Supporting Information for

Boron-Containing MFI-type Zeolites with a Hierarchical Nanosheet Assembly for Lipase Immobilization

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Experimental Details

Synthesis of hierarchical [Si, B]-MFI zeolite nanosheets using aerosil as a silica source: Initially, an aqueous NaOH solution was mixed with 50 % of the total amount of distilled water in a polypropylene bottle. To this mixture, the template (i.e., $C_{22\text{-}6\text{-}6}Br_2$) was added under stirring. Afterwards, the mixture was stirred for 20 minutes at room temperature. In a separate beaker, boric acid was dissolved in sulfuric acid and 50 % of the remaining water solution under stirring. After complete dissolution of boric acid, this mixture was then added at once into the above mixture in the polypropylene bottle. This mixture was then stirred at 450 to 650 rpm for 1 h at 333 K. Subsequently, it was cooled down to room temperature and the silica source, viz. aerosil was gradually added under stirring at 450 rpm to 650 rpm. After adding the aerosil, the mixture was stirred for 1 h at 333 K at 1000 rpm to ensure good mixing. After one hour, the stirring was reduced to 650 rpm in order to reduce the foaming and the synthesis mixture was stirred for another hour. Subsequently, ca. 15 g of this synthesis mixture was transferred into a 23 ml stainless steel autoclave containing a Teflon inner cylinder. In this work, synthesis was carried out in a preheated oven at 423 K. After 6 days of crystallization, the autoclaves were removed from the oven and immediately cooled in the water bath. The solid product was recovered by filtration, washed thoroughly with distilled water and dried at 348 K overnight and calcined at 823 K for 5 h under airflow. The molar compositions of the gels in these syntheses were $1SiO_2$: $0.30Na_2O$: $0.10C_{22-6-6}$: $(0.01\text{-}0.084)B_2O_3$: $0.18H_2SO_4$. In order to compare the lipase immobilization efficiency and biocatalytic activity of hierarchical boron-containing MFI zeolite nanosheets, microporous boron-containing MFI zeolite (i.e., conventional) with Si/B = 50 in the gel (i.e., Na-[Si, B]-MFI50) was also synthesized similar to the above-mentioned procedure except that tetrapropylammonium bromide (TPABr) was employed as template instead of $C_{22-6-6}Br_{2.}$

Surface functionalization of microporous Na-[Si, B]-MFI zeolite and hierarchical Na-[Si, B]-MFI zeolite nanosheets: Microporous boron-containing MFI zeolite prepared with Si/B = 50 in the gel (i.e., Na-[Si, B]-MFI50), hierarchical boron-containing MFI zeolite nanosheets prepared with Si/B = 50 and 25 (i.e., Na-[Si, B]-MFI50-NS and Na-[Si, B]-MFI25-NS, respectively) were functionalized similar to the procedure described in our previous publication.[S1] In a typical experiment, 275 mg of above-mentioned calcined catalyst was activated at 150 °C under vacuum in a schlenk vessel for 6 h. Afterwards, 25 ml of dry toluene and 0.48 g (2.2 mmol) of 3-aminopropyltriethoxysilane (APTS) were added to the flask under argon atmosphere. Subsequently, the reaction was performed under reflux and stirring overnight. Thereafter, the solid was filtered and washed with 200 ml of ethanol at ambient atmosphere and then dried at 50 °C under vacuum for 3 h. For further functionalization with glutaraldehyde (GA), 150 mg of with APTS modified material was suspended in 15 ml of a 1 wt. % of GA solution for 4 hours under stirring. The solid was filtered and washed with 300 ml of deionized water. The final product was obtained after drying overnight at 25 °C under vacuum. After functionalization, the modified samples were named as Na-[Si, B]-MFI50-APTS-GA, Na-[Si, B]-MFI50-NS-APTS-GA and Na-[Si, B]-MFI25-NS-APTS-GA. The C, H and N content of the functionalized samples were measured by CHN elemental analysis and the results are listed in Table S1.

Immobilization of thermomyces lanuginosus lipase (TLL) via covalent bonding: Sodium phosphate buffer (100 mM, pH =7.2) was used for enzyme immobilization and storage of the immobilized enzyme. To immobilize lipase on the functionalized supports, 20 mg of the sample was suspended in 2.0 ml of buffer solution, which contained a defined amount of TLL. The suspension was shaken overnight at 25°C and 150 rpm in a water bath. Thereafter, the solid and the supernatant buffer solution were separated. Furthermore, the material was washed three times with 2.0 ml of fresh buffer solution. The activity of the immobilized functionalized supports was measured by hydrolysis of *p*-nitrophenylpalmitate (pNPP) as described in our previous publications.[S1,S2] Per definition one unit (U) is equivalent to the amount of lipase releasing one µmol of nitrophenol at 25 °C and pH 7.2 per minute. Furthermore, every sample was measured three times and the mean value and the standard deviation of the reaction rate were used for calculation of the activity. The activity of immobilized lipase, immobilized amount and the concentration of used TLL are described as U per gram of support. The immobilization efficiency and the activity of the biocatalysts under study are summarized in Table S2.

Biotransformation: The transesterification[S1] of vinyl propionate and 1-butanol to butyl propionate was employed to test the biocatalytic activity of immobilized lipase in the above-mentioned functionalized catalysts (i.e., Na-[Si, B]-MFI50-APTS-GA, Na-[Si, B]-MFI50-NS-APTS-GA and Na-[Si, B]-MFI25-NS-APTS-GA). The reaction was performed with 20 mg of functionalized catalyst containing immobilized TLL in 3.0 ml of hexane and an equimolar amount (1:1 M ratio) of 1-butanol and vinyl propionate. Biotransformation was performed in a batch reactor at 40 °C. To follow the progress of the reaction, small aliquots (20 µl) of solution were withdrawn from the reaction vessel for analysis at certain time intervals. The analysis was performed in a Varian gas chromatograph equipped with a CP-sil 5 fused silica column employing *n*-decane as internal standard. The yields of butyl propionate obtained over the lipase-immobilized catalysts during transesterification reaction are depicted in Figure S2.

Characterization: Powder X-ray diffraction patterns, small angle X-ray scattering (SAXS) measurements, scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and N_2-sorption measurements of the boron-containing MFI zeolite nanosheets were performed under similar conditions using the same equipment's as described in ref. [5]. Elemental analysis (silicon and boron) was performed by SpectroCiros ICP-OES spectrometer, while CHN analysis of functionalized catalysts was performed using Euro EA 3000 (Euro Vektor) Instrument. Diffuse Reflectance Fourier Transform Infrared (DRIFT) spectra of the functionalized supports were measured on JASCO FT/IR-4100 equipped with an ATR cell and diffuse reflectance accessory with CaF2 as background in the range from 4000 cm^{-1} to 500 cm^{-1}. In addition, ^{29}Si HPDEC and ^{11}B MAS NMR spectroscopic measurements were performed on Agilent DD2 500 MHz WB spectrometer at frequencies of 99.30 MHz and 160.36 MHz, respectively. ^{29}Si HPDEC MAS NMR spectra were recorded using a 6 mm MAS NMR probe with a sample spinning rate of 5 kHz, pulse length of 3.9 μs, recycle delay of 60 s and total accumulations of 1200 for each sample. ^{11}B MAS NMR measurements were performed using a 3.2 mm MAS NMR probe with a sample spinning of 15 kHz. Spectra were obtained by applying one pulse technique with a pulse length of 1 μs, recycle delay of 1 s. A total of 4000 scans were accumulated for each sample.

Figures and Tables

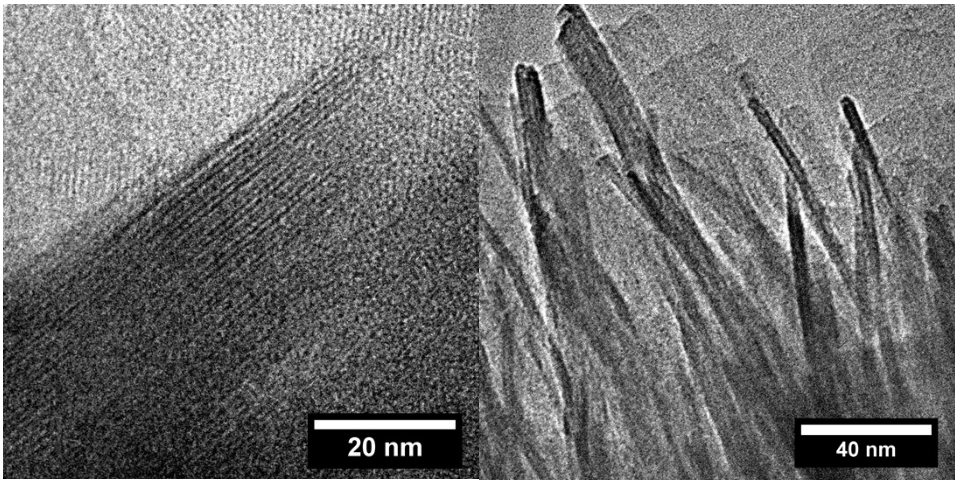

Fig. S1. TEM image of as-synthesized B-MFI zeolite nanosheets prepared with Si/B = 50 in the synthesis mixture (Na-[Si, B]-MFI50-NS).

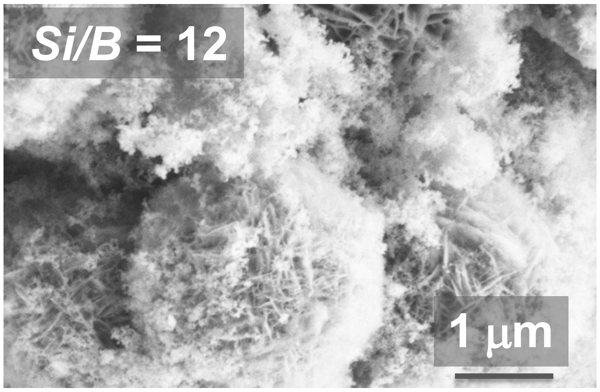

Fig. S2. SEM image of as-synthesized B-MFI zeolite nanosheets prepared with Si/B = 12 in the synthesis mixture.

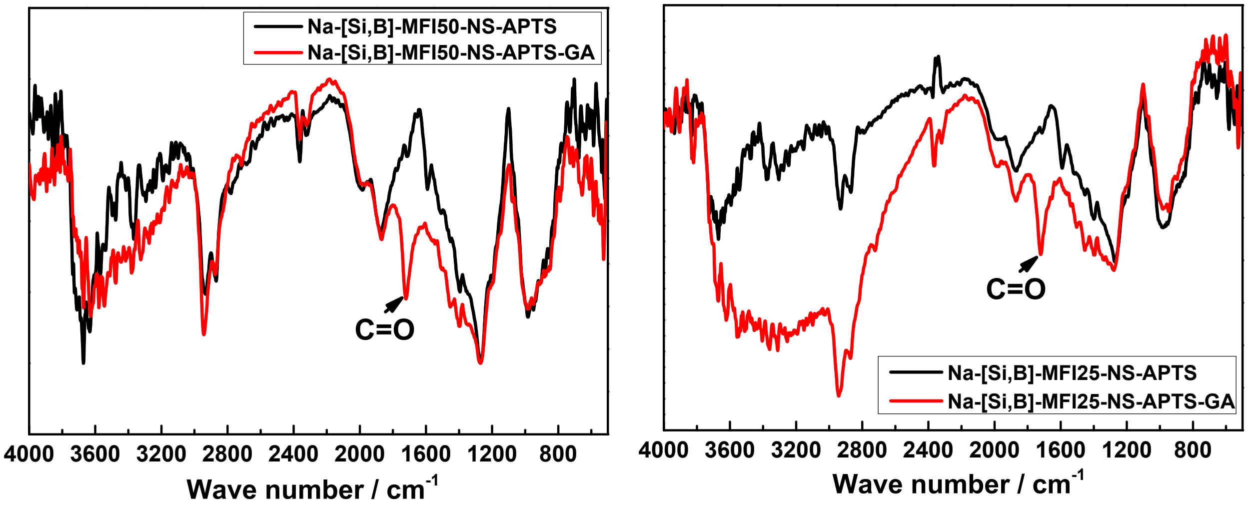

Fig. S3. DRIFT spectra of functionalized Na-[Si, B]-MFI50-NS (left) and Na-[Si, B]-MFI25-NS (right), respectively.

Table S1. Result of the functionalization of the supports by elemental analysis (CHN)

Sample	C / %	H / %	N / %	N^a / mmol g^{-1}
Na-[Si, B]-MFI50-APTS-GA	4.20	0.69	0.05	0.036
Na-[Si, B]-MFI50-NS-APTS-GA	9.87	1.44	0.87	0.62
Na-[Si, B]-MFI25-NS-APTS-GA	12.57	1.87	1.29	0.92

Table S2. Lipase immobilization performed via covalent bonding method[a]

Sample	Immobilization efficiency / %	Loading / U g^{-1}	Activity / U g^{-1}	Percent of efficient activity / %
Na-[Si, B]-MFI50-APTS-GA	1.6	5.1	1.71	19
Na-[Si, B]-MFI50-NS-APTS-GA	2.7	8.7	12.7	146
Na-[Si, B]-MFI25-NS-APTS-GA	7.8	25.3	7.47	29.5

a) The immobilization was performed in a lipase solution with concentration of 320 U $g_{support}^{-1}$

References

S1. Z. Zhou, F. Piepenbreier, V. R. R. Marthala, K. Karbacher, M. Hartmann, *Catal. Today*, 2015, **243**, 173.

S2. Z. Zhou, R. N. klupp Taylor, S. Kullmann, H. Bao, M. Hartmann, *Adv. Mater.,* 2011, **23**, 2627.