

Recycling of hydrodehalogenation catalyst used for detoxification of halogenated aromatic contaminants based on circular economy principles

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Abstract

The presentation deals with the application and facile recycling of commercially available Al-Ni alloy highly effective for the destruction of halogenated recalcitrant aromatic compounds from contaminated aqueous streams. The described destruction of non-biodegradable halogenated aromatic contaminants is based on reductive dehalogenation accompanied by formation of completely dehalogenated biodegradable products even at room temperature and ambient pressure. Mentioned Al-Ni alloy is converted to Raney nickel and soluble aluminate salts during dehalogenation process. Inactivated Raney nickel is efficiently recycled using mechanical activation by milling with Al powder with subsequent thermal processing. The Al-Ni based hydrodehalogenation reaction was applied to the samples of real wastewater showing high efficiency for chlorinated benzenes removal. The recyclable Raney Al-Ni alloy provides an alternative to less efficient bimetallic couples or costly precious metal-based hydrodehalogenation catalysts.

Keywords: hydrodechlorination, chlorobenzoic acid, mechano-thermal synthesis, ball-milling

Introduction

The emissions of halogenated compounds like halogenated aromatics such as polychlorinated or polybrominated dibenzo-p-dioxines, dibenzofuranes (PCDD/Fs, PBDD/Fs), and polychlorinated biphenyls (PCBs) are the most hazardous to living organisms¹.

Despite not leading to complete mineralization of halogen-derivates, reductive dehalogenation has been shown as a powerful method for degradation of halogenated aromatics. Several studies pointed on zero-valent metals (Fe^0 , Cu^0 , Al^0)²⁻⁴ or bimetallic mixtures (Ag-Fe , Cu-Ni , Ni-Fe , Pd-Fe)⁵⁻²³ as suitable candidates for dehalogenation of halogenated aromatics.

The Raney nickel was found to be able to completely dehalogenation of 4-chlorophenol without the use of external reducing agent in slightly acidic environment⁴.

Promising results were also obtained using Ni/Fe or Pd/Fe bimetallic couples, where iron acts as an electron donor and the other metal as a hydrogenation catalyst^{7,10,11}.

One of the most promising and technologically feasible ways of chlorinated contaminants removal is a reductive hydrodehalogenation reaction (HDH) utilizing the Raney Al-Ni alloy (50:50 wt% Al-Ni)¹²⁻³⁰. It is an alternative to costly precious-metal based heterogeneous catalysts. The alloy is an air stable and thus overcomes the storage problems of the Raney nickel or nano zero-valent iron (n-ZVI). Its utilization in basic environment also excludes the leaching of toxic nickel. Its reductive strength may be even higher in dilute NaOH solution, capable of reducing aromatics at room or elevated temperature^{18,20-21}. In specific cases cleavage of the C-C bond was observed²⁹, as well. Using additives enables lowering of the required quantity of the alloy for complete conversion, and to modulate the reaction's kinetics²².

Potential large-scale applicability of the Raney Al-Ni alloy is for now also economically unfavorable; especially in the case for low contaminated waters. The main reason is the cost of the Raney Al-Ni alloy

preparation via the metallurgical route, which requires working with high temperatures and molten metals. Moreover, atomization from the melt must be then utilized to isolate the alloy in a form of powder. Even though the preparation process for Raney Al-Ni alloy is well-known and used world-wide, it can be effectively optimized via mechanical activation; which makes it less demanding and greener. Mechanical activation increases the reactivity of starting mixture what allows to omit additives and to apply lower calcination temperature, and time for subsequent chemical conversion^{27–29}.

In this article, we focused on hydrodechlorination (HDC) of chlorobenzoic acid (Ar-Cl) using commercial Raney Al-Ni alloy and on comparison of HDC action of mechano-thermally prepared Raney Al-Ni alloy.

Experimental part

Materials

The commercial samples of the Raney Al-Ni alloy (50:50 wt% Al-Ni) (99.999%) and NaBH₄ were obtained from Sigma-Aldrich company. For the comparative experiments, nickel (Fichema, 98%) and aluminum (Sigma-Aldrich, 99%) powders were purchased. Halogenated aromatic compounds were obtained in 98% purity (Sigma-Aldrich, Germany).

Mechano-thermal synthesis of the Raney Al-Ni alloy

The Raney Al-Ni alloy (50:50 wt% Al-Ni) was prepared as follows - aluminum (5 g, 0.185 mol) and nickel (or spent Al-Ni from dehalogenation process) (5 g, 0.085 mol) powders were loaded into stainless steel milling chamber of inner volume 250 mL. To this, methanol (0.5 g, 0.015 mol) was added as a process controlling agent along with 100 g of stainless-steel milling balls (ball-to-powder ratio of 10:1). The mixture was then co-milled in an argon atmosphere for 90 min at 500 RPMs in the laboratory planetary mill Pulverisette 6 (Fritsch, Germany). The mixture activated for 90 min was then isothermally treated at 700°C in an argon atmosphere for 15 min for complete crystallization of the alloy. A dark gray microcrystalline powder was obtained.

Hydrodechlorination experiments

The hydrodechlorination reactions were carried out on stock solutions of corresponding Ar-Cl in distilled water. In a typical experiment, 100 mL of freshly prepared 1 mM stock solution of Ar-Cl were placed into 100 mL round-bottomed flask. To this, a corresponding amount of alkaline reagent (NaOH and/or NaBH₄) was added and the mixture was magnetically stirred at 25 °C and 300 rpm till dissolution of solids (see Table 2 for more details). Then, to the resulting basic solution, the appropriate quantity of alloy was added, and the mixture was stirred at 25 °C and 300 rpm for appropriate reaction time (see Table 2 for more details). The obtained reaction mixture was decanted and the undissolved part was used in the next cycle. The decanted solution was acidified using 16% H₂SO₄ to pH ~ 2 – 3 and analyzed using HPLC and NMR spectroscopy.

Analytical techniques

¹H NMR spectroscopy

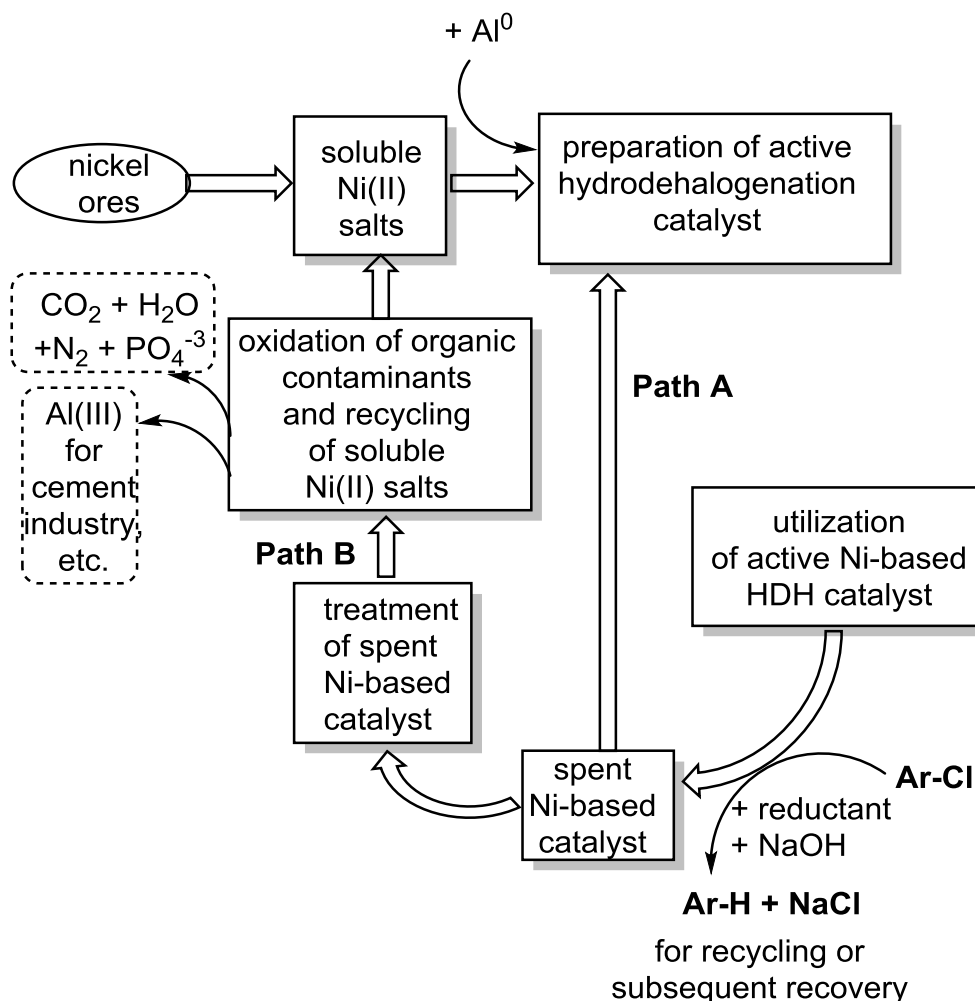
The ¹H NMR spectra were measured using solutions in CDCl₃ on a Bruker Ascend 500 spectrometer (equipped with Z-gradient 5 mm TBI 500 MHz S1 probe) at frequency 500.13 MHz for ¹H and compared with literature data.

Liquid chromatography (HPLC)

The levels of selected compounds were determined by liquid chromatography using the Shimadzu Prominence HPLC machine equipped with a UV–Vis 2-channel detector and the Gemini C6-phenyl 3 μm 100 × 3 mm chromatographic column (Phenomenex, USA) at a flowrate of 1 mL/min. 0.1% aqueous solution of phosphoric acid (solvent A) and acetonitrile (solvent B) were used as mobile phases. Analyses were performed at room temperature (24 – 25 °C) with pre-defined injection volume of 1.3 μL. The compounds were detected at 230 nm. The calibration was performed in the range of 0 – 1 mmol/dm³.

Results and discussion

The recycling of discussed Raney Al-Ni hydrodechlorination catalyst according to the circular economy principles is depicted in Scheme 1.



Scheme 1: Scheme of pathways evaluated for spent Ni-based HDC catalyst.

In our experiments, we started with fresh commercial Raney Al-Ni catalyst. The lifetime of this catalyst is quite limited in described HDC process due to the leaching of oxidized aluminum in the form of soluble (III) salts. It should be mentioned that the commercial Raney Al-Ni is a mixture of two intermetallic phases (Al₃Ni and Al₃Ni₂). However, only aluminum in active Al₃Ni phase works as reductant according to the equation²¹⁻²²:



In order to obtain Al-Ni alloy from powdered metals with requested catalytic properties, several mechanical alloyings in the Al-Ni system were performed utilizing a planetary ball-mill. Even though most of the published studies on mechanical alloying of the Al-Ni system did not suggest the use of a process controlling agent (PCA), it was found that under the studied conditions (see Experimental part), dry milling led to immediate welding of aluminum which then agglomerates on cooling. To avoid this phenomenon, methanol was added to the mixture as a commonly used PCA. However, the formation of new phases Al₃Ni and Al₃Ni₂ in the Al/Ni system was observed even after short annealing at 700 °C.

Despite its powerful reducing ability in a basic environment, the halogenated aromatics removal capability of the Raney Al-Ni alloy is limited by the leachability of aluminum. This is mostly affected by

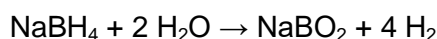
the temperature and particle size of the alloy. The main goal of our study was to verify kinetics and the leachability of aluminum from commercial and mechano-thermally prepared Raney alloy³⁰; see Table 1.

Table 1: Evaluation of the kinetics of the hydrodehalogenation reaction for the studied chlorobenzoic acid removal (using 0.8 g of alloy and 1 g NaOH per mmol of Ar-Cl)³⁰.

Chlorobenzoic acid regioisomer	Pseudo-first order kinetic constant (x 10 ⁻³ min ⁻¹)	
	commercial	mechano-thermal
2-chlorobenzoic acid	8.31	27.96
2,6-dichlorobenzoic acid	5.11	121.20

Reusability of commercial Al-Ni alloy

We demonstrate the reusability of Al-Ni alloy according to Path A using 2-chlorobenzoic acid (2-CBA), when excess of alloy (800 mg per mmol of 2-CBA as Ar-Cl) was repeatedly used for dechlorination in four cycles during max. 30 h operation at different reaction conditions to obtain the best results (Table 2)³⁰. Despite this, after exhaustion of the Raney Al-Ni alloy reducing capability (Table 2, Entry 1, 4th cycle), the formed Raney nickel with a high surface area can further act as hydrodechlorination reagent in the presence of external reducing agent, such as NaBH₄. Freshly activated Raney nickel serves as a hydrogenation catalyst and hydrogen gas is produced by the reaction of NaBH₄ with water according to the equation:



which allows for its utilization in the HDH reaction.

The used rests of Al-Ni alloy obtained after 4th cycle of action were collected, dried on air and used in mechano-thermal synthesis instead of commercial nickel powder. The obtained Al-Ni alloy was tested and successfully proved as effective HDC agent, even with slightly lower HDC durability compared with Al-Ni prepared from fresh metal powders (Table 2, Entry 3). The subsequent recycling of contaminated nickel was performed according to Path B using hydrometallurgical treatment, refining of Ni(II) salt and its recycling was published elsewhere³¹. Dissolved aluminum is removed by neutralization of obtained filtrate with subsequent filtration of insoluble Al(OH)₃. We suppose its utilization in cement production.

Table 2: The removal efficiency for repeatedly used Al-Ni alloy (0.8 g Al-Ni per mmol Ar-Cl was added in the 1st cycle).

Entry	Cycle	Reagent	Dosage (g)	Reaction time (h)	Reaction temp. (°C)	Removal efficiency (%)
1	1 st cycle	NaOH	0.1	2	25	> 99
	2 nd cycle	NaOH	0.2	4	25	> 99
	3 rd cycle	NaOH	0.2	18	25	82 (61 % after 8 h of action)
	4 th cycle	NaOH	0.2	6	40	21
2	1 st cycle	NaOH	0.1	2	25	> 99
	2 nd cycle	NaOH	0.1	4	25	> 99
	3 rd cycle	NaOH	0.2	6	25	97
	4 th cycle	NaBH ₄	0.1	18	40	99
3	1 st cycle	NaOH	0.1	2	25	> 99
	2 nd cycle	NaOH	0.1	4	25	93 (58 % after 2 h of action)
	3 rd cycle	NaOH	0.1	6	25	66
	4 th cycle	NaBH ₄	0.1	18	40	48

Conclusions

An innovative mechano-thermal approach for the Raney Al-Ni alloy preparation and recycling was applied in order to verify the technology as an alternative production way and for the material's dehalogenation efficiency.

The mixture of elemental aluminum and (used) nickel (catalyst), mechanically activated for 90 minutes, was processed by subsequent annealing at 700 °C in argon atmosphere to successfully yield well-crystalline Raney Al-Ni alloy. This consisted of Al₃Ni and Al₃Ni₂ intermetallic phases. Performed experiments proved the robustness of the HDH reaction based on commercial or recycled Al-Ni alloy.

As we demonstrated, only NaOH (eventually NaBH₄) and powdered aluminum metal is consumed within described exhaustive dehalogenation of aromatic halogenated compounds. Corresponding readily biodegradable dehalogenated product (Ar-H), sodium halogenide (eventually sodium borate) and aluminum hydroxide were the sole by-products of this described dehalogenation process. The produced deactivated nickel powder is fully recyclable using described mechano-thermal or mentioned hydrometallurgical process.

The described mechano-thermal Al-Ni synthesis is much less energy consuming compared with conventional Al-Ni alloy production comprising dissolving of metallic nickel in melt aluminum³² at approximately 1000 °C.

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