

## Electronic Supplementary Information

### **Direct synthesis of the organic and Ge free Al containing BOG zeolite (ITQ-47) and its application for transformation of biomass derived molecules**

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## Experimental Procedures

### Material synthesis

Preparation of Si/B-ITQ-47 seed according to US patent, tetraethylorthosilicate (TEOS) was purchased from Aladdin®, germanium dioxide, boric acid and phosphazene base P1-t-Bu were obtained from Sigma-Aldrich®, and Si/B-ITQ-47 zeolite used as seeds in the synthesis was supplied by Instituto de Tecnología Química (UPV-CSIC). Si/Al-BOG zeolite is hydrothermally synthesized from the starting gel with a molar ratio of  $\text{SiO}_2:0.25\text{-}0.27\text{Na}_2\text{O}:0.012\text{-}0.020\text{Al}_2\text{O}_3:20\text{H}_2\text{O}$  and Si/B-ITQ-47 seed crystals (5 wt% based on total silica amount). In a typical preparation, 0.214 g of NaOH (97%, Aladdin®) was dissolved in 2 mL of  $\text{H}_2\text{O}$ , followed by the addition of 0.602 g of fumed  $\text{SiO}_2$  (HL-300, GBS®). Then 0.021 g of  $\text{NaAlO}_2$  (Aladdin®) was dissolved in 1.52 mL of  $\text{H}_2\text{O}$  added to the gel. After forming the homogeneous aluminosilicate gel, 0.030 g of Si/B-ITQ-47 as seeds were introduced into the gel under stirring at room temperature. After stirring for 10 min, the appropriate  $\text{H}_2\text{O}$  was added until reaching the  $\text{H}_2\text{O}/\text{SiO}_2=20$ . Then the mixture was transferred into a Teflon lined stainless-steel autoclave for crystallization at 125 °C for 14 days under static conditions. The solid was collected by centrifugation or filtration, washed exhaustively with deionized water, and dried at 100 °C for 5 h to obtain the as-made Si/Al-BOG zeolite. When Si/Al-BOG zeolite was used as seeds for synthesizing BOG-structure zeolite, the synthesis gel ( $\text{SiO}_2:0.26 \text{Na}_2\text{O}:0.016 \text{Al}_2\text{O}_3:15 \text{H}_2\text{O}$ ) was heated at 125 °C for 12 days. The washed and dried solid was identified as Si/Al-BOG-2<sup>nd</sup>.

Further studies on the synthesis of  $S_{\text{cal}}$ -Si/Al-BOG with Si/B-ITQ-47-cal seed. The synthesis procedure was similar to that described previously for the Si/Al-BOG prepared in OSDA-free gel, but 6.7 wt% of Si/B-ITQ-47-cal seed was added to the synthesis gel giving the following composition:  $\text{SiO}_2:0.26 \text{Na}_2\text{O}:0.013 \text{Al}_2\text{O}_3:20 \text{H}_2\text{O}$ . Zeolite crystallization was observed at 13 days under hydrothermal conditions at 125 °C.

Post-synthesis treatment of the Si/B-ITQ-47-cal to obtain exchanged Al-ITQ-47: 0.5 g of the Si/B-ITQ-47-cal was added to 36 mL of 8% aluminum nitrate solution. The mixture was transferred to steel autoclaves coated with Teflon and entered into an oven at 140 °C for 3 days. It was then washed with 2000 mL of distilled water and dried at 100 °C overnight.

### Characterization and methods

#### ICP measurement

The bulk Si/Al ratio and content elements in the samples were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Varian 715-ES spectrometer. It can be 30 mg of sample and disintegrate in 1 mL of  $\text{HNO}_3$  (65%, Merck, Emsure®), 1 mL of HF (40%, Merck Suprapur®) and 3 mL of HCl (30%, Merck Suprapur®). The sample was dissolved in this mixed acid aqueous solution at room temperature 24 h. The next day it diluted to a total volume of 60 mL with Milli-Q water. And then, we analyzed the metals that are ordered using straight patterns of calibration of 20/50/100 ppm made from a pattern of commercial 1000 ppm.

## Solid-state NMR Experiments

All the solid-state NMR experiments were performed on a Bruker AVANCEIII 500 MHz spectrometer at resonance frequencies of 500.57, 130.44, and 99.44 MHz for  $^1\text{H}$ ,  $^{27}\text{Al}$ , and  $^{29}\text{Si}$  nucleus, respectively. All the  $^{27}\text{Al}$  magic-angle-spinning (MAS) NMR spectra were recorded using a small-flip-angle technique with a pulse length of 0.26  $\mu\text{s}$  ( $\pi/12$ ) and a recycle delay of 1 s on a 4 mm triple-resonance MAS probe operating at a spinning rate of 10 kHz. Whereas all the  $^{29}\text{Si}$  MAS NMR spectra with high power proton decoupling were recorded using a  $\pi/2$  pulse length of 3.9  $\mu\text{s}$  and a recycle delay of 80 s with a 7 mm MAS probe at a spinning rate of 4 kHz. The chemical shifts of  $^{27}\text{Al}$  and  $^{29}\text{Si}$  were externally referenced to 1 M aqueous  $\text{Al}(\text{NO}_3)_3$ , and kaolinite (-91.5 ppm), respectively.

## Catalytic study

### Materials used in the reactivity evaluation

Commercial  $\text{NH}_4$ -Beta (CP811, Si/Al=12.5),  $\text{NH}_4$ -ZSM-5 (CBV3024E, Si/Al=15) and  $\text{NH}_4$ -MOR (CBV20A, Si/Al=10) zeolites are purchased from Zeolyst®. They are calcined for 6 h at 550 °C, reached at a rate of 2 °C per minute under mildly flowing air, to obtain the protonic form before reaction.

### Procedure for the catalytic test

In a typical experiment, 0.83 g L-lactic acid (LA, 9.21 mmol, 98%, abcr®) dissolved in 0.83 g water was added in a 25 mL round bottom flask, equipped with a magnetic stirrer and a Dean-Stark apparatus. Then 10 mL of o-xylene(99%, Scharlau®) was added as well as 0.2 g calcined zeolite. Then the mixture was heated at the reflux temperature of o-xylene (144 °C) for 4 h. After the reaction, the mixture was homogenized by the addition of 10 mL of acetonitrile (99%, Scharlab®). The zeolite was removed by centrifugation, and the catalyst was extracted thoroughly using a soxhlet apparatus with acetonitrile as the solvent. The organic extract was weighed and considered in the molar balance. The crude of the reaction was mixed with this organic extract and analyzed by three independent analytical methods ( $^1\text{H}$ -NMR, HPLC and chiral GC) for determining product yields and LA conversion. The molar balance accounts for  $\geq 93\%$  in all experiments.

Two 1 mL the homogeneous worked-up reaction mixture were taken and dried in a mildly flowing  $\text{N}_2$ -atmosphere to remove o-xylene and acetonitrile solvents. One dry sample was dissolved in 0.5 mL of  $\text{DMSO-d}_6$  (99.9 atom % D, Sigma-Aldrich®) and measured on a Bruker Avance300 spectrometer to obtain  $^1\text{H}$ -NMR data. GC analysis was performed on a VARIAN 3900 with a chiral  $\beta$ -DEX capillary column, equipped with an FID detector held at 275 °C, and System Control-3900 software. The injection port temperature was 225 °C, and the initial column temperature was set at 70 °C. This temperature was held for 5 minutes before being ramped to 150 °C at 15 °C/min. After 5 minutes at 150 °C, the oven was ramped to 180 °C at 25 °C/min and held there for 24 min. This chiral GC methodology allows us to separate L,L-lactide, D,D-lactide and D,L-lactide. Another dry sample was dissolved in 1 mL of ultra-pure water and analyzed with Reverse Phase-HPLC on an Agilent 1100 Series Products Spectra System equipped with PL Hi-Plex H Guard column 50x7.7mm, PL Hi-Plex H

300x7.7mm column and a 1260 Infinity UV-Vis detector at 210 nm. 0.001M H<sub>2</sub>SO<sub>4</sub> solvent was used as the mobile phase, and the flow rate was 0.6 mL/min.

The product yield, L-lactic acid conversion and oligomeric side-product formation were determined by <sup>1</sup>H-NMR integration, relative to the total amount of lactyl-containing products present. The chromatography data was used as a secondary confirmation tool confirming the yield of L,L-lactide and L-lactic acid conversion.

#### **Acidity quantification of H-Si/Al-BOG by catalyst poisoning**

Five powder samples of H-Si/Al-BOG were treated with 0, 25, 50, 100, and 200 μmol/g of pyridine, respectively. Firstly, 0.2 g of the H-Si/Al-BOG was first degassed at 200 °C for 2 h to remove adsorbed moisture and cooled to 30 °C under N<sub>2</sub> flow. It was then treated with varying amounts of a freshly made solution of pyridine in dichloromethane. The mixture was then heated at 50 °C under stirring for 30 min and then dried at 80 °C in an oil bath to remove the dichloromethane. The obtained dried powder was used for L-lactic acid to L,L-lactide reaction as per the above experimental conditions. L,L-lactide yield (%) was plotted and fitted to a straight line with the amount (μmol/g) pyridine used to treat the H-Si/Al-BOG. The amount of the treated pyridine at which the conversion reached to zero corresponding to the intercept of the fitting line's x-axis was considered as the concentration of the acidic sites.

## Characterization of the zeolites

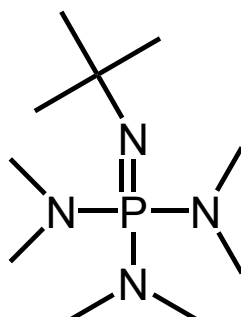
**Table S1.** The element analysis of Si/B-ITQ-47, Si/B-ITQ-47-cal and exchanged Al-ITQ-47.

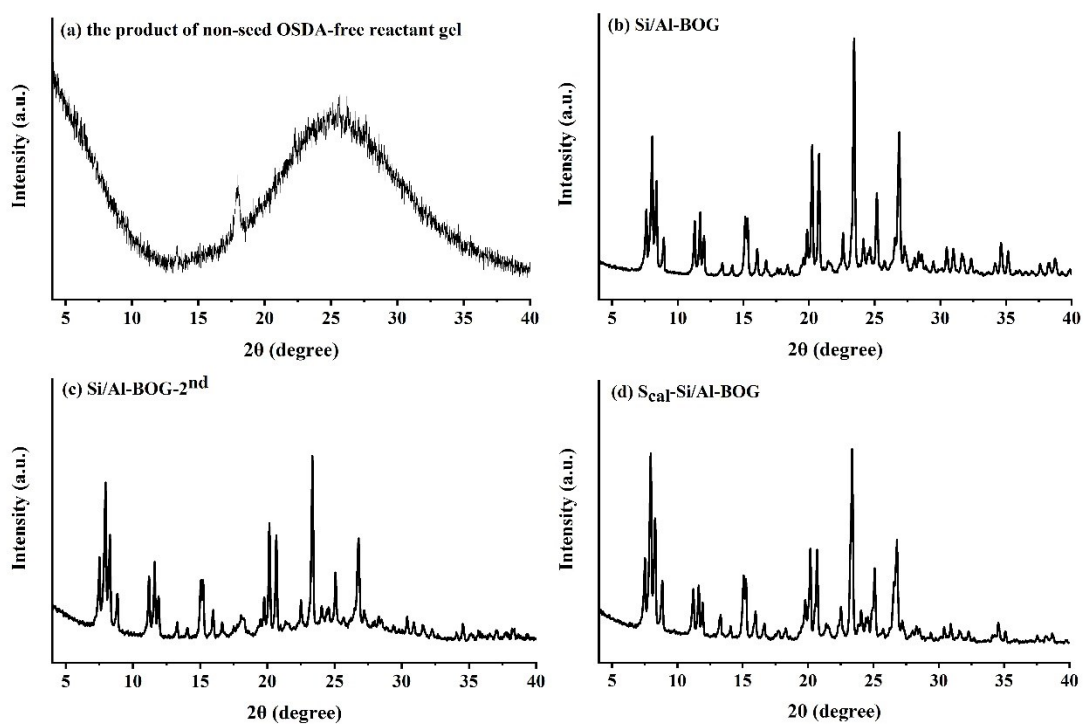
Zeolite		Si/B-ITQ-47	Si/B-ITQ-47-cal	Exchanged Al-ITQ-47
ICP analysis(wt%)	Si	37.07	37.14	40.78
	Al	0.000	0.000	1.726
	B	0.700	0.664	0.019
	Ge	2.079	2.031	0.386
	P	1.659	1.524	0.090
	Na	0.000	0.000	0.001
Elemental analysis(wt%)	C	7.57	0.86	undetected
	N	3.40	undetected	undetected
Theoretical C/P=10 <sup>a</sup>	Real C/P	11.32	1.45	-
Theoretical N/P=4 <sup>a</sup>	Real N/P	5.09	-	-
Removble contents	C+N+P	12.63	2.38	0.090
Si/B ratio	ICP	20.38	21.53	Si/Al=22.69

**Table S2.** The element analysis of Si/Al-BOG, H-Si/Al-BOG, S<sub>cal</sub>-Si/Al-BOG and Si/Al-BOG-2<sup>nd</sup>.

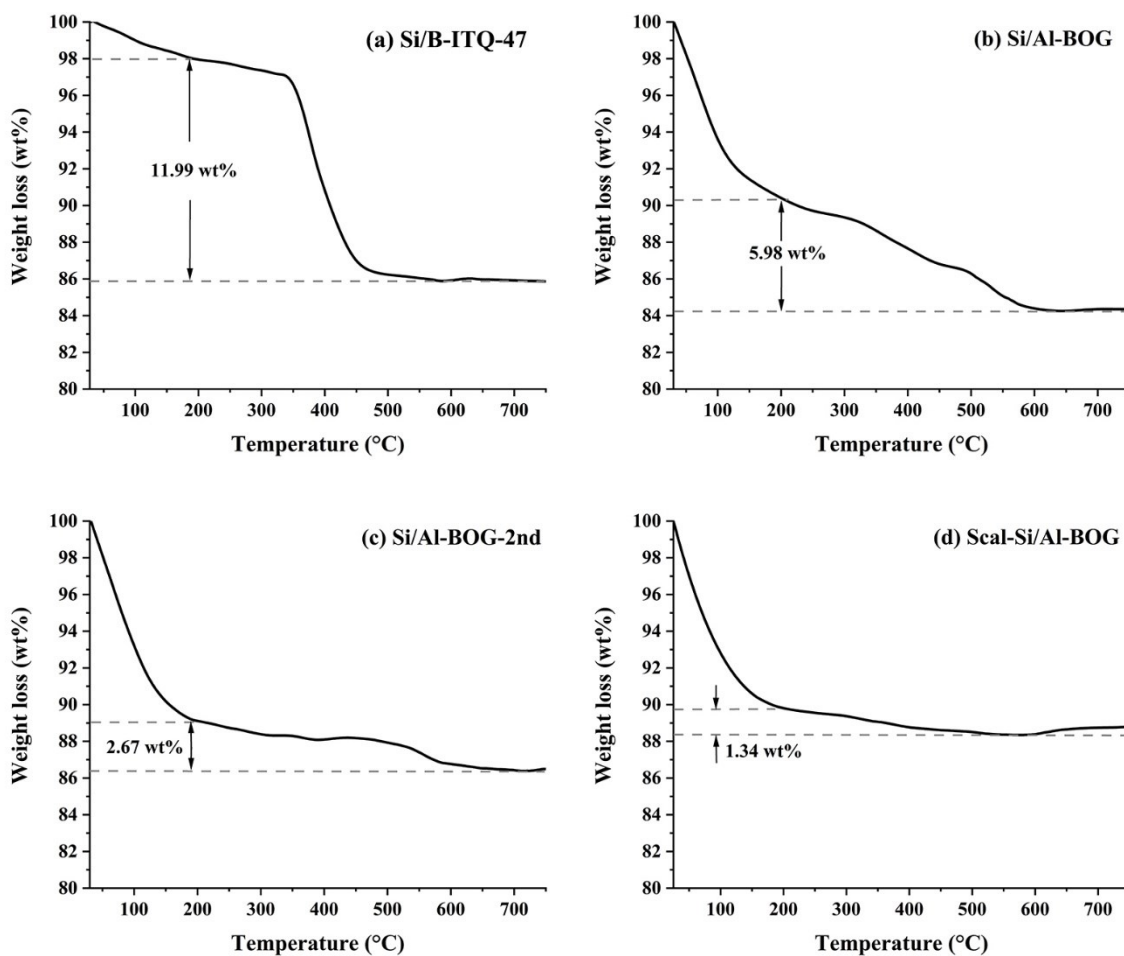
Zeolite		Si/Al-BOG	H-Si/Al-BOG	S <sub>cal</sub> -Si/Al-BOG	Si/Al-BOG-2 <sup>nd</sup>
ICP analysis(wt%)	Si	35.47	34.56	34.24	31.20
	Al	3.745	3.910	3.014	3.843
	B	0.195	0.180	0.275	0.078
	Ge	0.365	0.550	0.498	0.239
	P	0.513	0.530	0.797	0.267
	Na	1.407	0.012	1.864	2.731
Elemental analysis(wt%)	C	2.98	undetected	0.46	1.81
	N	1.66	undetected	undetected	0.54
Theoretical C/P=10 <sup>a</sup>	Real C/P	14.98	-	1.49	17.48
Theoretical N/P=4 <sup>a</sup>	Real N/P	7.17	-	-	4.47
Removble contents	C+N+P	5.15	0.530	1.26	2.62
Si/Al ratio	ICP	9.09	8.49	10.90	7.80

a: structure of phosphazene P1-t-Bu: C<sub>10</sub>N<sub>4</sub>PH<sub>30</sub>



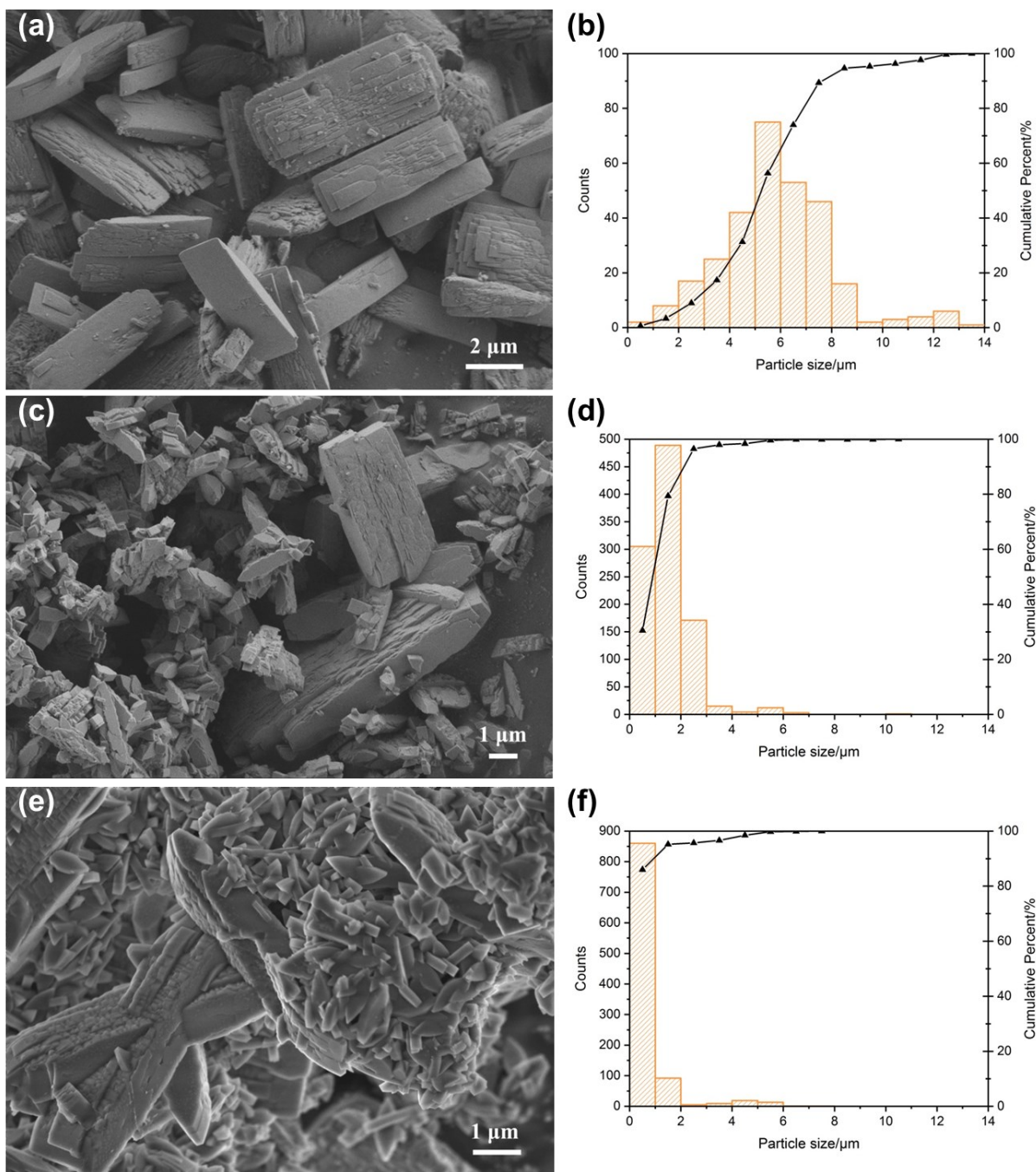


**Fig. S1.** Powder XRD patterns of (a) the as-made product obtained by the non-seed OSDA-free initial reaction gel ( $\text{SiO}_2 : 0.26 \text{ Na}_2\text{O} : 0.0125 \text{ Al}_2\text{O}_3 : 20 \text{ H}_2\text{O}$ ), (b) Si/Al-BOG, (c) Si/Al-BOG-2<sup>nd</sup>, (d) S<sub>cal</sub>-Si/Al-BOG.



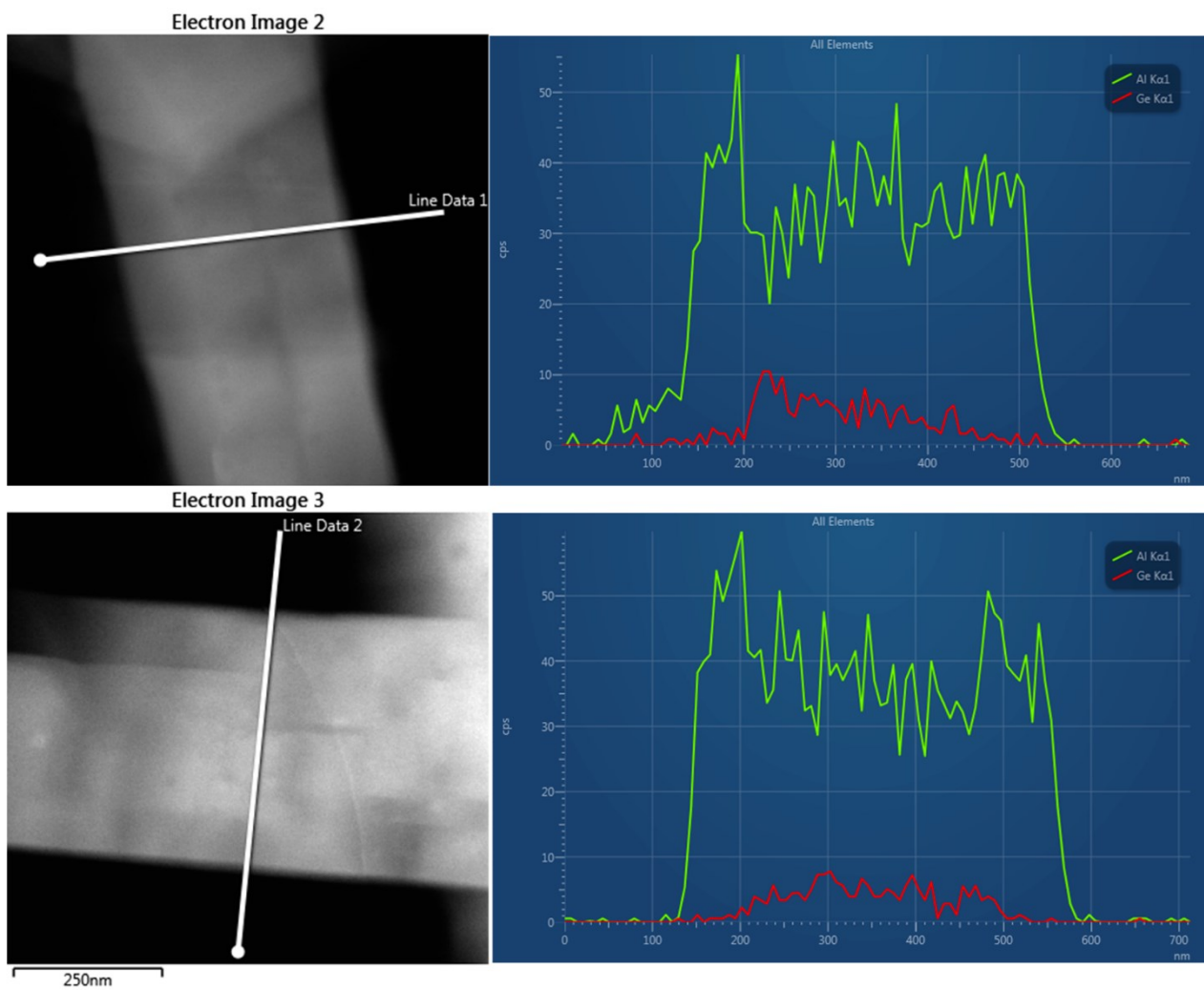
**Fig. S2.** Thermogravimetric analysis of (a) Si/B-ITQ-47, (b) Si/Al-BOG, (c) Si/Al-BOG-2<sup>nd</sup>, (d) S<sub>cal</sub>-Si/Al-BOG.



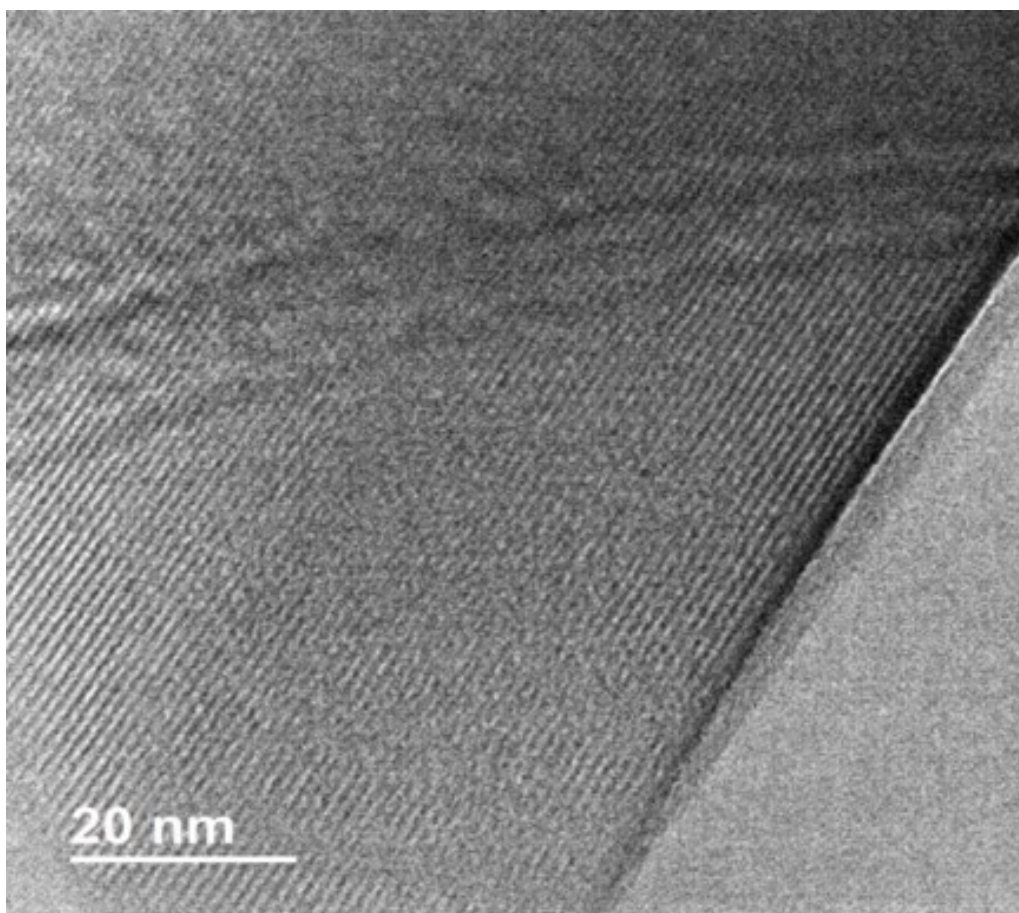


**Fig. S3.** The SEM images and distribution curves of particle size of (a, b) Si/B-ITQ-47, (c, d) Si/Al-BOG, (e, f) S<sub>cal</sub>-Si/Al-BOG.

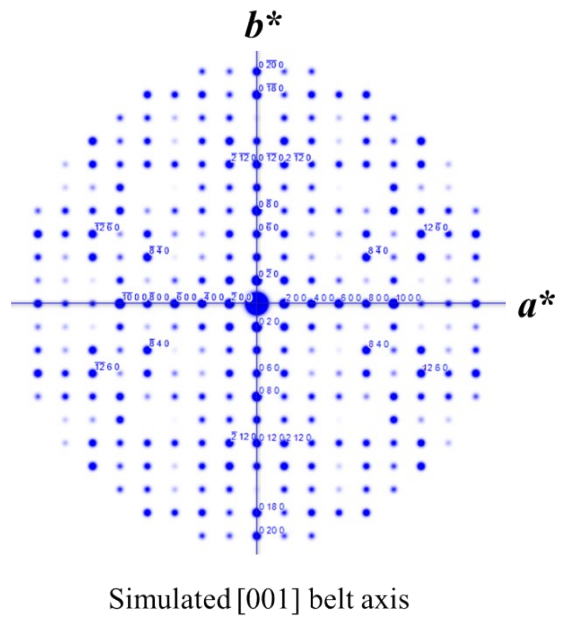
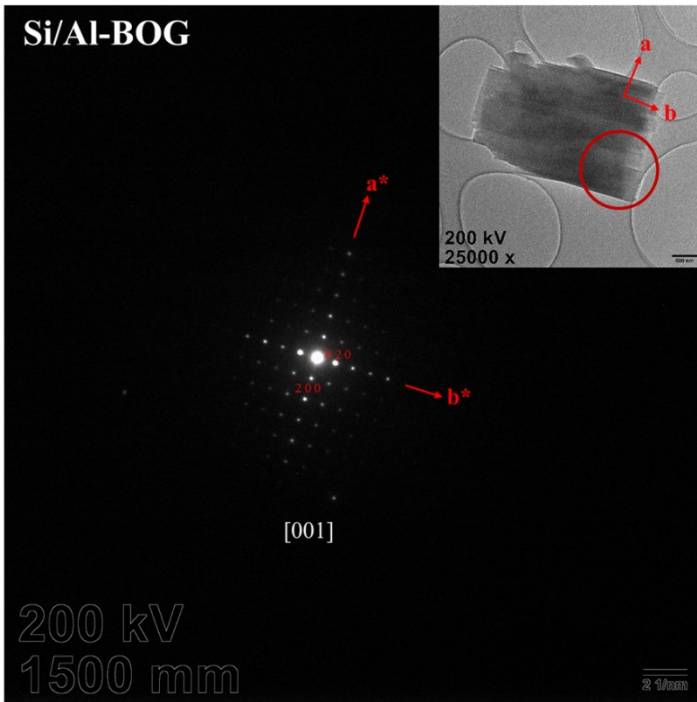
Note: The distribution curves of particle size are obtained from randomly selected SEM images, from which Si/B-ITQ-47 was selected three hundred particles for statistics, Si/Al-BOG and S<sub>cal</sub>-Si/Al-BOG were selected one thousand particles for statistics.



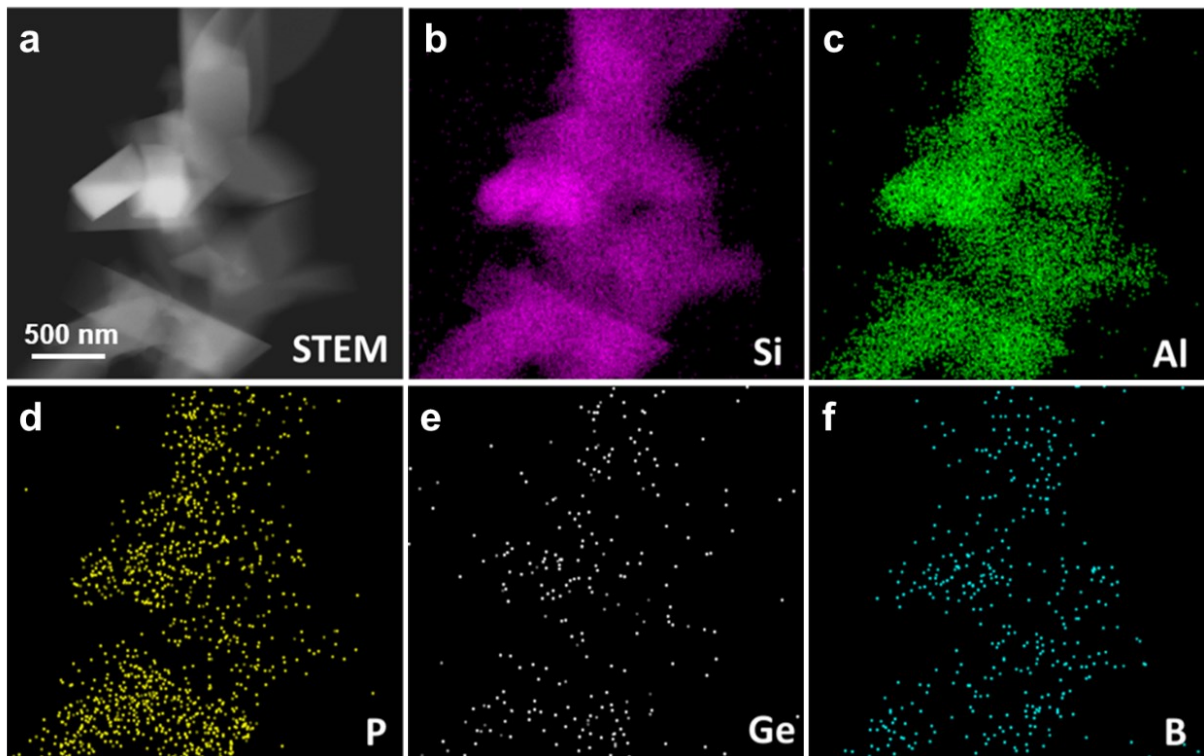
**Fig. S4.** EDS line-scans results of Si/Al-BOG crystallites. In the line profiles of Al and Ge, an enrichment of Ge in the core region is observed, indicating formation of core-shell type structure.



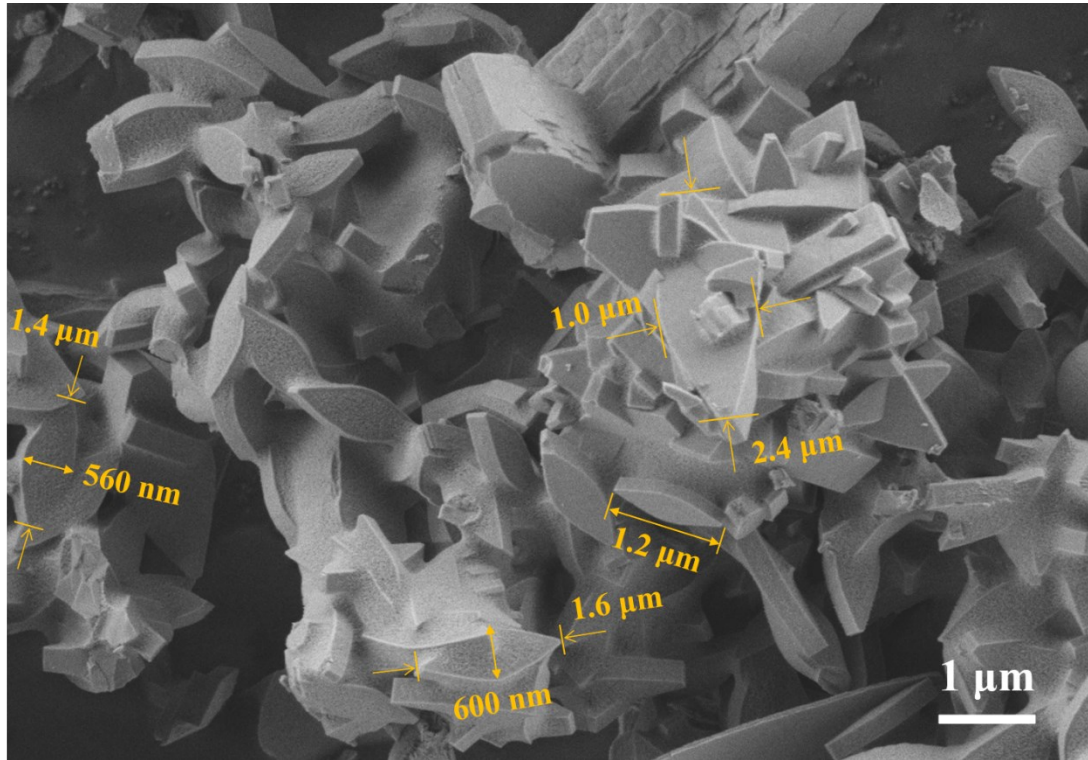
**Fig. S5.** High resolution TEM image for calcined Si/Al-BOG, showing the regular lattice fringes of the zeolite crystallite.



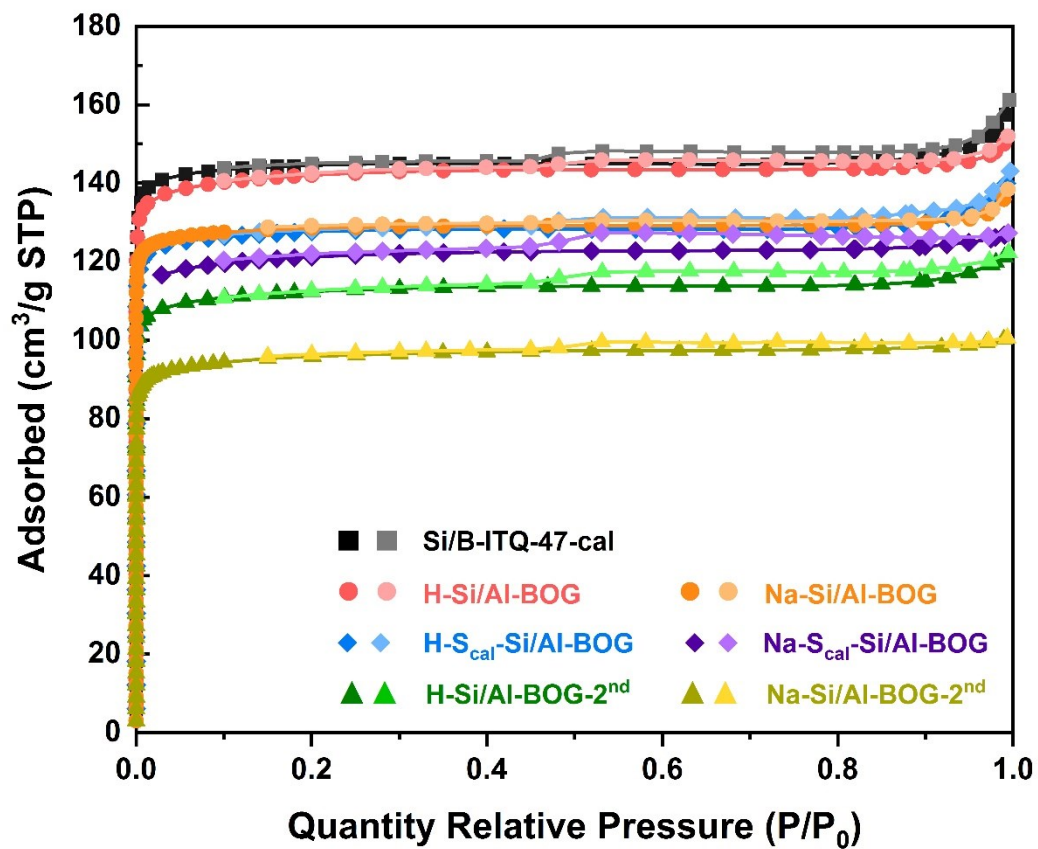
**Fig. S6.** The diffraction patterns and simulated [001] belt axis of Si/Al-BOG.



**Fig. S7.** The images of STEM-EDS observations of small crystallites without core-shell structure.



**Fig. S8.** The SEM image of Si/Al-BOG-2<sup>nd</sup>.



**Fig. S9.** N<sub>2</sub> adsorption–desorption isotherm of Si/B-ITQ-47-cal, H-Si/Al-BOG, H-Si/Al-BOG-2<sup>nd</sup>, H-S<sub>cal</sub>-Si/Al-BOG, Na-Si/Al-BOG, Na-Si/Al-BOG-2<sup>nd</sup> and Na-S<sub>cal</sub>-Si/Al-BOG.

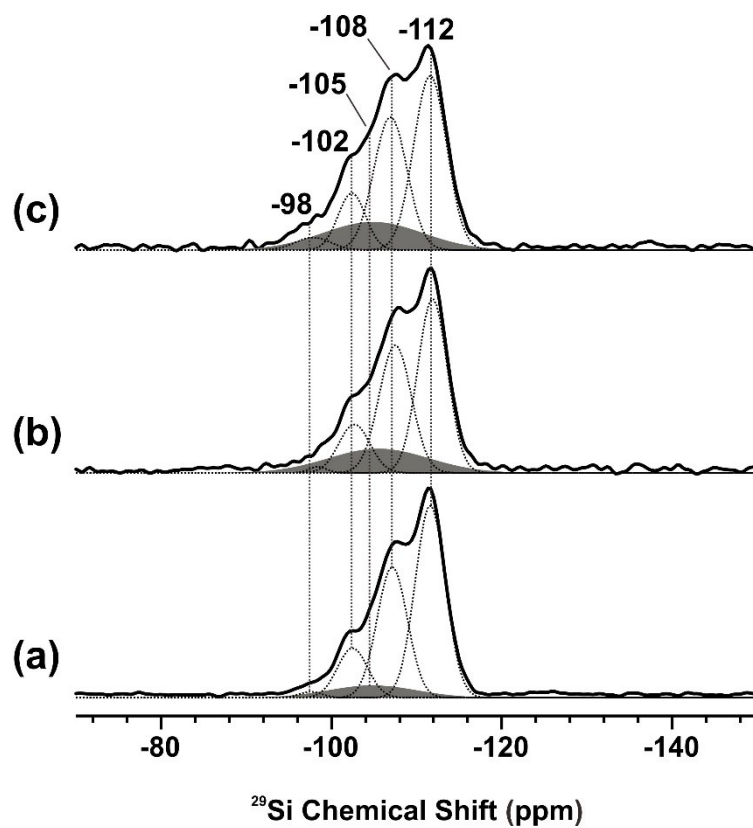
**Table S3.** The summarized texture property of Si/B-ITQ-47-cal, Na-Si/Al-BOG, H-Si/Al-BOG, Na-Si/Al-BOG-2<sup>nd</sup>, H-Si/Al-BOG-2<sup>nd</sup>, Na-S<sub>cal</sub>-Si/Al-BOG and H-S<sub>cal</sub>-Si/Al-BOG.

	Si/B-ITQ- 47-cal	Na-Si/Al- BOG	H-Si/Al- BOG	Na-Si/Al- BOG-2 <sup>nd</sup>	H-Si/Al- BOG-2 <sup>nd</sup>	Na-S <sub>cal</sub> - Si/Al-BOG	H-S <sub>cal</sub> - Si/Al-BOG
BET Surface Area(m <sup>2</sup> /g)	600.5	522.3	582.2	391.4	457.8	496.4	527.9
t-Plot Micropore Area(m <sup>2</sup> /g)	591.9	501.5	578.1	390.7	451.9	494.3	524.0
t-Plot External surface area(m <sup>2</sup> /g)	8.6	2.0	4.1	0.7	5.9	2.1	4.0
t-Plot Micropore volume(cm <sup>3</sup> /g)	0.22	0.20	0.22	0.15	0.17	0.19	0.20

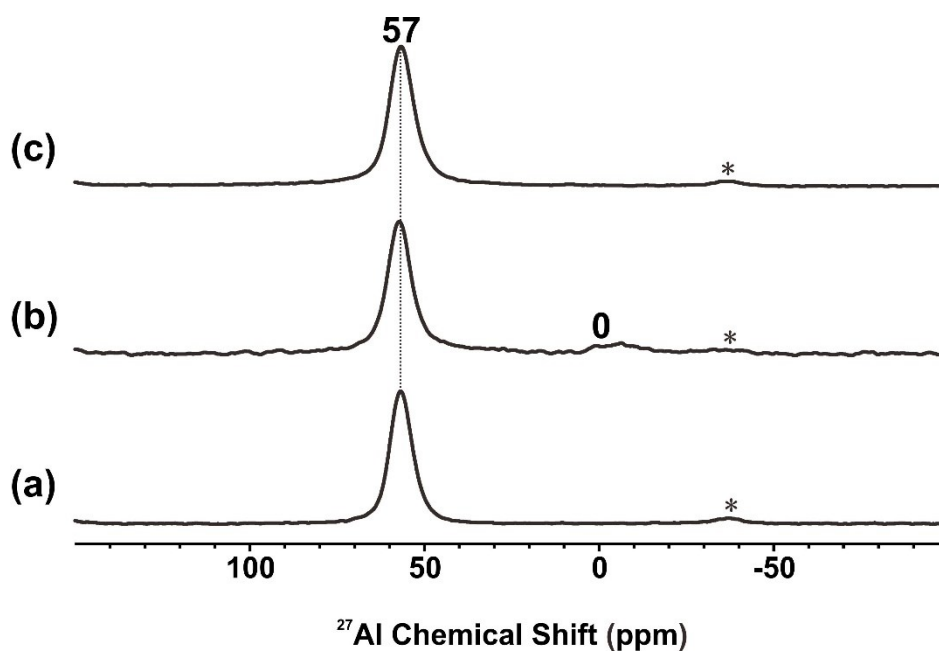


**Table S4.** Summarized  $^{29}\text{Si}$  MAS NMR data for Si/Al-BOG, Si/Al-BOG-2<sup>nd</sup> and S<sub>cal</sub>-Si/Al-BOG.

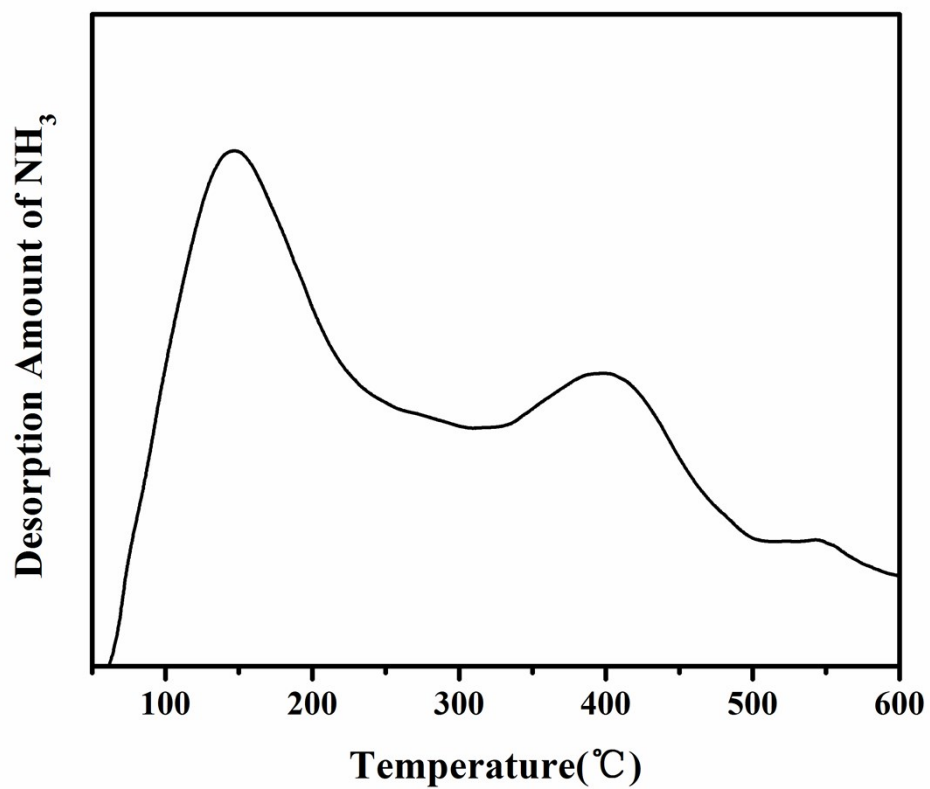
Samples	$^{29}\text{Si}$ NMR peak/ppm relative concentration (%)				
	Amorphous state		Crystalline state		
	-105	-98	-102	-108	-112
Si/Al-BOG	8.8	1.1	12.0	31.7	46.5
Si/Al-BOG -2 <sup>nd</sup>	18.8	2.9	10.4	29.5	38.3
S <sub>cal</sub> -Si/Al-BOG	18.2	0.8	11.3	31.0	38.7



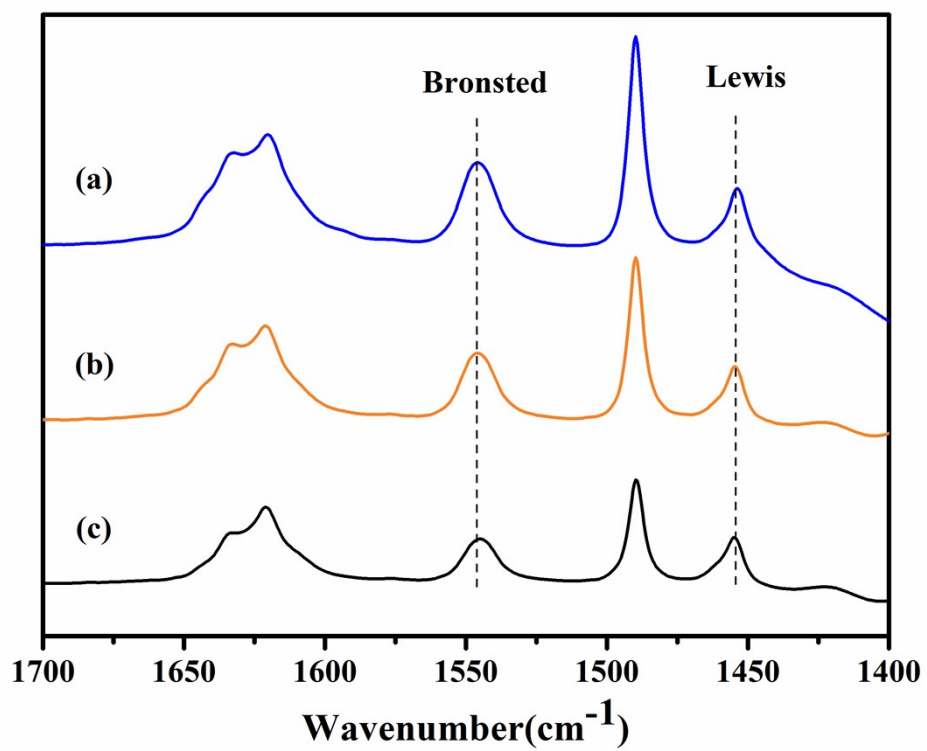
**Fig. S10.** Solid State  $^{29}\text{Si}$  MAS NMR spectra of (a) Si/Al-BOG, (b)  $S_{\text{cal}}$ -Si/Al-BOG, and (c) Si/Al-BOG-2<sup>nd</sup>.



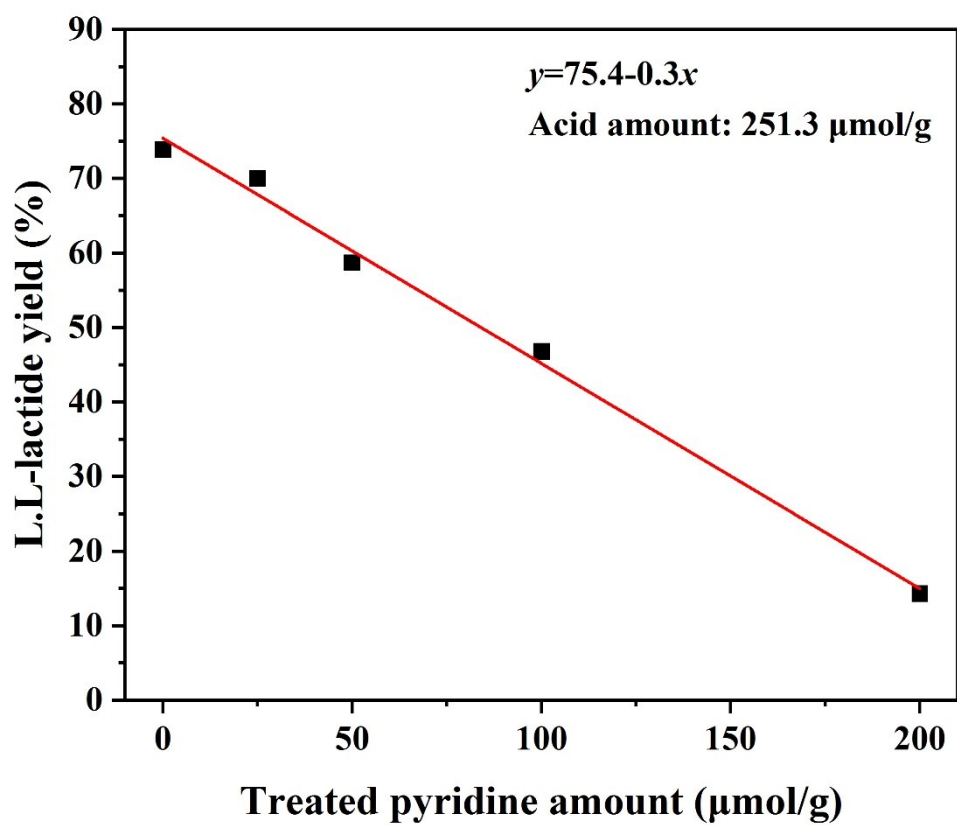
**Fig. S11.** Solid State  $^{27}\text{Al}$  MAS NMR spectra of (a) Si/Al-BOG, (b)  $S_{\text{cal}}$ -Si/Al-BOG, and (c) Si/Al-BOG-2<sup>nd</sup>.



**Fig. S12.** TPD-NH<sub>3</sub> profile of H-Si/Al-BOG zeolite.



**Fig. S13.** Infrared spectra of adsorption of pyridine on H-Si/Al-BOG zeolite at desorption temperatures of (a) 150 °C, (b) 250 °C and (c) 350 °C. Absorbances resulting exclusively from pyridine adsorbed on Brønsted and Lewis acid sites are indicated.



**Fig. S14.** Conversion of L-lactic acid to L.L-lactide reaction by H-Si/Al-BOG after treatment with varying amounts of pyridine.

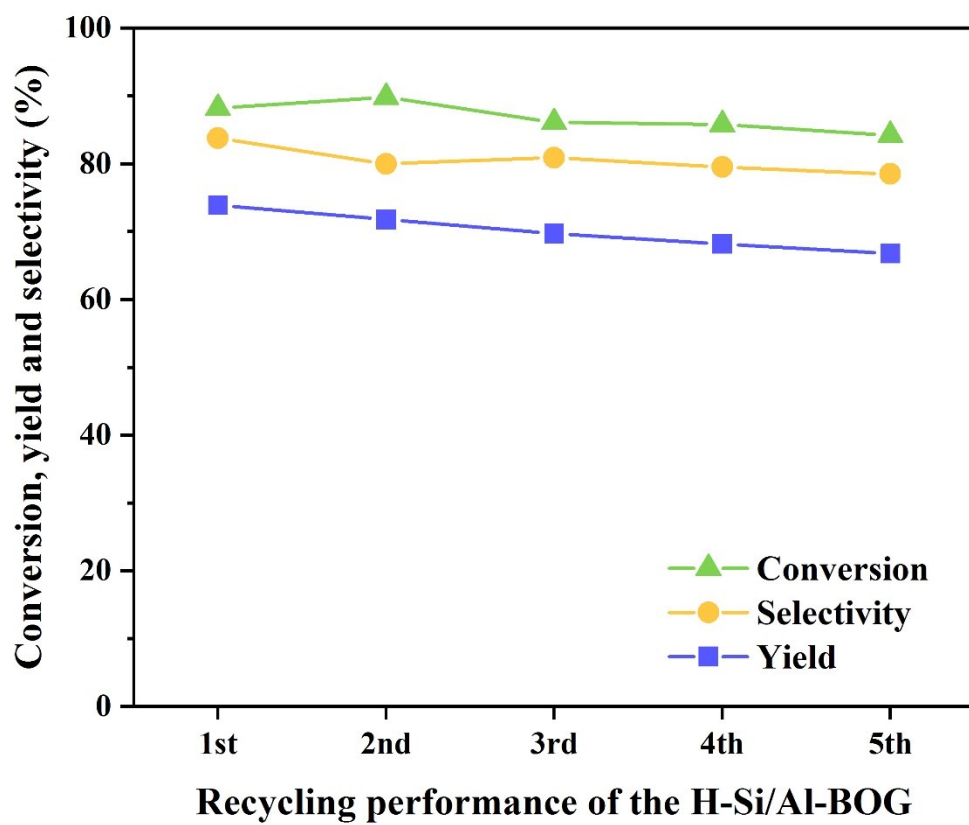
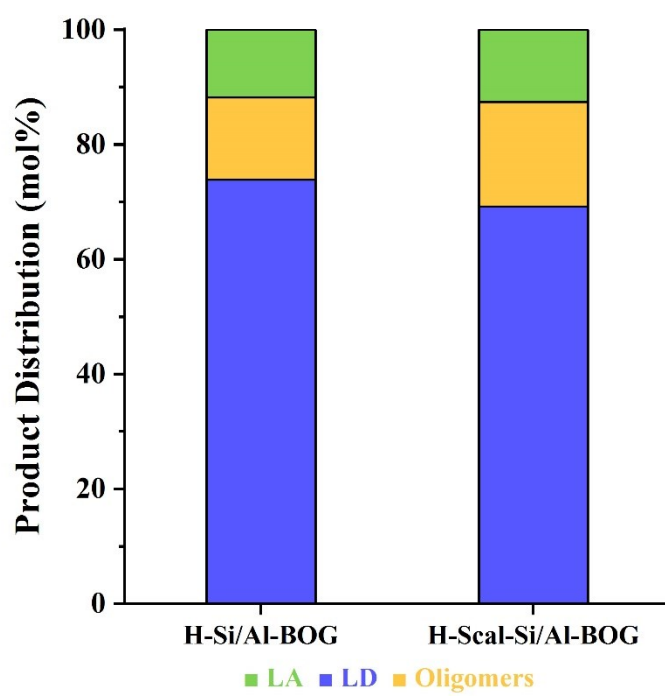
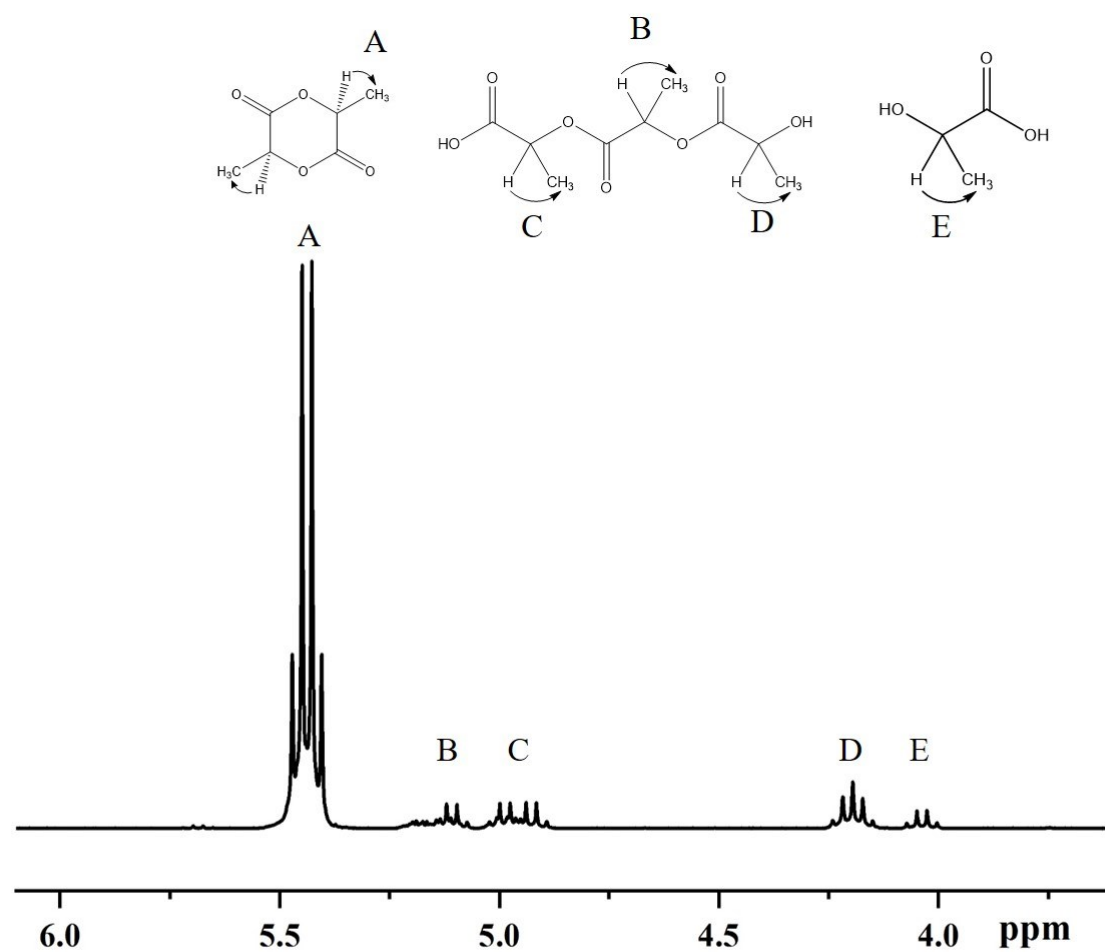


Fig. S15. The recycling performance of the H-Si/Al-BOG.



**Fig. S16.** Product distribution of L-lactic acid (LA) to L,L-lactide (LD) over H-Si/Al-BOG and H-S<sub>caI</sub>-Si/Al-BOG.



**Fig. S17.** Reaction result using H-Si/Al-BOG as the catalyst by  $^1\text{H}$  NMR in  $\text{DMSO-d}_6$ : The methine  $[-\text{CH}-\text{CH}_3]$  quartet region of various compounds in the reaction mixtures. Methine proton signals of A: lactide, B: centers of oligomers, C: carboxylic end groups of oligomers. D: hydroxyl end groups of oligomers, and E: lactic acid.



## **Author Contributions**

J. J was in charge of funding acquisition and project administration; J. J, C. Z. and A. C designed the experiment; Q.H, N.C and Z.C carried out the experiment works; Q.H, L.L, K.S.A and S.I were in charge of data analysis; X. Y. and A. Z. were in charge of solid state NMR data acquisition and analyzing; L.L and Q.H took the STEM and TEM images; C.M took electron diffraction to find the crystallography axis. W.L, J.H and Y. L drew the TOC and Scheme 1. Q.H, J.J, S. I. and A.C. were responsible for planning the work and manuscript writing.