Supplementary Information

Enhancement of (Stereo)Selectivity in Dynamic Kinetic Resolution Using Core-Shell Nanozeolite@enzyme as Bi-functional Catalyst

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Experimental process

The one-pot DKR of racemic 1-PE was carried out in a glass reactor with a magnetic stirring under microwave irradiation at a desired temperature. Typically, racemic 1-PE (0.10 - 0.4 mmol) and acyl donor (0.20 - 0.8 mmol) were firstly added into n-hexane (4.0 mL). And then, 20 mg of the core-shell bi-functional catalysts (Hβ-PDDA@CALB)MSs were added into the above-mentioned reaction mixture. The reaction mixture was irradiated by microwave under magnetic stirring at 50 - 60 ^{o}C for a desired time. For mixed catalyst system, 0.2 mmol racemic 1-PE and 0.4 mmol acyl donor were firstly added into n-hexane (4.0 mL). And then, 20 mg of Hβ-ZMSs and 10 mg of Novozym®435 were added into the above-mentioned reaction mixture. The reaction mixture was irradiated by microwave under magnetic stirring at 50 ^{o}C for a desired time. The DKR processes of 1-(4-bromophenyl)-ethanol and 1-(p-tolyl) ethanol catalyzed by (Hβ-PDDA@CALB)MSs and mixed catalysts using VA as acyl donor are the same as those of 1-PE at 50 ^{o}C.

Yields and enantiomeric excess (*ee*) of products (ee_p) and *ee* of substrates (ee_s) were monitored by gas chromatography (GC, Shimadzu GC 2010 Plus) on a CP-CHIRASIL-DEX CB chiral column (25 m × 0.25 μm, CP7502) with FID detection and calculated with area normalization method. The ee_s and conversion of substrate, and the selectivity, yield and *ee* of the R-ester, as well as the enzyme activity (EA) of free and immobilized CALB were calculated by the following equations:

$$ee_s = \frac{[\text{Substrate}]_{(R,t)} - [\text{Substrate}]_{(S,t)}}{[\text{Substrate}]_{(R,t)} + [\text{Substrate}]_{(S,t)}} \times 100\% \quad (1)$$

$$\text{Conv.} = \frac{[\text{Product}]_{(t)} + [\text{By-product}]_{(t)}}{[\text{Product}]_{(t)} + [\text{By-product}]_{(t)} + [\text{Substrate}]_{(t)}} \times 100\% \quad (2)$$

$$\text{Selec.} = \frac{[\text{Product}]_{(t)}}{[\text{Product}]_{(t)} + [\text{By-product}]_{(t)}} \times 100\% \quad (3)$$

$$\text{Y.} = \text{Conv.} \times \text{Selec.} \quad (4)$$

$$ee_p = \frac{[\text{Product}]_{(R,t)} - [\text{Product}]_{(S,t)}}{[\text{Product}]_{(R,t)} + [\text{Product}]_{(S,t)}} \times 100\% \quad (5)$$

$$\text{EA} = \frac{[\text{Product}]_{(t)} \times \text{V}}{\text{t} \times \text{m}_{\text{CALB}}} \quad (6)$$

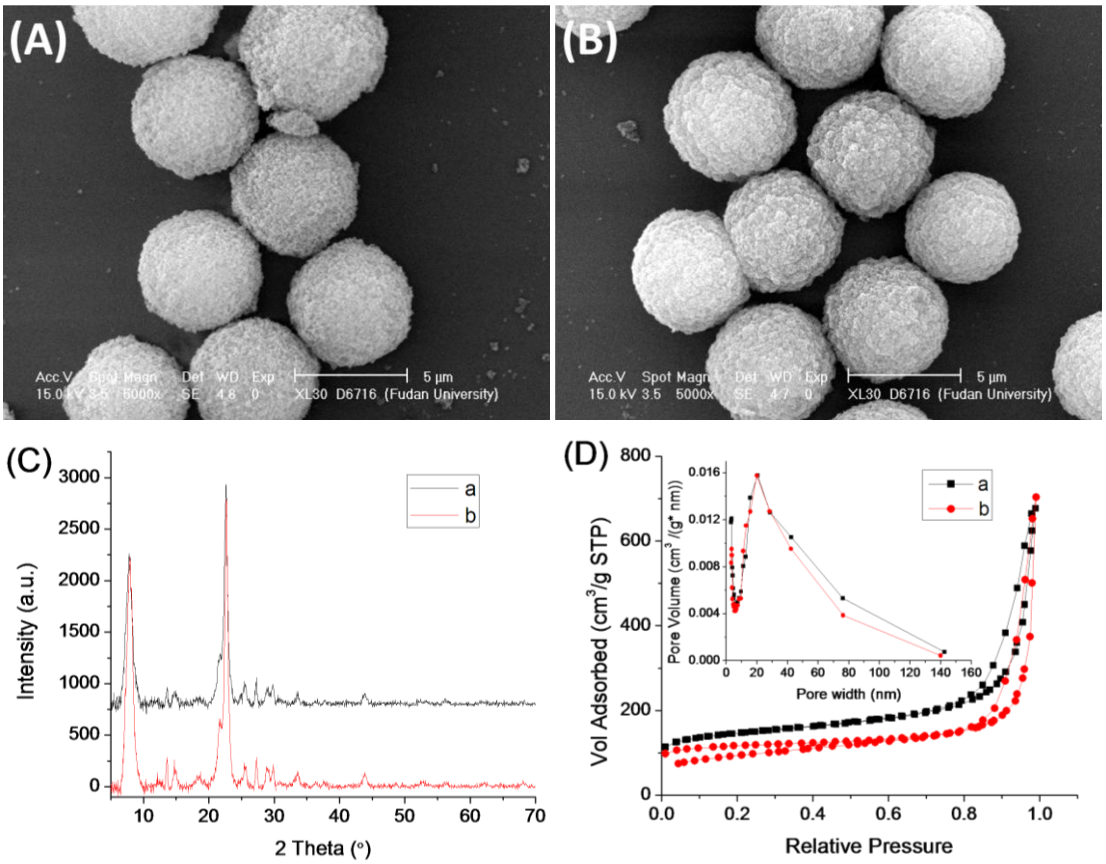


Fig. S1 SEM images of (A) Hβ-ZMSs and (B) (Hβ-PDDA@CALB)MSs as well as XRD patterns (C) and N_2 adsorption/desorption isotherms and pore size distributions (D) of (a) Hβ-ZMSs and (b) (Hβ-PDDA@CALB)MSs.

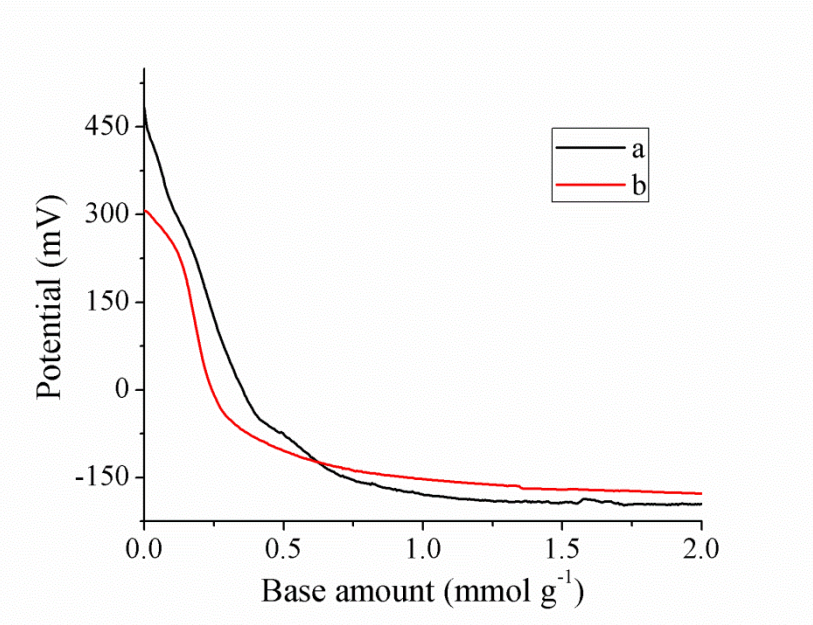


Fig. S2 Potentiometric titration curves of (a) Hβ-ZMSs (b) (Hβ-PDDA)MSs. Typically, the solid (0.10 g) was suspended in 25 mL of acetonitrile, and agitated for 3 h. Then, the suspension was titrated with 0.025 mol L^{-1} n-butylamine in acetonitrile at a rate of 0.1 mL min^{-1} on a potentiometeric titration meter (ZDJ-5, Shanghai Leici instrument Factory). The electrode potential variation was measured with a manual continuous titration model using a double junction electrode. The addition continued until no further change of voltage was recorded. The initial electrode potential (E_i) indicates the maximum acid strength and the value of meq amine/g solid at the beginning of the plateau indicates the total acid amount.

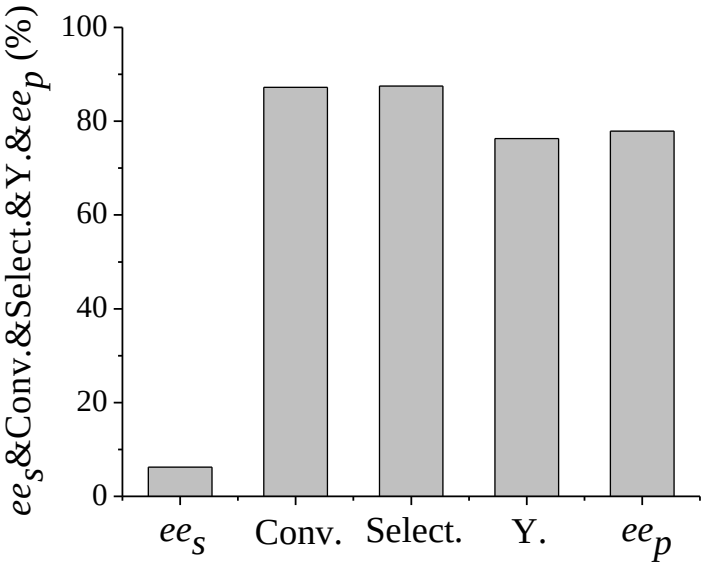


Fig. S3 DKR result of 1-PE catalyzed by mixed (Hβ-PDDA)MSs and Novozyme® 435 catalysts using VA as acyl donor at 50 ^{o}C. The concentrations of 1-PE and VA are 50 and 100 mmol L^{-1}, respectively. The reaction time is 1 h.

Table S1. The physical and textural properties of Hβ-ZMSs and (Hβ-PDDA@CALB)MSs.

Catalyst	S_{BET}[a] ($m^2\ g^{-1}$)	$S_{micropore}$ ($m^2\ g^{-1}$)	$S_{external}$ ($m^2\ g^{-1}$)	$V_{micropore}$[b] ($cm^3\ g^{-1}$)	$V_{mesopore}$[b] ($cm^3\ g^{-1}$)
Hβ-ZMSs	605	459	146	0.23	0.63
(Hβ-PDDA@CALB)MSs	397	285	111	0.14	0.43

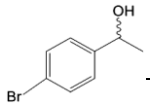
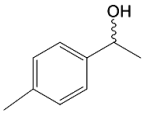
[a] Micropore area and external surface area were calculated by t-plot method. [b] Micropore and mesopore volumes were obtained by t-plot method and desorption data using BJH model between 1.7 and 300 nm width, respectively.

Table S2. The immobilized amount and EA of CALB on Hβ-ZMSs and (Hβ-PDDA)MSs as well as the EA of free CALB.

	Immobilized amount of CALB[a] (mg g^{-1})	EA of immobilized CALB[b] (μmol mg^{-1} min^{-1})
Free CALB	--	0.17
Hβ-ZMS@CALB	210	not detected
(Hβ-PDDA@CALB)MS	83	0.80

[a] The immobilization of CALB achieved in the aqueous solution of 2 mL containing 6 mg of CALB and 20 mg of Hβ-ZMSs or (Hβ-PDDA)MSs at 35 ℃. The immobilization amounts of CALB was obtained through measuring the UV absorbance of the protein solution at λ = 220 nm before and after adsorption. To accurately calculate the adsorption amount, the curve was calibrated by using a series of CALB solutions with different concentrations before measurement. The immobilized amount of CALB was expressed as: mg enzyme (g carrier) $^{-1}$, which is abbreviated as mg g^{-1}. [b] The EA of CALB immobilized on the Hβ-ZMSs and (Hβ-PDDA)MSs and free CALB were identified by their catalytic performances in the trans-esterification of rac-1-PE. In the catalytic process, 0.20 mmol of rac-1-PE and 0.40 mmol of VA were added into n-hexane (4.0 mL), and then, the immobilized/free CALB were added into the reaction medium. The reaction mixture was irradiated by microwave under magnetic stirring at 50 ℃ for 15 min. The activity of CALB was obtained and normalized against the time and the amount of CALB. The activity unit was expressed as: μmol product (mg enzyme) $^{-1}$ (reaction min)$^{-1}$, which is abbreviated as μmol mg^{-1} min^{-1}.

Table S3. DKR results of 1-(4-bromophenyl)-ethanol and 1-(p-tolyl) ethanol catalyzed by (Hβ-PDDA@CALB)MSs and mixed catalysts using VA as acyl donor at 50 °C.[a]

Substrate	Catalyst	t (h)	Results of DKR				
			ee_s (%)	Conv. (%)	Select. (%)	Y. (%)	ee_p (%)
	(Hβ-PDDA@CALB)MSs	1	66.4	47.4	93.6	44.4	97.9
		2	64.3	62.7	94.2	59.1	96.6
		3	69.0	69.8	93.5	65.2	95.5
	Hβ-ZMSs + Novozyme®435	0.25	48.9	60.1	92.7	55.7	88.9
		0.5	12.5	83.6	91.8	76.7	79.4
		1	7.3	94.9	88.5	84.0	58.2
	(Hβ-PDDA@CALB)MSs	1	11.4	44.6	84.7	37.8	77.1
		2	15.5	67.6	84.4	57.1	76.5
		3	15.8	77.6	84.8	65.8	76.0
	Hβ-ZMSs + Novozyme®435[b]	0.25	5.3	81.5	68.8	56.1	26.2
		0.5	18.6	97.7	58.8	57.4	2.3

[a] The concentrations of substrate and VA are 50 and 100 mmol L^{-1}, respectively. [b] 10 mg Hβ-ZMSs and 5 mg Novozyme®435 are used.