

Review

Applicability of Nickel-Based Catalytic Systems for Hydrodehalogenation of Recalcitrant Halogenated Aromatic Compounds

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Abstract: This review summarizes recent applications of nickel as a nonprecious metal catalyst in hydrodehalogenation (HDH) reactions of halogenated aromatic compounds (Ar-Xs). Nickel-based HDH catalysts were developed for reductive treatment of both waste containing concentrated Ar-Xs (mainly polychlorinated benzenes) and for wastewater contaminated with Ar-Xs. Ni-catalyzed HDH enables the production of corresponding nonhalogenated aromatic products (Ar-Hs), which are principally further applicable/recyclable and/or Ar-Hs, which are much more biodegradable and can be mineralized during aerobic wastewater treatment. Developed HDH methods enable the utilization of both gaseous hydrogen via the direct HDH process or other chemical reductants as a source of hydrogen utilized in the transfer of the hydrodehalogenation process. This review highlights recent and major developments in Ni-catalyzed hydrodehalogenation topic since 1990.

Keywords: hydrodehalogenation; hydrodechlorination; nickel; bimetallic systems; nanocatalysts; Al-Ni



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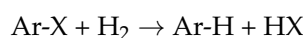


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1. Introduction

Ar-Xs are commercially important chemicals that are used as inert solvents (chlorobenzene or o-dichlorobenzene), end products and intermediates in the manufacture of plastics, dyes and a diversity of agrochemicals, flame retardants or other specialty fine chemicals. Ar-Xs are xenobiotic, highly stable in the environment, resistant to biodegradation, often exhibit considerable toxicity and have long been regarded as a major source of environmental pollution [1]. The presence of Ar-Xs in effluent discharges is of increasing concern, due to the ecological effects and impact on public health. The upcoming restrictive legislation evokes urgency to the development of effective removal strategies [1].

Catalytic hydrodehalogenation (HDH) is an effective means of detoxifying halogenated waste. Catalytic HDH represents a modern approach whereby the hazardous Ar-X is transformed into an easier biodegradable or even recyclable product (Ar-H) in a closed system with limited toxic emissions or enabling the detoxification of aqueous contaminants for subsequent biological treatment. HDH is a burgeoning area in an environmental catalysis focused on the treating of environmental pollutants in the past two decades. HDH involves hydrogenolysis of C-X bonds, lowering the toxicity and generating biodegradable or even reusable raw material Ar-H from Ar-X. It requires an external source of hydrogen and is typically promoted using hydrogenation catalyst (Pd, Pt, etc.) [1]:



To date, incineration has largely been the preferred technology for destroying dangerous waste contaminated with Ar-Xs but the requisite high decomposition efficiency (>99.9999%) is difficult to achieve in case of halogenated aromatic compound [2]. From an economic viewpoint, considering incineration as the principal means of halogenated

organic waste treatment, a move to a catalytic hydrodehalogenation-based treatment represents immediate cost saving in terms of fuel and/or possible chemical recovery [1].

In addition, effective HDH enables the application of halogen as the protective and/or directive group in aromatic substitution reactions in syntheses of specialty organic fine chemicals, for example of herbicide Dicamba [3].

Considering the high cost of noble catalysts and the difficulties of platinum metals-based catalysts preparation, it is essential to develop the intensification method to optimize the HDH technique using an inexpensive catalyst. Advancement in the Ni-based HDH field provides an attractive inexpensive alternative to HDH based on precious (platinum-based) metal catalysis by expanding their application space in a range of halogenated waste treatment methods [1–5]. In addition, the toxicity of nickel is lower in comparison with platinum group metals [6–9]. Since Ni is ubiquitously present in the environment, the exposure to low doses of Ni is unavoidable and may not be harmful to humans in low concentrations [10]. It has been published that the daily dietary human's intake of nickel varies between 25–300 μg Ni. Nickel ranks as the 24th element in the order of abundance in the earth's crust [11]. Due to the above-mentioned reasons, Ni-based hydrogenation catalysts are broadly used for thickening of vegetable oils for margarine production [12].

Direct HDH using excess of H_2 gas and transfer HDH are the two employed strategies for reductive treatment of Ar-Xs.

2. Ni-Catalyzed HDH Using Gaseous H_2

Direct HDH for Ar-Xs was studied using nickel supported on support such as alumina [13–23], silica [24–33], carbon [13,34] or unsupported in the form of Raney nickel [35–37] using pressurized hydrogen and an elevated temperature in the gas phase.

Ni is a much less active HDH catalyst in comparison with platinum metals. For this reason, the Ni-catalyzed HDH of Ar-Xs is performed at a higher temperature in the gaseous phase. Using mild reaction conditions (120 $^\circ\text{C}$ /0.1 MPa of H_2), the Ni-catalyzed hydrogenation of 4-chloronitrobenzene produces 4-chloroaniline selectively using both Ni/ SiO_2 or Ni/ Al_2O_3 and no HDH reaction was observed [38]. Due to the lower reductive activity of nickel compared with platinum metals [13,14], however, Ni-based heterogeneous catalysts are much more selective in HDH of (poly)chlorinated benzenes producing 100% of less chlorinated benzenes and benzene with no benzene ring reduction [29,39]. Although even powdered nickel is active for HDH process [40], most of the published research works studied the activity of supported Ni catalysts [41]. The lower Ni consumption, higher mechanical strength and higher thermal stability of supported Ni-based HDH catalysts give main reasons for research focused on effect of suitable inorganic supports. In addition, appropriate inorganic support provides higher specific area suitable for smaller Ni particle size formation during preparation of supported HDH catalyst which can favorably cause the catalytic activity.

The product selectivity and catalyst stability can also be influenced by the sort of catalyst support. As observed by Amorim et al. [39], specific hydrodechlorination (HDC) rates over the supported Ni system increased with the decreasing specific metal area and usually increase with the Ni particle size [42,43].

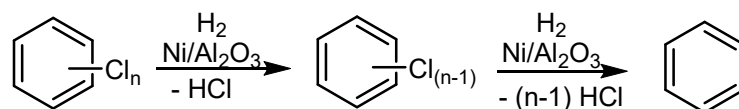
2.1. Gas Phase HDH Catalyzed by Nickel on Alumina

Nickel on γ -alumina has a lower activity than when supported on active carbon; the difference is about one order of magnitude at 200 $^\circ\text{C}$. The Ni content 5–10 wt% on alumina appears to be a suitable choice for the treatment of chlorinated aromatic compounds [13].

Nevertheless, HDH in the gaseous phase using Ni supported on Al_2O_3 was intensively studied and often compared with the action of Pd/ Al_2O_3 or Pd/ SiO_2 .

Using Pd(1 wt%)/ Al_2O_3 enables 99% HDC of Ph-Cl at 140 $^\circ\text{C}$ and ambient pressure of gaseous hydrogen with 86% selectivity for cyclohexane [44]. As was published by Keane, Ni(3 wt%)/ Al_2O_3 catalyst reduces Ph-Cl at 160 $^\circ\text{C}$ and ambient pressure of gaseous hydrogen with 100% selectivity for benzene [1].

The involvement of spillover hydrogen (dissociated atomic hydrogen on Ni support [1]) was examined in gas phase HDC of chlorobenzene (CB) and 1,3-dichlorobenzene (1,3-DCB) over Ni. The catalytic action of single component Ni, Ni/Al₂O₃ and physical mixtures of Ni and Pd with Al₂O₃ has been considered. Inclusion of Al₂O₃ with Ni and Ni/Al₂O₃ increased the spillover with an associated increase in the specific HDH rate (up to a factor of 10) and enhanced selectivity to benzene from 1,3-DCB [14] (Scheme 1).



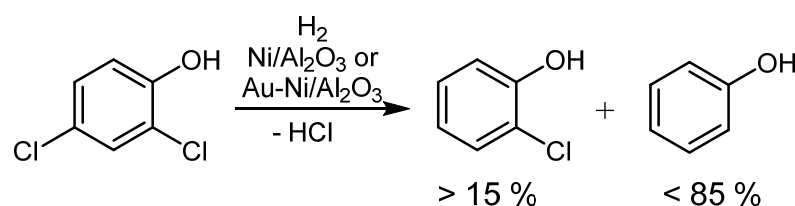
Scheme 1. HDC of (poly)chlorinated benzenes catalyzed by Ni on alumina at temperature over 200 °C [13–17].

De Jong and Louw compared HDC activity of Ni supported on carbon and γ -alumina with Pt- and Pd-based HDC catalysts [13]. They observed that the HDC activity of Ni-based catalyst is similar to Pt or Pd ones at temperature 250 °C. Generally, the HDC activity of tested Ni supported catalysts increase with increasing content of supported Ni. The main differences in HDC activity of Ni and platinum group metal-based catalysts were found at lower temperature range (150–220 °C) where platinum group metals based HDC catalysts are much more efficient [13]. Cesteros et al. studied the course of HDC of 1,2,4-trichlorobenzene (1,2,4-TCB) related to the amount of H₂ available at the reaction temperature [15]. This research proved that the most selective Ni/Al₂O₃- and Ni/NiAl₂O₄-based catalysts for HDC of 1,2,4-TCB to benzene are those which embody the highest amounts of H₂ desorbing at lower temperatures [15,16]. Fresh and reactivated Ni/NiAl₂O₄ hydrogenates 1,2,4-TCB to cyclohexane in 30 min at 250 °C, an irreversible partial chlorination of the catalytic surface making the hydrogenation of the aromatic ring difficult [15]. Catalyst containing 10% Ni supported on γ -Al₂O₃ enables complete gas phase HDC of chlorobenzene, chlorophenols, chloroanilines and chlorotoluenes at 250 °C, on the other hand, 4-chlorotrifluoromethylbenzene was selectively dechlorinated to trifluoromethylbenzene under the same reaction conditions [17].

Using different mesoporous Al-MCM-41 materials as the support for Ni catalysts, Cesteros et al. performed complete and selective HDC of 1,2,4-TCB to benzene at temperature above 225 °C. The number of converted 1,2,4-TCB molecules per second divided by the total number of surface Ni atoms (TOF) varied between $1.2\text{--}8.0 \times 10^{-4} \text{ s}^{-1}$ [16].

An electrophilic substitution reaction was assumed for the gas-phase HDC of substituted chlorobenzenes on Ni/ γ -Al₂O₃ [17].

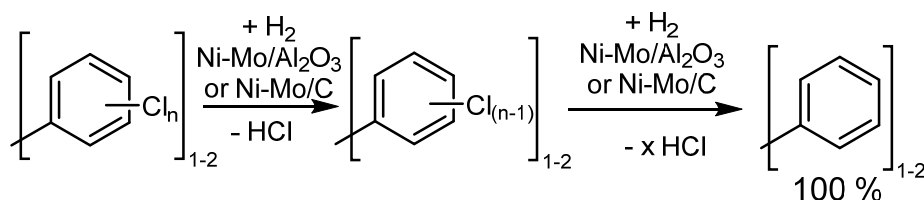
The catalytic gas-phase HDC of 2,4-dichlorophenol (2,4-DCP) has been explored over Ni/Al₂O₃ and Au–Ni/Al₂O₃ at 200 °C Hydrogen chemisorption on Au–Ni/Al₂O₃ was approximately five times lower than that recorded for Ni/Al₂O₃, but both catalysts show equivalent initial HDC activities. Ni/Al₂O₃ exhibits an irreversible progressive deactivation where partial HDC to 2-CP is increasingly favored over complete HDC to phenol. However, at least 15 mol% of 2-CP was observed (except benzene) in the obtained reaction mixture in each case. In contrast, thermal treatment of Au–Ni/Al₂O₃ in H₂ after the reaction increases HDC activity with a preferential complete HDC to phenol. This result was also achieved by a direct treatment of Au–Ni/Al₂O₃ with HCl [18] (Scheme 2).



Scheme 2. 2,4-Dichlorophenol stepwise dechlorinated with 2-chlorophenol as intermediate to phenol using Ni/Al₂O₃ or Au–Ni/Al₂O₃ (the selectivity to 2-CP is over 15%) [18].

For comparison of reactivity of Pd- and Ni-based HDC catalysts, complete Pd/ Al_2O_3 catalyzed HDC of 2,4-DCP was finished even after 30 min using Pd(9.2 wt%)/ Al_2O_3 catalyst (dosage 0.5 g Pd/ Al_2O_3 per liter containing 2,4-DCP/NaOH = $\frac{1}{2}$ and Cl/Pd ratio below 200) at 330 K (liquid phase) and ambient pressure of H_2 [45]. A more robust Ni-based catalyst for gas phase HDH was discovered with the testing standard hydrodesulfurization Ni-Mo/ Al_2O_3 catalyst HDS-9A (American Cyanamid Co., Wayne, NJ, USA) [19]. Even if it works at 320–350 °C and higher H_2 pressure (2–10 MPa), it is tolerant to the sulfur impurities in the treated halogenated waste. This catalyst is able to form HDH hexachlorobenzene, 1,2,3-trichlorobenzene, 1,2-dichlorobenzene, chlorobenzene [4,20] and polychlorinated biphenyls, although the reaction time for complete conversion to the benzene is around 8 h [21].

Using carbon as the support for Ni-Mo sulphides (sulphided Ni-Mo/C), the HDH of dichlorobenzenes, dichlorotoluene and dichlorobiphenyls proceeds smoothly in a range of 210–230 °C under hydrogen pressure of 3 MPa producing corresponding aromatic products (benzene, toluene, biphenyl) [22] (Scheme 3).



Scheme 3. HDC of (poly)chlorinated benzenes, toluenes or polychlorinated biphenyls using commercial hydrodesulfurization catalyst HDS-9A or Ni-Mo/C at 320–350 °C and 2–10 MPa of H_2 [4,21,22,33].

A number of Ni-Mg-Al and Ni-Al hydrotalcite-like precursors were prepared and their catalytic properties in the gas-phase HDH of 1,2,4-TCB was studied at 250 °C. It was documented that increasing the MgO content in the prepared catalyst greatly increased both the activity and selectivity to benzene and the high stability of the prepared catalyst. The positive effect of MgO was explained because MgO modifies the electronic properties of the Ni particles causing H_2 desorption at lower temperatures and also chemisorbs the HCl produced during the HDC reaction [23].

2.2. HDH Catalyzed by Nickel on Silica

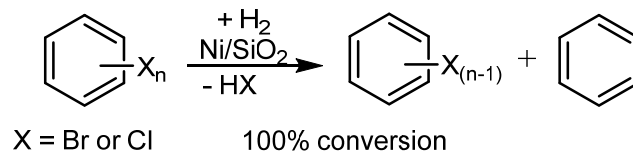
HDH of chlorobenzene, bromobenzene, their mixtures, and the three chlorobromobenzene isomers was examined over the temperature range $200\text{ °C} \leq T \leq 330\text{ °C}$ using Ni/ SiO_2 where the Ni loading was varied from 6.2 to 15.2% wt/wt. Each catalyst was 100% selective in terms of HDH and there was no evidence of cyclohexane formation [1,24–27].

In case of HDC of chlorobenzene (Ph-Cl), using 3 wt% Ni on SiO_2 , Keane calculated HDC to benzene reaction rate as pseudo first order rate constant $k = 20,000\text{ mol}_{\text{Ph-Cl}}\text{h}^{-1}\text{g}^{-1}$ at 150 °C [1]. Using similar conditions and Pd/ Al_2O_3 catalyst, Prati and Rossi describe HDC conversion of Ph-Cl ca. 98–99% with selectivity 86–89% for benzene (and 11–14% cyclohexane) using $0.27\text{ mmol min}^{-1}$ PhCl and 2.5 mmol min^{-1} H_2 per gram of Pd(1 wt%)/ Al_2O_3 catalyst at $T = 413\text{ K}$ [44].

The comparison of HDC activity of Ni- and Pd-based catalysts supported on SiO_2 is possible to make comparing published data measured by Keane (Ni/ SiO_2) [1,27] and Aramendia (Pd/ $\text{AlPO}_4\text{-SiO}_2$) [46]. Ni/ SiO_2 has lower activity compared with Pd/ SiO_2 in conversion of polychlorinated benzenes to nonchlorinated product(s). In case of Ni/ SiO_2 , the mixture of less chlorinated benzenes with benzene is produced during gas phase HDC [27].

Keane et al. described that Ni/ SiO_2 inclines to a temporal loss of activity during HDH reaction above 290 °C which was accompanied by Ni particle growth and structural modification with a consequent disturbance to the H_2 adsorption/desorption surface

dynamics [28]. The main reason for deactivation of Ni/SiO₂ based HDH catalysts seems to be the need to work at a high temperature (often higher than 300 °C) which is accompanied by sintering of catalytically active Ni particles and disruption of H₂/catalyst interaction [29] (Scheme 4).

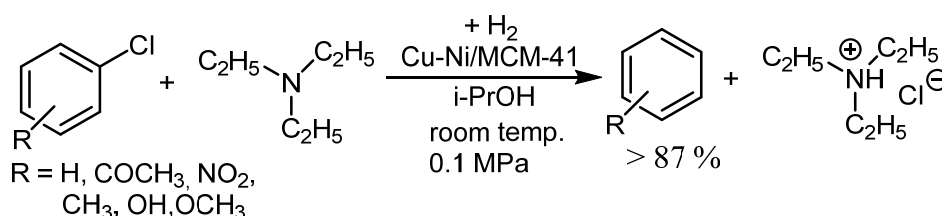


Scheme 4. Gas phase HDH of (poly)brominated or (poly)chlorinated benzenes catalyzed by Ni on silica [24–29].

The changes in catalytic support seem to have a minimal negative effect on HDH reaction at the reaction conditions. This was confirmed in the study of Kim et al. [30–32], where mesoporous alumina and silica Ni-based catalysts, with a well-defined and uniform surface of the inorganic support, were prepared and tested for HDH of 1,2-dichlorobenzene.

Mesoporous silica Ni-based catalyst was obtained by the sol-gel method using Ni(II) complexed by polyethyleneoxide added into SBA-15 as silica precursor [31]. Mesoporous alumina Ni-based catalyst was prepared by mixing of nickel and magnesium stearate with alumina sol and subsequent calcination of obtained precipitate at 550 °C [32].

Both the prepared mesoporous-nickel materials were well defined, however, their HDH activity and stability were limited and worse than other elsewhere published Ni-supported HDH catalysts at 350 °C [30]. Even in the case of Ni/SiO₂ catalytic systems, the selection and addition of the second appropriate metal to nickel for HDH catalyst preparation increases the stability in the HDH process. Cu/Ni catalyst prepared using well-defined mesoporous silica (MCM-41) as the support was proved to be highly active and stable for HDC of Ar–Cl's even at room temperature and ambient H₂ pressure especially in isopropylalcohol with the addition of triethylamine as the base [33] (Scheme 5). The activity of catalyst remains unchanged after three recycling steps.



Scheme 5. HDC of chlorobenzene at room temperature and ambient pressure using Cu–Ni supported on mesoporous silica MCM-41 [33].

2.3. HDH Using Ni on Active Carbon

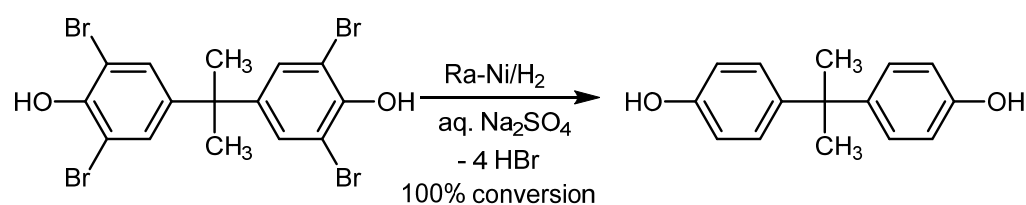
For 5 wt% PhCl in octane in gas phase mixed with hydrogen, Pd on active carbon (10 wt% Pd) was found to be the most active HDC catalyst, with complete reaction even at 200 °C, giving HCl, benzene and cyclohexane as HDC products. Using 10 wt% Ni on active carbon hydrodehalogenates Ph–Cl completely at 250 °C. Products are HCl and benzene. Ni (10 wt%) on γ -Al₂O₃ has a lower HDC activity for Ph–Cl producing benzene quantitatively at 350 °C. The alumina-supported Ni catalyst (10 wt% Ni) has a high activity to Ph–Cl but cracking above ca. 350 °C results in rapid deactivation, probably due to coke formation [13]. Carbon-supported Ni catalysts prepared using Ni–Al layered double hydroxide/carbon nanocomposite precursors displayed excellent activity in liquid phase HDC Ph–Cl with TOF in range 0.1–7.1 × 10² s^{−1} depending on structure and Ni/C ratio of prepared catalysts [47].

2.4. Raney Nickel Based HDH

Attempts were made to dehalogenate Ar-Xs even in the liquid phase especially using more active forms of Ni catalysts. It was published that at a low temperature (70 °C) working in the liquid phase, the HDH activity increased in order: Ni/SiO₂ < Ni/Al₂O₃ < Raney Ni < Ni/C [34].

Using liquid phase conditions and a reaction temperature between 60–70 °C, the Raney Ni-catalyzed HDH proceeds well using an elevated pressure of hydrogen (1 MPa) in the presence of alkaline hydroxide for the removal of produced HX by neutralization. Under the liquid phase conditions, a gradual loss of catalyst activity was observed in all probability due to the covering of the catalyst's surface with NaX. After aqueous treatment causing NaX dissolution, the catalyst activity was restored [34].

Rapid HDH of tetrabromobisphenol A catalyzed by the suspension of the Raney Ni catalyst and on cathode electrochemically produced nascent hydrogen was published using co-action of ultrasound [35] (Scheme 6).



Scheme 6. HDH of tetrabromobisphenol A using electrolytically produced H₂ and the Raney nickel slurry as the HDH catalysts enhanced with ultrasound [35].

Recently, Ma et al. published a straightforward HDC of chlorinated phenols catalyzed by Raney Ni (20 mg per mmol of 4-CP and 1.1 mmol of NaOH) at room temperature and ambient pressure of hydrogen in an alkaline aqueous solution. The employed Raney Ni was successfully reused more than five times without a significant effect on HDC conversion. The authors observed that the applied combination of triethyl amine, together with NaOH as the base, is the most effective combination in this HDC process due to the minimizing of Al/Ni leaching from the Raney Ni catalyst during the HDC process [36]. For comparison, the complete HDC was observed after 30 min using 5% Pd/C (5 mg per mmol 4-CP in co-action of 1.05 eq. of NaOH) at room temperature and ambient pressure of hydrogen [48]. Using Rh nanoparticles (2.45 mg Rh/L) under the same reaction conditions, the complete non-selective HDC of 4-CP (100 mg/L) was achieved after 1 h, producing phenol, cyclohexanone and cyclohexanol [49].

The HDH of lipophilic Ar-Xs catalyzed by Ra-Ni is significantly enhanced by the addition of excess of aqueous NaOH or KOH for neutralizing of the produced HX with the addition of the phase-transfer catalyst to enable facile transport of hydroxide anions into the immiscible organic phase containing Ar-Xs [37].

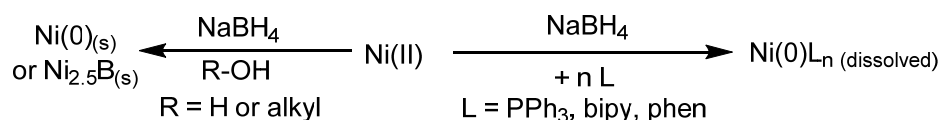
3. Hydrogentransfer in Ni-Catalyzed Hydrodehalogenation Reactions

Transfer HDH reaction, described as the addition of hydrogen to a molecule from a non-H₂ hydrogen source, is a convenient and powerful method to obtain various non-halogenated compounds (Ar-Hs) from starting Ar-Xs. It is an attractive alternative to direct HDH. The reasons for this are (i) the transfer HDH method does not require potentially hazardous pressurized H₂ gas nor elaborate experimental setups, (ii) the hydrogen donors are readily available, inexpensive and easy to handle, (iii) the major side product is potentially recyclable, and (iv) the usually used catalysts are readily accessible and not sensitive [50–54].

For transfer hydrogenation reactions, in-situ generated Ni(0) is generally used which is more active in comparison with Ni/Al₂O₃, Ni/SiO₂ or Ni/TiO₂ [55,56].

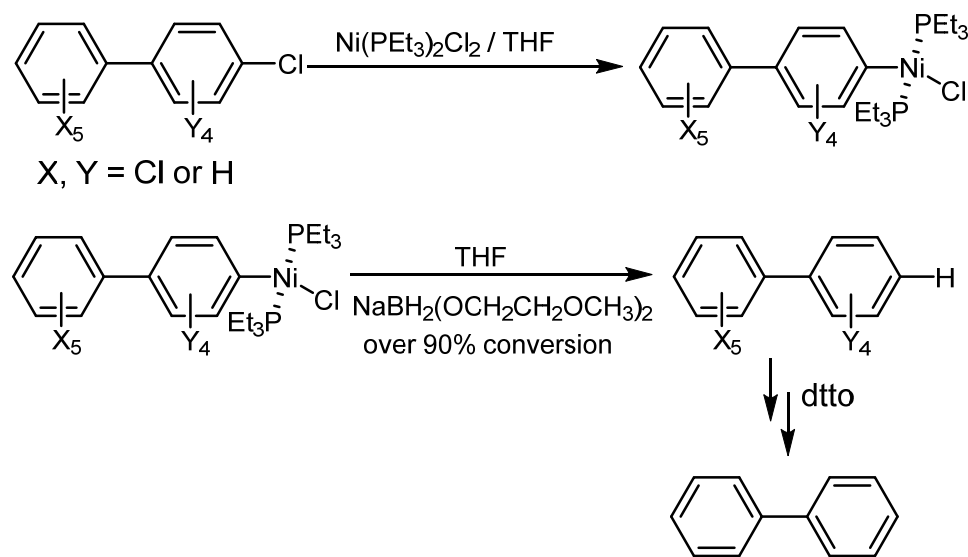
Powerful reductants such as ionic metal hydrides (NaBH_4 and its derivatives, CaH_2) or several electropositive metals are usually used in the published Ni-catalyzed transfer HDHs in contaminated water or organic solvents [51–57].

It is known that simple Ni(II) salts react with NaBH_4 in water or an ethanol solution to form a black precipitate (nickel or nickel boride) which is a powerful hydrogenation catalyst under heterogeneous conditions. Solvents of a greater coordinating power, such as N,N-dimethylformamide, Ni(II) chloride and NaBH_4 reportedly constitute a soluble hydrogenation catalyst [51] (Figure 1 and Scheme 7).



Scheme 7. Reduction of Ni(II) salts produced colloidal Ni(0) or soluble complex of Ni(0) depending on used solvent and/or ligands, respectively [51].

Tabaei et al. studied the effective HDH of polychlorinated biphenyls (PCBs) in tetrahydrofuran (THF) solution using an excess of $\text{NaBH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ and the addition of NiCl_2 at 68 °C after ten hours of action [58]. Using the same reaction conditions, 1,2,4-trichlorobenzene was hydrodechlorinated with a high efficiency to benzene and chlorobenzene [59] (Scheme 8).



Scheme 8. $\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$ catalyzed HDC of polychlorinated biphenyls in THF [59].

Scrivanti et al. later even published the complete HDH of 1,2,3-trichlorobenzene using an excess of NaBH_4 , the catalytic amount of $\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2$ salt with the co-action of an extra two equivalents of Ph_3P in ethanol/pyridine solution at 70 °C after several hours of action. The formation of Ni(0) stabilized with Ph_3P is proposed as a catalytically active Ni(0)-based species which oxidatively inserts into the C–Cl bond and enables its subsequent reduction [60] (Scheme 9).

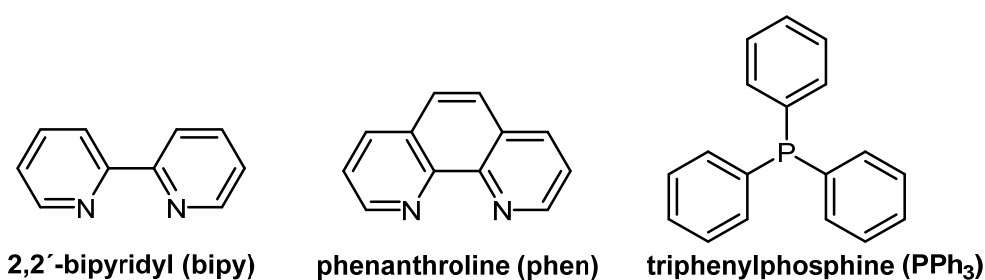
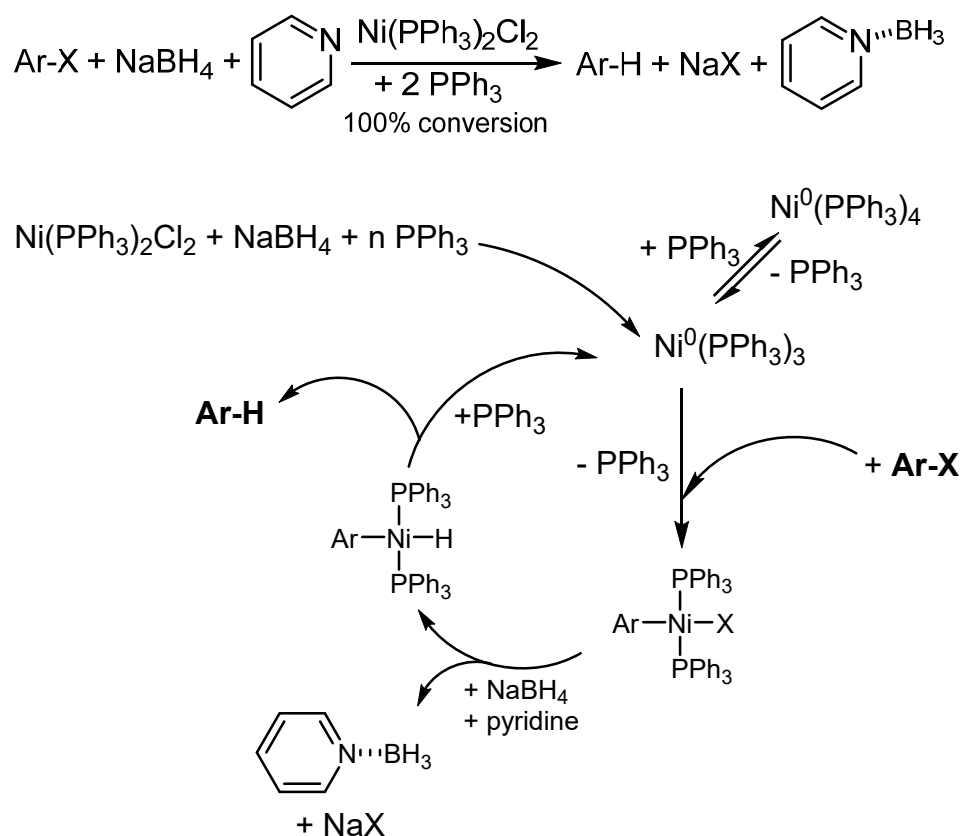
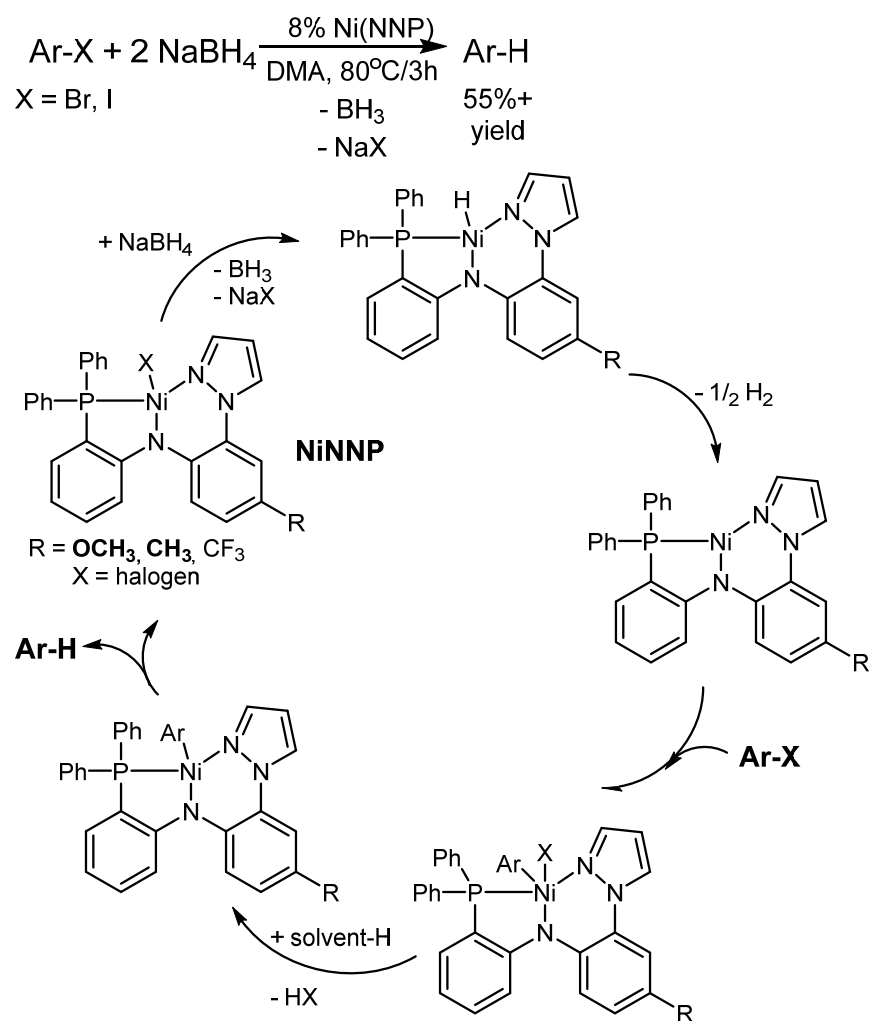


Figure 1. The structures of broadly used ligands of nickel complexes catalytically active for HDH [61–67].



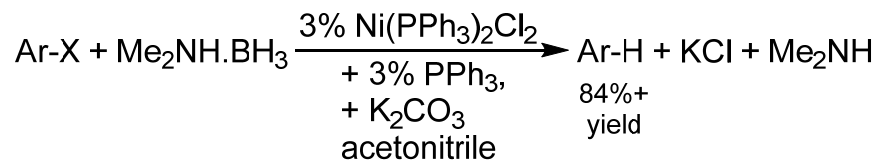
Scheme 9. HDH of Ar-X using Ni(PPh₃)₂Cl₂ with 2 equivalents of PPh₃ in ethanol/pyridine with subsequent addition of excess NaBH₄ (benzene was produced with 100% conversion using 2 mmol 1,2,3-TCB dissolved in 10 mL ethanol/pyridine 9/1 with addition of 0.05 mmol Ni(PPh₃)₂Cl₂, 0.1 mmol PPh₃ and 7 mmol NaBH₄ at 70 °C/3 h) [60].

Recently, a series of Ni(NNP) pincer complexes with HDH activity in co-action of excess of NaBH₄ as a reductant was described by Wang and Gardinier [61]. This system (especially in case if R = methoxy or methyl) was recognized as effective mainly for hydrodebromination of Ar-Br_s and hydrodeiodination of Ar-I_s but is very slow in case of HDC of Ar-Cl_s in N,N-dimethylacetamide (DMA) even at 80 °C [61] (Scheme 10).



Scheme 10. HDH of Ar–Br or Ar–I using Ni(NNP) complex and NaBH₄ and the proposed reaction pathway [61].

The main drawback of above-mentioned methods seems to be poor utilization of used NaBH₄ reductant. Only one hydride from NaBH₄ reductant is used for HDH of Ar–X with subsequent loss of untapped BH₃. This drawback is potentially removed by the method described by Lipshutz et al. using Me₂NH·BH₃ as the reductant, Ni(PPh₃)₂Cl₂ as the source of Ni-catalyst and K₂CO₃ as the HX scavenger in acetonitrile [62]. This method affords facile HDH of aromatic iodides, bromides and even chlorides (Scheme 11).

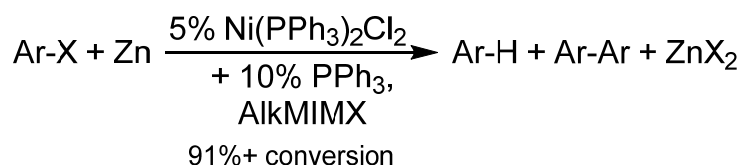


Scheme 11. The efficient HDH caused by borane-dimethylamine catalyzed by in-situ prepared Ni(PPh₃)_n [62].

Sakai et al. described facile HDH of Ar–Xs using an excess of zinc powder and aqueous NaOH in ethanol catalyzed by colloidal nickel produced in-situ from added NiBr₂ at 60 °C. The oxidative addition of Ni into Ar–X bond is considered with subsequent reduction to Ar–H and recycling of catalytically active nickel [63].

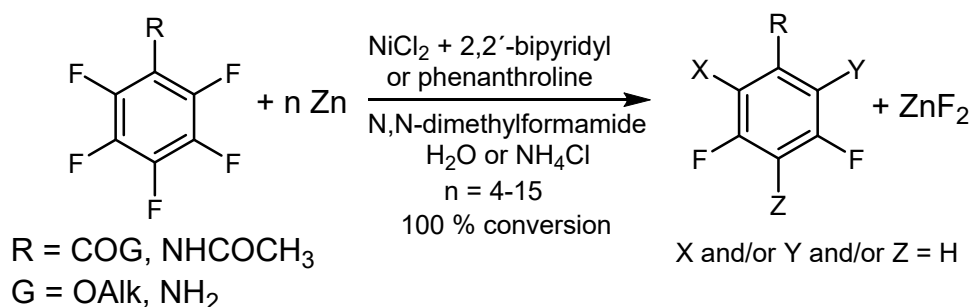
Prichodko et al. published the promoting effect of ionic liquids for Ni-catalyzed HDH using powdered zinc in the role of reductant and Ni(PPh₃)₂Cl₂ with co-action of PPh₃

as HDH catalyst. In the described procedure, different Ni(L)_nCl₂ (L = Bpy, Phen, PPh₃) complexes were tested as Ni-based HDH and/or homocoupling catalysts in 1-alkyl-3-methylimidazolium chloride or other ionic liquids (1-alkyl-3-methylimidazolium halides, AlkMIMXs) and compared with the application of N,N-dimethylacetamide as the polar aprotic solvent [64] (Scheme 12). The calculated TON is 18–20.



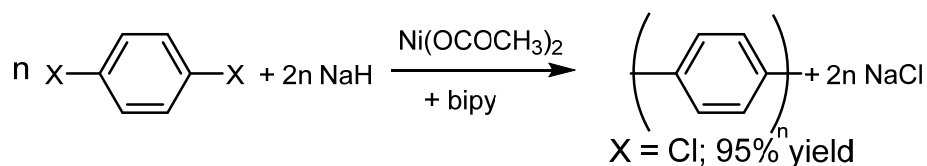
Scheme 12. Ni(0)-catalyzed HDH using powdered zinc as reductant [64].

Shteingarts and Adonin described effective co-action of Zn powder as the reductant and NiX₂ together with appropriate ligand (2,2'-bipyridyl (bipy) or phenanthroline (phen)) for partial aromatic hydrodefluorination in case of polyfluorinated aromates [60,61]. Using this Ni-based HDH system, (the hydride complex HNiXL_n probably operates as the reductant [65,66]) (Scheme 13).



Scheme 13. Regioselective hydrodefluorination of perfluorinated acetanilides or derivatives of perfluorinated benzoic acids [65,66].

It is well known that the catalytic system based on complexes of Ni(II) with bipy even enables polymerization of dichloroaromates in tetrahydrofuran using NaH as the reductant [67] (Scheme 14).



Scheme 14. Ni-based HDC of p-dichlorobenzene produces polyphenylene [67].

Tetrabromodiphenyl ethers dissolved in minute concentrations in a methanolic solution of triethylamine were hydrodebrominated by hydrogen produced upon irradiation of dispersed Ni-graphite carbon nitride C₃N₄ catalyst [68].

Based on recognition of Ni(II) role in coenzyme F₄₃₀, some artificial models were synthesized and tested as biomimetic catalysts in HDH reactions. Only slow partial HDC of hexachlorobenzene to pentachlorobenzene using Ni-complex F₄₃₀ with Ti(III) citrate as the electron donor was, however, observed. The authors proved that Co-complex such as vitamin B₁₂ is much more effective in HDH reactions using Ti(III) citrate [69]. Based on the structure of coenzyme F₄₃₀, structurally simpler complexes were tested as possible biomimetic HDH catalysts [51].

Ni(II) complexes of several tetraazacycles were reported to form soluble complexes with NaBH₄, but no catalytic activity was ascribed to these compounds. The 2,6-disubstituted

pyridine-based Ni(II) complexes (Figure 2) were described as effective homogeneous HDH catalysts for polychlorobenzenes reduction using NaBH_4 or hydrazine in mixtures of polar organic solvents (acetonitrile, ethanol) or their aqueous solutions [70,71].

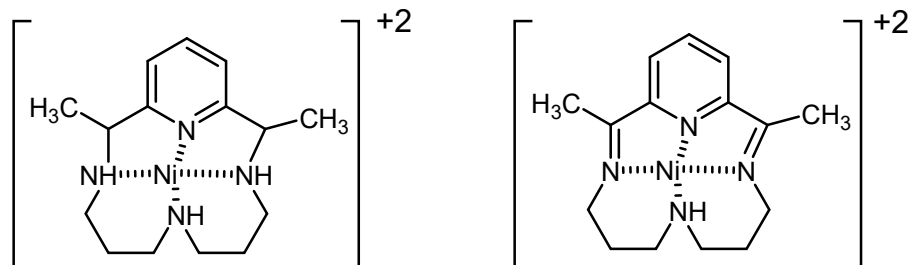
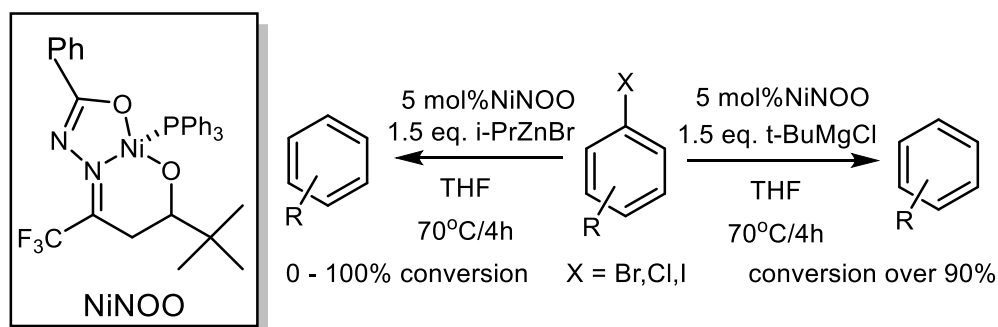


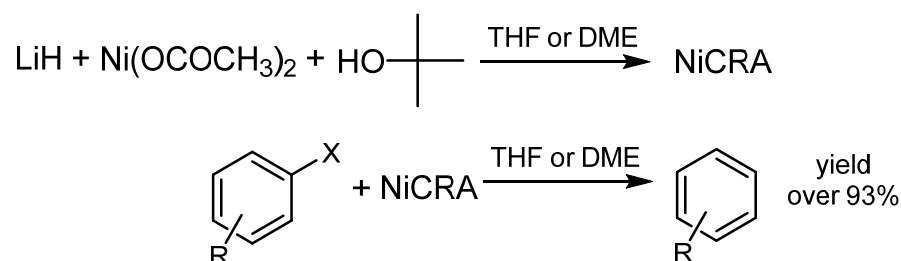
Figure 2. The structures of Ni(II) complexes catalytically active for HDH of polychlorinated benzenes [65,66].

Isopropyl zinc bromide and especially tert-butyl magnesium bromide used as reductants and Ni(II) 1-benzoyl-5-hydroxypyrazoline complex (NiNOO) as the catalyst enable facile dehalogenation not only of halogenobenzene derivatives in tetrahydrofuran but even of hexachlorobenzene [72] (Scheme 15). The use of sufficient excess (over 6 eq.) of *t*-BuMgCl enables even complete HDC of hexachlorobenzene.



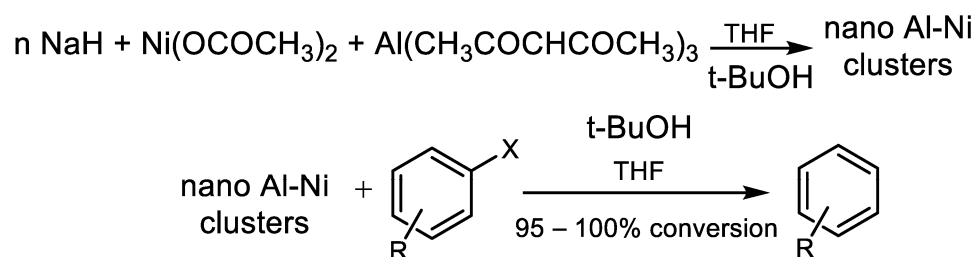
Scheme 15. NiNOO complex mediated HDH using isopropylzinc bromide or tert-butylmagnesium chloride as reductants [72].

LiH-based HDH catalyzed by Ni-complex produced by the reaction of tert-butyl alcohol with LiH and nickel acetate in hot tetrahydrofuran or 1,2-dimethoxyethane was recognized as being very effective for halogenobenzenes or halogenonaphthalene [73–78] (Scheme 16).



Scheme 16. NiCRA produced by the reaction of alkali metal hydride with soluble Ni(II) salt, Al(III)acetylacetonate and *t*-BuOH in ethers smoothly hydrodehalogenates Ar-Xs [73–78].

Subsequent research of Fort et al. developed a new HDH system based on Ni–Al clusters produced in-situ from Ni(II) acetate and Al(III) acetylacetonate using sodium alkoxide/sodium hydride in THF [79–82] (Scheme 17).



Scheme 17. HDH of Ar-Xs mediated by nano Al-Ni clusters produced in-situ from Ni(II) and Al(III) in THF using excess of NaH (100% conv. to benzene starting from di-, tri- or tetrachlorobenzene using 10 mol% of nano Al-Ni and 2.5-fold mol excess of NaH per C-Cl unit) [79–81].

4. Decontamination Methods Based on Transfer HDH for Treatment of Contaminated Aqueous Solutions

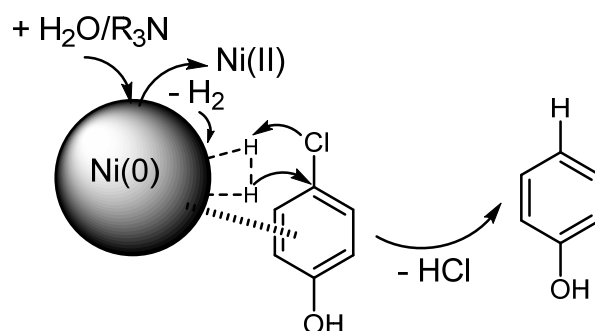
Probably over 90% of hazardous waste is aqueous and its toxic effect is dependent on the kind and concentration of contaminants dissolved or dispersed in produced waste water [82,83].

4.1. Raney Nickel Applications in Transfer HDH

Ma et al. published a smooth HDH of chlorophenols with H_2 in an alkaline aqueous solution using suspension of the Raney nickel catalyst [84]. The used Ra-Ni is recyclable 5-times without loss of HDC activity.

Wang et al. reported an increase in the HDH rate using ultrasonic action on triclosan catalyzed by Raney Ni saturated with gaseous H_2 [85].

Raut et al. published effective HDC of 4-chlorophenol (30 mg/L) caused by a high excess of Raney Ni (3 g/L) in an aqueous solution by co-action of trialkyl amines (45 mg/L) without the addition of other reductants [86]. The observed HDC was explained by the partial dissolution of Raney Ni in an aqueous trialkylamine solution with subsequent H_2 formation which adsorbed on catalytically active nickel sponge and caused HDC of 4-chlorophenol (Scheme 18). The proposed mechanism is based on the observed increase of dissolved Ni in the reaction mixture during described HDC process [86].



Scheme 18. Dissolution of Ni in $\text{R}_3\text{N}/\text{H}_2\text{O}$ produces H_2 reductant causing HDH of 4-chlorophenol (86% HDC conversion decreases to 38% after 3th recycling of used Ra-Ni) [86].

For comparison of HDC activity, Ra-Ni (1 g/L) or Pd(5%)/C (1 g/L) were tested for HDC of 4-CP (30 mg/L). After 24 h of action, Pd/C caused complete HDC of 4-CP whereas Ra-Ni achieved 84% conversion to phenol [86].

Study of Ma et al. [87] compares activity of Raney nickel and Pd/C as HDH catalysts. It was found that HDH of halogenated benzenes or halogenated phenols using 120 mg Ra-Ni is usually more rapid in case of application 20 mg Pd/C under otherwise same reaction conditions. Beside this, the tested catalysts differ in hydrogenolytic scission reactivity of Ar-X.

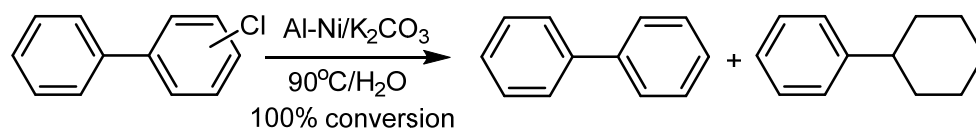
4.2. Utilization of Raney Al–Ni Alloy in HDH Processes

Another simply available HDH system applicable for Ar–X contaminated wastewater, serve alloys or bimetals containing electropositive metal and nickel applied as HDH catalyst.

For effective HDH of Ar–Xs, the Raney Al–Ni alloy was broadly studied in alkaline aqueous solution contaminated with Ar–X. Raney Al–Ni alloy is commercially simply available and low-cost. This alloy contains 50 wt% of Al and 50 wt% of Ni bound in the form of Al_3Ni and Al_3Ni_2 . Different bases such as NaOH or KOH [88–104], alkali metal carbonates [89,94,95], NaF [100] or some alkaline salts of complexing agents [91,101] were proved for HDH processes. It was observed that Raney Al–Ni alloy is, especially in diluted aq. NaOH or KOH, a very effective and universal HDH agent enabling quantitative HDH of Ar–Br, Ar–Cl compounds at elevated temperature [89,90,95,96,99,102,104] or even at room temperature [81–94,98,103].

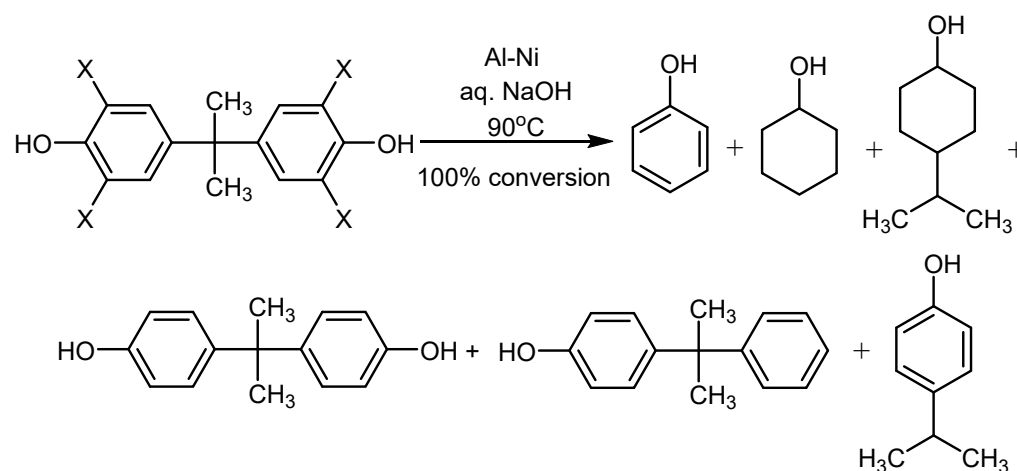
According to the mentioned articles studying Al–Ni alloy HDH properties, the above-mentioned Al–Ni alloy is a quite robust HDH agent in diluted aqueous solutions of alkali metal hydroxides. Raney Al–Ni alloy was reported as an applicable reduction agent for complete HDH of halogenated anilines [88,91], (poly)chlorinated benzoic acids [100], chlorinated benzenes [88], mono- and dichloro-biphenyls [95,97], polybrominated diphenyl ethers [89], (poly)halogenated phenols or polyhalogenated bisphenol A [89,90,92,100,101], chlorinated benzils [103] and halogenated benzophenones [96].

HDH is accompanied by reduction of other reducible functional groups, carbon-carbon bond cleavage or hydrogenation of aromatic ring, especially at elevated temperature. HDH of chlorobiphenyls produces biphenyl together with phenylcyclohexane [95,97] using excess of Al–Ni at temperature above 60 °C (Scheme 19).



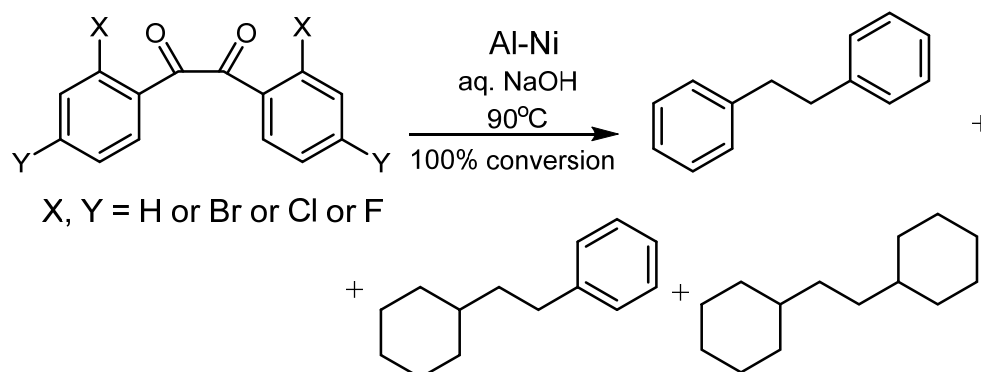
Scheme 19. HDC of monochlorobiphenyls using Raney Al–Ni alloy in hot aqueous alkali metal carbonate solution [95,97].

Tetrachloro- or tetrabromo-bisphenol A are converted into a mixture of nonhalogenated phenols and cyclohexanols using Al–Ni even in 1% aqueous alkali metal or alkali earth metal hydroxide at a temperature 60 °C or higher [89] (Scheme 20).



Scheme 20. Raney Al–Ni alloy mediated HDH of tetrabromo- or tetrachlorobisphenols A (X = Br or Cl) accompanied by carbon-carbon and carbon-oxygen cleavage reactions [89].

Halogenated benzil is reduced to the mixture of 1,2-diphenylethane, 1-cyclohexyl-2-phenylethane and 1,2-diphenylethane [104] in 1% aqueous KOH at 90 °C (Scheme 21).

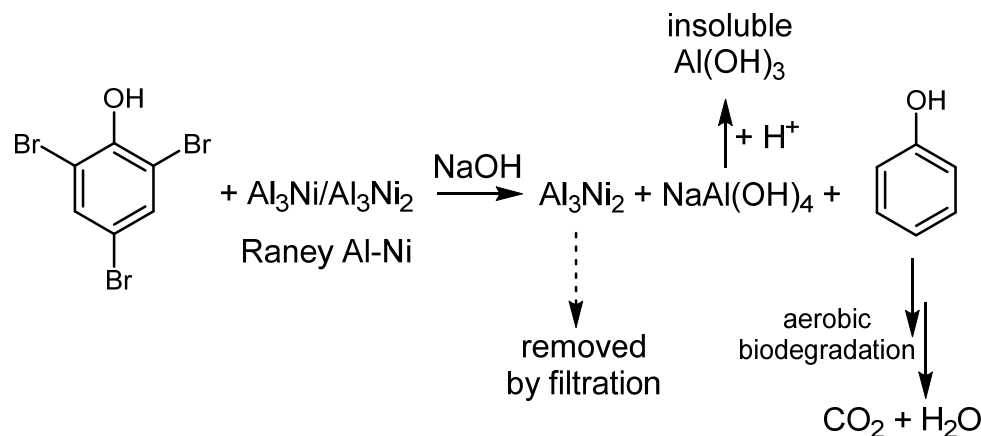


Scheme 21. Raney Al–Ni alloy based HDH of polyhalogenated benzil in hot aqueous alkali metal hydroxide solution [104].

Under the same reaction conditions, chlorinated benzophenones are reduced to dicyclohexylmethane, benzylcyclohexane and diphenylmethane [96].

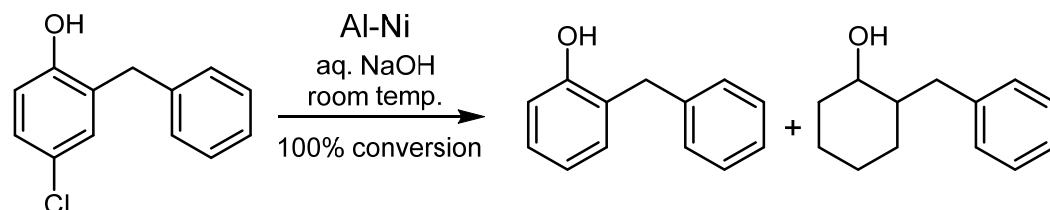
At least (poly)halogenated anilines, (poly)chlorinated benzenes, (poly)chlorinated benzoic acids and polyhalogenated phenols are selectively reduced, however, to the corresponding nonhalogenated aromatic compounds at room temperature using a low excess of Al–Ni alloy in 1–2% aqueous NaOH or KOH solutions, as we observed [88,91–94,98,103].

In case of 2,4,6-tribromophenol, the interconnection of HDH with subsequent biodegradation of produced phenol was tested after removal of insoluble part of Raney Al–Ni alloy (Al_3Ni_2) and coagulation/flocculation of insoluble Al(III) hydroxide [92] (Scheme 22).



Scheme 22. Al–Ni-based HDH of 2,4,6-tribromophenol with subsequent removal of used metals and biodegradation of produced phenol [92].

In case of Chlorophene, the HDC reaction is accompanied by formation of 2-benzylcyclohexanol even at room temperature [94] (Scheme 23).



Scheme 23. Raney Al–Ni alloy based HDC of Chlorophene is accompanied by reduction of aromatic ring even at a room temperature [94].

Only in the case of 2-chlorophenol, KF instead of the corresponding hydroxide was proved as an applicable base for complete HDH after 2 h of action of a high excess of Al–Ni alloy (10 g Al–Ni per 50 mg of 2-CP mixed with 40 mmol KF) [100]. In contrast, this configuration of HDH enables recycling of the huge excess used and during HDC process undissolved Al–Ni after washing of the produced insoluble AlF_3 layer from Al–Ni surface with $\text{Ca}(\text{OH})_2$ suspension.

It was observed that alkaline salts (alkali metal borate or phosphate) inhibit HDH process utilizing Al–Ni alloy. This inhibition is likely caused by the formation of insoluble Al(III) salts which cover active Al–Ni surface. Alkali metal salts (of citric or ethylenediaminetetraacetic (EDTA) acid) which enables both corrosion of metallic Al and formation of soluble Al(III) salts enables complete HDH, as was observed [91] and citations herein, [101].

For complete HDH of halogenated anilines and phenols, the effective molar ratio of reactants NaOH (or KOH):Al (used as Al–Ni alloy):Ar–X is 10:2:1. This ratio enables complete HDH of Ar–Xs until 120 min under vigorous stirring at room temperature. On the other hand, we observed that in case of halogenated anilines the quantity of Al–Ni can be significantly decreased after addition of glucose [93]. Used glucose inhibits dissolution of metallic Al in alkaline aqueous solution and caused formation of Ni nanoparticles, as we documented. We suppose that formation of nanoparticles Ni saturated with H_2 enables effective HDH of halogenated anilines [93].

The application of glucose enables decrease of Al–Ni alloy quantity in case of reactive Ar–Xs, such as brominated anilines and 3-chloro- or 2-chloro-anilines but not 4-chloroaniline [93]. These mentioned reactive Ar–Xs are simply hydrodehalogenated even using Devarda's Al–Cu–Zn alloy, as we published earlier [88]. HDH of hardly reducible chlorinated compounds such as 4-chloroaniline or other polychlorinated aromatic compounds is not promoted by the addition of glucose, as we described earlier [91]. In this context the hardly reducible compounds (4-chloroaniline, etc.) are not hydrodehalogenated even using Devarda's Al–Cu–Zn alloy [88,91]. The effective HDH of 4-chloroaniline or other hardly reducible Ar–Xs at room temperature requires the reductive action of Raney Al–Ni alloy bound in Al_3Ni . The mentioned crucial role of Al–Ni we explained as HDH of adsorbed Ar–Xs on $\text{Al}_3\text{Ni}/\text{Al}_3\text{Ni}_2$ surface immersed in diluted aqueous NaOH solution working as a galvanic couple composed by soluble Al anode and stable and catalytically active Ni cathode [88,98].

The applicability of Raney Al–Ni alloy was successfully tested including the treatment of contaminated water streams on a pilot plant scale [103].

4.3. Ni-Based Bimetals Applied in Transfer HDH

For effective HDH treatment, applicable for degradation of Ar–Xs in contaminated water, several research teams have tested monometallic (Al, Fe, Mg, Zn) [4,105–107] or bimetallic reduction systems prepared by plating of electropositive metal surfaces with Pt or Pd (Pd/Zn, Pt/Fe, Pd/Fe, Pd/Mg, Pd/Al) [108–112].

Applying non-plated electropositive metals, the kinetic of HDH in Ar–Xs is slow even when using nanoparticles. This means that effective HDH requires a significant excess of the used electropositive metal [4,105–108].

The performance of bimetallic HDH systems for Ar–Xs is usually explained by the dissolution of electropositive zero-valent metal with the production of nascent hydrogen and the functioning of precious metal (commonly from platinum group metals (PGMs) as a HDH catalyst [109–112]. PGMs used for plating of electropositive metals as HDC catalysts are quite sensitive to poisoning and very expensive [6,7,109–112].

Due to these reasons, cheaper bimetallic reductants have been examined in recent years based on Ni in the role of HDC catalysts for plating of electropositive metals Ni/Fe and Ni/Zn [108,113–121]. It was even reported by Cheng et al. [122] that addition of micronized Ni(0) could re-activate zerovalent iron particles that have lost their reduction activity.

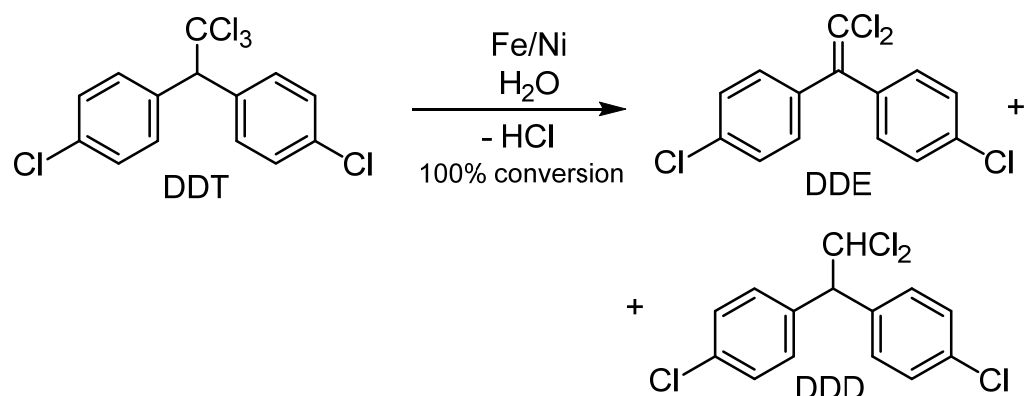
The accepted model describing mechanism of action of Fe/Ni bimetal in HDH processes involved utilization of accelerated corrosion of metallic iron especially on Fe-Ni local galvanic couples as the first step. Dissolution of iron is accompanied by formation of hydrogen which is adsorbed on Ni surface. The produced Ni nano and/or micro-particles saturated with hydrogen subsequently work as the HDH agent [113–121]. This mechanism is supported by the observation that compounds producing insoluble Fe-salts (for example humic acids [113] inhibit the HDH rate.

Apart from the above-mentioned, in the case of HDH of pentachlorophenol, the authors used sole nano iron or mixture of nickel and iron nanoparticles instead of plated Ni/Fe and compare HDH based on the size of the added nickel nanoparticles. The authors observed an increase of HDH with a decreased size of Ni and no HDH in the case of sole Ni nanoparticles application without the addition of nano Fe [115].

Ni/Fe bimetallic (nano)particles are quite popular and broadly tested in recent years due to sufficient efficiency, simple preparation and low cost together with low toxicity of iron [113–120]. This was demonstrated as effective for HDH of chlorinated phenols [113,115,121], DDT [114], the anti-inflammatory drug Diclofenac [116], polychlorinated biphenyls [117], polybrominated diphenyl ethers [119] and chlorinated nitrobenzenes [120] at room temperature.

The choice of pH is quite problematic because metallic iron corrodes mainly in a neutral or acidic aqueous solution, but the HDH reaction is promoted by the addition of a base which removes produced HX [113–121].

In case of HDH of DDT Fe/Ni bimetal caused only partial HDC in the CCl_3 group of DDT structure [114] and authors suggested reductive effect of both $\text{Fe}(\text{OH})_2/\text{Ni}$ or Fe/Ni . The source of reductant depends on pH. While in acidic reaction mixture Fe/Ni as main active HDH reagent is assumed, in alkaline solution $\text{Fe}(\text{OH})_2/\text{Ni}$ seems to be predominant HDH agent [114] (Scheme 24).



Scheme 24. HDC (formation of DDD) accompanied by dehydrochlorination (DDE) was observed in case of DDT treatment with Fe/Ni bimetal [114].

Liu et al. elucidated the decrease of 2,2',4,4'-tetrabromodiphenylether HDH reaction rate with increasing pH by the formation of insoluble iron (hydr)oxides on Fe/Ni surface which inhibit further corrosion of Fe^0 and the production of hydrogen fundamental of the HDH process [119]. Even using optimal HDH conditions, the authors only identified partially debrominated products (4-bromodiphenylether and 2-bromodiphenylether) [119].

Ghauch et al. demonstrated that even Fenton-like oxidation is promoted by Fe/Ni bimetal in the case of aerobic treatment of the Diclofenac solution which is documented by the determination of hydroxylated Diclofenac in the obtained reaction mixture using LC-MS [116]. In contrast, when oxygen was excluded in the reaction mixture during Fe/Ni-based HDH, only products of HDC were observed after Fe/Ni treatment [116].

Lin et al. observed the enhancement of the HDH rate during pentachlorophenol reduction induced by Fe/Ni with the co-action of cationic surfactant [118]. The authors

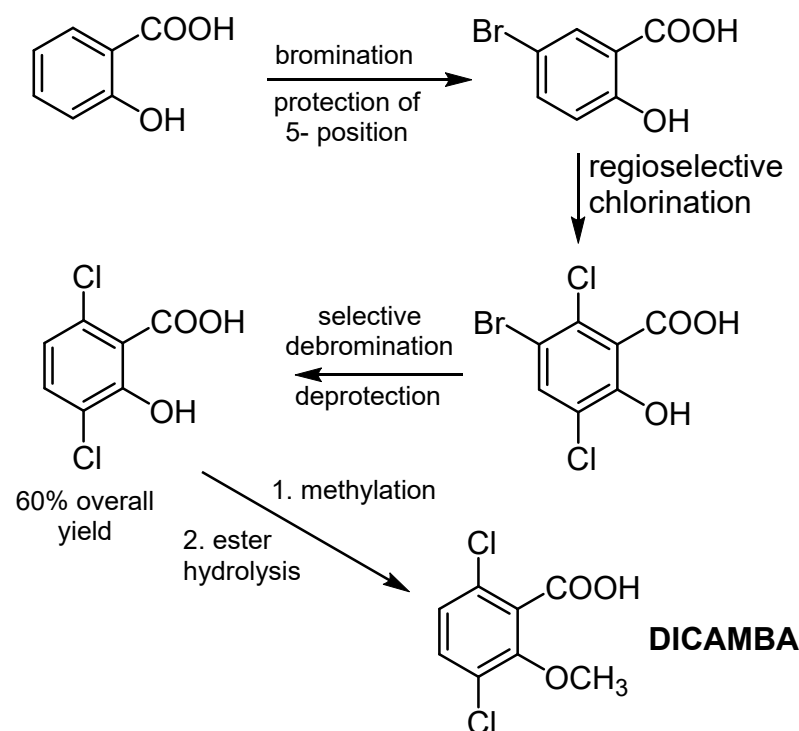
explained this observation by an increase of the specific surface area of Fe/Ni particles in co-action with the cationic surfactant and the higher adsorption rate of pentachlorophenol in this manner prepared Fe/Ni particles and their stabilization [118].

5. The Role of HDH for Application of Halide as Protecting and Directing Group

The above-mentioned Ni-based HDH methods seem to be suitable, not only for detoxification of Ar-Xs containing waste or treatment of polluted water streams, but especially these effective at room temperature for removal of halogen used as the protecting, respective directing, group in aromatic chemistry of organic fine chemicals syntheses [3,123,124].

Applying broadly used electrophilic aromatic substitution reaction is linked with the problem of selective introduction of functional group(s) with the aim to obtain aromatic compounds with the desired chemical structure. The desired orientation of bound substituent(s) may be achieved by blocking the most reactive position in the aromatic ring of the substrate, the carrying out desired substitution reaction followed finally by the removal of the protective group.

Ni-based HDH could be the method of choice for room-temperature and selective removal of halogen used as the protective group including possibility of deuteration for the syntheses of 2- or 3-substituted anilines or acetanilides [124,125], 2,6- or 3,4-disubstituted anilines [125,126], 2-substituted benzoic acids [3,124] (Scheme 25), 2-substituted benzonitrile [124], hydroxydiphenylmethanes [124], hydroxydiphenyls [124], 2-substituted phenols [123–125], 2,4- or 2,5-disubstituted phenols [123–125], 2,5-disubstituted quino-line [125].

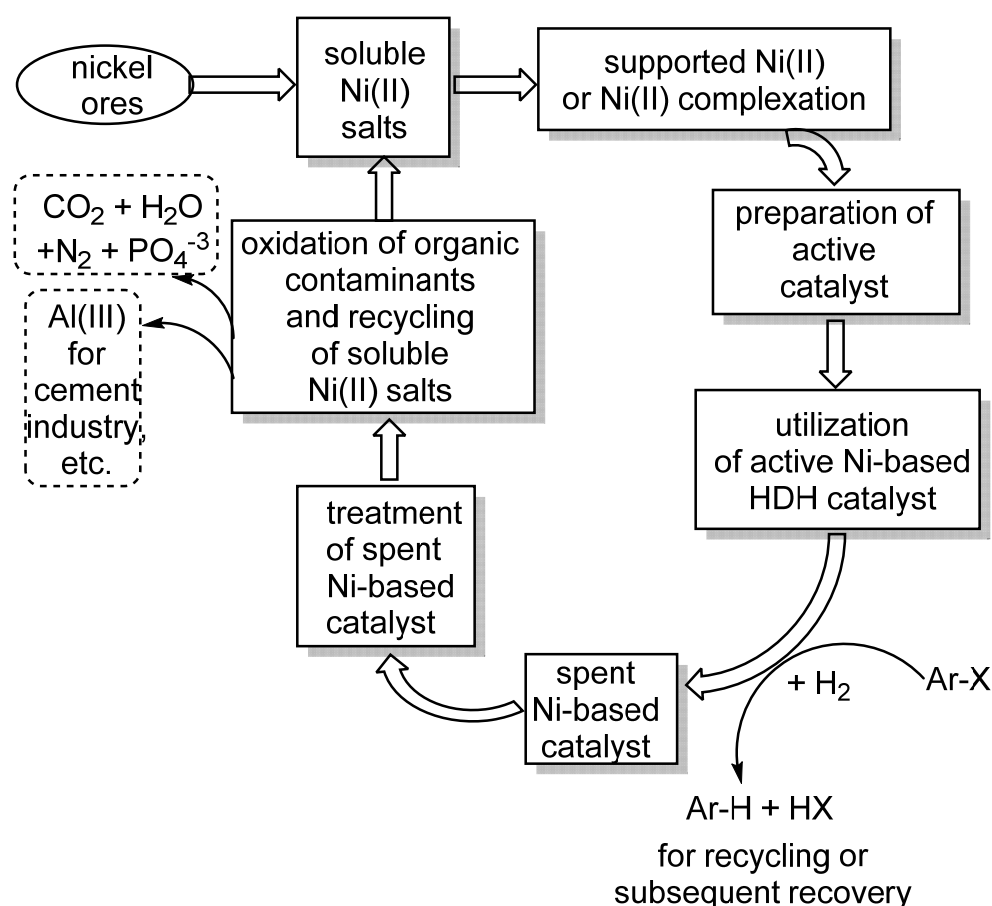


Scheme 25. An example of bromine utilization as protecting group for subsequent regioselective chlorination in alternative synthesis of herbicide Dicamba [3].

6. Available Methods for Recycling of Spent Ni Catalysts

Each of the above-mentioned HDH methods based on application of Ni catalysts is limited with the durability of the applied catalyst. Even metallic nickel is much cheaper in comparison with platinum metals-based catalysts (actual price about 20,000 USD/t), and for sustainability of HDH methods the recycling of used Ni is required. For this purpose, hydrometallurgical processes would seem to be suitable energy-saving alternatives to the common pyrometallurgical ones [127–131]. Hydrometallurgical processing methods

are environmentally friendly due to the low energy requirements, low gas emissions and waste generations and complete recovery of the metals [127]. They are based mainly on mineral acid leaching (hydrochloric, nitric or sulfuric acid) with appropriate co-action of oxidant (hydrogen peroxide, persulfate, etc.) [127–132] (Scheme 26). The obtained refined nickel salts such as nickel chloride, nitrate or sulfate are usually used for preparation of Ni-based HDH catalysts and eventually reduced directly to metallic nickel by the action of electropositive metal, NaH_2PO_2 or NaBH_4 [51,60,63,128–131].



Scheme 26. Applying the principle of circular economy in Ni-catalyzed HDH process.

7. Conclusions

Ni-catalyzed gas phase HDH was developed for reductive treatment of concentrated streams of waste halogenated aromatic compounds (Ar-Xs) produced as by-products or non-simply-recyclable mixtures such as distillation residue from the production of perchloroethylene, application of *o*-dichlorobenzene as the solvent, etc. The above-mentioned Ni-based gas phase HDH method potentially enables subsequent recycling of the obtained HDH products (Ar-Hs) as raw materials in organic technology. In the last years, however, the occurrence of published articles dealing with gas phase Ni-based HDH is rare. Gas phase HDH is included as part of soil remediation (REACH) technology, for example [133]. It was proved that standard supported Ni–Mo catalysts used for hydrosulfurization are effective even for HDC which offers broad utilization in reductive treatment of Ar-Xs contaminants produced by pyrolysis of plastic waste [134].

It is possible that the necessity of special apparatus, application of catalyst and supply of hydrogen disadvantages gas phase HDH as hazardous waste treatment method towards incineration. The waste incineration is probably cheaper as non-catalytic thermal oxidative technology consuming air oxygen and sometimes even natural gas as the supporting fuel. On the other hand, incineration produces low quantities of toxic and thermodynamically

stable organic by-products such as polyhalogenated dibenzo-p-dioxines and/or polyhalogenated dibenzofurans and polyaromatic compounds. Nevertheless, these stable organic by-products are reactive enough for effective destruction via liquid phase HDH methods. HDH in the liquid phase seems to be applicable for treatment of waste containing halogenated aromatic contaminants due to the lower temperature used with subsequent lower detrition of the used Ni catalyst.

In the future, it is likely that new findings dealing with searching of the new suitable supports and looking for synergistic effects of additional elements [18,33,135] for improvement of catalytical activity, selectivity and catalyst stability could be expected in the area of Ni-catalyzed HDH processes using gaseous hydrogen.

Special techniques were developed for transfer HDH of some Ar-Xs in organic solvents using Ni-based complexes and reductants such as metal hydrides or Zn(0). These techniques are demanding, however, on the high quantity of the used anhydrous solvents, auxiliary compounds such as ligands (triphenylphosphine, 2,2'-bipyridyl or phenanthroline), proton sponges (pyridine) and due to this reason, cause poor atom economy, and lack the opportunity for broader technological applications of these HDH techniques [132]. On the other hand, if used Ni(Ph₃P)_n HDH catalyst and used reductant were recyclable, the above-mentioned techniques utilizing organic solvents working under homogeneous conditions could be a promising detoxification method for treatment of waste Ar-Xs in the near future.

Reductive degradation of Ar-Xs-based contaminants in alkaline aqueous solution or mixed alkaline alcohol/water solution using Raney Al-Ni alloy seems to be ready for use in treatment processes. The only limitation could be the complicated recycling of produced Ni-waste which needs several hydrometallurgical steps with exceptional subsequent high temperature treatment [100,130,131].

In contrast, the yet published application of Fe/Ni bimetals for Ar-Xs HDH seems to be quite problematic, with inconsistent HDH results and often producing only partially dehalogenated products. Other authors advert to unreplaceable role of Ni in iron-based HDH [136]. Due to these reasons, even though Fe/Ni bimetal is a cheap reductant, it should be more deeply investigated for HDH applications especially in HDH of mixtures of Ar-Xs. Ni-based bimetals containing other electropositive metals such as Mg or Al could in all probability be more profitable for efficient HDH of Ar-Xs in contaminated wastewaters.

In conclusion, nickel as a cheap nonprecious metal with HDH efficiency impeding to platinum group metals in HDH reactions seems to be potentially broadly applicable for significant decreasing of environmental impacts joined with the utilization of halogenated aromatic compounds.

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References

1. Keane, M.A. Supported Transition Metal Catalysts for Hydrodechlorination Reactions. *ChemCatChem* **2011**, *3*, 800–821. [[CrossRef](#)]
2. Converti, A.; Zilli, M.; De Favari, D.M.; Ferraiola, G. Hydrogenolysis of Organochlorinated Pollutants: Kinetics and thermodynamics. *J. Hazard. Mater.* **1991**, *27*, 127–135. [[CrossRef](#)]
3. Walker, D.P.; Harris, G.D., Jr.; Carroll, J.N.; Boehm, T.L.; McReynolds, M.D.; Struble, J.R.; van Herpt, J.; van Zwieten, D.; Koeller, K.J.; Bore, M. A new process to prepare 3,6-dichloro-2-hydroxybenzoic acid, the penultimate intermediate in the synthesis of herbicide dicamba. *Tetrahedron Lett.* **2019**, *60*, 1032–1036. [[CrossRef](#)]

4. Alonso, F.; Beletskaya, I.P.; Yus, M. Metal-Mediated Reductive Hydrodehalogenation of Organic Halides. *Chem. Rev.* **2002**, *102*, 4009–4091. [[CrossRef](#)]
5. Buono, F.; Nguyen, T.; Qu, B.; Wu, H.; Haddad, N. Recent Advances in Nonprecious Metal Catalysis. *Org. Proc. Res. Dev.* **2021**, *25*, 1471–1495. [[CrossRef](#)]
6. Zimmermann, S.; Wolff, C.; Sures, B. Toxicity of platinum, palladium and rhodium to *Daphnia magna* in single and binary metal exposure experiments. *Environ. Pollut.* **2017**, *224*, 368–376. [[CrossRef](#)] [[PubMed](#)]
7. Pawlak, J.; Lodyga-Chruścińska, E.; Chrustowicz, J. Fate of platinum metals in the environment. *J. Trace Elem. Med. Biol.* **2014**, *28*, 247–254. [[CrossRef](#)]
8. Harasim, P.; Filipek, T. Nickel in the environment. *J. Elem.* **2015**, *20*, 525–534. [[CrossRef](#)]
9. Shahzad, B.; Tanveer, M.; Rehman, A.; Cheema, S.A.; Fahad, S.; Rehman, S.; Sharma, A. Nickel; whether toxic or essential for plants and environment-A review. *Plant Physiol. Biochem.* **2018**, *132*, 641–651. [[CrossRef](#)] [[PubMed](#)]
10. Denkhaus, E.; Salnikow, K. Nickel essentiality, toxicity, and carcinogenicity. *Crit. Rev. Oncol. Hemat.* **2002**, *42*, 35–56. [[CrossRef](#)]
11. Li, Y.; Zamble, D.B. Nickel Homeostasis and Nickel Regulation: An Overview. *Chem. Rev.* **2009**, *109*, 4617–4643. [[CrossRef](#)] [[PubMed](#)]
12. Konkol, M.; Wróbel, W.; Bicki, R.; Golebiowski, A. The Influence of the Hydrogen Pressure on Kinetics of the Canola Oil Hydrogenation on Industrial Nickel Catalyst. *Catalysts* **2016**, *6*, 55. [[CrossRef](#)]
13. de Jong, V.; Louw, R. Performance of supported nickel and other metal catalysts in the hydrodechlorination of chlorobenzene and 1-chlorohexane. *Appl. Catal. A Gen.* **2004**, *271*, 153–163. [[CrossRef](#)]
14. Amorim, C.; Keane, M.A. Catalytic hydrodechlorination of chloroaromatic gas streams promoted by Pd and Ni: The role of hydrogen spillover. *J. Hazard. Mater.* **2012**, *211–212*, 208–217. [[CrossRef](#)] [[PubMed](#)]
15. Cesteros, Y.; Salagre, P.; Medina, F.; Sueiras, J.E. Synthesis and characterization of several Ni/NiAl₂O₄ catalysts active for the 1,2,4-trichlorobenzene hydrodechlorination. *Appl. Catal. B Environ.* **2000**, *25*, 213–227. [[CrossRef](#)]
16. Cesteros, Y.; Salagre, P.; Medina, F.; Sueiras, J.E. TPD study about the surface modification of some Ni/spinel catalysts in the hydrodechlorination of 1,2,4-trichlorobenzene. Influence on hydrogenation ability. *Catal. Lett.* **2000**, *67*, 147–153. [[CrossRef](#)]
17. Suzdorf, A.R.; Morozov, S.V.; Anshits, N.N.; Tsiganova, S.I. Gas-phase hydrodechlorination of chlorinated aromatic-compounds on nickel-catalysts. *Catal. Lett.* **1994**, *29*, 49–55. [[CrossRef](#)]
18. Keane, M.A.; Gomez-Quero, S.; Cardenas-Lizana, F.; Shen, W. Alumina-Supported Ni–Au: Surface Synergistic Effects in Catalytic Hydrodechlorination. *ChemCatChem* **2009**, *1*, 270–278. [[CrossRef](#)]
19. Novak, M.; Zdrzil, M. Effects of sulfidation and synergism in hydrodechlorination of o-dichlorobenzene over alumina catalyst. *Bull. Soc. Chim. Belg.* **1993**, *102*, 271–279. [[CrossRef](#)]
20. Murena, F. Catalytic hydroprocessing of chlorobenzene: The effect of thiophene. *J. Hazard. Mater.* **2000**, *75*, 49–57. [[CrossRef](#)]
21. Schioppa, E.; Murena, F.; Gioia, F. Mass-transfer resistances in the catalytic hydrodechlorination of polychlorobiphenyls. Experimental results of 2-chlorobiphenyl hydrodechlorination in a slurry reactor and in a rotating basket reactor. *Ind. Eng. Chem. Res.* **2001**, *40*, 2011–2016. [[CrossRef](#)]
22. Gryglewicz, S.; Piechocki, W. Hydrodechlorination of dichlorobenzenes and their derivatives over Ni–Mo/C catalyst: Kinetic analysis and effect of molecular structure of reactant. *Chemosphere* **2011**, *83*, 334–339. [[CrossRef](#)]
23. Cesteros, Y.; Salagre, P.; Medina, F.; Sueiras, J.E.; Tichit, D.; Coq, B. Hydrodechlorination of 1,2,4-trichlorobenzene on nickel-based catalysts prepared from several Ni/Mg/Al hydrotalcite-like precursors. *Appl. Catal. B Environ.* **2001**, *32*, 25–35. [[CrossRef](#)]
24. Menini, C.; Park, C.; Shin, E.J.; Tavoularis, G.; Keane, M.A. Catalytic hydrodehalogenation as a detoxification methodology. *Catal. Today* **2000**, *62*, 355–366. [[CrossRef](#)]
25. Park, C.; Menini, C.; Valverde, J.L.; Keane, M.A. Carbon–Chlorine and Carbon–Bromine Bond Cleavage in the Catalytic Hydrodehalogenation of Halogenated Aromatics. *J. Catal.* **2002**, *211*, 451–463. [[CrossRef](#)]
26. Keane, M.A.; Pina, G.; Tavoularis, G. The catalytic hydrodechlorination of mono-, di- and trichlorobenzenes over supported nickel. *Appl. Catal. B Environ.* **2004**, *48*, 275–280. [[CrossRef](#)]
27. Keane, M.A. Hydrodehalogenation of haloarenes over Silica supported Pd and Ni. A consideration of catalytic activity/selectivity and haloarene reactivity. *Appl. Catal. A Gen.* **2004**, *271*, 109–118. [[CrossRef](#)]
28. Murthy, K.V.; Patterson, P.M.; Jacobs, G.; Davis, B.H.; Keane, M.A. An exploration of activity loss during hydrodechlorination and hydrodebromination over Ni/SiO₂. *J. Catal.* **2004**, *223*, 74–85. [[CrossRef](#)]
29. Murthy, K.V.; Patterson, P.M.; Keane, M.A. C–X bond reactivity in the catalytic hydrodehalogenation of haloarenes over unsupported and silica supported Ni. *J. Mol. Catal. A Chem.* **2005**, *225*, 149–160. [[CrossRef](#)]
30. Kim, P.; Kim, Y.; Kang, T.; Song, I.K.; Yi, J. Preparation of nickel-mesoporous materials and their application to the hydrodechlorination of chlorinated organic compounds. *Catal. Surv. Asia* **2007**, *11*, 49–58. [[CrossRef](#)]
31. Kim, P.; Joo, J.B.; Kim, H.; Kim, W.; Kim, Y.; Song, I.K.; Yi, J. Preparation of mesoporous Ni-alumina catalyst by one-step sol-gel method: Control of textural properties and catalytic application to the hydrodechlorination of o-dichlorobenzene. *Catal. Lett.* **2005**, *104*, 181–189. [[CrossRef](#)]
32. Park, Y.; Kang, T.; Kim, P.; Yi, J. Encapsulation method for the dispersion of NiO onto ordered mesoporous silica, SBA-15, using polyethylene oxide (PEO). *J. Colloid Interface Sci.* **2006**, *295*, 464–471. [[CrossRef](#)]
33. Rath, D.; Parida, K.M. Copper and Nickel Modified MCM-41 an Efficient Catalyst for Hydrodehalogenation of Chlorobenzene at Room Temperature. *Ind. Eng. Chem. Res.* **2011**, *50*, 2839–2849. [[CrossRef](#)]

34. Wu, W.; Xu, J.; Ohnishi, R. Complete hydrodechlorination of chlorobenzene and its derivatives over supported nickel catalysts under liquid phase conditions. *Appl. Catal. B Environ.* **2005**, *60*, 129–137. [[CrossRef](#)]
35. Wang, W.; Wang, K.; Huang, D.; Zhou, C.; Zhang, W.; Niu, J. Ultrasonication-Enhanced Reduction of Tetrabromobisphenol A by Activating Nascent H₂ on Raney Ni Catalyst: Kinetics, Mechanisms, and Hydrogenation Pathways. *ACS EST Eng.* **2021**, *1*, 884–894. [[CrossRef](#)]
36. Ma, X.; Liu, S.; Liu, Y.; Li, X.; Li, Q.; Gu, G.; Xia, C. Promoted liquid-phase hydrodechlorination of chlorophenol over Raney Ni via controlling base: Performance, mechanism, and application. *Chemosphere* **2020**, *242*, 125202. [[CrossRef](#)]
37. Marques, C.A.; Selva, M.; Tundo, P. Hydrodehalogenation of polyhalogenated aromatics under multiphase conditions with H-2 and metal catalyst: Kinetics and selectivity. *Gazz. Chim. Ital.* **1996**, *126*, 317–327.
38. Cardenas-Lizana, F.; Gomez-Quero, S.; Keane, M.A. Clean production of chloroanilines by selective gas phase hydrogenation over supported Ni catalysts. *Appl. Catal. A Gen.* **2008**, *334*, 199–206. [[CrossRef](#)]
39. Amorim, C.; Wang, X.; Keane, M.A. Application of Hydrodechlorination in Environmental Pollution Control: Comparison of the Performance of Supported and Unsupported Pd and Ni Catalysts. *Chin. J. Catal.* **2011**, *32*, 746–755. [[CrossRef](#)]
40. Birke, P.; Wilfried, R.; Heubner, U.; Koppe, J.; Neumann, U.; Shoedel, R. DE Patent 4320462, 1995. *Chem. Abstr.* **1995**, *123*, 231952.
41. Keane, M.A.; Larsson, R. Isokinetic behaviour in gas phase catalytic hydrodechlorination of chlorobenzene over supported nickel. *J. Mol. Catal. A Chem.* **2007**, *268*, 87–94. [[CrossRef](#)]
42. Keane, M.A.; Park, C.; Menini, C. Structure sensitivity in the hydrodechlorination of chlorobenzene over supported nickel. *Catal. Lett.* **2003**, *88*, 89–94. [[CrossRef](#)]
43. Shin, E.-J.; Keane, M.A. Structure sensitivity in the hydrodechlorination of chlorophenols. *React. Kinet. Catal. Lett.* **2000**, *69*, 3–8. [[CrossRef](#)]
44. Prati, L.; Rossi, M. Reductive catalytic dehalogenation of light chlorocarbons. *Appl. Catal. B* **1999**, *23*, 135–142. [[CrossRef](#)]
45. Keane, M.A. A review of catalytic approaches to waste minimization: Case study-liquid-phase catalytic treatment of chlorophenols. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1211–1222. [[CrossRef](#)]
46. Aramendia, M.A.; Borau, V.; Garcia, I.M.; Jimenez, C.; Lafont, F.; Marinas, A.; Marinas, J.M.; Urbano, F.J. Influence of the Reaction Conditions and Catalytic Properties on the Liquid-Phase Hydrodechlorination of Chlorobenzene over Palladium-Supported Catalysts: Activity and Deactivation. *J. Catal.* **1999**, *187*, 392–399. [[CrossRef](#)]
47. Wang, J.; Fan, G.; Li, F. Carbon-supported Ni catalysts with enhanced metal dispersion and catalytic performance for hydrodechlorination of chlorobenzene. *RSC Adv.* **2012**, *2*, 9976–9985. [[CrossRef](#)]
48. Xia, C.; Liu, Y.; Zhou, S.; Yang, C.; Liu, S.; Guo, S.; Liu, Q.; Yu, J.; Chen, J. The influence of ion effects on the Pd-catalyzed hydrodechlorination of 4-chlorophenol in aqueous solutions. *Catal. Commun.* **2009**, *10*, 1443–1445. [[CrossRef](#)]
49. Baeza, J.A.; Calvo, L.; Gilarranz, M.A.; Rodriguez, J.J. Effect of size and oxidation state of size-controlled rhodium nanoparticles on the aqueous-phase hydrodechlorination of 4-chlorophenol. *Chem. Eng. J.* **2014**, *240*, 271–280. [[CrossRef](#)]
50. Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, *115*, 6621–6686. [[CrossRef](#)]
51. Stiles, M. Nickel Complexes as Soluble Catalysts for Reductive Dehalogenation of Aromatic Halides. *J. Org. Chem.* **1994**, *59*, 5381–5385. [[CrossRef](#)]
52. Tak, H.; Lee, H.; Kang, J.; Cho, J. A high-spin nickel(II) borohydride complex in dehalogenation. *Inorg. Chem. Front.* **2016**, *3*, 157–163. [[CrossRef](#)]
53. Vcelak, J.; Hetflejš, J. Dehalogenation of chloroarenes with sodium dihydrobis(2-methoxyethoxy)aluminate in the presence of transition metal compounds. *Collect. Czech. Chem. Commun.* **1994**, *59*, 1645–1653. [[CrossRef](#)]
54. King, C.M.; King, R.B.; Bhattacharyya, N.K.; Newton, M.G. Organonickel chemistry in the catalytic hydrodechlorination of polychlorobiphenyls (PCBs): Ligand steric effects and molecular structure of reaction intermediates. *J. Organomet. Chem.* **2000**, *600*, 63. [[CrossRef](#)]
55. Alonso, F.; Riente, P.; Sirvent, J.A.; Yus, M. Nickel nanoparticles in hydrogen-transfer reductions: Characterisation and nature of the catalyst. *Appl. Catal. A Gen.* **2010**, *378*, 42–51. [[CrossRef](#)]
56. Alonso, F.; Foubelo, F.; González-Gómez, J.C.; Martínez, R.; Ramón, D.J.; Riente, P.; Yus, M. Efficiency in chemistry: From hydrogen autotransfer to multicomponent catalysis. *Mol. Divers.* **2010**, *14*, 411–424. [[CrossRef](#)]
57. Alonso, F.; Riente, P.; Yus, M. Nickel Nanoparticles in Hydrogen Transfer Reactions. *Acc. Chem. Res.* **2011**, *44*, 379–391. [[CrossRef](#)] [[PubMed](#)]
58. Tabaei, S.-M.H.; Pittman, C.U., Jr.; Mead, K.T. Dehalogenation of Organic Compounds. 3. Dechlorination of Polychlorinated Biphenyls, 4-Chlorobiphenyl, and Chloro-p-xylene with Alkoxyborohydrides. *J. Org. Chem.* **1992**, *57*, 6669–6671. [[CrossRef](#)]
59. Tabaei, S.-M.H.; Pittman, C.U., Jr. Dehalogenation of Organic Compounds. 4. Dechlorination of Pentachlorophenol and 1,2,4-Trichlorobenzene with Transition Metal-Promoted Alkoxyborohydrides. *Tetrahedron Lett.* **1993**, *34*, 3263–3266. [[CrossRef](#)]
60. Scrivanti, A.; Vicentini, B.; Beghetto, V.; Chessa, G.; Matteoli, U. Hydrodehalogenation of aromatic chlorides with NaBH₄, in the presence of Ni(0) catalysts. *Inorg. Chem. Commun.* **1998**, *1*, 246–248. [[CrossRef](#)]
61. Wang, D.; Gardinier, J.R. The Electronic Properties of Ni(PNN) Pincer Complexes Modulate Activity in Catalytic Hydrodehalogenation Reactions. *Eur. J. Inorg. Chem.* **2020**, *2020*, 4425–4434. [[CrossRef](#)]
62. Lipshutz, B.H.; Tomioka, T.; Pfeiffer, S.S. Mild and selective reductions of aryl halides catalyzed by low-valent nickel complexes. *Tetrahedron Lett.* **2001**, *42*, 7737–7740. [[CrossRef](#)]

63. Sakai, M.; Lee, M.-S.; Yamaguchi, K.; Kawai, Y. Metallic Nickel-Catalyzed Reduction of Aryl Halides with Zinc Powder and Ethanol. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1739. [[CrossRef](#)]
64. Prikhodko, S.A.; Popov, A.G.; Adonin, N.Y. Effects arising from the replacement of aprotic dipolar solvents with ionic liquids in the nickel-catalyzed reduction of aryl chlorides. *Mol. Catal.* **2018**, *461*, 19–25. [[CrossRef](#)]
65. Prikhodko, S.A.; Adonin, N.Y.; Parmon, V.N. Reaction of pentafluoroacetanilide with zinc catalyzed by nickel complexes. *Russ. Chem. Bull.* **2009**, *58*, 2304–2310. [[CrossRef](#)]
66. Shteingarts, V.D. Recent advances in practice and theory of polyfluoroarene hydrodehalogenation. *J. Fluorine Chem.* **2007**, *128*, 797–805. [[CrossRef](#)]
67. Yamamoto, T.; Hayashida, N.; Maruyama, T. Ni-catalyzed dehalogenation polycondensation of dihaloaromatic compounds with NaH. *Macromol. Chem. Phys.* **1997**, *198*, 341–351. [[CrossRef](#)]
68. Wei, Y.; Gong, Y.; Zhao, X.; Wang, Y.; Duan, R.; Chen, C.; Song, W.; Zhao, J. Ligand directed debromination of tetrabromodiphenyl ether mediated by nickel under visible irradiation. *Environ. Sci. Nano* **2019**, *6*, 1585–1593. [[CrossRef](#)]
69. Gantzer, C.J.; Wackett, L.P. Reductive Dechlorination Catalyzed by Bacterial Transition-Metal Coenzymes. *Environ. Sci. Technol.* **1991**, *25*, 715–722. [[CrossRef](#)]
70. Shiraiishi, K.; Yamamoto, T. New pi-conjugated polymers constituted of dialkoxybenzodithiophene units: Synthesis and electronic properties. *Synth. Met.* **2002**, *130*, 139–147. [[CrossRef](#)]
71. Freeman, P.K.; Ramnath, N.; Richardson, A.D. The Photochemistry of Polyhaloarenes. 10. The Photochemistry of Pentachlorobenzene. *J. Org. Chem.* **1991**, *56*, 3643–3646. [[CrossRef](#)]
72. Weidauer, M.; Irran, E.; Someya, C.I.; Haberberger, M.; Enthaler, S. Nickel-catalyzed hydrodehalogenation of aryl halides. *J. Organomet. Chem.* **2013**, *729*, 53–59. [[CrossRef](#)]
73. Janiak, C.; Deblon, S.; Uehlin, L. Synthesis of 6,6'-diamino-2,2'-biquinoline and 2,2'-bi-1,6-naphthyridine. *Synth.-Stuttg.* **1999**, *1999*, 959–964.
74. Fort, Y. Lithium Hydride Containing Complex Reducing Agent—A New And Simple Activation of Commercial Lithium Hydride. *Tetrahedron Lett.* **1995**, *36*, 6051–6054. [[CrossRef](#)]
75. Caubere, P. Complex Reducing Agents—their Applications and their Outcome in the Field of Carbonylations. *Pure Appl. Chem.* **1985**, *57*, 1875–1882. [[CrossRef](#)]
76. Dubois, J.M.; Fort, Y.; Tillement, O. FR Patent 2768638. *Chem. Abstr.* **1999**, *130*, 254063.
77. Li, H.; Liao, S.; Xu, Y. Catalytic Hydrogenolysis of Aromatic Halides with Sodium Hydride of Nanometric Size. *Chem. Lett.* **1996**, *25*, 1059–1060. [[CrossRef](#)]
78. Li, H.; Liao, S.; Yu, D.; Qiao, Z. An effective method for the hydrodehalogenation of organic halides. *Chin. Sci. Bull.* **1997**, *42*, 966–967. [[CrossRef](#)]
79. Massicot, F.; Schneider, R.; Fort, Y.; Illy, S.; Tillement, O. Synergistic Effect in Bimetallic Ni±Al Clusters. Application to Efficient Catalytic Reductive Dehalogenation of Polychlorinated Arenes. *Tetrahedron* **2000**, *56*, 4765–4768. [[CrossRef](#)]
80. Gazellot, P.; Leclercq, C.; Fort, Y.; Caubere, P. Subnanometer Nickel Clusters in Complex Reducing Agents. *J. Mol. Catal. A Chem.* **1994**, *93*, 79–83. [[CrossRef](#)]
81. Illy, S.; Tillement, O.; Dubois, J.M.; Massicot, F.; Fort, Y.; Ghanbaja, J. First direct evidence of size-dependent structural transition in nanosized nickel particles. *Philos. Mag. A* **1999**, *79*, 1021–1031. [[CrossRef](#)]
82. Kastanek, F.; Maleterova, Y.; Kastanek, P.; Rott, J.; Jiricny, V.; Jiratova, K. Complex treatment of wastewater and groundwater contaminated by halogenated organic compounds. *Desalination* **2007**, *211*, 261–271. [[CrossRef](#)]
83. Keane, M.A. Advances in greener separation processes - case study: Recovery of chlorinated aromatic compounds. *Green Chem.* **2003**, *5*, 309–317. [[CrossRef](#)]
84. Ma, X.; Liu, S.; Liu, Y.; Li, X.; Xu, J.; Gu, G.; Xia, C. Water: The most effective solvent for liquid-phase hydrodechlorination of chlorophenols over Raney Ni catalyst. *Appl. Catal. B* **2015**, *165*, 351–359. [[CrossRef](#)]
85. Wang, W.; Wu, Y.; Wang, K.; Pei, Y.; Niu, J. Ultrasonic-enhanced nascent H₂ activation on Raney Ni for the degradation of triclosan. *Chin. Sci. Bull. Chin.* **2021**, *66*, 1923–1932. [[CrossRef](#)]
86. Raut, S.S.; Shetty, R.; Raju, N.M.; Kamble, S.P.; Kulkarni, P.S. Screening of zero valent mono/bimetallic catalysts and recommendation of Raney Ni (without reducing agent) for dechlorination of 4-chlorophenol. *Chemosphere* **2020**, *250*, 126298. [[CrossRef](#)] [[PubMed](#)]
87. Ma, X.; Liu, S.; Liu, Y.; Gu, G.; Xia, C. Comparative study on catalytic hydrodehalogenation of halogenated aromatic compounds over Pd(5 wt%)/C and Raney Ni catalysts. *Sci. Rep.* **2016**, *6*, 1–11. [[CrossRef](#)]
88. Weidlich, T.; Kamenicka, B.; Melanova, K.; Cizmancova, V.; Komersova, A.; Cermak, J. Hydrodechlorination of Different Chloroaromatic Compounds at Room Temperature and Ambient Pressure—Differences in Reactivity of Cu- and Ni-Based Al Alloys in an Alkaline Aqueous Solution. *Catalysts* **2020**, *10*, 994. [[CrossRef](#)]
89. Liu, G.B.; Zhao, H.Y.; Dai, L.; Thiemann, T. A convenient method for the reductive degradation of mono-, di-, and tribromodiphenyl ethers, tetrabromo- and tetrachlorobisphenol A with Raney Ni-Al alloy. *Ark. J. Chem. Res.* **2009**, *13*, 211–226. [[CrossRef](#)]
90. Liu, G.B.; Zhao, H.Y.; Zhang, J.; Thiemann, T. Raney Ni-Al alloy mediated hydrodehalogenation and aromatic ring hydrogenation of halogenated phenols in aqueous medium. *J. Chem. Res.* **2009**, *6*, 342–344. [[CrossRef](#)]

91. Weidlich, T.; Prokes, L. Facile dehalogenation of halogenated anilines and their derivatives using Al–Ni alloy in alkaline aqueous solution. *Cent. Eur. J. Chem.* **2011**, *9*, 590–597. [[CrossRef](#)]
92. Weidlich, T.; Prokes, L.; Pospisilova, D. Debromination of 2,4,6-tribromophenol coupled with biodegradation. *Cent. Eur. J. Chem.* **2013**, *11*, 979–987. [[CrossRef](#)]
93. Weidlich, T.; Oprsal, J.; Krejcova, A.; Jasurek, B. Effect of glucose on lowering Al–Ni alloy consumption in dehalogenation of halogenoanilines. *Monatsh. Chem.* **2015**, *146*, 613–620. [[CrossRef](#)]
94. Perko, J.; Kamenicka, B.; Weidlich, T. Degradation of the antibacterial agents triclosan and chlorophene using hydrodechlorination by Al-based alloys. *Monatsh. Chem.* **2018**, *149*, 1777–1786. [[CrossRef](#)]
95. Liu, G.-B.; Tsukinoki, T.; Kanda, T.; Mitoma, Y.; Tashiro, M. Organic Reaction in Water. Part 2. A New Method for Dechlorination of Chlorobiphenyls Using a Raney Ni–Al Alloy in Dilute Aqueous Alkaline Solution. *Tetrahedron Lett.* **1998**, *39*, 5991–5994. [[CrossRef](#)]
96. Liu, G.B.; Zhao, H.-Y.; Zhu, J.-D.; He, H.-J.; Yang, H.-J.; Thiemann, T.; Tashiro, H.; Tashiro, M. New Method for the Reduction of Benzophenones with Raney Ni–Al Alloy in Water. *Synth. Commun.* **2008**, *38*, 1651–1661. [[CrossRef](#)]
97. Liu, G.B.; Tashiro, M.; Thiemann, T. A facile method for the dechlorination of mono- and dichlorobiphenyls using Raney Ni–Al alloy in dilute aqueous solutions of alkali hydroxides or alkali metal carbonates. *Tetrahedron* **2009**, *65*, 2497–2505. [[CrossRef](#)]
98. Hegedus, M.; Gaborova, K.; Weidlich, T.; Kalivoda, P.; Briancin, J.; Tothova, E. Rapid hydrodehalogenation of chlorinated benzoic acids using mechano-thermally prepared Raney alloy with enhanced kinetics. *J. Environ. Chem. Eng.* **2021**, *9*. [[CrossRef](#)]
99. Liu, G.B.; Dai, L.; Gao, X.; Li, M.K.; Thiemann, T. Reductive degradation of tetrabromobisphenol A (TBBPA) in aqueous medium. *Green Chem.* **2006**, *8*, 781–783. [[CrossRef](#)]
100. Yang, B.; Zhang, F.; Deng, S.; Yu, G.; Zhang, H.; Xiao, J.; Shi, L.; Shen, J. A facile method for the highly efficient hydrodechlorination of 2-chlorophenol using Al–Ni alloy in the presence of fluorine ion. *Chem. Eng. J.* **2012**, *209*, 79–85. [[CrossRef](#)]
101. Yang, B.; Zhang, J.; Zhang, Y.; Deng, S.; Yu, G.; Wu, J.; Zhang, H.; Liu, J. Promoting effect of EDTA on catalytic activity of highly stable Al–Ni bimetal alloy for dechlorination of 2-chlorophenol. *Chem. Eng. J.* **2014**, *250*, 222–229. [[CrossRef](#)]
102. Keefer, L.K.; Lunn, G. Nickel–Aluminum Alloy as a Reducing Agent. *Chem. Rev.* **1989**, *89*, 459–502. [[CrossRef](#)]
103. Hegedus, M.; Lacina, P.; Ploteny, M.; Lev, J.; Kamenicka, B.; Weidlich, T. Fast and efficient hydrodehalogenation of chlorinated benzenes in real wastewaters using Raney alloy. *J. Water Proc. Eng.* **2020**, *38*, 101645. [[CrossRef](#)]
104. Liu, G.-B.; Zhao, H.-Y.; Dai, L.; Thiemann, T.; Tashiro, H.; Tashiro, M. Raney Ni–Al alloy-mediated reduction of benzils in water. *J. Chem. Res.* **2009**, *9*, 579–581. [[CrossRef](#)]
105. Nidheesh, P.V.; Khatri, J.; Anatha Singh, T.S.; Gandhimathi, R.; Ramesh, S.T. Review of zero-valent aluminium based water and wastewater treatment methods. *Chemosphere* **2018**, *200*, 621–631. [[CrossRef](#)]
106. Shih, Y.-H.; Hsu, C.-Y.; Su, Y.-F. Reduction of hexachlorobenzene by nanoscale zero-valent iron: Kinetics, pH effect, and degradation mechanism. *Sep. Pur. Technol.* **2011**, *76*, 268–274. [[CrossRef](#)]
107. Roy, H.M.; Wai, C.M.; Yuan, T.; Kim, J.-K.; Marshall, W.D. Catalytic hydrodechlorination of chlorophenols in aqueous solution under mild conditions. *Appl. Catal. A Gen.* **2004**, *271*, 137–143. [[CrossRef](#)]
108. Choi, J.H.; Kim, Y.H. Reduction of 2,4,6-trichlorophenol with zero-valent zinc and catalyzed zinc. *J. Hazard. Mater.* **2009**, *166*, 984–991. [[CrossRef](#)]
109. Shih, Y.H.; Chen, M.Y.; Su, Y.F. Pentachlorophenol reduction by Pd/Fe bimetallic nanoparticles: Effect of copper, nickel, and ferric cations. *Appl. Catal. B Environ.* **2011**, *105*, 24–29. [[CrossRef](#)]
110. Agarwal, S.; Al-Abed, S.R.; Dionysiou, D.D. Enhanced corrosion based Pd/Mg bimetallic systems for dichlorination of PCBs. *Environ. Sci. Technol.* **2007**, *41*, 3722–3727. [[CrossRef](#)]
111. Zhuang, Y.; Ahn, S.; Seyfferth, A.L.; Masue-Slowey, Y.; Fendorf, S.; Luthy, R.G. Dehalogenation of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyl by Bimetallic, Impregnated, and Nanoscale Zerovalent Iron. *Environ. Sci. Technol.* **2011**, *45*, 4896–4903. [[CrossRef](#)]
112. Yang, B.; Deng, S.; Yu, G.; Zhang, H.; Wu, J.; Zhuo, Q. Bimetallic Pd/Al particles for highly efficient hydrodechlorination of 2-chlorobiphenyl in acidic aqueous solution. *J. Hazard. Mater.* **2011**, *189*, 76–83. [[CrossRef](#)]
113. Zhang, Z.; Cissoko, N.; Wo, J.; Xu, X. Factors influencing the dechlorination of 2,4-dichlorophenol by Ni–Fe nanoparticles in the presence of humic acid. *J. Hazard. Mater.* **2009**, *165*, 78–86. [[CrossRef](#)]
114. Tian, H.; Li, J.; Mu, Z.; Li, L.; Hao, Z. Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles. *Sep. Purif. Technol.* **2009**, *66*, 84–89. [[CrossRef](#)]
115. Cheng, R.; Zhou, W.; Wang, J.-L.; Qi, D.; Guo, L.; Zhang, W.-X.; Qian, Y. Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: Role of nano-Ni and its size effect. *J. Hazard. Mater.* **2010**, *180*, 79–85. [[CrossRef](#)] [[PubMed](#)]
116. Ghauch, A.; Assi, H.A.; Bdeir, S. Aqueous removal of diclofenac by plated elemental iron: Bimetallic systems. *J. Hazard. Mater.* **2010**, *182*, 64–74. [[CrossRef](#)]
117. Zhang, Z.; Hu, S.; Ali, S.; Tang, J.; Xu, X. Catalytic dechlorination of Aroclor 1242 by Ni/Fe bimetallic nanoparticles. *J. Colloid Interface Sci.* **2012**, *385*, 160–165. [[CrossRef](#)] [[PubMed](#)]
118. Lin, C.; Shih, Y.; MacFarlane, J. Amphiphilic compounds enhance the dechlorination of pentachlorophenol with Ni/Fe bimetallic nanoparticles. *Chem. Eng. J.* **2015**, *262*, 59–67. [[CrossRef](#)]

119. Liu, Z.; Gu, C.; Ye, M.; Bian, Y.; Cheng, Y.; Wang, F.; Yang, X.; Song, Y.; Jiang, X. Debromination of polybrominated diphenyl ethers by attapulgite-supported Fe/Ni bimetallic nanoparticles: Influencing factors, kinetics and mechanism. *J. Hazard. Mater.* **2015**, *298*, 328–337. [[CrossRef](#)]
120. Huang, B.; Qian, W.; Yu, C.; Wang, T.; Zeng, G.; Lei, C. Effective catalytic hydrodechlorination of o-, p- and m-chloronitrobenzene over Ni/Fe nanoparticles: Effects of experimental parameter and molecule structure on the reduction kinetics and mechanisms. *Chem. Eng. J.* **2016**, *306*, 607–618. [[CrossRef](#)]
121. Li, Y.; Li, X.; Han, D.; Huang, W.; Yang, C. New insights into the role of Ni loading on the surface structure and the reactivity of nZVI toward tetrabromo- and tetrachlorobisphenol A. *Chem. Eng. J.* **2017**, *311*, 173–182. [[CrossRef](#)]
122. Cheng, S.F.; Wu, S.C. Feasibility of using metals to remediate water containing TCE. *Chemosphere* **2001**, *43*, 1023–1028. [[CrossRef](#)]
123. Tashiro, M.; Fukata, G. Selective Electrophilic Aromatic Substitutions via Positional Protective Groups. A Review. *Org. Prep. Proc. Int.* **1976**, *8*, 51–74. [[CrossRef](#)]
124. Ramanathan, A.; Jimenez, L.S. Reductive Dehalogenation of Aryl Bromides and Chlorides and Their Use as Aryl Blocking Groups. *Synthesis* **2010**, 217–220. [[CrossRef](#)]
125. Choi, H.Y.; Chi, Y. A Facile Debromination Reaction: Can Bromide Now Be Used as a Protective Group in Aromatic Systems? *J. Am. Chem. Soc.* **2001**, *123*, 9202–9203. [[CrossRef](#)] [[PubMed](#)]
126. Effenberger, F. How Attractive is Bromine as a Protecting Group in Aromatic Chemistry? *Angew. Chem.* **2002**, *41*, 1699–1700. [[CrossRef](#)]
127. Ramos-Cano, J.; González-Zamarripa, G.; Carrillo-Pedroza, R.; de Jesús Soria-Aguilar, M.; Hurtado-Macías, A.; Cano-Vielma, A. Kinetics and statistical analysis of nickel leaching from spent catalyst in nitric acid solution. *Int. J. Min. Proc.* **2016**, *148*, 41–47. [[CrossRef](#)]
128. Martinez Stagnaro, S.Y.; Mesquida, C.D.; Stábile, F.M.; Zysler, R.; Ramos, S.B.; Giaveno, A. Recovery and characterization of nickel particles by chemical reduction method from wastes generated in electroless industry. *J. Hazard. Mater.* **2019**, *376*, 133–140. [[CrossRef](#)]
129. Coman, V.; Robotin, B.; Ilea, P. Nickel recovery/removal from industrial wastes: A review. *Res. Conserv. Rec.* **2013**, *73*, 229–238. [[CrossRef](#)]
130. Weidlich, T.; Kamenicka, B. Recycling of Spent Hydrodehalogenation Catalysts—Problems Dealing with Separation of Aluminium. *Inz. Min. J. Pol. Min. Eng. Soc.* **2019**, *1*, 177–182. [[CrossRef](#)]
131. Bendova, H.; Weidlich, T. Application of diffusion dialysis in hydrometallurgical separation of nickel from spent Raney Ni catalyst. *Sep. Sci. Technol.* **2018**, *53*, 1218–1222. [[CrossRef](#)]
132. Sheldon, R.A. Atom efficiency and catalysis in organic synthesis. *Pure Appl. Chem.* **2000**, *72*, 1233–1246. [[CrossRef](#)]
133. Wee, H.-Y.; Cunningham, J. Remediation of contaminated soil by solvent extraction and catalytic hydrodehalogenation: Semicontinuous process with solvent recycle. *Environ. Prog. Sustain. Energy* **2011**, *30*, 589–598. [[CrossRef](#)]
134. Altarawneh, M.; Ahmed, O.H.; Al-Harashseh, M.; Jiang, Z.-T.; Huang, N.M.; Lim, H.N.; Dlugogorski, B.Z. Co-pyrolysis of polyethylene with products from thermaldecomposition of brominated flame retardants. *Chemosphere* **2020**, *254*, 1267662. [[CrossRef](#)] [[PubMed](#)]
135. Cecilia, J.A.; Infantes-Molina, A.; Rodríguez-Castellón, E. Hydrodechlorination of polychlorinated molecules using transition metal phosphide catalysts. *J. Hazard. Mater.* **2015**, *296*, 112–119. [[CrossRef](#)]
136. Balda, M.; Kopinke, F.-D. The role of nickel traces in fine chemicals for hydrodechlorination reactions with zero-valent iron. *Chem. Eng. J.* **2020**, *388*, 124185. [[CrossRef](#)]