# Hexagonal Boron Nitride as a Solid Acid-Base Catalyst

**Atsushi Takagaki,**[a,*] **Shusaku Torii,**[a] **Keiko Jimura,**[b] **Shigenobu Hayashi,**[b] **Ryuji Kikuchi,**[a] **S. Ted Oyama**[a]

[a]*Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[b]*Research Institute for Material and Chemical Measurement, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

**Corresponding author: +81-3-5841-7300, atakagak@chemsys.t.u-tokyo.ac.jp*

**Abstract:** This study investigated the use of hexagonal boron nitride (h-BN) as a novel catalyst with base and acid functionalities. For use as a solid catalyst, the layered structure of h-BN was disrupted by ball-milling, exposing boron and nitrogen edge sites as well as increasing the surface area. FTIR, XPS and $^1$H MAS NMR indicated that amino- and hydroxyl groups were formed adjacently on the surface of h-BN by ball milling. The ball-milled h-BN was found to function as a solid acid–base catalyst. The coexistence of acid and base sites enhanced its activity for the nitroaldol reaction.

**Keywords:** Acid-base catalysis, boron nitride, nitroaldol reaction.

## 1. Introduction

It is highly desirable to design well-defined acid-base pairs, and understand its acid-base cooperative catalysis. In this study, hexagonal-boron nitride (h-BN) was investigated as a new candidate for acid-base bifunctional catalysis [1]. Hexagonal boron nitride h-BN is a layered compound isostructural with graphite, and has been widely studied for diverse applications outside of catalysis such as electronic and optical devices, coating materials with high-temperature oxidation resistance, adsorbents for organic compounds useful in water cleaning, and materials for hydrogen storage. Unlike graphite, BN has unshared electron pairs localized on the nitrogen atoms, resulting in a polarized nature. Owing to the strong chemical bonding between the atoms and physical bonding between the layers, BN is chemically and thermally stable, electrically insulating, and mechanically robust. However, this study focuses on the chemically polarized nature of h-BN. Nitrogen and boron composing h-BN are expected to function as base and acid sites, respectively by an appropriate treatment. A top-down ball-milling method was chosen to disrupt the structure of bulk h-BN, resulting in exposure of the edge sites of the planar h-BN. This study reveals that amino and hydroxyl groups were simultaneously formed at adjacent positions on the h-BN surface by using the simple ball-milling method, and these groups functioned as efficient cooperative acid-base sites for the nitroaldol reaction [1].

## 2. Experimental

A quantity of 0.8 g of commercially available h-BN (Wako) was ball-milled at 400 rpm for 6-24 h. The samples prepared were denoted as h-BN bm6-24 h respectively. The physical properties of h-BN and ball-milled h-BN were measured using XRD, $N_2$ adsorption, FTIR, XPS, and $^1$H MAS NMR. For nitroaldol reaction, *p*-methoxybenzaldehyde (0.5 mmol), nitromethane (1.25 mmol), toluene (2 mL), catalyst (50 mg) and *n*-decane (0.1 mmol) were added. The mixture was stirred at 100 $^{o}$C for 8 h.

## 3. Results and discussion

Fig. 1(a) shows FTIR spectra for pristine h-BN and ball-milled h-BN (h-BN bm12h). The IR spectrum of pristine h-BN exhibited only lattice vibration modes derived from covalent bonds between nitrogen and boron atoms. A significant difference before and after ball-milling was the appearance of bands centered at 3400 cm$^{-1}$ and 3200 cm$^{-1}$,which can be assigned to O–H and N-H stretching bands, respectively [2]. This clearly indicates formation of hydroxyl- and amino groups [3]. From the results of the FTIR measurements, the surface structure of ball-milled h-BN is suggested as shown in Fig. 1(b), which involves cleavage of B–N–B bonds and simultaneous formation of B–OH and –$NH_2$ groups. The cleavage of B–N–B bonds is expected to proceed by reaction with moisture in air. This oxidative cleavage of B–N–B bonds is in good agreement with the FTIR results previously reported [4]. Fig.1(c) shows XPS spectra of B1s of h-BN samples before and after ball-milling. The XPS spectrum of B1s of pristine h-BN showed single peak at 191.1 eV. For ball-milled h-BN sample, the shape of B1s spectrum became asymmetric with a shoulder at higher binding energy (192.9 eV), indicating the appearance of oxidized boron on the surface. A new peak could be assigned to fully oxidized boron ($B^{3+}$) on the edge sites. The ratio of O/$B^{3+}$ ratio were calculated to be around 1.7 for h-BN bm12h. This indicates that the surface structure for h-BN bm12h consists of a mixture of mono- and di-hydrolyzed boron with hydroxyl and amino groups. Fig. 1(d) shows $^1$H MAS NMR spectrum for h-BN bm12h . The two peaks composing the main peak can be attributed to –OH (3.7 ppm) and $–NH_2$ (6.7 ppm). The amounts of acid and base sites were 3.34 and 1.96 mmol $g^{-1}$, respectively. The ratio of acid sites over base site was 1.7, which well corresponded with the previous IR and XPS results.

The catalytic activity of the BN and the ball-milled catalysts was evaluated by the nitroaldol reaction using *p*-methoxybenzaldehyde (1a) and nitromethane (2a) as substrates (Table 1). Boric acid and an amine, which are homogenous counterparts, were also used for comparison. It is noteworthy that only ball-milled BN catalyzed the reaction whereas the pristine BN showed no activity at all. The ball-milled BN catalysts displayed activity and high selectivity (76-79%) for the corresponding *p*-methoxy-*β*-nitrostylene (3a). The BN bm12h showed the highest activity (84% conv.) with high selectivity (77%) for 3a. These results clearly indicated that disruption of the layered structure resulted in the formation of reaction sites of the catalysts, and led to significant improvement of the catalytic activity.

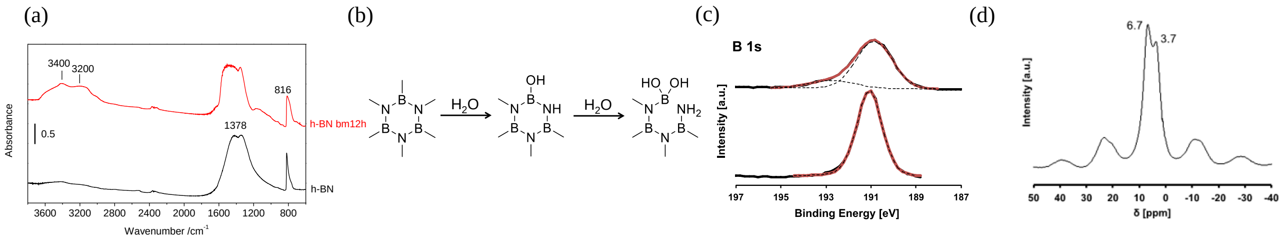
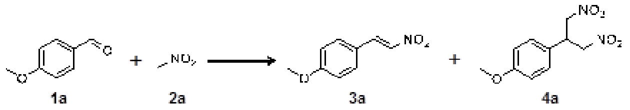


**Figure 1.** (a) FTIR spectra for pristine h-BN and ball-milled BN, (b) simultaneous formation of hydroxyl and amino groups via cleavage of B-N bonds, (c) B1s XPS spectra of h-BN and h-BN bm12h and (d) $^1$H MAS NMR spectrum of h-BN bm12h

**Table 1.** Results of nitroaldol reaction using h-BN catalysts.



| Catalyst | $S_{BET}$ /$m^2$ $g^{-1}$ | 1a Conv. /% | Selectivity /% 3a | Selectivity /% 4a |
|---|---|---|---|---|
| BN | 3 | 9 | <1 | 0 |
| BNbm6h | 341 | 25 | 79 | <1 |
| BNbm12h | 404 | 84 | 77 | <1 |
| BNbm24h | 155 | 45 | 76 | <1 |
| $H_3BO_3$ (50 μmol) | | 6 | 0 | 0 |
| *n*-butylamine (50 μmol) | | 9 | 27 | 0 |

## 4. Conclusions

The layered structure of h-BN was successfully disrupted by planetary ball-milling. The results of FTIR, XPS and NMR confirmed the cleavage of B–N bonds, forming –B–OH and $–NH_2$ groups that could function as acid and base sites, respectively. The ball-milled h-BN showed high activity and selectivity for nitroaldol reaction, whereas non-treated h-BN did not show activity. Coexistence of acid and base on the catalyst is expected to enhance the activity of the catalyst.

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