ACTIVATED BORANE MATERIALS FOR HETEROGENEOUS CATALYTIC DEHALOGENATION

DOI: 10.66951/PNOC2840, https://doi.org/10.66951/PNOC2840

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Abstract

In this contribution, we review our catalytic studies of activated borane (**ActB**) materials with different Lewis acid strength of their active centers utilized as heterogeneous catalysts for reductive dehalogenation of sp^3 C-X bonds using triethylsilane as the reductant. The increased Lewis acidity of the materials enabled lowering the reaction temperatures and expansion of the substrate scope even on perfluorinated pollutants.

Introduction

Reactions catalyzed by acidic catalysts play a significant role in chemistry, including a number of industrial processes. Heterogeneous catalysis predominates in these cases due to the many advantages it offers. On the other hand, strong molecular Lewis acids, such as borane derivatives, particularly $B(C_6F_5)_3$ (BCF),[1] have been used in a number of reactions as homogeneous catalysts. Our collaborating group recently introduced a new class of materials named after activated carbon – "activated borane" (**ActB**) – due to a similar nature of these porous amorphous polymers. **ActB**s are prepared by co-thermolysis of decaborane(14) (*nido*-$B_{10}H_{14}$) and various hydrocarbons.[2] **ActB**s possess relatively strong Lewis acid centers, likely corresponding to tricoordinated boron atoms in the material's structure. Thanks to these properties, they can be used as heterogeneous catalysts for reactions similar to those where its molecular analog BCF is employed. We have previously studied catalytic properies of **ActB**s formed from toluene, cyclohexane and *n*-hexane in reductive deoxygenation/hydrosilylation reactions of carbonyl substrates and also in dehydration of ethanol to ethylene.[3] As a next step, we studied reductive dehalogenation of aliphatic organohalides using triethylsilane as a method of catalytic removal/conversion of harmful halogenated substances.[4]

Preparation of ActB and its postsynthetic modification by bromine

The standard **ActB-Tol** material was prepared by heating a solution of *nido*-$B_{10}H_{14}$ in dry toluene to 250 °C in a stainless-steel autoclave for 24 h (Fig. 1). After this time, a black-brown powder appeared, which was Soxhlet-extracted with toluene and dried under vacuum. **ActB-Tol** was subsequently treated with excess of neat bromine under argon atmosphere for 24 h and the obtained solid was washed with toluene and dried under vacuum to afford the brominated material **ActB-Br**. Analyses of the new material revealed that the porous character was retained during the bromination, although the BET specific surface area decreased from 827 to 391 m^2g^{-1}. This was accompanied by changes in textural properties observable by SEM (insets in Fig. 1).

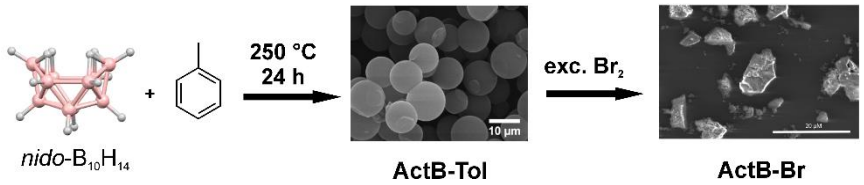


Figure 1. Preparation of ActB-Tol and its post-synthetic modification by bromine to give ActB-Br. SEM images are displayed for both materials obtained.
Gutmann-Beckett evaluation of Lewis acid strength of the boron active centres in the material revealed an increase (cf. ^{31}P chemical shift of the TEPO probe was 70.5 ppm for **ActB-Tol** and 73.0 ppm for **ActB-Br**).[5]

Catalytic dehalogenation

The proposed mechanism for the Lewis acid-catalysed reductive dehalogenation is depicted in Fig. 2. Activation of the Si-H bond in the silane is accompanied by the formation of carbocation by abstraction of the halogen atom from the substrate.

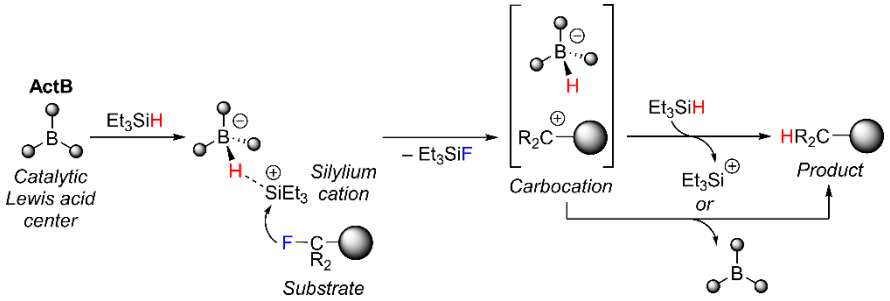


Figure 2. Proposed mechanism of the reductive dehalogenation (defluorination) using silane reductant catalysed by boron Lewis acid.

Reaction of α,α,α-trifluorotoluene with Et_3SiH was chosen as a model process. While the parent **ActB-Tol** gave 56% conversion of C–F bonds to Si–F bonds at 140 °C, **ActB-Br** reached complete C–F conversion already at 60 ◦C within 1 h, as confirmed by ^{19}F NMR, at the same substrate-to-catalyst ratio (Fig. 3).[5] The original material **ActB-Tol** was evaluated also with simple linear or cyclic aliphatic fluoro- and chloro-derivatives, while it proved sufficiently active at higher temperatures achieved conveniently by microwave heating (Fig. 3).[4] On the other hand, the more active ActB-Br has been screened for catalytic degradation of various fluorinated molecules, including the perfluorinated ones, which constitute some of the notorious persistent pollutants – such as the GenX precursor **11** (Fig. 4).[5]

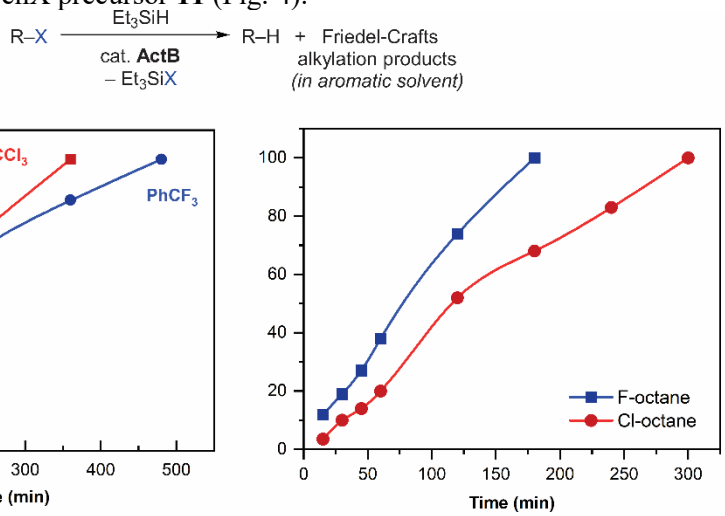


Figure 3. Selected catalytic dehalogenations using Et_3SiH catalysed by **ActB-Tol** – kinetic profiles at 140 °C using 20 mg of **ActB-Tol** per 1 mmol substrate.

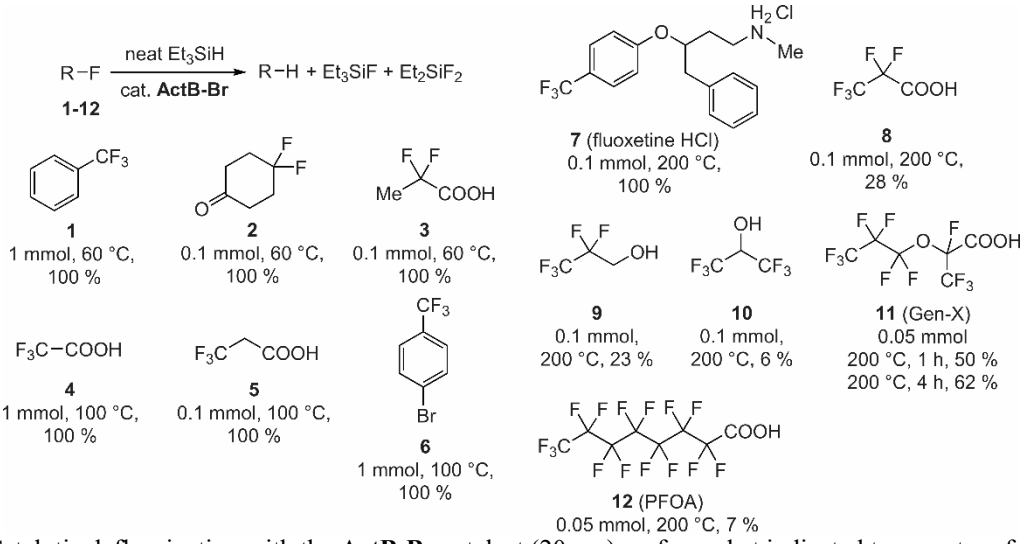


Figure 4. Catalytic defluorination with the **ActB-Br** catalyst (20 mg) performed at indicated temperature for 1 h in neat Et_3SiH (2 mL) as a solvent.

Notably, TON of 4098 was achieved for $PhCF_3$ and 156 for the GenX precursor **11**. The catalyst could be re-used by feeding new batches of the substrate (6 consecutive runs without observable loss of activity).

Conclusions

We demonstrated that bromination of an amorphous polymer based on borane clusters, **ActB**, is an effective strategy to enhance its Lewis acidity, leading to a marked improvement in catalytic performance in defluorination reactions. The increased Lewis acidity enabled lowering the reaction temperatures and expansion of the substrate scope even on perfluorinated pollutants.

Acknowledgement

This work has been funded by a grant from the Programme Johannes Amos Comenius under the Ministry of Education, Youth and Sports of the Czech Republic CZ.02.01.01/00/22_008/0004558 Advanced MUltiscaLe materials for key EnablingTechnologies.

Financial support by the Czech Science Foundation (grant no. 23-05818S) is acknowledged.

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