

Enhancing β -hydroxy ketone selectivity in aldol condensation of furfural and acetone over N-B-O sites in calcined boron nitride

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1. Experimental details

1.1. Materials and Equipment

Unless otherwise stated, the following materials were used without further purification. Furfural (98%), acetone (99.5%), 3-pentanone (99%), ethanol (99.5%), toluene (99.5%), cyclohexanone (99%), cyclopentanone (99%), butanone (99%), 2,4-dimethyl-3-pentanone (98%), and N,N-dimethylformamide (DMF 99.8%) were bought from Sigma-Aldrich Chemicals Co. Ltd.. BN (99.9%), B₂O₃ (98%), MgO (99.9%), La₂O₃ (99.9%), H₃BO₃ (99.5%) were purchased from Macklin Chemicals Co. Ltd..

Hydrothermal autoclave reactor (HT-100-SS1), temperature controller (iTC-10A), and high-pressure autoclave reactor (NS50-P5-T3-SS1-SV) were provided by Anhui Kemi Machinery Technology Co. Ltd. (Hefei, China, <http://www.ahkemi.com>).

1.2. Catalyst preparation

1.2.1. The synthesis of calcined BN catalysts

0.8 g of the commercial BN powder for each treatment was spread evenly in a boat-type corundum crucible reactor (50×20×20 mm). The crucible does not need any lid, so as to the sample can be fully exposed to the air. Then the crucible was placed in the center of the hearth of the muffle furnace (SX2-12-12N, 30 L, Shanghai YeTuo Technology Co. Ltd.), and calcined in air from the room temperature to the target calcination temperatures with a heating rate of 5 °C/min. After calcining samples at the constant target temperature for 3 hours, the muffle furnace was naturally cooled to room temperature. The obtained catalyst was ground into powder and collected in dry and clean EP (Eppendorf) tubes without special isolation of air and moisture, and the aldol reaction test was carried out within five days. During this process, the moisture in ambient air was measured by a hygrometer (UNI-T Co. Ltd., Type-A13T) and described as the relative humidity, which was around 55-65% at the temperature of 24-27 °C. The as-prepared catalyst was labeled as **BN-X**, where X was the calcined temperature. In addition, BN was calcined at 900 °C for 6 hours using the above method to give the sample **BN-900-6h** as a reference.

BN was also calcined for 3 hours under the N₂ purge at 750 °C to give the sample

BN-N₂750 for comparison. For a typical synthesis, 0.8 g of the commercial BN powder was weighed and packed in the middle of a 32 mm diameter quartz tube reactor by being fixed with quartz wool at both ends of the sample. The quartz tube reactor was placed in a tubular heating furnace (Shanghai TONGCOO, TCGC-1700) and fed with N₂ (purity: 99.99%) at a flow rate of 15 mL/min. After standing at room temperature for 15 min, the sample was heated to 750 °C with a ramp of 5 °C/min for 3 hours. During this period, continuously introduce N₂ with a flow rate of 15 mL/min until the end of the calcination, and the tubular heating furnace was cooled to room temperature naturally. The obtained catalyst was ground into powder and collected in dry and clean EP (Eppendorf) tubes without special isolation of air and moisture, and the aldol reaction test was carried out within five days. The moisture in ambient air was measured by a hygrometer (UNI-T Co. Ltd., Type-A13T) and described as the relative humidity, which was around 55-65% at the temperature of 24-27 °C. The collected catalyst was labeled as **BN-N₂750**.

1.2.2. The synthesis of impregnated B₂O₃/BN catalysts

All B₂O₃/BN catalysts were prepared by an impregnation method. For a typical procedure: Add 0.8 g of commercial BN powder to a solution of H₃BO₃ of nominal mass dissolved in 50 mL of ethanol. After ultrasonic dispersion for 3 minutes, the suspension was stirred at 70 °C until the liquid completely evaporated. The resulting solid was dried at 120 °C overnight and then packed in the middle of a 32 mm diameter quartz tube reactor by being fixed with quartz wool at both ends of the sample. The quartz tube reactor was placed in a tubular heating furnace (Shanghai TONGCOO, TCGC-1700) and fed with Ar (purity: 99.99%) at a flow rate of 15 mL/min. After standing at room temperature for 15 min, the sample was heated to 300 °C with a ramp of 10 °C/min for 2 hours. During this period, continuously introduce Ar with a flow rate of 15 mL/min until the end of the calcination, and the tubular heating furnace was cooled to room temperature naturally. The obtained catalyst was ground into powder and collected in dry and clean EP (Eppendorf) tubes without special isolation of air and moisture, and the aldol reaction test was carried out within five days. The moisture in ambient air was measured by a hygrometer (UNI-T Co. Ltd., Type-A13T) and described as the relative humidity, which was around 55-65% at the temperature of 24-27 °C. The as-prepared catalyst was labeled as **xB₂O₃/BN**, where x represented the B₂O₃ loading based on catalyst mass.

1.2.3. The hydrothermal (HT) treatment on the catalysts

The hydrothermal (HT) treatment was applied to remove the excessive O-B-O sites in the structure of catalysts. For a typical procedure: 0.3 g of catalyst and 50 mL deionized water were packed into the 100 mL hydrothermal autoclave reactor. The reactor was placed in an oven at 140 °C for a period of time and then naturally cooled down to room temperature. The solid was taken out by filtration or centrifugation and labeled as **catalyst-HTx**, where x represented the time for hydrothermal treatment.

1.3. Catalytic process and the analysis of products

All aldol experiments were conducted in a 25 mL high-pressure autoclave reactor equipped with a quartz lining. For a typical reaction: 960 mg of furfural, 6.3 g of acetone or other substrates, and 500 mg catalyst were added into the reactor, which was sealed

and then purged by N₂. The reaction was carried out under the set temperature and one atmosphere of nitrogen at a stirring speed of 800 rpm. After reaction, the reactor was placed in ice water to cool to room temperature. The mixture in the reactor was collected with ethanol and toluene was added as an internal standard. The composition of the product was quantified by a Shimadzu GC-2010 plus gas chromatograph equipped with a HP-5 capillary column and flame ionization detector, and qualitatively characterized by an Agilent 7000D gas chromatography-mass spectrometer equipped with a DB-5MS capillary column. Carbon balance is determined as $[M(C8) + 2 * M(C13)] / M(C5)$ and M indicates the moles of products. Conversion, yield, and selectivity were calculated on basis of the following equations:

$$\text{Conversion}(\%) = \left(1 - \frac{\text{Mole of furfural remaining}}{\text{Mole of furfural fed}}\right) \times 100$$

$$\text{Yield}(\%) = \frac{\text{Mole of product}}{\text{Mole of furfural fed}} \times 100$$

$$\text{Selectivity}(\%) = \frac{\text{Mole of product} \times 100}{\text{Mole of furfural fed} - \text{Mole of furfural remaining}}$$

Reusability tests of catalysts were carried out as follows: After each reaction, the catalyst was separated from the post-reaction mixture by filtration, and washed several times with ethanol and acetone, then dried in an oven at 60 °C. The dried catalyst was weighed and ground, and all substrates were fed according to the furfural/acetone mass ratio of 0.152 and the furfural/catalyst mass ratio of 1.92. The next steps were the same as the catalytic process described above.

1.4. Characterization techniques

Nitrogen adsorption-desorption experiments were obtained on the Quantachrome Autosorb-1C apparatus at 77 K, and the BET and BJH methods were used to calculate the specific surface area and pore volume of catalysts from the equilibrium curves, respectively.

The powder X-ray diffraction (**XRD**) patterns of samples were collected on the Rigaku Miniflex 600 diffractometer (Japan) equipped with a graphite-filtered Cu K α radiation operated at 45 kV and 200 mA. The scanning of diffraction angle ranges from 10 degree to 90 degree with a step of 0.01 degree.

Fourier transform infrared spectroscopy (**FT-IR**) from 4000 to 600 cm⁻¹ was obtained on a Nicolet 8700 Thermo Scientific FT-IR spectrometer with a resolution of 0.4 cm⁻¹ to detect the presence of diverse functional groups in the BN structural framework.

X-ray photoelectron spectra (**XPS**) were carried out on the Thermo Scientific Escalab 250 X-ray photoelectron spectrometer (ESCALAB250) using monochromatic Al K α radiation. The binding energies were calibrated using the C 1s peak at 284.8 eV as the reference. The experimental errors were within ± 0.1 eV.

The stability of pristine BN was investigated by temperature-programmed oxidation (**TPO**) on the home-built adsorption instrument coupled with FT-IR and mass

spectrometry as the detectors to detect the escaping components in the carrier gas. Before each test, 200 mg of the sample was pretreated at 400 °C for 1 hour under Ar purge. The TPO curves were collected at 40-900 °C at a heating rate of 10 °C/min under Ar and O₂ mixed steam.

The basicity and acidity of catalysts were investigated by CO₂-temperature-programmed desorption (**CO₂-TPD**) and NH₃-temperature-programmed desorption (**NH₃-TPD**) respectively using the home-built adsorption instrument coupled with FT-IR as the detector. Before each test, 200 mg of the sample was pretreated at 400 °C for 1 hour under Ar purge and then subjected to Ar and CO₂ or NH₃ mixed steam at 40 °C for 1 hour. Then the desorption curves were collected at 40–800 °C at a heating rate of 10 °C/min.

The number of acid sites was measured by NH₃-TPD as previously reported.¹ The desorbed NH₃ was absorbed by 0.005 mol/L dilute sulfuric acid aqueous solution, which was then conducted reverse-titration with 0.01 mol/L NaOH solution three times to quantify an average value of the acidity representing the total acid sites in the unit of mmol/g.

The Boron *K*-edge X-ray absorption near edge structure (**XANES**) spectra were collected at the 4B9B beamline of the Beijing Synchrotron Radiation Facility (BSRF).

The in-situ diffuse reflection infrared Fourier transform spectroscopy (**DRIFTS**) experiments of the absorption of C=O compounds (acetone, 3-pentanone, and DMF) on catalysts were conducted on the FTIR spectrometer (Thermo Nicolet iS50) equipped with a homemade in-situ cell. Before each test, 50 mg of the sample was pretreated at 200 °C for 1 hour under Ar purge and then subjected to the mixed steam of Ar and the C=O compounds bubbling at 24 °C for 20 minutes, and the gas phase DRIFTS spectra of the C=O compounds was collected at this time. After that, the inlet flow was switched to Ar to purge the samples at 24 °C until the characteristic bond in the gas phase spectra vanished, and the absorption DRIFTS spectra of diverse C=O compounds were collected at this time.

Table S1. A variety of catalysts used for aldol reaction and performance of calcined BN catalyst in this work.

Category	Catalysts	Reaction conditions	Conversion (%)	Yield or selectivity (%)	Reuse number	Ref.
Base	NaOH or KOH	2 mmol furfural, 1 mmol cyclopentanone, 15 mL H ₂ O, 30 °C, 40 min, 20 mol% catalyst	100	96% yield of dehydrated product	0	2
	CaMg(CO ₃) ₂ activated dolomite	3.3 g acetone, 5.5 g furfural, 0.5 g catalyst, 60 g H ₂ O and methanol (1/1.5wt), 50 °C, 90 min	90	85% total yield of dehydrated product	Decline of 20% after 4 cycles	3
	MgO-ZrO ₂ , MgO-Al ₂ O ₃ , CaO-ZrO ₂	0.25 L H ₂ O, 5 wt% furfural and acetone (1/1 mole ratio), 1MPa N ₂ , 24 h, 50 °C	81.4	76% total yield of dehydrated product	Decline of 50% after 2 cycles	4
Acid	UiO-66(Zr) MOFs	130 °C, 4 h, furfural/catalyst=2 wt, methyl-isobutyl ketone/furfural molar ratio=4	99.4	99% yield of dehydrated product	Decline 50% conversion after 4 cycles	5
	Acid Zeolites (ZSM-5, MOR, BETA)	0.2 mol levulinic acid, 0.1 mol furfural, 100 mL H ₂ O, 0.1 mol Na ₂ CO ₃ , 1.8 g catalyst, 70 °C, 1.5 MPa N ₂ , 24 h	95	50% yield of dehydrated product	Decline 10% conversion after 4 cycles	6
	BN-850	960 mg furfural, 6.3 g acetone, 500 mg BN-850, 40 °C, 12 h, 1 atm N ₂	98.9	79.6% selectivity of hydrated product	Decline 15% conversion after 3 cycles	This work
Base and acid	Cellulose nanocrystals (-COOH & -	5 mmol catalyst (N-content), 50 mmol furfural, 2 mL	10 ⁻³ site yields (S ⁻¹)	80% selectivity of dehydrated	Decline 50% conversion	7

NH ₂)	acetone, 2 mL acetonitrile, 1 atm N ₂ , 60 °C, 6 h		product after 2 cycles	
MCM-41 functionalized with aminosilanes (- OH and -NH ₂)	0.1 mmol 4- nitrobenzaldehyde, 2 mL acetone, 10 mol% catalyst (amine loading), 1 atm N ₂ , 50 °C, 4 h	5.9±0.1 (h ⁻¹)	100% selectivity of dehydrated product	8
Pd/BN- phosphor (B- NH ₂ , N ₂ P=O and N ₃ P-OH)	20 mg catalyst, 0.5 mL acetone, 5 mL ethanol, 0.75 MPa H ₂ , 150 °C, 2 h	58.24	90% selectivity of dehydrated product	Decline 8% conversion after 2 cycles 9
Oxides (MgO, MgO-Al ₂ O ₃ , Na ₂ CO ₃),	6 mmol sodium levulinate, 4 mmol furfural, 3 mL H ₂ O, 0.1 g catalyst, 85 °C, 3 h, 1 atm Ar.	100	70-80% selectivity of dehydrated product	10
Oxides (CeO ₂ , Nb ₂ O ₅ , SnO ₂ , ZnO, TiO ₂ , ZrO ₂ , and WO ₃),		15-35	10-40% selectivity of hydrated product, 5- 60% selectivity of dehydrated product	
acidic zeolites (HY, Hβ, HZSM-5, H- MOR, and SAPO-34)		10-35	13-50% selectivity of hydrated product, 10- 30% selectivity of dehydrated product	

Table S2. BET surface areas and pore volumes of pristine and calcined BN, and impregnated B₂O₃/BN.

Sample	S _{BET} / m ² g ⁻¹	Pore volume / mL g ⁻¹
BN	27.54	0.110
BN-750	15.32	0.096
BN-800	13.58	0.058

BN-850	12.86	0.056
BN-900	12.51	0.036
25B ₂ O ₃ /BN	22.67	0.109
35B ₂ O ₃ /BN	21.29	0.096

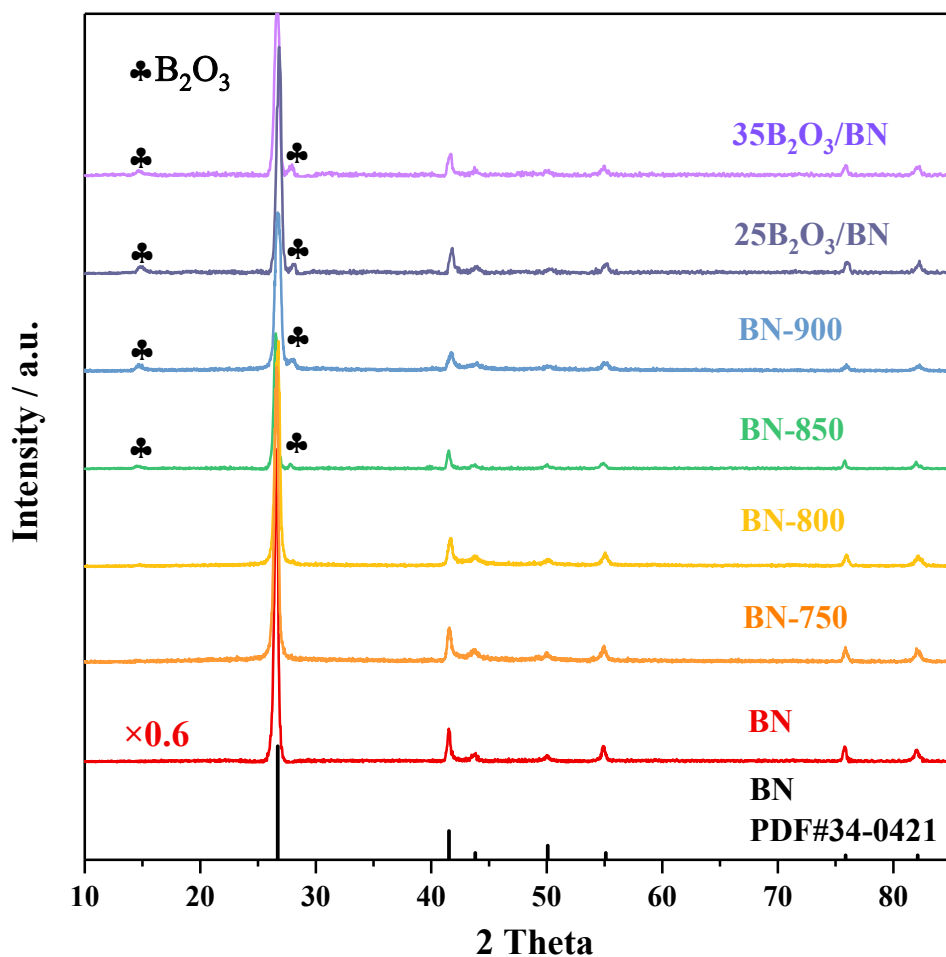
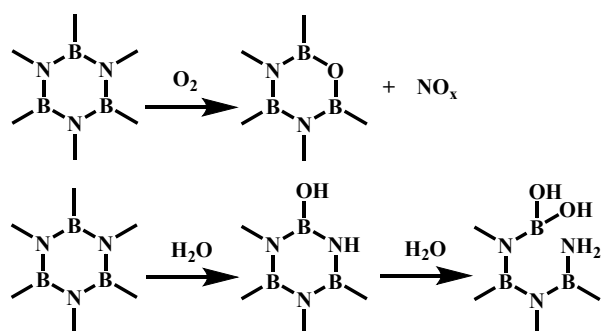


Fig. S1. XRD patterns of pristine and calcined BN, and impregnated B₂O₃/BN.

Table S3. Peak area fitting of Fig. 2b.

Sample	Peak position / °C	Peak area
BN	676	0.713
BN-750	710	2.227
BN-800	125	0.266
BN-850	124	0.106
BN-900	123	0.020



Scheme S1. The formation of B-OH groups and defects via cleavage of B-N bonds.

In the process of calcining BN in a muffle furnace in air, the above reactions were proposed to occur on the surface. The moisture and O₂ in the air will participate in the breaking of the N-B bond and the formation of the B-O bond and the N-H bond. During the calcination of BN, the change of -NB₃→-B₂N-H→-BNH₂ occurs at the N site. The less electron-deficient B bonding with N, the weaker the delocalization effect of the lone electron pair on N, and the stronger the base. Therefore, calcination at 750 °C exhibited an increase in the CO₂ desorption temperature (Fig. 2b).

Table S4. Binding energies and peak areas for N 1s XPS spectra in Fig. 2e.

Sample	Binding energy / eV	Assignment	Fitted peak area	Defect ratio / %
BN	398.3	N-B	33554.74	(N-H)/[(N-H)+(N-B)]=7.5%
	399.2	N-H	2838.74	
BN-750	398.3	N-B	55320.41	(N-H)/[(N-H)+(N-B)]=16.7%
	399.2	N-H	5118.90	
BN-800	398.3	N-B	59507.52	(N-H)/[(N-H)+(N-B)]=3.9%
	399.2	N-H	2420.52	
BN-850	398.3	N-B	61646.32	(N-H)/[(N-H)+(N-B)]=3.1%
	399.2	N-H	2007.63	
BN-900	398.3	N-B	49365.73	(N-H)/[(N-H)+(N-B)]=3.0%
	399.2	N-H	1573.76	

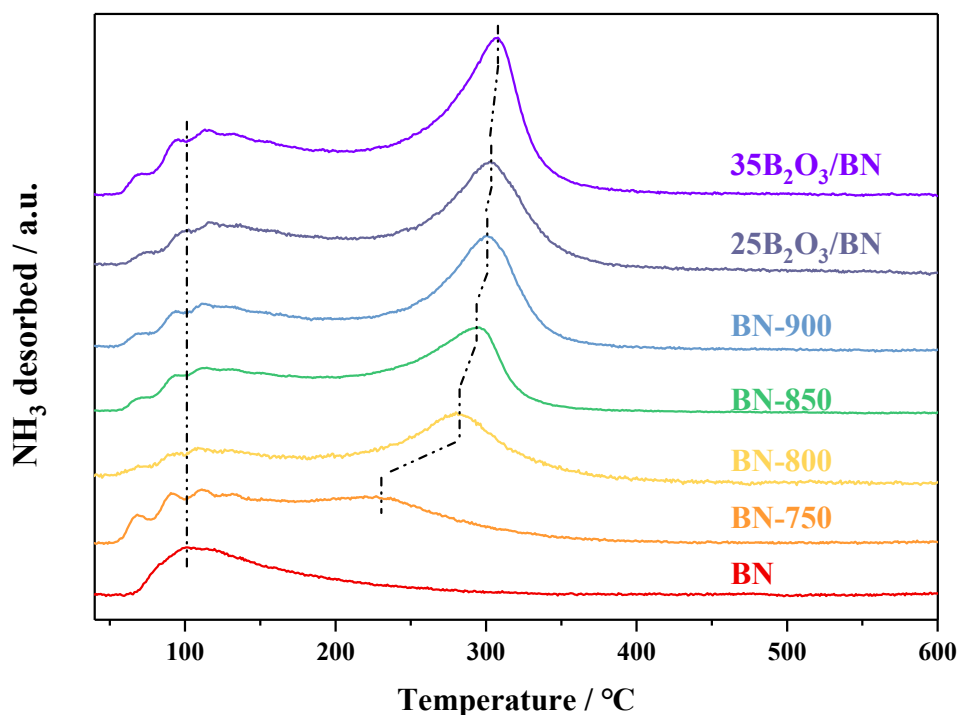


Fig. S2. NH_3 -TPD profiles of BN-based materials.

Table S5. The number of acid sites on pristine and calcined BN, and impregnated $\text{B}_2\text{O}_3/\text{BN}$ determined by NH_3 -TPD.

Sample	Acidity / $\text{mmol}\cdot\text{g}^{-1}$
BN	0.039
BN-750	0.092
BN-800	0.137
BN-850	0.180
BN-900	0.216
$25\text{B}_2\text{O}_3/\text{BN}$	0.229
$35\text{B}_2\text{O}_3/\text{BN}$	0.262

The acidic sites of BN-based catalysts were characterized using NH_3 -TPD (Fig. S2). The pristine BN exhibits an NH_3 desorption peak at around $110\text{ }^\circ\text{C}$, indicating that there is a small amount of weakly acidic sites on the pristine BN, which can be attributed to the B-O-H defects at the edge of the BN structure by FTIR characterization. After high-temperature calcination, the NH_3 desorption peak at $110\text{ }^\circ\text{C}$ attributed to the stable B-O-H defects always exists. Meanwhile, a group of stronger NH_3 desorption peaks appears in the range of $230\text{-}320\text{ }^\circ\text{C}$, and the higher the calcination temperature is, the more intensive the NH_3 desorption peak exhibits and moves towards the higher temperature. This phenomenon indicates that the oxygen defect sites introduced by the calcination significantly increase the number and strength of acid sites on BN-based materials.¹¹

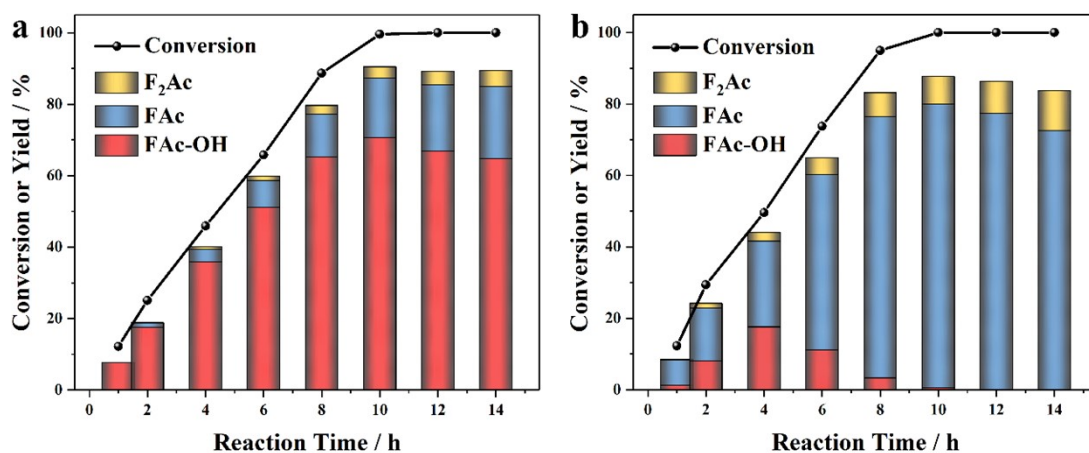


Fig. S3. Parallel tests between (a) BN-850 and (b) impregnated 35B₂O₃/BN. Reaction conditions: 960 mg furfural, 6.3 g acetone, 500 mg BN-850 or 35B₂O₃/BN, 60 °C, 1 atm N₂.

The parallel tests of BN-850 and impregnated 35B₂O₃/BN as a comparison were the confirmatory experiments for the assumption that β-hydroxy ketones are more likely to dehydrate at the O-B-O sites rather than N-B-O sites (Fig. S3). The product distributions show significant differences at the nearly equal conversions of BN-850 and 35B₂O₃/BN. The hydrated FAc-OH dominates the product distribution on BN-850, while the dehydrated product FAc occupies the predominant proportion on 35B₂O₃/BN.

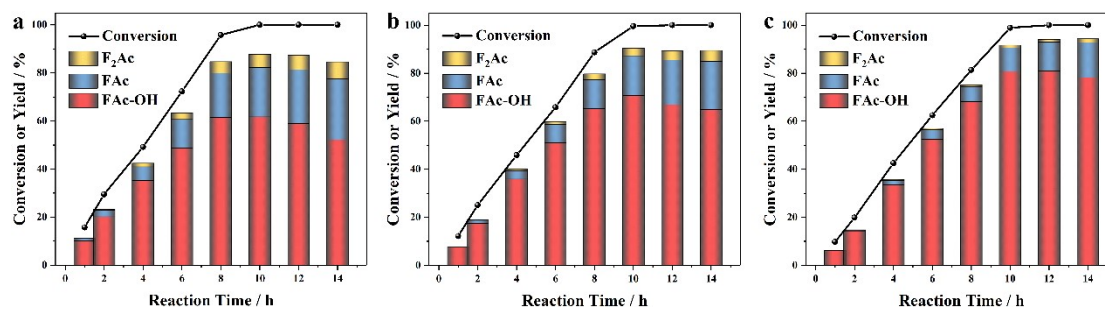


Fig. S4. Effect of temperature and reaction time on aldol condensation catalyzed by BN-850. Reaction conditions: 960 mg furfural, 6.3 g acetone, 500 mg BN-850. Reaction conditions: 960 mg furfural, 6.3 g acetone, 500 mg BN-850, (a)60 °C, (b) 50 °C, (c) 40 °C.

The effects of reaction temperature and time shown in Fig. S4 determine that both the higher temperature and the longer reaction time will enhance the dehydration of the aldol reaction.

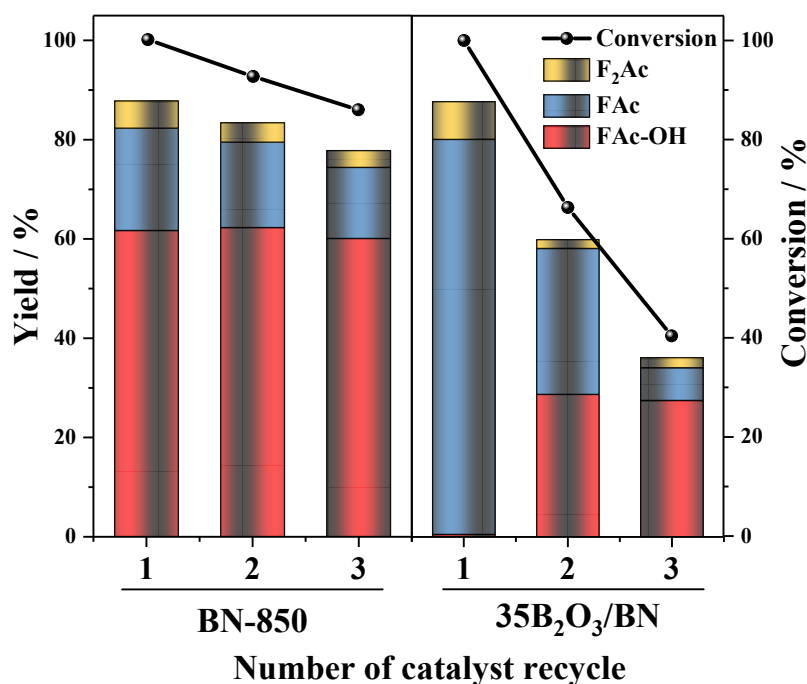


Fig. S5. Recycling tests of BN-850 and impregnated 35B₂O₃/BN.

The stability test of the calcined BN and B₂O₃-impregnated BN catalyst is shown in Fig. S5. After three cycles, the furfural conversion of BN-850 decreased from 100% to 85.9%. The yield of the dehydration product FAc gradually declined with the increase of the recycling number, but the yield of the hydrated product FAc-OH remained unchanged and maintained above 60%. Compared with various solid acid and base catalysts from other papers in Table S1, BN-850 demonstrates moderate stability on reactivity, but its selectivity for the target hydration products is outstanding. The furfural conversion of 35B₂O₃/BN diminished from 100% to 40.4%, and the product distribution of 35B₂O₃/BN significantly changed in the three cycles. The main product in the first cycle was the dehydrated FAc with a yield of 80%. In the second cycle, FAc and FAc-OH were afforded almost equal selectivity. In the third cycle, the main product was the hydrated product FAc-OH with a yield of 27.5%. The drop in the activity of BN-850 is significantly smaller than that of 35B₂O₃/BN, indicating that the reactive sites on calcined BN are more stable and less prone to loss under hydrothermal conditions. This may be due to the chemical bonding between the N-B-O sites and the BN support. XPS is utilized to investigate the effect of the hydrothermal process on the B₂O₃-impregnated BN catalyst, demonstrating that the relative content of O-B-O sites on the 35B₂O₃/BN surface decreased significantly after hydrothermal treatment, which may account for the inhibition of the dehydration of β -hydroxy ketone. This result suggests that the more stable N-B-O sites are more prone to the aldol reaction while suppressing dehydration.

Table S6. Binding energies and peak areas for N 1s XPS spectra in Fig. 3b, Fig. 4a, and Fig. 4b, as well as the product selectivities.

Sample	Binding energy / eV	Assignment	Fitted peak area	Relative content of N-B-O and O-B-O	Hydration Selev. / %	Dehydration Selev. / %
BN	190.5	N-B-N	17485.33	(N-B-O)/[(N-B-O)+(O-B-O)]=1.000	0	0
	192.0	N-B-O	408.23			
BN-750	190.5	N-B-N	18397.82	(N-B-O)/[(N-B-O)+(O-B-O)]=1.000	79.6	2.8
	192.0	N-B-O	1103.12			
BN-800	190.5	N-B-N	16356.10	(N-B-O)/[(N-B-O)+(O-B-O)]=1.000	78.8	4.9
	192.0	N-B-O	1822.59			
BN-850	190.5	N-B-N	14131.83	(N-B-O)/[(N-B-O)+(O-B-O)]=0.750	72.4	7.7
	192.0	N-B-O	1723.97			
	193.8	O-B-O	574.33			
BN-900	190.5	N-B-N	31683.90	(N-B-O)/[(N-B-O)+(O-B-O)]=0.423	52.3	30.5
	192.0	N-B-O	2775.30			
	193.8	O-B-O	3793.90			
BN-900-6h	190.5	N-B-N	23633.52	(N-B-O)/[(N-B-O)+(O-B-O)]=0.306	36.4	46.7
	192.0	N-B-O	3316.79			
	193.8	O-B-O	7521.36			
BN-900-HT10	190.5	N-B-N	39456.82	(N-B-O)/[(N-B-O)+(O-B-O)]=0.488	60.3	24.2
	192.0	N-B-O	2771.99			
	193.8	O-B-O	2905.37			
BN-900-HT20	190.5	N-B-N	18397.82	(N-B-O)/[(N-B-O)+(O-B-O)]=1.000	80.5	6.8
	192.0	N-B-O	1103.13			
35B ₂ O ₃ /BN	190.5	N-B-N	14726.41	(N-B-O)/[(N-B-O)+(O-B-O)]=0.191	33.5	50.4
	192.0	N-B-O	941.92			
	193.8	O-B-O	3971.32			
25B ₂ O ₃ /BN	190.5	N-B-N	10031.64	(N-B-O)/[(N-B-O)+(O-B-O)]=0.401	53.3	34.9
	192.0	N-B-O	1374.56			
	193.8	O-B-O	2053.35			
25B ₂ O ₃ /BN-HT20	190.5	N-B-N	26878.37	(N-B-O)/[(N-B-O)+(O-B-O)]=1.000	78.9	9.7
	192.0	N-B-O	1405.35			

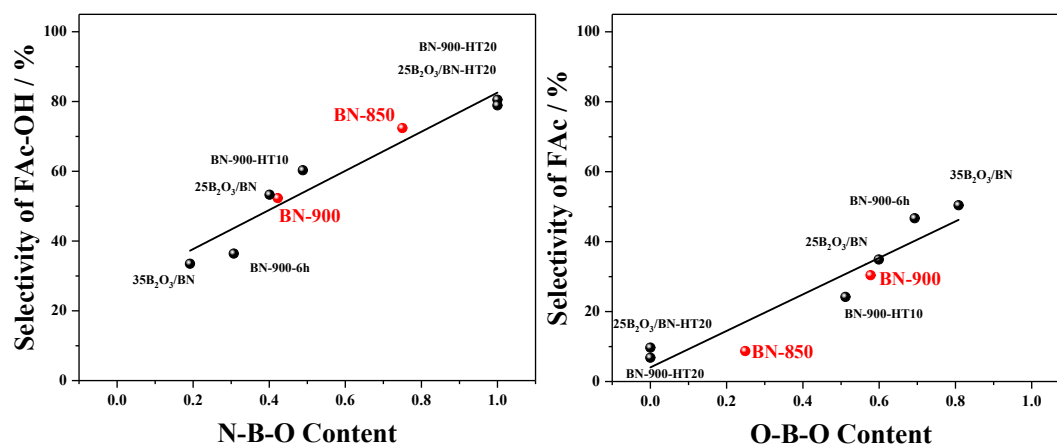


Fig. S6. Linear fitting curves of N-B-O and O-B-O relative content related to the selectivities of Fac-OH and Fac. HT: Hydrothermal treatment.

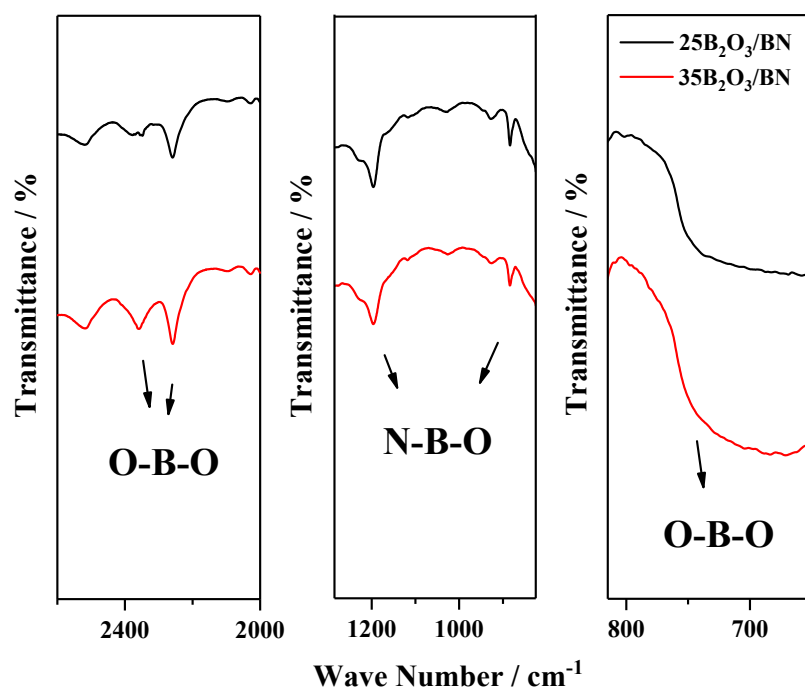


Fig. S7. Partially enlarged FTIR spectra between 900-1200 cm⁻¹, 700-800 cm⁻¹, and 2200-2400 cm⁻¹, of 25B₂O₃/BN and 35B₂O₃/BN.

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