

## Supporting information

### **Boron-incorporated nanosized SUZ-4 zeolite for DME carbonylation**

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## Sample preparation

For synthesizing the boron incorporated SUZ-4 zeolites, the following reagents were directly used without purification: Potassium hydroxide (85 wt.%, Sinopharm Chemical reagent Co., Ltd.); Sodium hydroxide (AR, Sinopharm Chemical reagent Co., Ltd.); Aluminum foil (99.9%, Aladdin); Ludox AS-40 (40 wt.% Sigma-Aldrich); tetraethylammoniumhydroxide solution (35 wt.%, Sigma-Aldrich). Boronic acid (AR, Sinopharm Chemical reagent Co., Ltd.)

SUZ-4 was synthesized according the method reported in literature<sup>1</sup>. Aluminum foil was diluted in a solution of KOH in distilled water. Another solution with tetraethylammoniumhydroxide solution and Ludox AS-40 was added quickly under vigorous stirring. The mixture was stirred for extra 60 min, forming the aluminosilicate gel with formulation of 7.9KOH:1.0Al<sub>2</sub>O<sub>3</sub>: 21.2SiO<sub>2</sub>:2.6TEAOH:500H<sub>2</sub>O.

For the B-SUZ-4, aluminum foil, boronic acid were diluted in a solution of KOH in distilled water. Another solution with tetraethylammoniumhydroxide solution and Ludox AS-40 was added quickly under vigorous stirring. The mixture was stirred for extra 60 min, forming the aluminosilicate gel with formulation of 7.9KOH:1.0Al<sub>2</sub>O<sub>3</sub>:1.5B<sub>2</sub>O<sub>3</sub>:21.2SiO<sub>2</sub>:4.68TEAOH:750H<sub>2</sub>O.

After stirring at 25 °C for 1 h, the gel was transferred into a 100 mL stainless steel autoclave and crystallized at 160 °C in a rotation mode (30 r/min). After the crystallization, the autoclave was quenched to room temperature by cold water. Then, the suspension was centrifuged, and the solid product was washed with deionized water and dried at 120 °C for 10h.

The OSDA was removed at 540 °C for 6 h in air. The NH<sub>4</sub><sup>+</sup>-form samples were obtained after three repeated ion exchange using 1 mol/L NH<sub>4</sub>Cl at 100 °C for 6 h. H(B)-SUZ-4 zeolite was obtained after calcination at 540 °C for 5 h in a flowing 20% O<sub>2</sub>/N<sub>2</sub> mixture.

## Catalyst test

DME carbonylation was carried out with a continuous flow fixed-bed reactor (i.d. 8 mm). 300 mg catalyst (40–60 mesh) was loaded into the reactor and treated with N<sub>2</sub> (30 mL/min) at 500 °C for 1 h. After cooling down to the reaction temperature, a mixture of 5 vol.% DME/50 vol.% CO/2.5 vol.% Ar/42.5 vol.% He was introduced via a mass-flow controller (6.25 mL/min) and the reactor was pressurized to 2.0 MPa. The effluent from the reactor was analyzed online using a gas chromatograph (Agilent 7890A) equipped with a 100% dimethylpolysiloxane column (HP-PONA, 50 m×0.20 mm×0.50 μm) that connected to a flame-ionization detector.

## Characterization techniques

The morphology of SUZ-4 was characterized by scanning electron microscope (Quanta 200F, FEI) at 20 KV and transmission electron microscopy (HITACHI HT7700) with an accelerating voltage of 100 kV. Smart lab (Rigaku) was used to get XRD patterns with an incident angle of 10°, the scanning rate of 5 °/min. Elemental analysis was performed using ICP-OES 7300DV (PerkinElmer). Thermal gravimetric (TG) analysis of the spent catalyst was conducted using a Diamond TG/ DTA6300 instrument (PerkinElmer). The sample was heated from room temperature to 800°C at a rate of 10°C·min<sup>-1</sup> under flowing air.

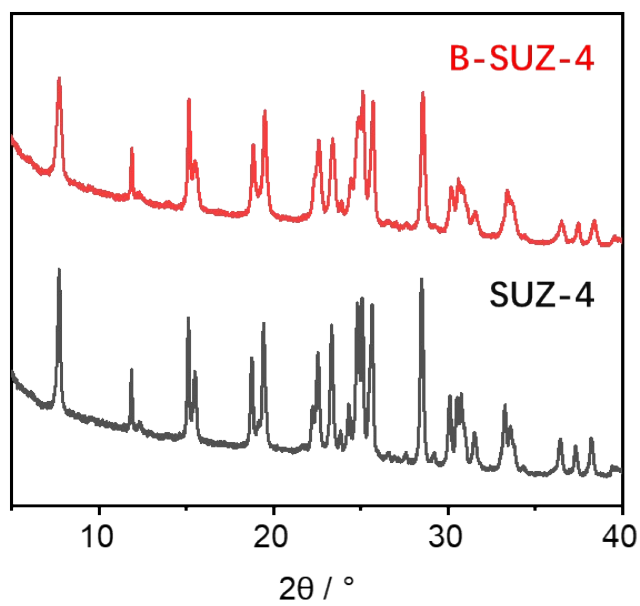
N<sub>2</sub> adsorption-desorption isotherms were recorded on a Micromeritics Autosorb iQ adsorption analyzer at -196°C. Before the measurement, the sample was outgassed at 300°C for 5 h. The total pore volume was calculated from the adsorption isotherms at P/P<sub>0</sub> = 0.99. The total micropore volumes were calculated using t-plot method.

Fourier transform infrared spectra (FT-IR) were collected using a Bruker Tensor 27 instrument equipped with a MCT detector.

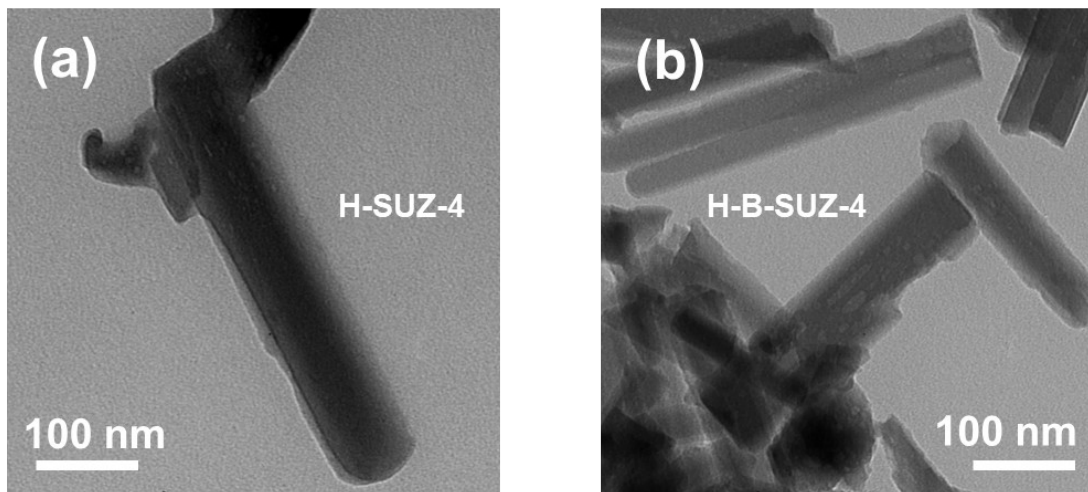
In the pyridine and NH<sub>3</sub> adsorption-desorption *in-situ* experiment, self-supported wafers of samples (20 mg) were placed into an *in-situ* quartz cell equipped with CaF<sub>2</sub> windows. The wafers were subsequently pretreated at 450 °C for 30 min in vacuum.

Afterwards, the wafers were put in contact with pyridine vapor at 450 °C until reaching to an equilibrium, and then the pyridine desorption was performed at 150 °C for 30 min, and FTIR spectra were recorded at 150 °C. Subsequently, the samples were heated to 300 °C, 450 °C for pyridine desorption. The spectra were collected at the corresponding temperature.

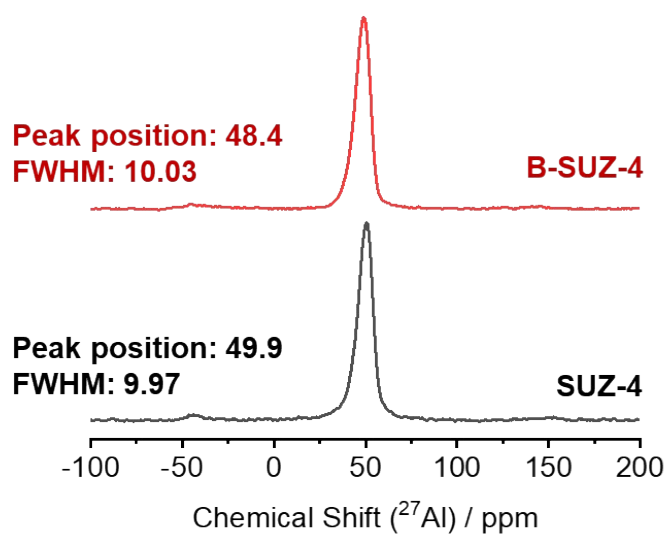
In the CO adsorption-desorption *in-situ* experiment, self-supported wafers of samples (38.3 mg) were placed into an *in-situ* quartz cell equipped with CaF<sub>2</sub> windows, The wafers were subsequently pretreated at 450 °C for 30 min in vacuum, and cooled down to room temperature. ~10 ml CO was injected in the vacuum line for twice and subsequently pumped out from the vacuum line. *In-situ* IR spectra are collected at dynamic vacuum.



**Fig. S1** XRD patterns of SUZ-4 and B-SUZ-4.

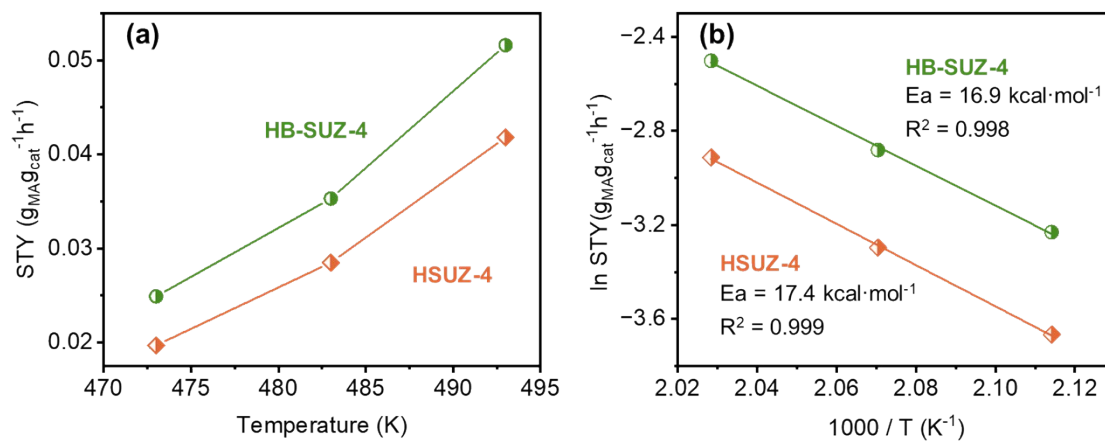


**Fig. S2** TEM images of HSUZ-4 and HB-SUZ-4.

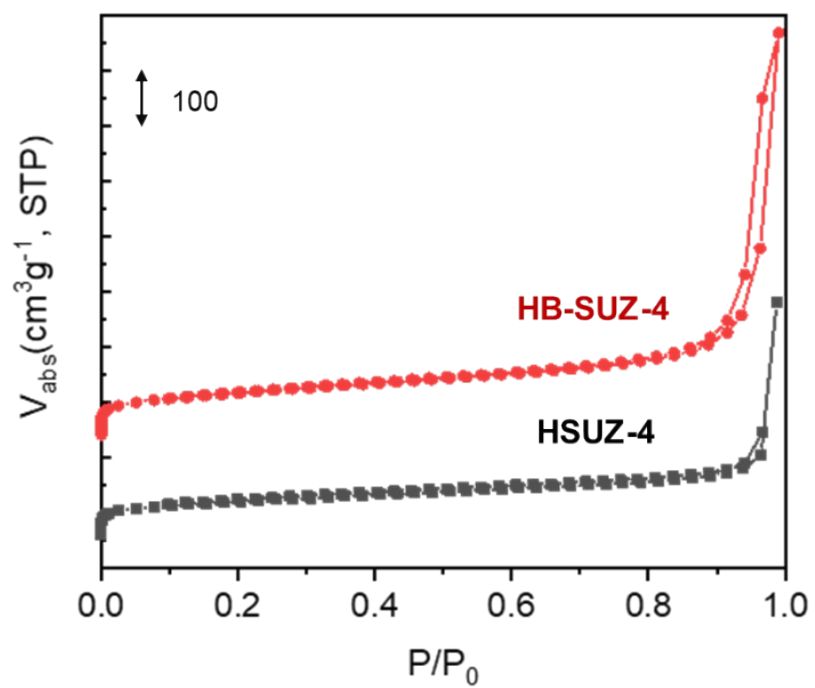


**Fig. S3**  $^{27}\text{Al}$  MAS NMR spectra of as-synthesized SUZ-4 and B-SUZ-4

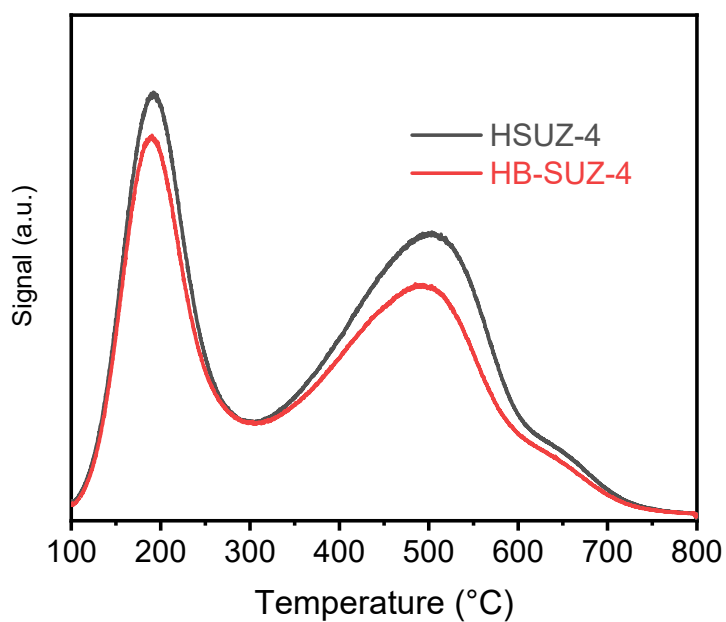




**Fig. S4** MA synthesis rate over HSUZ-4 and HB-SUZ-4 (a) and the apparent activation energies (b)



**Fig. S5**  $\text{N}_2$  sorption isotherms of HSUZ-4 and HB-SUZ-4.

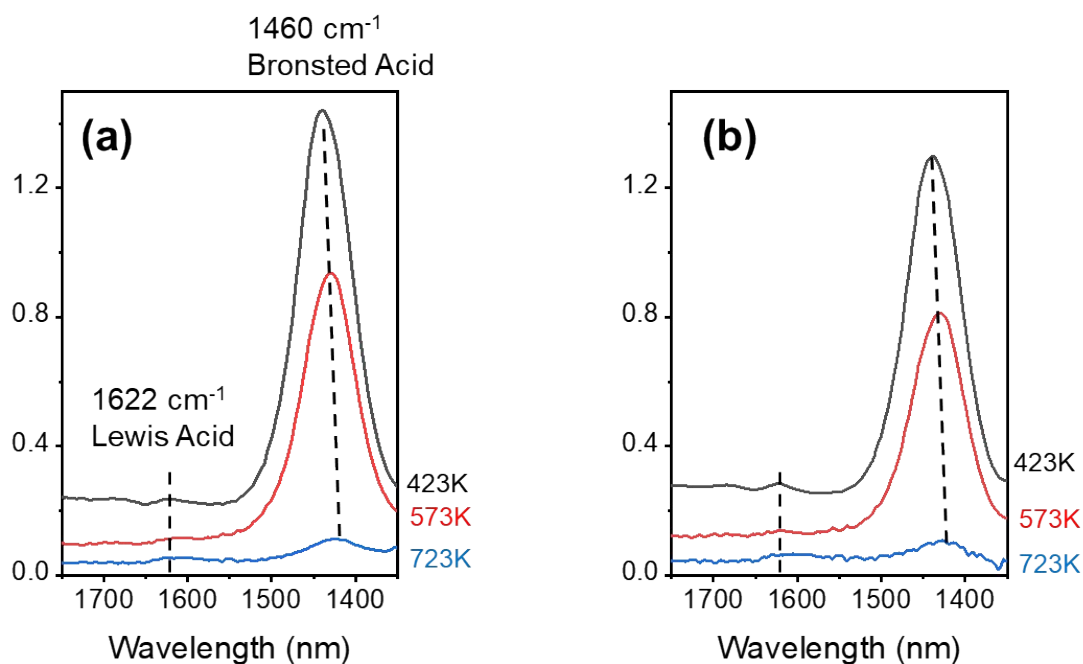


**Fig. S6** NH<sub>3</sub>-TPD profiles of HSUZ-4 and HB-SUZ-4.

**Table. S1** . Acid density and acid site distribution for HSUZ-4 and HB-SUZ-4

Sample	<sup>a</sup> Total acid density/mmole·g <sup>-1</sup>	<sup>b</sup> Acid site distribution/ %			Acid density /mmole·g <sup>-1</sup>	
		Al-OH	8-MR	10-MR	8-MR	10-MR
HSUZ-4	1.56	10.0	49.3	40.7	0.77	0.63
HB-SUZ-4	1.32	10.3	48.0	41.7	0.63	0.55

<sup>a</sup> Characterized by NH<sub>3</sub>-TPD; <sup>b</sup> calculated from the IR deconvolution result in Fig. 3b

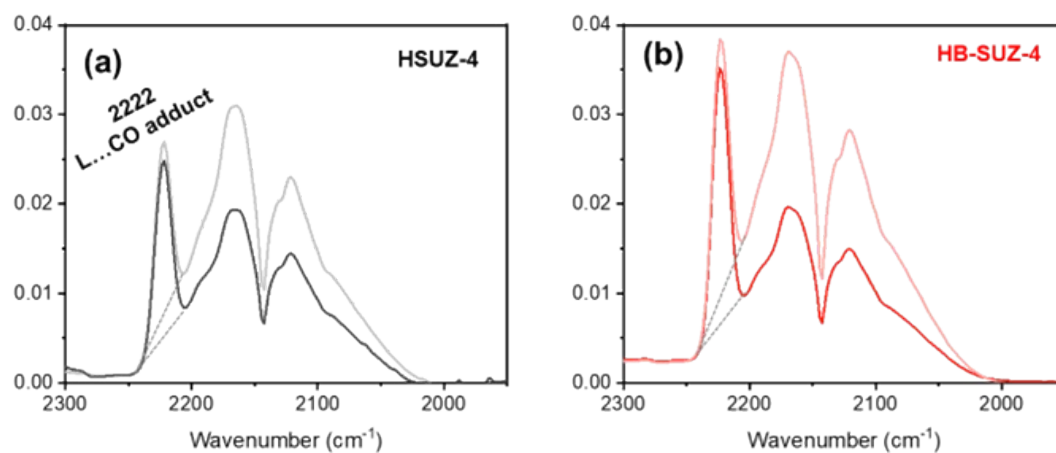


**Fig. S7** IR spectra of  $\text{NH}_3$  adsorbed on HSUZ-4 (a) and HB-SUZ-4 (b) following thermal treatment at 423 K, 573 K and 723 K.

**Table. S2** . Integrated 1622 and 1460  $\text{cm}^{-1}$  peak area of IR spectra of HSUZ-4 and HB-SUZ-4 with  $\text{NH}_3$  adsorbed following thermal treatment at 423, 573 and 723 K

Integrated band area/ $\text{cm}^{-1}$	HSUZ-4			HB-SUZ-4		
	423 K	573 K	723 K	423 K	573 K	723 K
1460 $\text{cm}^{-1}$ (B site)	89.800	55.703	2.472	78.130	48.025	5.131
1622 $\text{cm}^{-1}$ (L site)	0.512	0.387	-	4.638	0.501	-

Note: According to the calculation method proposed by Datka et al.<sup>2</sup>, that the acidity is proportionate to the integrated peak area, the Bronsted acid density of HSUZ-4 is 15% higher than that of HB-SUZ-4 at 423 K and 573 K. The Lewis acid density of HB-SUZ-4 is 8.2 times higher than that of HSUZ-4 at 423 K.



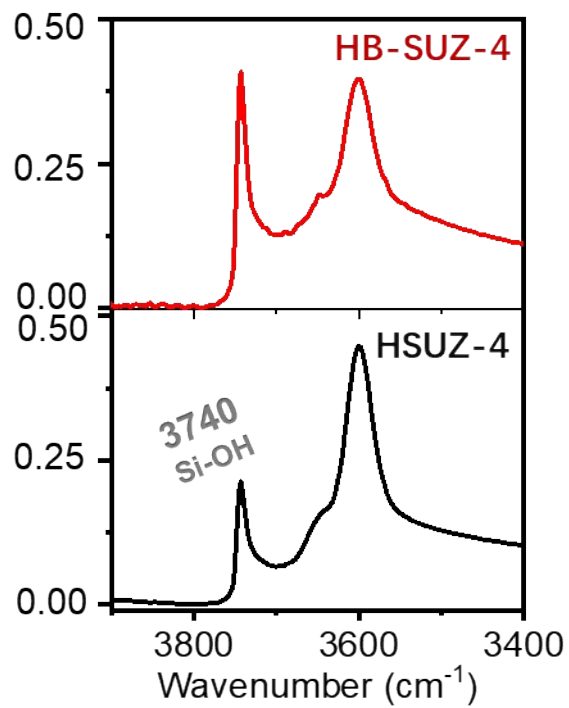
**Fig. S8** *in-situ* IR spectra of CO adsorption on HSUZ-4 (a) and HB-SUZ-4 (b) during CO injection at 298 K

**Table. S3.** Band area of 2222  $\text{cm}^{-1}$  *in-situ* IR spectra during CO desorption from HSUZ-4

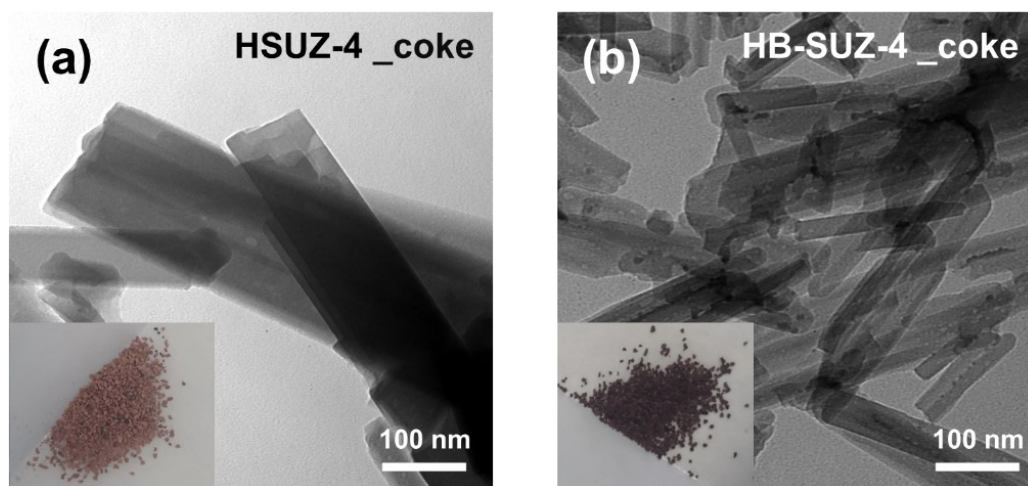
Spectrum in Fig. 3c	1	2	3	4	5	6	7	8	9
2222 $\text{cm}^{-1}$ band area/ $\text{cm}^{-1}$	0.281	0.281	0.276	0.266	0.125	0.057	0.033	0.022	0.016

**Table. S4.** Band area of 2222  $\text{cm}^{-1}$  *in-situ* IR spectra during CO desorption from HBSUZ-4

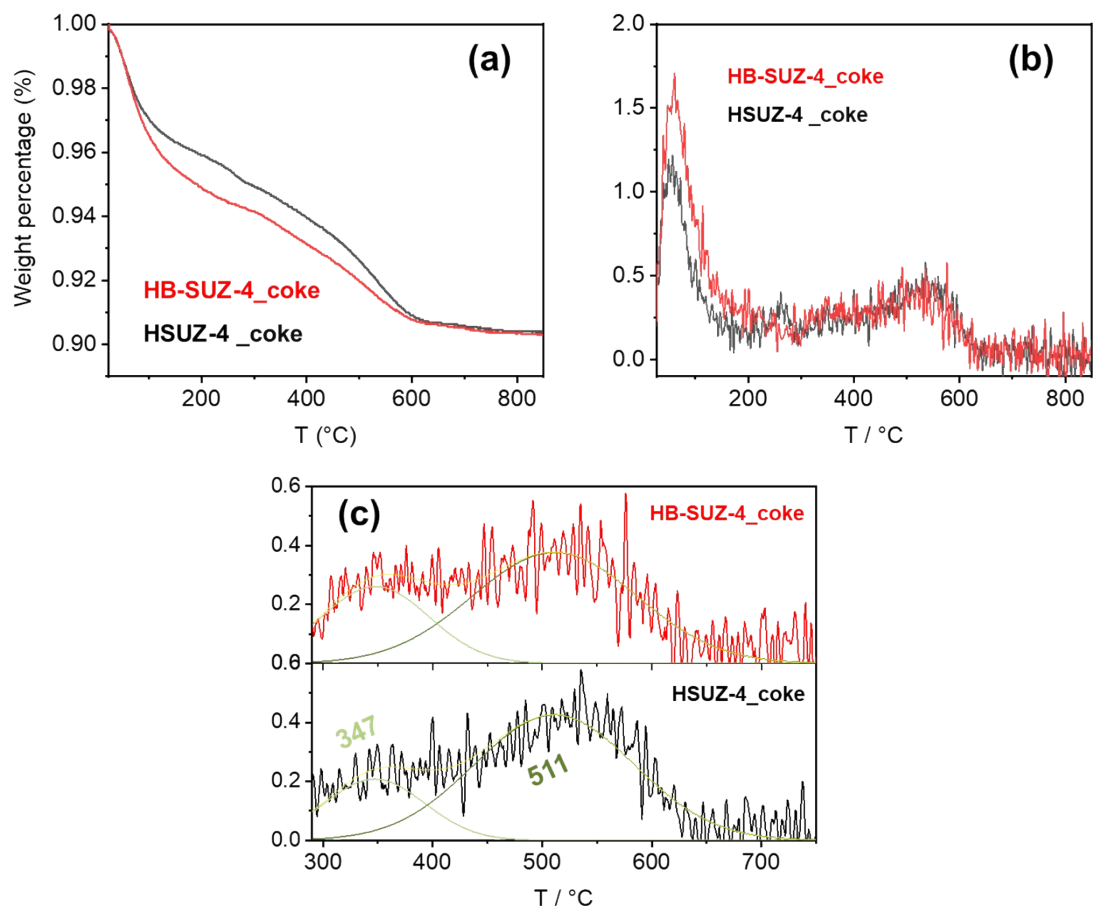
Spectrum in Fig. 3d	1	2	3	4	5	6	7	8	9
2222 $\text{cm}^{-1}$ band area/ $\text{cm}^{-1}$	0.413	0.412	0.394	0.286	0.166	0.107	0.052	0.019	0.014



**Fig. S9** IR spectra of HSUZ-4 and HB-SUZ-4 followed thermal treatment at 423 K in vacuum.



**Fig. S10** TEM images of the used catalysts after the reaction shown in Fig.2.

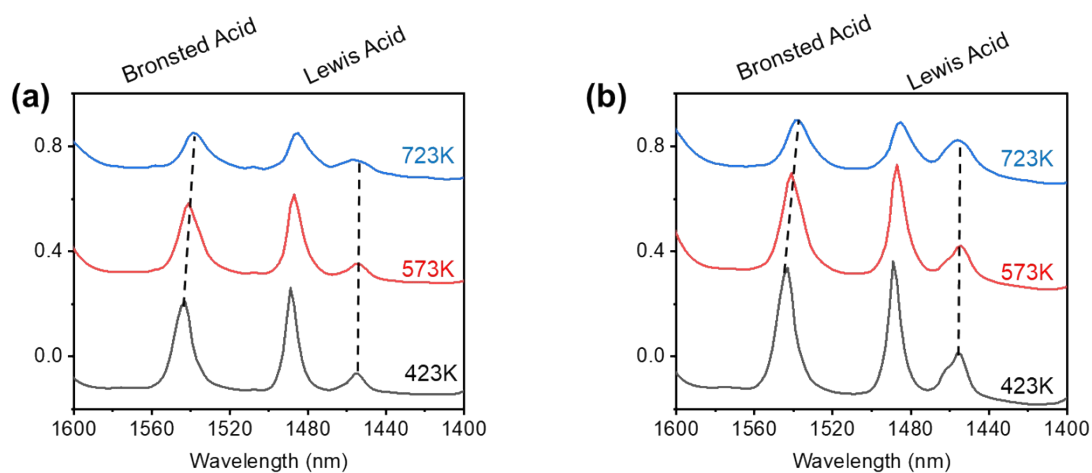


**Fig. S11** TG (a) and DTA (b, c) curves of the used catalysts after the reaction shown in Fig.2. (c) analysis of weightlessness peak above 300 °C.

**Table. S5.** The textural properties of zeolites after the reaction shown in Fig. 2a

	$S_{\text{BET}}$ m <sup>2</sup> /g	$S_{\text{micro}}$ m <sup>2</sup> /g	$S_{\text{ext}}$ m <sup>2</sup> /g	$V_{\text{micro}}$ cm <sup>3</sup> /g	$V_{\text{total}}$ cm <sup>3</sup> /g
HSUZ-4_coke	286.508	142.040	135.944	0.065	0.4956
HB-SUZ-4_coke	393.438	219.578	173.860	0.094	1.100





**Fig. S12** IR spectra of pyridine adsorbed on HSUZ-4 (a) and HB-SUZ-4 (b) following thermal treatment at 423K, 573K and 723K.

The samples were pretreated at 723 K in vacuum for 60 min, followed by pyridine introduced at 723 K. Then pyridine was desorbed at 423 K, 573 K and 723 K. Spectra were collected at the temperature for desorption. Bands at  $1547\text{ cm}^{-1}$  and  $1455\text{ cm}^{-1}$  refer to Bronsted and Lewis bonded pyridine respectively<sup>3</sup>. The integrated peak areas in the spectra collected 423 K, 573 K and 723 K reflect total acid, medium strong acid and super acid density.

**Table. S6.** Acidity of HSUZ-4 determined by pyridine sorption.

	<b>weak</b>	<b>Medium strong</b>	<b>Super acid</b>	<b>Total acid</b>
$C_B / \text{mmol} \cdot \text{g}^{-1}$	0.027	0.092	0.107	0.226
$C_L / \text{mmol} \cdot \text{g}^{-1}$	0.004	0	0.021	0.024

**Table. S7.** Acidity of HB-SUZ-4 determined by pyridine sorption.

	<b>weak</b>	<b>Medium strong</b>	<b>Super acid</b>	<b>Total acid</b>
$C_B / \text{mmol} \cdot \text{g}^{-1}$	0.027	0.124	0.131	0.283
$C_L / \text{mmol} \cdot \text{g}^{-1}$	0.019	0	0.054	0.073

## REFERENCES

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