Supplementary Information for

A supraparticle-based biomimetic cascade catalyst for continuous flow reaction

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**C Textural parameters of SPs prepared with different amounts of TEPA**

| Samples         | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $V$ (cm$^3$ g$^{-1}$) | Pore Size (nm) |
|-----------------|-----------------------------------|-----------------------|----------------|
| 8 wt% TEPA      | 102                               | 0.30                  | 5.1            |
| 12 wt% TEPA     | 30                                | 0.19                  | —              |

**Supplementary Figure 21.** N$_2$ sorption measurement results of SPs prepared with different amounts of TEPA. **a,** N$_2$ adsorption-desorption isotherms, offset vertically the prior one by 140. **b,** BJH pore size distribution plots, offset vertically the prior one by 0.6. **c,** Textural parameters of SPs.
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**Textural parameters of SPs prepared with different sizes of MSNs**

| Samples | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | V (cm$^3$ g$^{-1}$) | Pore Size (nm) |
|---------|---------------------------------|---------------------|----------------|
| 20 nm   | 124                             | 0.9                 | -              |
| 60 nm   | 201                             | 0.78                | 3.9            |
| 180 nm  | 340                             | 0.78                | 4.1            |
| 880 nm  | 20                              | 0.05                | -              |

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**Textural parameters of amine-modified MSNs and octyl-modified MSNs**

| Samples                | S$_{BET}$ (m$^2$ g$^{-1}$) | V (cm$^3$ g$^{-1}$) | Pore Size (nm) |
|------------------------|-----------------------------|---------------------|-----------------|
| amine-modified MSNs    | 327                         | 0.84                | 4.5             |
| octyl-modified MSNs    | 561                         | 1.47                | 4.7             |

**Supplementary Figure 28.** N$_2$ sorption measurement results of amine-modified MSNs and octyl-modified MSNs. **a,** N$_2$ adsorption-desorption isotherms. **b,** BJH pore size distribution plots. **c,** Textural parameters of amine-modified MSNs and octyl-modified MSNs.
**C Textural parameters of Pd/MSNs and CALB/MSNs**

| Samples   | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | V (cm$^3$ g$^{-1}$) | Pore Size (nm) |
|-----------|----------------------------------|---------------------|----------------|
| Pd/MSNs   | 281                              | 0.85                | 4.2            |
| CALB/MSNs | 416                              | 0.83                | 4.1            |

**Supplementary Figure 29.** $N_2$ sorption measurement results of Pd/MSNs and CALB/MSNs.  

- **a**, $N_2$ adsorption-desorption isotherms, offset vertically the prior one by 200.  
- **b**, BJH pore size distribution plots, offset vertically the prior one by 0.8.  
- **c**, Textural parameters of Pd/MSNs and CALB/MSNs.
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Supplementary Figure 31. Kinetic profiles of individual step and cascade reactions.

**a**, Kinetic results for acetophenone hydrogenation over Pd/SPs, reaction condition: 0.2 mmol acetophenone, 2.0 mL n-octane, 2 MPa H₂, 50 °C and the molar ratio of acetophenone to Pd (S/C) = 56:1. **b**, Kinetic results for kinetic resolution of 1-phenylethanol over CALB/SPs, reaction condition: 0.2 mmol 1-phenylethanol, 0.8 mmol vinyl acetate, 2.0 mL n-octane, 50 °C. **c**, Kinetic results for sequential hydrogenation-kinetic resolution of acetophenone over Pd-CALB/SPs, 0.2 mmol acetophenone, 0.8 mmol vinyl acetate, 2.0 mL n-octane, 2 MPa H₂, 50 °C and the molar ratio of acetophenone to Pd (S/C) = 56:1.
Supplementary Figure 3.2. Kinetic profiles of cascade of ketone hydrogenation and alcohols kinetic resolution over different catalysts in batch reactions. Reaction conditions: 60 mg catalyst, 0.20 mmol acetophenone, 0.80 mmol vinyl acetate, 2.0 mL n-octane, 2 MPa H₂, 50 °C. a, 30 mg Pd-CALB/MSNs. b, A physical mixture of 30 mg Pd/MSNs and 30 mg CALB/MSNs. c, 30 mg Pd-CALB@SPs. d, A physical mixture of 30 mg Pd/SPs and 30 mg CALB/SPs. e, 60 mg Pd-CALB/SPs.
Supplementary Figure 33. Characterization of Pd-CALB@SPs. 

a, TEM image showing the interior structure of fresh Pd-CALB@SPs (Pd NPs and CALB were co-localized on a single MSN particle). 

b, TEM image showing the interior structure of Pd-CALB@SPs after four reaction cycles. 

c, Pd 3d XPS spectra of fresh Pd-CALB@SPs. 

d, Pd 3d XPS spectra of Pd-CALB@SPs after four reaction recycles.
C Textural parameters of Pd-CALB/SPs prepared with differently sized MSNs

| Samples | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $V$ (cm$^3$ g$^{-1}$) | Pore Size (nm) |
|---------|------------------|----------------|--------------|
| 60 nm   | 241              | 0.63           | 5.1          |
| 180 nm  | 240              | 0.40           | 4.6          |

Supplementary Figure 34. N$_2$ sorption measurement results of Pd-CALB/SPs prepared with differently sized MSNs. a, N$_2$ adsorption-desorption isotherms, offset vertically the prior one by 200. b, BJH pore size distribution plots, offset vertically the prior one by 0.6. c, Textural parameters of Pd-CALB/SPs.
Supplementary Figure 35. Reaction results of sequential hydrogenation-kinetic resolution of acetophenone over SPs prepared with differently sized MSNs (at different reaction times). Reaction conditions: 60 mg catalyst, 0.20 mmol acetophenone, 0.80 mmol vinyl acetate, 2.0 mL n-octane, 2 MPa H₂, 50 °C. a, 2 h. b, 4 h. c, 6 h.
Supplementary Figure 36. Kinetic profiles of 1-phenylethanol hydrogenation and 1-phenylethyl acetate hydrogenation over Pd-CALB/SPs. Reaction condition: 60 mg catalyst, 2.0 mL n-octane, 2 MPa H₂, 50 °C. a, 0.2 mmol 1-phenylethanol. b, 0.2 mmol 1-phenylethyl acetate.
Supplementary Figure 37. Results of sequential hydrogenation-kinetic resolution of acetophenone over SPs prepared with different mass ratios of Pd/MSNs to CALB/MSNs (at different reaction time). Reaction conditions: 0.20 mmol acetophenone, 0.80 mmol vinyl acetate, 2 mL n-octane, 2 MPa H₂, 50 °C, 30 mg Pd/MSNs, 15 mg, 30 mg, 60 mg or 120 mg CALB/MSNs. a, 2 h. b, 4 h. c, 6 h. d, 8 h.
Supplementary Figure 3. Results of the cascade of hydrogenation and kinetic resolution over Pd/SPs and CALB/SPs in two-stage reactions. Reaction conditions: 0.1 M acetophenone, 0.4 M vinyl acetate in n-octane, 0.425 g Pd/SPs, 0.425 g CALB/SPs, 50 °C, 2 MPa H₂, flow rate from initial 3.0 mL h⁻¹ to 1.5 mL h⁻¹ at the end.
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Supplementary Figure 40. Characterization of Pd-CALB/SPs after 200 h of continuous flow reaction. 

**a**, TEM image of Pd/MSNs in Pd-CALB/SPs after 200 h of continuous flow reaction. 

**b**, Pd 3d XPS spectra of Pd-CALB/SPs before and after 200 h of continuous flow reaction.
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Supplementary Figure 43. Results of the cascade reaction for the synthesis of chiral 1-phenylethanol acetate over H-beta-CALB/SPs in a continuous flow system.

Reaction condition: 1 g H-beta-CALB/SPs packed in a fixed-bed reactor, 0.1 M 1-phenylethanol and 0.4 M vinyl acetate in n-octane, 45 °C, flow rate at 2.5 mL h⁻¹ from 0 to 300 h, flow rate at 2.0 mL h⁻¹ from 300 to 450 h and 1.5 mL h⁻¹ after 450 h.
Supplementary Figure 44. Characterization of Pd-CALB/SPs after 500 h of continuous flow reaction. a, SEM image of Pd-CALB/SPs after 500 h of continuous flow reaction. b, SEM image showing the interior structure of Pd-CALB/SPs after 500 h of continuous flow reaction. c, TEM image of Pd-CALB/SPs after 500 h of continuous flow reaction. d, N$_2$ adsorption-desorption isotherm of Pd-CALB/SPs after 500 h of continuous flow reaction. e, BJH pore size distribution plot of Pd-CALB/SPs after 500 h of continuous flow reaction. f, Mechanical strength for Pd-CALB/SPs before and after 500 h of continuous flow reaction. Error bars indicate the standard error from 20 samples averages. g, TG curves of Pd-CALB/SPs after 500 h of continuous flow reaction. h, Pd 3$d$ XPS spectra of Pd-CALB/SPs before and after 500 h of continuous flow reaction.
Supplementary Figure 45. Results of testing CALB activity in the eluent from sequential amine racemization-kinetic resolution. Reaction condition: 0.1 mmol 4-methyl-2-pentanol, 0.4 mmol vinyl acetate and 10 mL outflow from the fixed-bed reaction (amine racemization and kinetic resolution over Pd-CALB/SPs), 50 °C.

Notes: To check whether the flow process leads to the leaching of CALB from Pd-CALB/SPs, we examined the catalytic activity of the outflow by adding another substrates (4-methyl-2-pentanol) instead of previous 1-phenylamine. As shown above, no new products were determined even during 12 h of reaction, indicating no significant CALB leaching from the fixed-bed reactor. Moreover, a protein assay was also performed to further examine the CALB leaching. The result was determined to be below the detection limit.
**Supplementary Table 1.** Results of ICP-MS analysis of Pd-CALB/SPs before and after 200 h of continuous flow reaction

| sample                                      | Pd (wt%) | P (wt%) |
|---------------------------------------------|----------|---------|
| Pd-CALB/SPs                                 | 0.63     | 0.12    |
| Pd-CALB/SPs after 200 h continuous flow     | 0.54     | 0.10    |

**Supplementary Table 2.** Results of ICP-MS analysis of Pd-CALB@SPs before and after four reaction recycles

| sample                                      | Pd (wt%) | P (wt%) |
|---------------------------------------------|----------|---------|
| Before reaction                             | 1.25     | 0.36    |
| After four reaction recycles                | 1.00     | 0.33    |

**Supplementary Table 3.** Loadings of Pd and CALB in various catalysts

| sample                                      | Pd (wt%) | CALB (mg g\(^{-1}\)) |
|---------------------------------------------|----------|-----------------------|
| Pd-CALB/MSNs                                | 1.25     | 47.3                  |
| Pd/MSNs                                     | 1.26     |                       |
| CALB/MSNs                                   |          | 46.5                  |
| Pd-CALB@SPs                                 | 1.25     | 47.3                  |
| Pd/SPs                                      | 1.26     |                       |
| CALB/SPs                                    |          | 46.5                  |
| Pd-CALB/SPs                                 | 0.63     | 23.3                  |
**Supplementary Table 4.** Results of ICP-MS analysis of Pd-CALB/SPs before and after 500 h of continuous flow reaction

| sample                        | Pd (wt%) | P (wt%) |
|-------------------------------|----------|---------|
| Before reaction               | 0.65     | 0.125   |
| After 500 h continuous-flow   | 0.55     | 0.09    |
Supplementary Methods

1. Chemicals
Toluene (AR), n-octane (AR), dimethyl sulfoxide (AR), cyclohexane (AR), p-xylene (AR), ethyl acetate (AR), sodium dihydrogen phosphate (NaH$_2$PO$_4$) and dibasic sodium phosphate (Na$_2$HPO$_4$) were procured from Sinopharm Chemical Reagent Co., LTD, (China). Concentrated hydrochloric acid (37 wt%) was bought from QiXian Hui Hong Yuan Chemical Co., LTD Company. Native Lipase B from Candida Antarctica (CALB) was purchased from Novozymes. Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$, Mv~5800), ammonium fluoride (NH$_4$F, AR), tetraethyl orthosilicate (TEOS, AR), n-hexylamine (99%), (octyl)-trimethoxysilane (97%), hexadecyltrimethylammonium chloride (CTAC, 97%), triethanolamine (TEA, AR), 3-aminopropyltriethoxysilane (APTES, 99%), sodium tetrachloropalladate (Na$_2$PdCl$_4$, 98%), sodium borohydride (NaBH$_4$, 98%), acetophenone (98%), 4'-methylacetophenone (98%), vinyl acetate (99%), ethyl methoxyacetate (98%), 1-phenylethylamine (98%), 1-(4-methylphenyl)ethyamine (97%), 1-(4-fluorophenyl)ethylamine (97%), 1,2,3,4-tetrahydro-1-naphthylamine (98%), 1-(4-methylphenyl)ethylamine (96%), dodecane (GC, >99%), hexadecane (98%), ethylene glycol (AR), ethanolamine (99.7%), ethylenediamine (AR), polyethylene glycol (M.W. 400), diethylenetriamine (97%), tetraethylenepentamine (TEPA), pentaethylenehexamine polyethyleneimine (PEI, M.W. 800, 98%), fluorescein isothiocyanate isomer I (FITC-I, CAS No. 3326-32-7) and Rhodamine B (CAS No. 81-88-9) were purchased from Aladdin (China). Chitosan (M.W. 800-1000), epoxy resin (Viscosity: 1100-1600 mpa.s), carboxymethylcellulose (CMC, M.W. 250000) were purchased from Macklin Biochemical Co., Ltd, (China). Nile red (CAS No. 7385-67-3) was purchased from Sigma-Aldrich. H-beta zeolite was purchased from Nankai University Catalyst Co., Ltd, (China). TiO$_2$ (P25) was purchased from Degussa.

Water used in this study was deionized water.

2. Characterization
Transmission electron microscopy (TEM) images were obtained on a JEM 2000EX (operated at 200 kV). Samples for TEM observations were prepared by dispersing the
sample powder in ethanol using ultrasound and then allowing a drop of the suspension to evaporate on a copper grid covered with a holey carbon film. Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6700F field-emission electron microscope. EDS elemental maps were recorded on this instrument. Nitrogen-sorption measurements were performed at −196 °C on a Micromeritics ASAP 2020 analyzer. Before measurement, all samples were outgassed at 150 °C under vacuum for 6 h. The specific surface area was calculated from the adsorption branch in the relative pressure range of 0.05-0.15 using the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was performed under an ultrahigh vacuum on a Kratos AXIS ULTRA DLD spectrometer with Al Ka radiation and a multichannel detector. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer over the range 4000–400 cm⁻¹ with 64 scans and a resolution of 2 cm⁻¹. The samples were performed under vacuum with a heating rate of 5 °C min⁻¹ to 150 °C for 2 h in vacuum, then recorded the spectra. Solid-state ¹³C-MAS NMR measurements were performed on Varian Infinity Plus 400 NMR spectrometer. The spinning rate was 4 kHz and a total number of 800 scans were recorded with 4 s recycle delay for each sample. Solid-state ¹H CP-MAS NMR measurements were performed on a Bruker AVANCE IIITM 600 MHz spectrometer. The spectra were recorded by hahn-echo method at an MAS rate of 12 kHz. The samples dehydration were carried out on glove box with 150 °C for 10 h, then packed on a zirconia rotor. Thermogravimetric (TG) measurement was performed on TA Q-600 instrument. UV-Vis determination was conducted on a TU-1900 spectrometer (China). Gas chromatography (GC) analysis was carried out on an Agilent 7890 analyzer (Agilent-19091G-B213, HP-CHIRAL-20B, CYCLODEX-B) with a flame ionization detector. The identification of products by mass spectrometry (MS) was performed on a GC-MS instrument (7890B-5977A, HP-5, Agilent). Confocal laser scanning microscopy (CLSM) images were obtained on a Carl Zeiss LSM880 instrument (Germany). The excitation wavelength of FITC-I is 488 nm (green). The excitation wavelength of Nile Red is 559 nm (red). The concentration of Rhodamine B in a
solution (a mixture of ethanol and water, 1:1 V/V) was 2×10⁻⁶ M and the excitation wavelength is 554 nm (red). The piston pump (LC-01P) used in this study was purchased from Jiangshen Technology Co., China. Viscosity measurements were performed at 25 °C on Brookfield DV-Ⅱ + Pro analyzer.

3. Material synthesis

**Preparation of spongy porous silica.** Mesoporous silica nanoparticles were prepared according to the reported method¹. Typically, 4.8 g P123 was dissolved in 168 mL HCl solution (1.30 M). Then, the resultant suspension was stirred at 40 °C until the solution became clear, followed by addition of 0.054 g NH₄F. After stirring at this temperature for 10 min, a mixture of 21.64 g n-octane and 8.1 g TEOS was then added into the above solution. The resulting mixture was keep stirred at 40 °C for 24 h and then transferred into an autoclave for further condensation at 100 °C for 48 h. The resultant solid was collected by filtration, then dried in air and calcined at 550 °C for 5 h, eventually leading to the spongy porous silica.

**Preparation of hydrophobic spongy porous silica.** 1.0 g as-synthesized spongy porous silica (dried at 120 °C for 4 h) were dispersed into 50 mL p-xylene using sonication for 20 min. Then, 4 mmol (octyl)-trimethoxysilane and 4 mmol n-hexylamine were added into this suspension. This mixture was stirred under a N₂ atmosphere at 130 °C for 10 h. The solid particles were collected through centrifugation, washed with toluene and dried, yielding octyl-modified spongy porous silica.

**Preparation of mesoporous silica nanospheres (MSNs).** MSNs were prepared according to a previously reported method². 0.36 g TEA was added into 112 mL CTAC aqueous solution (10 wt%). The resultant mixture was gently stirred at 60 °C for 1 h. Then, a solution of TEOS in cyclohexane (20 v/v%, 40 mL) was slowly added to the above suspension, which was maintained at 60 °C in a water bath for 12 h under magnetic stirring. The solid product was collected by centrifugation and washed for several times with ethanol. After calcination in air at 550 °C for 5 h (ramping rate, 2 °C min⁻¹), MSNs were obtained. To tune the sizes MSNs (60 or 180 nm), the temperature
for hydrolysis-condensation of TEOS was decreased down to 45 °C or increased up to 75 °C).

**Preparation of other SPs.** The MSNs was replaced by TiO$_2$ or microporous H-beta zeolite. Other procedures are the same as the synthesis of SPs made of silica nanoparticles.

**Preparation of amine-modified MSNs.** 1.0 g MSNs (dried at 120 °C for 4 h) were dispersed into 50 mL toluene. Then 1 mL APTES was added into this suspension. This mixture was stirred under N$_2$ atmosphere at 110 °C for 4 h. The solid particles were collected through centrifugation, and washed with toluene and dried, yielding amine-modified MSNs.

**Preparation of octyl-modified MSNs.** 1.0 g MSNs (dried at 120 °C for 4 h) were dispersed into 50 mL toluene. Then, 0.234 g (octyl)-trimethoxysilane and 0.101 g n-hexylamine were added into this suspension. The solid particles were collected through centrifugation, and washed with toluene and then dried, eventually yielding octyl-modified MSNs.

**Preparation of CALB-immobilized MSNs (CALB/MSNs).** 0.5 g octyl-functionalized MSNs were added into 45 mL enzyme solution consisting of 7.5 mL crude CALB (8.0 mg mL$^{-1}$ of protein) and 37.5 mL phosphate buffer solution (PBS: 0.05 M Na$_2$HPO$_4$-0.05 M NaH$_2$PO$_4$, pH = 7.4). To increase the dispersion of MSNs, 5 mL ethanol was also added this mixture. After slowly rotating at 25 °C for 12 h, the solid material was isolated by filtration, and washed three times with PBS (pH = 7.4, 0.05 M). After that, the obtained material was filtered out and dried under vacuum. The obtained material is denoted as CALB/MSNs. The loading of CALB on the solid materials was calculated on the basis of the difference in the CALB concentration in the PBS between before and after adsorption (Bradford method).

**Preparation of Pd NPs-supported MSNs (Pd/MSNs).** Pd nanoparticles (NPs) were supported on the amine-modified MSNs according to reported procedure.$^3$ 0.2 g amine-modified MSNs was dispersed into 50 mL of deionized water via sonication, leading to
a suspension. After this suspension was stirred for 10 min at 30 °C, 1.88 mL of fresh Na₂PdCl₄ aqueous solution (20 mM) was added dropwise. After stirring at 30 °C for 4 h, 3.0 mL of 0.1 M NaBH₄ solution was added. The resultant mixture was aged at this temperature for 20 h. The resultant solid was collected by centrifugation, washed with water and dried, yielding Pd/MSNs.

**Preparation of Au clusters labelled CALB.** Au clusters-labeled CALB were prepared according to the reported procedure⁴. In a typical synthesis, 2.0 mL of aqueous HAuCl₄ solution (2.5×10⁻³ M) was added to 9 mL of CALB solution (consisting of 1.5 mL crude CALB and 7.5 mL PBS, pH = 7.4, 0.05 M). The mixture was mixed by stirring for 5 min. Afterward, a few droplets of aqueous NaOH solution (0.1 M) were added to this mixture to adjust the pH to ~11. Then, the resultant mixture was heated to 90 °C under gentle stirring for 24 h, leading to an orange aqueous suspension. The solid was isolated from this suspension through centrifugation and then washed several times with PBS, eventually leading to Au clusters labeled CALB. The immobilization procedure of the Au clusters labeled CALB composites on MSNs was the same as the immobilization of CALB on MSNs.

**Preparation of fluorescently labelled silica materials.** 1.0 g silica materials (such as spongy porous silica, hydrophobic spongy porous silica, MSNs, CALB/MSNs or Pd/MSNs) and 0.001 mmol 3-aminopropyltriethoxysilane (APTES) were added into 20 ml toluene. After stirring under a N₂ atmosphere at 60 °C for 2 h, the resultant solid particles were collected through filtration, washed four times with toluene and dried, resulting in amino-modified silica particles. 0.5 g amino-modified silica particles and 0.005 g fluorescein isothiocyanate isomer I (FITC-I) were added into 50 mL ethanol. The mixture was stirred overnight at room temperature in the dark. After filtration, the solid was washed five times with ethanol and dried under vacuum, yielding FITC-I-labelled silica. For the preparation of Rhodamine B-labelled silica, samples were prepared by a similar method but with water as the solvent.

4. Mechanical stability test
0.2 g SPs were filled into a quartz column (diameter of 0.7 cm and length of 10 cm) and were subjected to be fluidized with N₂ at a superficial velocity of 0.3 m s⁻¹ for 24 h. Likewise, 0.5 g SPs were directly packed in a fixed-bed reactor and treated with flowing n-octane (flow rate: 6 mL h⁻¹) at 4 MPa N₂ (50 mL min⁻¹) for 48 h. After the treatment, the sample was collected for SEM observation and TG test.

5. Fluorescent permeability tests.
SPs were deposited on a glass slide. 30 μL Rhodamine B solution (2×10⁻⁵ M in a mixture of water and ethanol, V/V = 1:1) was gently dropped on the glass slide. The diffusion of Rhodamine B molecules into the interior of SPs was recorded by fluorescence microscopy at intervals.

6. Pd-CALB/SPs catalyzed cascade reactions.
Cascade of hydrogenation and kinetic resolution over Pd-CALB/SPs in batch system. 10 mg dodecane as an internal standard, 2 mL n-octane containing 0.1 M acetophenone and 0.4 M vinyl acetate were added to a 100 mL Teflon-lined steel autoclave. 30 mg Pd-CALB/MSNs, a physical mixture of 30 mg Pd/MSNs and 30 mg CALB/MSNs, 30 mg Pd-CALB@SPs, a physical mixture of 30 mg Pd/SPs and 30 mg CALB/SPs, 60 mg Pd-CALB/SPs (3.52-3.55 μmol Pd and 1.40-1.42 mg CLAB applied for all the reactions) were then added into the above solution, respectively. Before reaction, the autoclave was sealed and flushed with H₂ five times to remove the air. After being charged with a 2 MPa H₂ at room temperature, the autoclave was then heated to 50 °C while being stirred (600 rpm) for reaction to occur. The autoclave was allowed to cool to room temperature after reaction. The products were analyzed by GC at intervals and further confirmed with GC-MS. The catalyst was isolated from the reaction mixture via filtration, thoroughly washed with n-octane five times, and then dried at 50 °C under a vacuum, ready to be used in the next reaction cycle.

Sequential hydrogenation-kinetic resolution over Pd-CALB/SPs in continuous-flow system. In a typical reaction, 0.85 g Pd-CALB/SPs (0.050 mmol Pd; 19.8 mg CALB) and 0.2 g CALB/SPs (9.3 mg CALB) were mixed with quartz sand (120-160
mesh) to pack in a fixed-bed, at bottom and top of which were filled with quartz sand (40-60 mesh). Before reaction, the catalyst was flushed with H\textsubscript{2} at 2 MPa to remove air. Subsequently, a solution of ketone (0.1 M), vinyl acetate (0.4 M) and dodecane (internal standard) in n-octane as mobile phase was pumped through the inlet of the column reactor at a given flow rate and was allowed to pass through the column reactor whose temperature was kept at 50 °C. The outflow of the column reactor was sampled for GC analysis at regular intervals. The product was further confirmed with GC-MS.

**Cascade reaction for the synthesis of chiral 1-phenylethanol acetate over H-beta-CALB/SPs in continuous-flow system.** In a typical reaction, 1 g H-beta-CALB/SPs (CALB loading, 23.3 mg g\textsuperscript{-1}) was packed in a fixed-bed reactor. A solution of 1-phenylethanol (0.1 M) and vinyl acetate (0.4 M) in n-octane as mobile phase was pumped through the inlet of the column reactor at a given flow rate and was allowed to pass through the column reactor whose temperature was kept at 45 °C. The outflow of the column reactor was sampled for GC analysis at regular intervals. The product was further confirmed with GC-MS.

**Sequential amine racemization-kinetic resolution over Pd-CALB/SPs in the continuous-flow system.** In a typical reaction, 0.85 g Pd-CALB/SPs mixed with a small amount of quartz sand (120-160 mesh) were packed in a fixed-bed, at bottom and top of which were filled with quartz sand (40-60 mesh). Before reaction, the catalyst was flushed with 5% H\textsubscript{2}/95% N\textsubscript{2} at 1 MPa (10 mL min\textsuperscript{-1}) to remove air. Subsequently, a solution of amine (0.1 M), ethyl methoxyacetate (0.2 M) and n-hexadecane (internal standard) in toluene as mobile phase was pumped through the inlet of the column reactor at a given flow rate (flow rate at 1.2 mL h\textsuperscript{-1} within first 190 h, flow rate at 1.0 mL h\textsuperscript{-1} from 190 to 290 h, flow rate at 0.72 mL h\textsuperscript{-1} from 290 to 390 h and 0.6 mL h\textsuperscript{-1} after 500 h.) and was allowed to pass through the column reactor whose temperature was kept at 70 °C. After running for 500 h, about 466 mL of the amine solution was used. The outflow of the column reactor was sampled for GC analysis at regular intervals. The product was further confirmed with GC-MS.
Supplementary Mass Spectrometry Data

[Graph showing mass spectrometry data with m/z values and abundances]
Supplementary References

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