

# Solid base catalysis of ball-milled hexagonal-boron nitride

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It is highly desirable to design well-defined acid-base pairs, and understand its acid-base cooperative catalysis. Hexagonal boron nitride h-BN is a layered compound isostructural with graphite, and has been widely studied for diverse applications outside of catalysis. In this study, hexagonal-boron nitride (h-BN) was investigated as a new candidate for acid-base bifunctional catalysis.

A quantity of 0.8 g of commercially available h-BN was ball-milled at 400 rpm for 6-24 h. The samples prepared were denoted as h-BN bm6-24 h respectively.

Fourier-transform infrared spectroscopy (Fig. 1), X-ray photoelectron spectroscopy and proton magic-angle spinning nuclear magnetic resonance spectroscopy (<sup>1</sup>H MAS NMR) indicated simultaneous and adjacent formation of amino and hydroxyl groups by milling, which function as Brønsted base and acid sites, respectively (Scheme 1).

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-nitrostyrene (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.

Several nitroaldol reactions using a variety of mono-substituted benzaldehydes indicated that electron-donating groups enhanced the activity, suggesting that the formation of adjacent base and acid sites is responsible for the activity.

To summarize, 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.

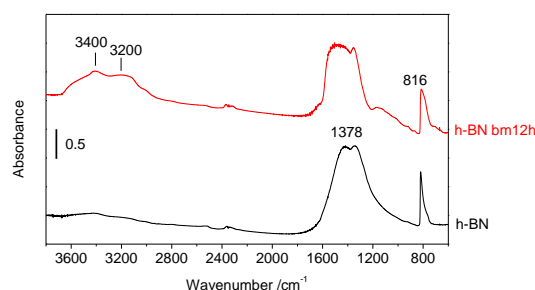
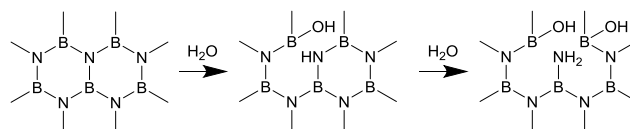


Fig.1 FTIR spectra for pristine h-BN and h-BN bm12h.



Scheme 1 Simultaneous formation of hydroxyl and amino groups via cleavage of B-N bonds

Table 1. Results of nitroaldol reaction using h-BN catalysts<sup>a</sup>.

Catalyst	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1</sup>	Conv. /%	Selec. /%	
			3a	4a
BN	3	9	<1	0
BNbm6h	341	25	79	<1
BNbm12h	404	84	77	<1
BNbm24h	155	45	76	<1
H <sub>3</sub> BO <sub>3</sub> <sup>b</sup>		6	0	0
<i>n</i> -butylamine <sup>b</sup>		9	27	0

<sup>a</sup> Reaction conditions: *p*-methoxybenzaldehyde (0.5 mmol), nitromethane (1.25 mmol), toluene (2 mL), catalyst (50 mg), 100 oC, 8 h.

<sup>b</sup> 0.05 mmol