst cartridges were filled with 100 mg of Pd@DOWEX 1x8 (Pd@**1**), Pd@DIAION PA308/L (Pd@**2**), Pd@DIAION HPA25 (Pd@**3**), Pd@ReliSorb QA405/EB (Pd@**4**), or Pd@DIAION WA21J (Pd@**5**). Before each measurement, the H-Cube microfluidic flow reactor was washed for 10 min with absolute ethanol under the required H_2 pressure. After stabilization at the pre-set actual reaction parameters, flow of the substrate solution was started. The reaction mixture was sampled at the outflow after 5 min flow time. Duplicate samples were collected and analyzed by gas chromatography.

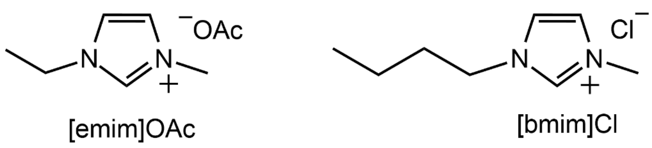
3. Results and discussion

3.1. Hydrodehalogenation reactions with Na-formate under batch conditions

The anion-exchange resins, **1**–**5**, were reacted with an aqueous solution of $(NH_4)_2[PdCl_4]$ followed by reduction with molecular hydrogen. The resulting palladium catalysts were tested in catalytic hydrodehalogenation of halobenzenes (Scheme 2) by transfer hydrogenation from aqueous sodium formate under batch conditions. Mixtures (50–50 % V/V) of water and one of the two ionic liquids, [emim]OAc (1-ethyl-3-methylimidazolium acetate) or [bmim]Cl (1-*n*-butyl-3-methylimidazolium chloride), shown on Scheme 3. The reaction parameters for hydrodehalogenation were optimized using Pd@DOWEX 1X8 catalyst (Pd@**1**). The catalyst showed high activity under mild conditions, with benzene as the exclusive product; no further hydrogenation (e.g. to cyclohexane) was detected. Representative results are summarized in Table 1.



Scheme 2. General scheme of hydrodehalogenation of halobenzenes.



Scheme 3. Ionic liquids used in this study.

Table 1
Hydrodehalogenation of halobenzenes with aqueous sodium formate under batch conditions using Pd@DOWEX 1x8 (Pd@**1**) as catalyst.

Entry	Substrate	Ionic Liquid	Conversion (%)
1	C_6H_5Cl	[emim]OAc	86
2	C_6H_5Br	[emim]OAc	70
3	C_6H_5I	[emim]OAc	12
4	C_6H_5F	[emim]OAc	0
5	C_6H_5Cl	–	70
6	C_6H_5Br	–	29
7	C_6H_5Cl	[bmim]Cl	96
8	C_6H_5Br	[bmim]Cl	61
9	C_6H_5Cl	[bmim]Cl	32[a]
10	C_6H_5Cl	[bmim]Cl	99[b]

Reaction conditions: 2.5 mmol substrate, 2.5 mmol HCO_2Na, 60 mg Pd@**1**, 0.5 mL water, 0.5 mL ionic liquid, 50 μL decane, 80 °C, 2 h. [a] RT; [b]0.5 mmol substrate; 19 h, RT.

The data in Table 1 show that at 80 °C hydrodehalogenation of chlorobenzene proceeded faster than that of bromobenzene both in water–[emim]OAc (Entries 1,2) and in water–[bmim]Cl mixtures (Entries 7,8). Iodobenzene showed low reactivity while fluorobenzene could not be dehalogenated at all (Entries 3,4). When no ionic liquid was used (Entries 5,6) only moderate yields were obtained with larger conversion of chlorobenzene than that of bromobenzene. It is remarkable, that the reaction could be successfully performed –albeit with lower rate– at room temperature (Entry 9). However, increased catalyst amount and longer reaction time still led to practically complete conversion of chlorobenzene (Entry 10). Using HCO_2Na as a hydrogen source, the reactivity of halobenzenes with Pd@**1** as the catalyst for dehalogenation, did not follow the C-X bond strength in the substrates. In separate reactions, the conversion of chlorobenzene was consistently higher than those for bromo- and iodobenzene. This phenomenon is often observed in halobenzene dehalogenations with Pd [11,29], and is attributed to inhibition by the halide ions produced in the reaction. Interestingly, dehalogenation of the studied halobenzenes was faster in water–IL mixtures than in water alone, and even somewhat faster with [bmim]Cl than with [emim]OAc, despite the presence of Cl^- in [bmim]Cl. The role of the ionic liquids may be in the solubilization of halobenzenes in the partly aqueous solvent resulting in faster reactions in the water–IL mixtures, or by forming an adsorbed IL film on the surface of the catalyst, similarly to the observations of Tundo et al [34]. Formation of surface-NHC species cannot be excluded either [38–40,69,70]. Furthermore, the ion-exchange resin supports (with the exception of **5**) are polymeric quaternary ammonium salts, and the reaction of Pd(II)-species with surface $–R_3N^+$ functional groups may result in highly reactive ion-pairs – similar to the findings of Januszkiewicz and Alper [71], Blum et al [72], and Jeffery [73] – leading to formation of Pd-nanoparticles in reaction with H_2 or aqueous Na-formate. (It may also be important, that under conditions of Table 1, 100% dechlorination of chlorobenzene yields 2.5 mmol HCl, in comparison to the 3.1 mmol Cl^- in 0.5 mL [bmim]Cl. However, the effect of total chloride concentration on the reaction rate was not investigated in this study.).

It is important to note, that in a control experiment on chlorobenzene hydrodehalogenation with the use of Pd@**1** catalyst and with water–

Table 2
Transfer hydrodehalogenation of halobenzene mixtures under batch conditions with Pd@DOWEX 1x8 (Pd@**1**) and Pd@DIAION WA21J (Pd@**5**) catalysts.

Entry	Catalyst	Conversion (%)		
		C_6H_5Cl	C_6H_5Br	C_6H_5I
1	Pd@**1**	21	11	22
2	Pd@**5**	19	13	21

Reaction conditions: Mixture of C_6H_5Cl, C_6H_5Br, C_6H_5I, 1.0 mmol each, 3.0 mmol HCO_2Na, 60 mg Pd@**1** or Pd@**5**, 0.5 mL water, 0.5 mL [emim]OAc, 50 μL decane, 80 °C, 2 h.

[bmim]Cl solvent under argon (i.e. in the absence or H_2 or Na-formate), after 2 h at 80 °C no benzene or cyclohexane was detected by gas chromatography, independent of the substrate concentration being 0.5 or 2.5 mmol. These results suggest that the contribution of the hydrogen content of the Pd catalyst (from its synthesis under H_2) is negligible to the conversion of chlorobenzene in the absence of other reducing agents, such as Na-formate of hydrogen.

When mixtures of halobenzenes were studied with the use of a water–[emim]OAc mixed solvent, and with Pd-catalysts supported on a strongly basic or a weakly basic anionite (Pd@**1** and Pd@**5**, respectively) the conversions of the three substrates did not significantly depend on the nature of the support, despite the fact that among our resin-supported catalysts Pd@**1** and Pd@**5** are the most different catalysts in terms of support type, functional group, and particle size. However, in these cases the reactivity order of $C_6H_5I \approx C_6H_5Cl > C_6H_5Br$ was observed (Table 2). A possible explanation of this finding is that in the simultaneous hydrodehalogenation of C_6H_5Cl, C_6H_5Br, and C_6H_5I, the resulting Cl^-, Br^- and I^- inhibit the dehalogenation of all three substrates (cross inhibition).

Reusability of the Pd@DOWEX 1x8 catalyst was studied by repeating the same procedure of chlorobenzene dehalogenation several times. To this end, the final reaction mixtures were extracted with diethyl ether (2×6 mL), the organic phase was removed with a Pasteur pipette, and traces of ether were taken away by stirring the residual catalyst suspension under vacuum. It should be mentioned, that magnetic stirring milled the beads of the supported catalyst into hardly settling powder, so complete catalyst recovery was hard to achieve. The subsequent reactions were started by the addition of a new batch of the substrate, HCO_2Na, and the internal standard (decane). As shown in Fig. 1, the catalyst could be recycled up to five consecutive cycles and a significant decrease of conversion was observed (from 96% in the 1st to 60% in the 5th run). We checked the extent of Pd leaching into the solution phase in chlorobenzene hydrodehalogenation with the use of Pd@**1**. After carrying out the 1st run (under identical conditions to those in Fig. 1), the resulting reaction mixture was passed through a 0.2 μm PTFE membrane filter (VWR Syringe Filter). With the use of ICP-OES, the Pd concentration of the filtrate was found 187.29 mg/mL, which is equivalent to 10. 9% of the total initial Pd content of the applied catalyst. Such a leaching of the catalytic Pd species from the support explains the larger part (but not all) of the experimentally observed activity loss (77.9 % conversion in the 2nd run compared to 95.8 % in the 1st). The lower activity of the catalyst from run to run may also be due to morphology changes of the resin-bound Pd particles and –at least in part– to the physical loss of the catalyst caused by the recovery procedure.

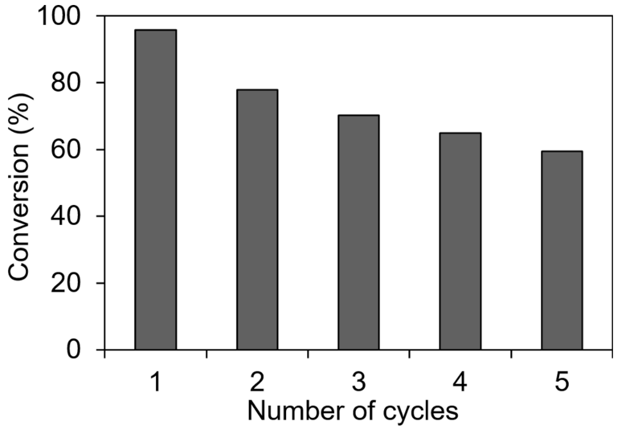


Fig. 1. Recycling of the Pd@DOWEX 1x8 (Pd@**1**) catalyst in repeated hydrodehalogenations of chlorobenzene. Reaction conditions: 60 mg Pd@**1** added in the first run. Other conditions: 2.5 mmol chlorobenzene, 2.5 mmol HCO_2Na, 0.5 mL water, 0.5 mL [emim]OAc, 50 μL decane in each run at 80 °C, 2 h.

Concentration of the hydrogen donor (HCO_2Na) in the water/IL phase had a profound effect on the reaction rate of catalytic hydrodehalogenations. For example, in the case of chlorobenzene, hydrodehalogenation with Pd@**1**, the conversion of the substrate increased rapidly with increasing amounts of the hydrogen donor, and already at a ratio of $n(HCO_2Na)/n(C_6H_5Cl) = 1/1$ (mol/mol), a conversion of 86% was determined (Fig. 2). This was further increased to 100% by raising the formate/chlorobenzene ratio to 2.0. However, at such high HCO_2Na concentrations the reaction mixture was inhomogeneous at room temperature; that is why we generally used one equivalent of HCO_2Na to the halobenzene substrate in this study.

Two resin-supported catalysts, Pd@**1** and Pd@**5** were compared in hydrodehalogenation of chlorobenzene with molecular H_2, and with hydrogen transfer from aqueous sodium formate. It can be seen from the data of Table 3, that in water–[emim]OAc mixed solvent, Pd@**1** showed substantially higher activity (90% to 98% conversion) than Pd@**5** (50% to 66% conversion) at all three investigated hydrogen pressures. However, upon addition of sodium formate, Pd@**5**, too, showed excellent catalytic activity both in the presence and absence of the ionic liquid (99% vs 97% conversion, respectively). This shows, that Pd@**1** is inherently a more active catalyst than Pd@**5** and this fact is manifested at 1 bar H_2 pressure, where the concentration of the reducing agent (H_2)

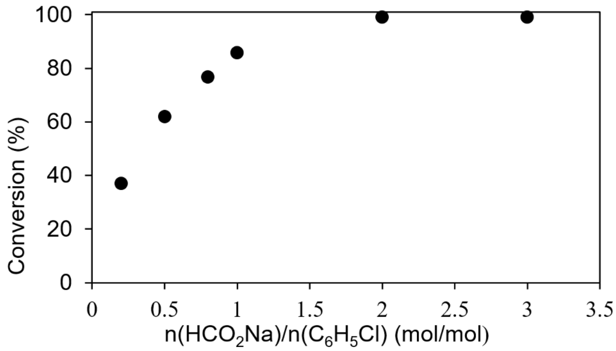


Fig. 2. Effect of the sodium formate to substrate molar ratio on the conversion of chlorobenzene in catalytic hydrodehalogenation. Reaction conditions: 2.5 mmol chorobenzene, 60 mg Pd@**1**, 0.5 mL water, 0.5 mL [emim]OAc, 50 μL decane, 80 °C, 2 h.

Table 3
Hydrodehalogenation of chlorobenzene using molecular hydrogen under batch conditions with Pd@DOWEX 1x8 (Pd@**1**) and Pd@DIAION WA21J (Pd@**5**) catalysts.

Entry	Catalyst	Conversion (%)		
		1 bar H_2	5 bar H_2	10 bar H_2
1	Pd@**1**	90	93	98
2	Pd@**5**	50	59 (99[a], 97[b])	66

Reaction conditions: 2.5 mmol C_6H_5Cl, 60 mg Pd@resin, 0.5 mL water, 0.5 mL [emim]OAc, 50 μL decane, 80 °C, 2 h; [a]with addition of 2.5 mmol HCO_2Na; [b]without ionic liquid, but with addition of 2.5 mmol HCO_2Na, and 0.5 mL water to replace the IL.

in the aqueous phase is low (0.81 mM at 20 °C). However, in the dehydrogenations with 2.5 M aqueous HCO_2Na the high concentration of the reducing agent drove the reactions almost to completion with both catalysts (Table 1, entry 7, and Table 3, entry 2^a and 2^b).

To obtain information on the possible effect of soluble quaternary ammonium salts (such as e.g. the IL-s used in this study), we carried out hydrodehalogenation of chlorobenzene with Pd@**1** catalyst under 1 bar H_2, with 1 mL of water as solvent, and 0.125 mmol of dodecyltetrabutylammonium bromide (DTAB) (other conditions as in Table 3). A 52% conversion was found, which is much less, than the 90 % conversion obtained in the presence of 0.5 mL [emim]OAc (Table 3, entry 1). This result also shows, that even if the interaction of the Pd(II)-precursor (s) with the surface ammonium groups is important in formation of the supported Pd-catalysts, the ionic liquid additives were much more effective in obtaining high conversions in chlorobenzene hydrodehalogenation than DTAB itself.

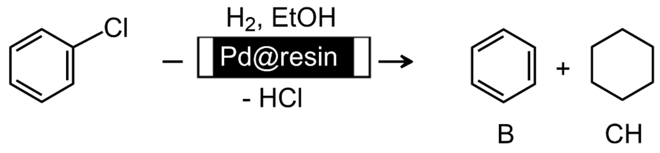
3.2. *Hydrodehalogenation reactions under flow conditions*

As detailed in the Introduction, several Pd-based catalysts immobilized on a variety of supports (among them non-functionalized and functionalized synthetic resins) were applied for catalysis of hydrodehalogenation. Most publications reported on batch processes [55–60], however, flow processes with Pd-catalysts on diverse supports for various reactions (e.g. hydrodehalogenation [30,74], hydrogenation [64–66], *C-C* cross coupling [54,62], and deuterodehalogenation [61]) were also described. In contrast, hydrodehalogenations with commercially available ion-exchange resin-supported Pd-catalysts in flow systems were not yet investigated. Therefore, it was of interest to compare our anion-exchange resin-supported Pd-catalysts to a standard hydrogenation catalyst also in the flow dehydrohalogenation of chlorobenzene. In addition to benzene (B), Scheme 4 also shows cyclohexane (CH) as possible product. For comparative experiments, the widely used 10% Pd/C (0.94 mmol Pd/g) catalyst was chosen. Flow hydrodehalogenations were studied with ethanol as solvent, since in the absence of IL-s the chlorinated substrates did not dissolve freely in 2.5 M aqueous Na-formate.

The resin-supported catalysts were packed into small stainless steel cartridges, and connected to an H-Cube microfluidic hydrogenation reactor. Each cartridge contained 100 mg of the Pd@resin catalyst. Ethanolic solution of the substrate (e.g. chlorobenzene) was passed through the catalyst column at the required temperature and H_2 pressure at various flow rates, all pre-set electronically. Results of the hydrodehalogenation of chlorobenzene (0.1 M in ethanol) with commercial 10% Pd/C catalyst are summarized in Table 4.

The conversion of chlorobenzene increased with increasing temperature, however, above 80 °C the activity of the catalyst did not increase further. Lower flow rates (longer residence time in the reactor) led to higher conversions. Conversely, the pressure of H_2 had no significant effect on the conversions.

The effect of substrate concentration on the reaction rate was also investigated (Table 5). The decrease of the substrate concentration from 0.1 M to 0.001 M increased the conversion but led to lower selectivity. Full conversion of chlorobenzene with 99% selectivity to benzene (B) was still achieved in case of 0.04 M C_6H_5Cl concentration (Entry 3). However, lower chlorobenzene concentrations led to formation of significant amounts of cyclohexane (CH), too. This can be rationalized by assuming a consecutive reaction chlorobenzene → benzene → cyclohexane, with the rate of formation of benzene considerably higher than its further reduction to cyclohexane. Strong adsorption of chlorobenzene on the catalyst surface may strongly hinder the further reduction of benzene. So at high substrate concentrations, when the total conversion is below 100%, cyclohexane does not appear as product (Table 5, entries 1 and 2). However, when all chlorobenzene is consumed (as is the case at low substrate concentrations), hydrogenation of benzene sets on and the product mixture contains increasingly higher amounts of cyclohexane with decreasing substrate concentrations.



Scheme 4. Hydrodehalogenation of chlorobenzene under flow conditions.

Table 4
Effect of the reaction parameters on the conversion of chlorobenzene in hydrodehalogenation with 10% Pd/C catalyst in flow reactor.

Entry	*P*(H_2) (bar)	*T* (°C)	Flow rate (mL/min)	Conversion (%)
Effect of temperature				
1	10	20	1.0	18
2	10	40	1.0	25
3	10	60	1.0	52
4	10	80	1.0	66
5	10	100	1.0	67
Effect of H_2 pressure				
6	20	80	1.0	73
7	40	80	1.0	70
8	60	80	1.0	70
9	80	80	1.0	68
10	100	80	1.0	69
Effect of flow rate				
11	10	80	0.6	71
12	10	80	0.7	70
13	10	80	0.8	67
14	10	80	1.0	66
15	10	80	1.5	57
16	10	80	2.0	54
17	10	80	3.0	49

Reaction conditions: 110 mg 10% Pd/C, 0.1 M C_6H_5Cl, 0.256 mM decane (internal standard), solvent: ethanol.

Table 5
Effect of substrate concentration on the rate and selectivity of chlorobenzene hydrodehalogenation (10% Pd/C).

Entry	Concentration (M)	Conversion (%)	B (%): CH (%)
1	0.10	66	100:0
2	0.05	85	100:0
3	0.04	100	99:1
4	0.03	100	96:4
5	0.02	100	84:16
6	0.01	100	45:55
7	0.005	100	30:70
8	0.001	100	22:78

Reaction conditions: 110 mg 10% Pd/C, 0.256 mM decane (internal standard), 80 °C, 10 bar H_2, 1 mL/min flow rate, solvent: ethanol.

The ion-exchange resin-supported Pd-catalysts, too, were tested in hydrodehalogenation of chlorobenzene with the use of an H-Cube microreactor under continuous flow conditions. The catalytic activity of Pd@**1**–**5** was studied at the optimum reaction parameters determined with Pd/C catalyst. The Pd-concentration in the effluent reaction mixture was below the ICP-OES detection limit. Influence of the solvent on the conversion was also investigated. In addition to EtOH, hydrodehalogenation of chlorobenzene was carried out also in EtOH–toluene = 1:1 (V/V), and in EtOH–water = 95:5 (V/V) mixed solvents. The results are shown in Table 6. In EtOH, all Pd@resin catalysts were moderately or highly active, and with the most effective catalysts, Pd@DIAION PA308/L (Pd@**2**) and Pd@DIAION HPA25 (Pd@**3**) at 0.01 M chlorobenzene concentration, over 70% conversions were obtained in one pass. The anionite supports **2** and **3** are very similar, containing quaternary alkylammonium functional groups, attached to strongly basic porous polystyrene-divinylbenzene matrix (Table S2). Addition of

Table 6
Hydrodehalogenation of chlorobenzene with Pd@**1**–**5** resin-supported and 10% Pd/C catalysts in flow reactor.

Entry	Catalyst	Conversion (%)		
		EtOH	50% toluene in EtOH	5% H_2O in EtOH
1	Pd@**1**	53	n.d.	n.d.
2	Pd@**2**	70	20	66
3	Pd@**3**	88	12	92
4	Pd@**4**	61	n.d.	n.d.
5	Pd@**5**	30	n.d.	n.d.
6	10% Pd/C	100	13	98

Reaction conditions: 100 mg Pd@resin, or 110 mg 10% Pd/C, 0.01 M C_6H_5Cl, T = 80 °C, $P(H_2) = 10$ bar H_2, flow rate = 1 mL/min, 0.256 mM decane (internal standard); n.d.: not determined.

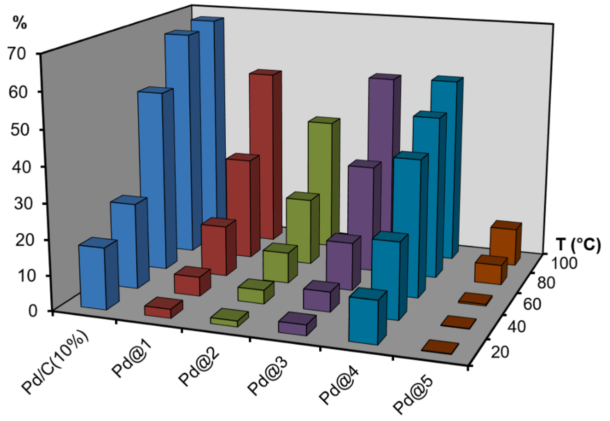


Fig. 3. Effect of the temperature on the catalytic activity of resin-supported Pd catalysts on hydrodehalogenation of chlorobenzene. Reaction conditions: 100 mg Pd@**1**–**5**, 0.1 M C_6H_5Cl, 0.256 mM decane (internal standard), $P(H_2) = 60$ bar, flow rate = 1 mL/min, solvent: ethanol.

Table 7
Hydrodehalogenation of chlorobenzene with new and used Pd catalysts.

Entry	Catalyst	Conversion of chlorobenzene (%)	
		new catalyst	1 month old catalyst
1	10% Pd/C	100	62
2	Pd@**2**	58	40
3	Pd@**3**	84	62

Reaction conditions: 110 mg 10% Pd/C or 100 mg Pd@resin 0.04 M C_6H_5Cl, 0.256 mM decane (internal standard), T = 80 °C $P(H_2) = 10$ bar, flow rate = 1 mL/min, solvent: ethanol.

5% water did not significantly change the conversions compared to neat EtOH. In contrast, in presence of toluene only low conversions (between 10–20%) were achieved. This was probably due to competing adsorption of toluene leading to displacement of chlorobenzene on the catalyst's surface resulting in concomitant decrease of the conversion.

The effect of temperature, hydrogen pressure and flow rate on chlorobenzene hydrodehalogenation with the resin-supported Pd-catalysts was also determined. Fig. 3 shows the effect of temperature with these catalysts.

It is seen from Fig. 3, that similar to the case of the 10% Pd/C catalyst, raising the temperature resulted in higher conversion with all five Pd@resin catalysts. However, important differences were also observed. While Pd@**4** was active already at 20 °C, Pd@**1**–**3** afforded only low conversions, and Pd@**5** did not show any activity at this temperature. In contrast, the activity of Pd@**1**, Pd@**3**, and Pd@**4** (containing 2.84, 3.46 and 3.08 w/w % Pd, respectively) rapidly increased with increasing temperatures, and their use at 100 °C led to 52 to 54% conversion, which is close to that obtained with the commercial 10% Pd/C catalysts (67%) of higher Pd content. The effect of flow rate (Figure S7) and hydrogen pressure (Figure S8) was basically the same as that observed in the case of 10% Pd/C (Table 4).

With the aim of establishing the reusability and the stability of the resin-supported catalysts in flow conditions, the same reaction was repeated after one month of regular use of the catalysts. After each use the catalysts were washed with ethanol, and stored in a CatCart catalyst container under ethanol. As shown by the data of Table 7, after one month, the activity of the anion-exchange resin-immobilized catalysts decreased modestly (18–22%) compared to the commercially available 10 %Pd/C (activity drop 38%).

3.3. *Hydrodehalogenation of chloroacetophenones*

Hydrogenation of acetophenones results in important products such as e.g. 2-phenylethanol via reduction of the ketone functionality, or ethylbenzene via deoxygenation [6,10,18,31,34,43,52]. The reaction may also yield the corresponding cyclohexane derivatives. In case of haloacetophenones, dehalogenation may also take place, further increasing the number of possible products. It was also found, that for certain supported Pd-catalysts, the reaction rate and selectivity were significantly influenced by the presence of water [10,52] or upon addition of modifiers (such as e.g. onium salts, polyethylene glycol, etc. [34]).

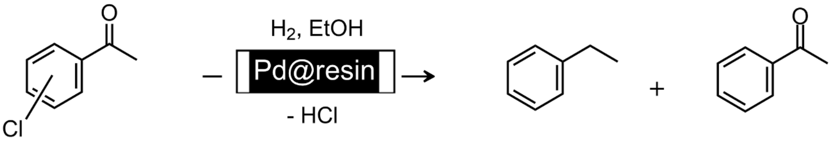
We compared the catalytic properties of commercial 10% Pd/C and of our anion exchange resin-supported Pd@DIAION HPA25 (Pd@**3**) catalyst, in hydrogenation of *o*-, *m*, and *p*-chloroacetophenone under flow conditions. As shown on Scheme 5, only two of the eleven possible products were detected under the reaction conditions of Table 8.

The resin-supported catalyst selectively yielded ethylbenzene as the sole product with all three substrates, that means that both aromatic dehalogenation and benzylic deoxygenation took place. However, in reactions of *m*- and *p*-chloroacetophenone, with the use of 10% Pd/C catalyst, acetophenone was also detected in addition to ethylbenzene (Entries 2,3). With the Pd@**3** catalyst we also studied the reactions at 30

Table 8
Hydrodechlorination of *o*-, *m*- and *p*-chloroacetophenone with palladium catalysts in flow reactor.

Entry	Substrate	10% Pd/C		Pd@DIAION HPA25 (Pd@**3**)	
		Conv.[a]	Selectivity[b]	Conv.[a]	Selectivity[b]
1	*o*-Cl-acetophenone	100	100	100(78[c])	100
2	*m*-Cl-acetophenone	100	88	99(63[c])	100
3	*p*-Cl-acetophenone	100	79	98(60[c])	100

Reaction conditions: 110 mg 10% Pd/C, or 100 mg Pd@**3**, 0.01 M substrate, 0.256 mM decane, EtOH, 80 °C, [c]30 °C, 10 bar H_2, 1 mL/min.
[a] Conversion of chloroacetophenone (%).
[b] Selectivity to ethylbenzene (%).



Scheme 5. General scheme of flow hydrodehalogenation of acetophenones.

°C, however, lowering the temperature only reduced the conversion to ethylbenzene but did not impact the 100% selectivity.

In hydrogenation of acetophenone, Rahaim and Maleczka observed, that with a Pd-nanoparticle catalyst, obtained from $Pd(OAc)_2$ and polymethyl hydrosiloxane (PMHS) as the reductant, in the absence of any additive the sole product was 1-phenylethanol (98% yield in 24 h). In contrast, addition of 1 equivalent of chlorobenzene not only speeded up the reaction but completely switched the selectivity to ethylbenzene (100% yield in 1 h). This striking effect was attributed to a slow and controlled release of HCl in the simultaneous dehydrochlorination of chlorobenzene [75]. We have observed a similar effect of chlorobenzene on the hydrogenation of acetophenone (Table S3). With Pd@**3** as the catalyst, hydrogenation of acetophenone yielded 74% ethylbenzene and 26% 1-phenylethanol in the absence of an additive. Conversely, with the addition of 10 mol% chlorobenzene, the ethylbenzene/1-phenylethanol selectivity shifted to 96:4. Together with the data shown in Table 8, this finding implies, that the resin-supported Pd@DIAION HPA25 (Pd@**3**) is a more effective catalyst than 10% Pd/C for deoxygenation of acetophenone to ethylbenzene (and remain effective even at 30 °C).

4. Conclusions

Practical and economical synthesis of anion-exchange resin-supported palladium catalysts was developed with the use of various anion-exchangers. The synthesis relies on the reduction of the dry, Pd^{2+}-loaded anionites under 5 bar H_2 in the absence of solvent. The obtained Pd@**1**–**5** catalysts showed high catalytic activity and selectivity, comparable to those of 10% Pd, in dehydrohalogenation of monohalobenzenes by hydrogen transfer from aqueous sodium formate (batch reaction), as well as in their dehalogenation with H_2 in a flow microreactor (with ethanol as solvent). The transfer hydrodehalogenations were significantly faster in the presence of ionic liquids than in pure aqueous systems. In flow reactions, hydrogenation of *o*-, *m*- and *p*-monochloroacetophenones with the ion-exchange resin-supported Pd-catalysts selectively yielded ethylbenzene with all three isomers, while in the case of 10% Pd/C, acetophenone was also produced with *m*- and *p*-chloroacetophenone as the substrate.

CRediT authorship contribution statement

Csilla Enikő Czégéni: Conceptualization, Supervision, Investigation, Writing – original draft, Writing – review & editing. **Henrietta Kovács:** Investigation, Writing – review & editing. **Gábor Papp:** Methodology, Visualization, Funding acquisition, Writing – review & editing. **Ágnes Kathó:** Conceptualization, Writing – review & editing. **Ferenc Joó:** Conceptualization, Funding acquisition, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data are available from the authors upon request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2023.121613.

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