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Development of Biomass-Derived Non-Noble Metal Catalysts for Selective Hydrodehalogenation of Alkyl and (Hetero)Aryl Halides

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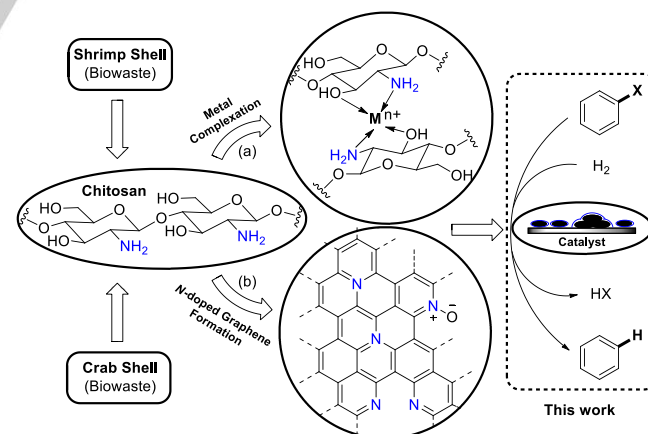
Abstract: Hydrodehalogenation represents a straightforward approach for detoxifications of anthropogenic harmful organohalide based pollutants as well as removal of halide protecting groups used in multistep synthesis. A novel sustainable catalytic material has been prepared from biowaste (chitosan) in a combination with earth-abundant cobalt salt. This heterogeneous catalyst was fully characterized by means of TEM, XRD as well as XPS analysis and applied successfully for hydrodehalogenation of alkyl and (hetero)aryl halides with broad scope (>40 examples) and excellent chemoselectivity using molecular hydrogen. The general usefulness of this methodology has been proven by the successful implementation for detoxification of non-degradable pesticides and fire retardants. In addition, its use in the multistep synthesis of (\pm)-*Peronatin B* (alkaloid) as deprotection tool showed its potential applicability.

Hydrodehalogenation constitutes an important organic transformation where a halogen atom is formally substituted with a hydrogen atom. It has become an enabling technology for degradation of anthropogenic and environmentally deleterious polyhalogenated organic pollutants (e.g. polychlorodioxins, polychlorophenols, etc.), which are often produced in industrial processes, as well as toxic and non- or slow degradable pesticides and fire retardants to their less noxious congeners.^[1,2] Furthermore, in organic synthesis, hydrodehalogenations are often used in deprotection chemistry, since halides can selectively block one of two reaction sites with similar reactivity without strongly influencing the electronics of the system.^[2,3] In addition, stereoselective hydrodehalogenation of prochiral *gem*-dihalo-organic compounds affords chiral halo-organic compounds.^[4]

Hydrodehalogenation reactions have been performed with various methods, such as metal-halogen exchange,^[2,5] metal-mediated reduction,^[2,6] photochemical reduction^[7] and reductive radical dehalogenation.^[8] Some of these reactions suffer from the use of toxic and explosive reagents, production of stoichiometric metal waste, poor selectivity and low functional group tolerance. Nevertheless, there has been an intense research interest in developing more efficient and reliable transition metal catalyzed hydrodehalogenation (mostly, Pd,^[9]

Rh,^[10] Ru,^[11] Ni,^[4,12] and Fe^[13]) using Grignard reagents,^[12c,13] alcohol and base,^[9a,10c,11a,c] hydrides,^[4,9b,c,12b,d,14] formic acid^[9h] or its salt,^[9e] hydrazine^[9d] and molecular hydrogen.^[9c,f,g,10a,b,11b,12a] Obviously, from an ecological perspective, the later reagent is considered to be the most efficient, clean and atom-economical reductant.^[15]

Since the last decade, the implementation of cheap, earth abundant non-noble metals for (de)hydrogenation reactions attracts significant interest in homogeneous and heterogeneous catalysis.^[16] Complementary to molecularly defined organometallic complexes, recently heterogeneous materials based on Fe and Co are also applied in advanced organic synthesis.^[17] For example, we developed novel nanostructured heterogeneous catalysts modified by *N*-doped graphenes for several redox reactions including hydrogenation of nitroarenes, ketones, nitriles as well as oxidations of alcohols.^[18] A key issue for catalytic activity of these materials is the synergistic combination of metal nanoparticles with the nitrogen doped carbon matrix, which results from the original organic ligand via pyrolysis. Although most of these systems, which show excellent selectivity and functional group tolerance, are based on cheap metals, the use of sophisticated organic ligands such as phenanthroline constitutes a drawback. In addition, the variation of the metal loading in these catalysts is limited and higher metal contents are difficult to achieve.



Scheme 1. Development of biomass-derived heterogeneous catalyst and its potential application in hydrodehalogenation

Among the various organic ligands suitable for the generation of nitrogen-doped carbon, we considered chitosan, a polymer of (*D*)-glucosamine, especially useful. Advantageously, this biomass derived product is sustainable, biodegradable, non-

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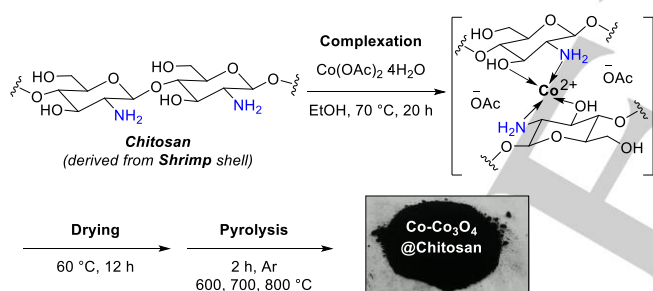
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toxic and inexpensive.^[19] It is mostly obtained from shrimp or crab shell derived chitin, which in fact represents a bio-waste generated in fishery plants.^[19] Among the various interesting properties, chitosan has high affinity for binding transition metal ions (Scheme 1, a).^[20] In 2010, Titirici and co-workers described the hydrothermal treatment followed by calcination of chitosan for the preparation of carbonaceous materials.^[21] Later on, it has been shown that it serves as an excellent precursor for the generation of *N*-doped graphene (Scheme 1, b).^[22]

Based on these and our own efforts,^[18] we became interested to prepare novel nanoparticles modified by pyrolyzed chitosan. To the best of our knowledge such systems have not been prepared or tested in catalysis so far. More specifically, herein, we report a straightforward concept for the synthesis of novel inexpensive and sustainable heterogeneous catalysts based on complexation of cobalt salt to chitosan and subsequent pyrolysis. The material obtained under optimal conditions (Co(OAc)₂/chitosan, 1:8.6; pyrolyzed at 700 °C) constitutes the first general cobalt catalyst for hydrodehalogenation reactions of a variety of organic halides.

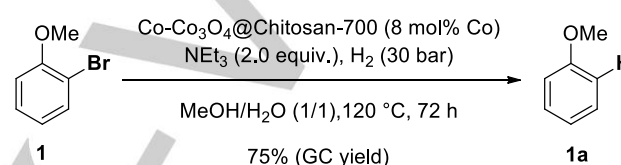
Initially, three novel materials were prepared in a sequential process comprising of (a) reflux of a mixture of Co(OAc)₂·4H₂O (OAc = acetate) and commercial chitosan derived from shrimp shell in ethanol at 70 °C delivering metal-chitosan complex,^[20a] (b) drying at 60 °C and (c) pyrolysis of dried material at high temperatures (600, 700 and 800 °C) (Scheme 2).



Scheme 2. Synthesis of Co-Co₃O₄@Chitosan materials

Having different potential catalysts in hand, we wanted to demonstrate their usefulness for synthetic organic transformations. Although cobalt-catalyzed hydrodehalogenation reactions of organohalides have rarely been explored,^[23] the Vit-B₁₂ co-factor-mediated dehalogenation in biological systems^[24] inspired us to test our materials for this type of reactions. In a preliminary test, 2-bromoanisole (**1**) was treated with hydrogen gas (50 bar) in the presence of Co-Co₃O₄@Chitosan-700 under similar conditions previously optimized for the reduction of nitroarenes^[18b] (4 mol% Co loading, 2.0 equiv. NEt₃ in ethanol/H₂O (3/1) at 120 °C for 20 h). To our delight, the formation of desired debrominated product, anisole (**1a**), was observed in 36% GC yield.^[25] Next, the testing of the catalysts prepared at variable pyrolysis temperatures (600, 700 and 800 °C) showed Co-Co₃O₄@Chitosan-700 to be the best one (Table S1, entries 1-3).^[25] To improve the yield further on,

various organic solvents alone as well as in combination with water were tested (Table S2, entries 1-9).^[25] Slightly better results were obtained in MeOH/H₂O (1/1). Moreover, many different organic and inorganic bases were screened to improve the yield of anisole (**1a**), but triethylamine remained the best option (Table S3, entries 1-9).^[25] Variation of catalyst loading, solvent ratio, pressure and also prolonging the reaction time resulted in 75% GC yield of anisole (**1a**) (Scheme 3). For the success of this hydrodehalogenation reaction, the catalyst, Co-Co₃O₄@Chitosan-700, is crucial. No reactivity was observed in the presence of Co(OAc)₂, CoBr₂, Co(OAc)₂-Chitosan complex, pyrolyzed Chitosan@700 and pure Co₃O₄ (Table S5, entries 1-5).^[25] Notably, without hydrogen only traces of anisole (4%) were detected (Table S5, entry 6).^[25] The necessity of the base was proven when the reaction was performed in the absence of NEt₃ affording anisole (**1a**) in 16% yield only (Table S5, entry 7).^[25]

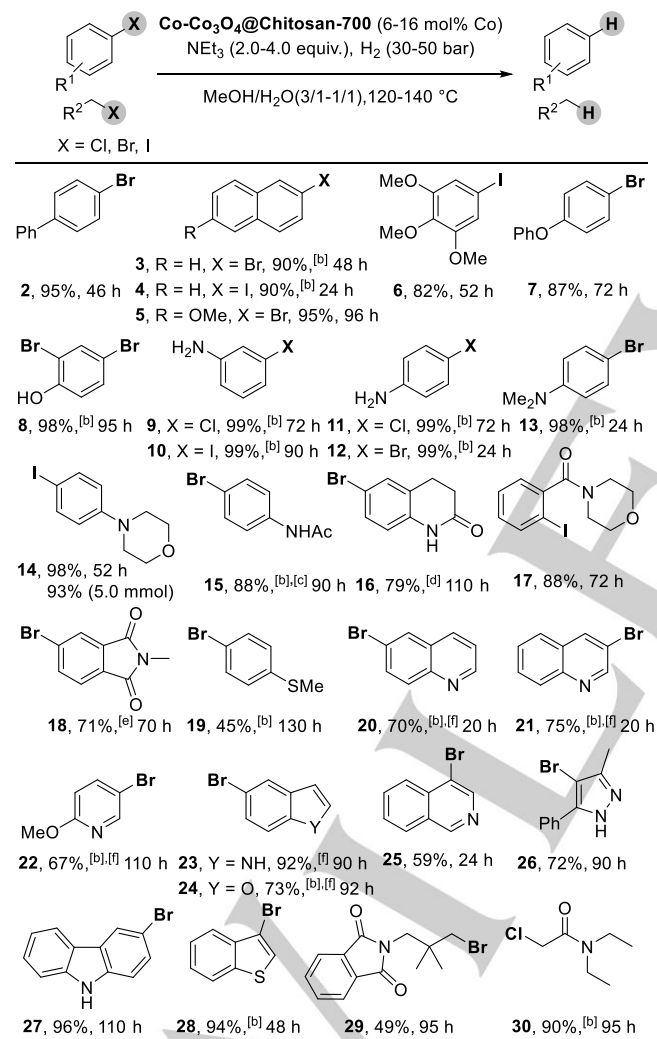


Scheme 3. Investigation of hydrodebromination of 2-bromoanisole.

After that, the most active material obtained by pyrolysis at 700 °C was characterized in detail. To investigate its structure, high-angle annular dark field (HAADF) and annular bright field (ABF) measurements with the help of spherical aberration (Cs)-corrected scanning transmission electron microscopic (STEM) were carried out, which show the image of cobalt composites (Figure S2b) and the structure of carbon (Figure S2a).^[25] Interestingly, three different types of cobalt phases are formed: metallic cobalt, cobalt oxide and Co particles with metallic core and an oxidic shell as seen by contrast and chemical analysis (Figure S2a,b).^[25] Furthermore, it is obvious that the metallic cobalt particles are embedded in graphitic layers with thickness of more than 50 nm as demonstrated by ABF imaging (Figure S2a).^[25] Nevertheless, thickness of the graphitic layers can vary region wise (Figure S2).^[25] The phase, where metallic cobalt is partially enveloped by cobalt oxide embedded in a graphitic carbon matrix can be best shown by EDXS mapping (Figure S3a-f).^[25] In this case, the observed cobalt structures from partially oxidized to completely metallic cobalt, can be explained by different states of oxidation effects based on Kirkendall effect.^[26] In further investigation of the chemical composition of this material, X-ray photoelectron spectroscopy (XPS) measurements reveal the presence of carbon, nitrogen and cobalt on the surface and few layers underneath (Figure S6,7).^[25] Importantly, the N1s spectra display at least two different peaks: the higher binding energy peak can be explained by the bonding to the cobalt ions (Co-N_x), whereas the lower binding energy peak is observed in unpyrolyzed chitosan, too, and correlated to the amine nitrogen (NH₂) (Figure S7b,9b).^[25] However, the measured Co2p spectra, which agree with the reported Co₃O₄ data,^[27] show only the presence of

Co₃O₄ species (Figure S7c).^[25] Finally, to obtain the composition of the cobalt composite, X-ray diffraction study was also performed to reveal the presence of metallic cobalt (cubic phase) as major constituent along with Co₃O₄ (Figure S10).^[25]

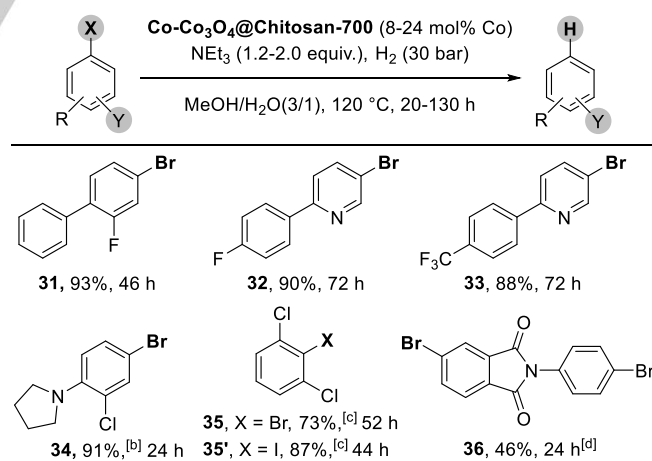
Next, we started to explore the scope and limitations of the hydrodehalogenation reactions, which are summarized in the Scheme 4 and 5. In this investigation, we successfully employed various chloro-, bromo- and iodo-substituted alkyl- and aryl substrates. For example, 4-bromobiphenyl (**2**) is converted to the corresponding non-bromo-congener in 95% yield. Among polyaromatic substrates, bromo- and iodonaphthalene derivatives (**3-5**), were successfully employed for hydrodehalogenation. Highly electron-rich 3,4,5-trimethoxyiodobenzene (**6**) and 4-bromobiphenylether (**7**) could be converted to the corresponding hydrodehalogenated derivatives



^[a]Reaction conditions: Substrate **2-30** (1 equiv.), **Co-Co₃O₄@Chitosan-700** (6-16 mol% Co), **NEt₃** (2.0-4.0 equiv.) were added to **MeOH/H₂O** (3/1-1/1) and stirred under **H₂** (30-50 bar) at 120-140°C for 20-130 h. All yields are isolated yields unless otherwise mentioned.^[25] ^[b]GC yields using hexadecane as internal standard; ^[c]aniline (6% GC yield) was obtained. ^[d]EtOH/H₂O (3/1) was used. ^[e]toluene/H₂O (3/1) was used. ^[f]K₃PO₄ (2.0 equiv.) was used as base. Ac = Acyl, Me = Methyl, Ph = Phenyl.

in good yields as well (82 and 87% respectively). Apart from mono-brominated substrates, 2,4-dibromophenol (**8**) was successfully degraded to phenol using a larger amount of the catalyst and base. Gratifyingly, all haloarenes substituted with amine functionality (**9-14**) were well tolerated delivering expected products in quantitative yields, including a large scale (5.0 mmol) entry for the substrate **14**. In addition, various amides and *N*-methylphthalimide featuring bromo- and iodo-substituents (**15-18**) remained effective substrates for this transformation. Finally, 4-bromothioanisole (**19**) also showed reactivity, albeit lower yield (45%). The dehalogenation of different heteroaromatic compounds is of general interest for the decomposition of agrochemicals and pharmaceuticals. As a model substance for this class of compounds, 6-bromoquinoline (**20**) was employed under the standard reaction conditions. In the presence of triethylamine as base, quinoline was obtained in a reasonable yield (31%) along with 1,2,3,4- tetrahydroquinoline (10%) as over reduced product.^[25] However, in the presence of K₃PO₄, 6-bromoquinoline (**20**) can be converted to quinoline in good yield (70%) without further reduction. Under the similar conditions, 3-bromoquinoline (**21**), 5-bromo-2-methoxypyridine (**22**), 5-bromoindole (**23**) and 5-bromobenzofuran (**24**) were hydrodebrominated in moderate to excellent yield. Moreover, 4-bromoisquinoline (**25**) reacted under standard reaction conditions to afford the desired isoquinoline. The substrate pyrazole featuring bromine functionality (**26**) delivered the desired product in good yield (72%) with the recovery of 18% starting material, while 3-bromocarbazole (**27**) and 3-bromobenzo[*b*]thiophene (**28**) afforded the expected products in excellent yields. Apart from all these (hetero)aryl halides, the non-activated alkyl bromide **29** was also successfully hydrodehalogenated, albeit in moderate 49% yield (20% starting material recovered). As a model compound for *Metazachlor* (herbicide), 2-chloro-*N,N*-diethylacetamide (**30**) was successfully converted to the non-chlorinated product.

Scheme 5. Chemoselective Hydrodehalogenation of Aryl halides^[a]



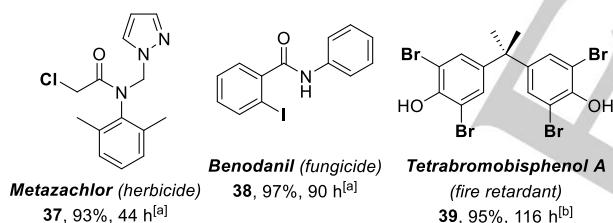
^[a]Reaction conditions: Substrate **31-36** (0.3-0.5 mmol, 1 equiv.), **Co-Co₃O₄@Chitosan-700** (8-24 mol% Co), **NEt₃** (1.2-2.0 equiv.) were added to **MeOH/H₂O** (3/1) and stirred under **H₂** (30 bar) at 120°C for 24-72 h. All yields are isolated yields unless otherwise mentioned.^[25] ^[b]Overall yield of debrominated and didehalogenated products obtained in 6:1 ratio; ^[c]GC yields using hexadecane as internal standard; ^[d]toluene/H₂O (3/1) was used.

The chemo- and regioselective partial hydrodehalogenation of polyhalogenated organic compounds to their congeners is highly challenging. With the developed catalytic method, substrates featuring with fluoro- and bromo-substituents (**31-33**) selectively underwent hydrodebromination in the presence of stable fluorine substituent. An arylamine substrate **34** featuring *o*-chloro- and *p*-bromo-substituents afforded the corresponding hydrodebromination and dihydrodehalogenation products in good selectivity (6:1), while Raney nickel delivered the product of complete dihydrodehalogenation accompanied with arene hydrogenation product under similar conditions.^[25] Furthermore, 2,6-dichloro-substituted bromo- and iodobenzene (**35-35'**) delivered desired product upon selective hydrodebromination and hydrodeiodination in the presence of chlorine substituents. Gratifyingly, *N*-arylphthalimide substrate **36** featuring bromine substituents on both phenyl rings underwent selectively hydrodebromination on the phthalimide phenyl ring, albeit moderate yield (46%) due to hydrolysis of the starting material under basic conditions.

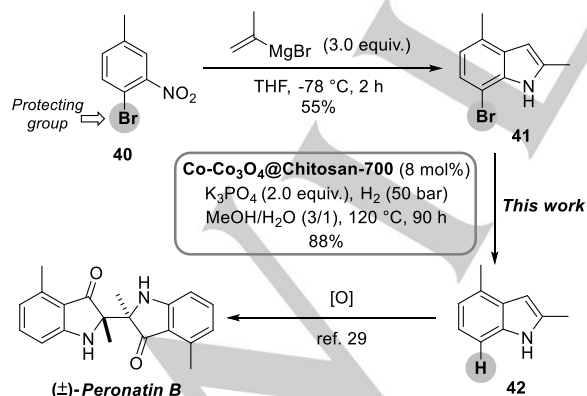
Since the stability and recyclability are important parameters for the application of heterogeneous catalysts, the Co-Co₃O₄@Chitosan-700 material was tested four times for the hydrodebromination of 4-bromo-*N,N*-dimethylaniline (**13**) (Figure S13).^[25] Although ICP analysis revealed only small amounts of leaching after the first run (5 ppm) and no measurable leaching after the 2nd, 3rd and 4th run, significant drops of reactivity were observed (Figure S13).^[25] This different reactivity is explained by the structural change of the catalyst (Figure S4,5,11,12).^[25]

Scheme 6. Applications of Hydrodehalogenation

a) Detoxifications of Pesticides and Fire Retardants



b) Application in Alkaloid Synthesis



^[a]Reaction conditions: Substrate **37-38** (1.0 equiv.), Co-Co₃O₄@Chitosan-700 (8 mol% Co), NEt₃ (2.0 equiv.), H₂ (30-50 bar), MeOH/H₂O (3/1), 120 °C (isolated yields).^[25] ^[b]Reaction conditions: Substrate **39** (1.0 equiv.), Co-Co₃O₄@Chitosan-700 (4x8 mol% Co), NEt₃ (4x2.0 equiv.), H₂ (30 bar), MeOH/H₂O (3/1), 120 °C (isolated yield).^[25]

Halogen-containing pesticides and fire retardants, which are often toxic and long persistent, have an adverse effect on the eco-system, entering in food chain. However, it is highly desirable to degrade these chemicals before being accumulated in the body by contamination with the drinking water or foods. As representative examples, two pesticides, *Metazachlor* (herbicide) (**37**) and *Benodanil* (fungicide) (**38**) and a fire retardant, *Tetrabromobisphenol A* (**39**), have been converted to their corresponding non-halogen variants employing this methodology (Scheme 6a).

Hydrodehalogenation reactions have been frequently applied in the multistep syntheses of complex natural products as deprotection toolkit.^[28] As an example, one of the steps involved in the synthesis of (±)-*Peronatin B*, an indole-based alkaloid, was halogen deprotection (Scheme 6b).^[28b,29] For this deprotection step, stoichiometric amounts of toxic Bu₃SnH and AIBN initiator had to be used.^[28b] As an alternative, the hydrodebromination of the indole derivative (**41**) can be carried out in more benign pathway employing our developed protocol.

In conclusion, we have prepared and characterized a new cobalt catalyst from cheap and readily available biowaste (chitosan). This heterogeneous material showed interesting reactivity for the hydrodehalogenation of alkyl and (hetero)aryl halides with broad scope and good chemoselectivity using molecular hydrogen as a green reducing agent. The usefulness of this novel protocol is demonstrated by efficient detoxification of a harmful fire retardant and pesticides. The implementation in the multistep synthesis of (±)-*Peronatin B* further highlights this methodology as a deprotection tool.

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Keywords: Non-noble metal • cobalt • chitosan • hydrogen • hydrodehalogenation

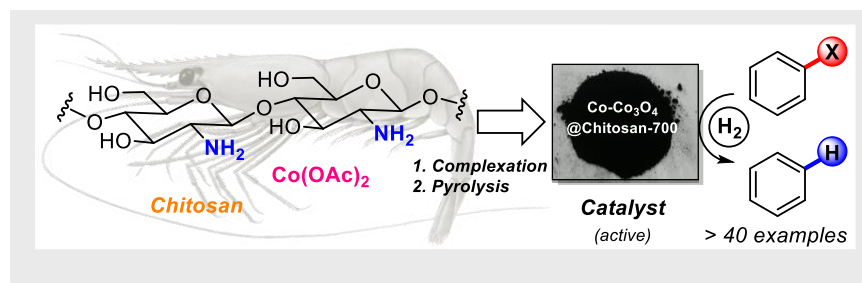
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**Development of Biomass-Derived
Non-Noble Metal Catalysts for
Selective Hydrodehalogenation of
alkyl- and (Hetero)Aryl halides**

Biomass to Catalyst: A novel sustainable catalytic material was prepared from chitosan (biomass) and earth-abundant cobalt salt and characterized by means of TEM, XRD as well as XPS analysis. This material constitutes the first general cobalt catalyst for hydrodehalogenation reactions of a variety of organic halides with broad scope (>40 examples), including harmful pesticides and fire retardant, and excellent chemoselectivity using molecular hydrogen.