Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Dynamic Kinetic Resolution of Aromatic *sec*-Alcohols by using a Heterogeneous Palladium Racemization Catalyst and Lipase

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Chemicals and reagents

Novozym® 435 (immobilized lipase B from *Candida antarctica*) were purchased from Sigma-Aldrich Inc. (USA) and used without any other treatments.

Experimental

Catalyst preparation

Synthesis of oleylamine-capped Pd nanoparticles (NPs). Oleylamine-capped Pd NPs were synthesized following the similar method as we reported previously.[1] Briefly, 75 mg of palladium (II) acetylacetonate [Pd(acac)$_2$] was mixed with 5 mL of oleylamine under a nitrogen flow. The formed solution was heated to 333 K in 10 min, resulting in a nearly colorless solution. 300 mg of *tert*-butylamine borane (TBAB) was dissolved in 2 mL of oleylamine and quickly injected into the clear Pd-oleylamine solution. A visible color change from colorless to a brown-black was observed. The temperature was raised to 363 K (3 K/min) and kept at this temperature for 60 min. After the solution was cooled down to room temperature, 30 mL of ethanol was added and the product was centrifuged at 8000 rpm for 8 min. The Pd NPs colloids were then re-dispersed in 50 mL of *n*-hexane.

Synthesis of Pd@SBA-15. SBA-15 silica was synthesized according to the method reported by Zhao et al..[2] The immobilization of Pd NPs onto SBA-15 proceeded as follows: 0.65 g of SBA-15 was added into the oleylamine-capped Pd NP colloid (13 mg Pd) dispersed in 25 mL of *n*-hexane. After being ultrasonicated for 2 h, the solution was stirred for another 10 h at room temperature. The color of the silica turned dark while the supernatant solution became colorless, indicating that the oleylamine-capped Pd NPs were immobilized on the support. After *n*-hexane was removed by rotary evaporation, the product was refluxed in 25 mL of acetic acid at 343 K for 10 h to remove the excess oleylamine. Afterward, 40 mL of ethanol was added and stirred for 5 min. The slurry was obtained by centrifugation and washing with plenty of ethanol. Finally, the as-synthesized Pd@SBA-15 was dried at 373 K for 4 h.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna 550 spectrometer by KBr technique. The crystalline structure was determined by X-ray diffraction (XRD; Rigaku D/Max-RB with Cu Kα radiation). The catalyst shapes and morphologies were observed by the transmission electron microscopy (TEM; JEOL JEM2100). The surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS; ULVAC-PHI PHI5000 VersaProbe system using Al Kα radiation). All the binding energy (BE) values were calibrated by using C 1*s* = 284.6 eV as a reference. N_2 adsorption-desorption isotherms were obtained at 77 K using a Quantachrome NOVA 4000e apparatus. By N_2 adsorption, the Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was calculated by using the multiple-point BET method in the relative pressure range of P/P_0 = 0.05-0.2. The pore volume and pore size distribution curve were obtained by the Barrett-Joyner-Halenda model.

Activity Test

Racemization of (S)-1-phenylethanol (S-PE). Racemization reactions were carried out in 10-mL stainless steel autoclaves containing Pd@SBA-15 (50 mg Pd), 0.5 mmol of *S*-PE, 4 mL of solvent, and 0.01-0.04 MPa of hydrogen at 343 K. To easily obtain hydrogen pressures below 0.1 MPa, a 5% hydrogen dilution in argon was used as reactive gas. Microwave-assisted reaction was carried out in a closed glass tube by using a commercially available microwave synthesis equipment (MAS-1 SINEO). The reaction mixture was flushed with a 5%H_2/Ar flow before vial was closed. The hydrogen partial pressure inside vial was 0.03 MPa. The reaction temperature was controlled by a continuous focused microwave power delivery system with power from 0-1360 W and a microwave frequency source of 2450 MHz. The processes were monitored on a gas chromatography (Shimadzu GC-17A) with a CP-CHIRASIL-DEX CB chiral column (25 m × 0.25 μm, CP7502) and FID detection using *n*-decane as an internal standard.

Dynamic kinetic resolution (DKR) of racemic 1-phenylethanol (rac-PE). Typial DKR reactions were carried out under the same conditions as above but with 0.5 mmol of *rac*-PE as reactant, 100 mg of Novozyme® 435 as acylation catalyst and 1.5 mmol of vinyl acetate as acyl donor. After cooling to room temperature at the end of the reaction, the catalyst was separated by centrifugation and washed with *n*-hexane for further characterizations and applications. The products were analyzed by the GC as mentioned above.

References

1. Y. Xu, J. Q. Ma, Y. F. Xu, L. Xu, L. Xu, H. X. Li and H. Li, *RSC Adv.*, 2013, **3**, 851.
2. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.

Supporting Figures

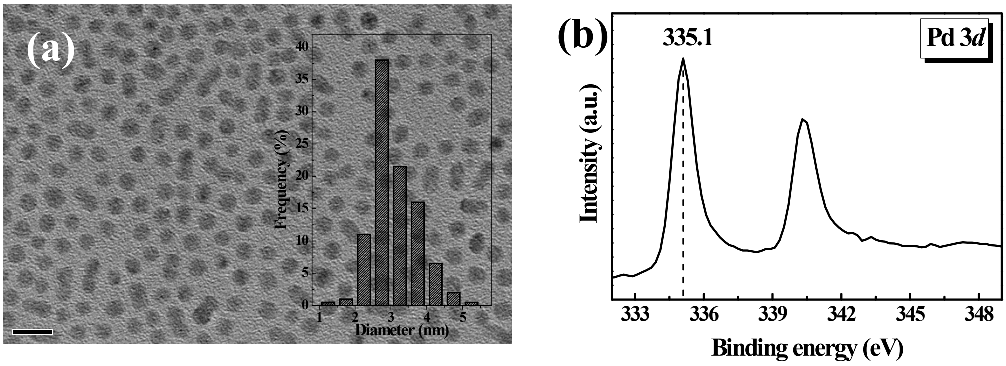


Fig. S1 (a) TEM image and the corresponding particle size distribution, (b) XPS spectrum of the as-prepared Pd nanoparticles.

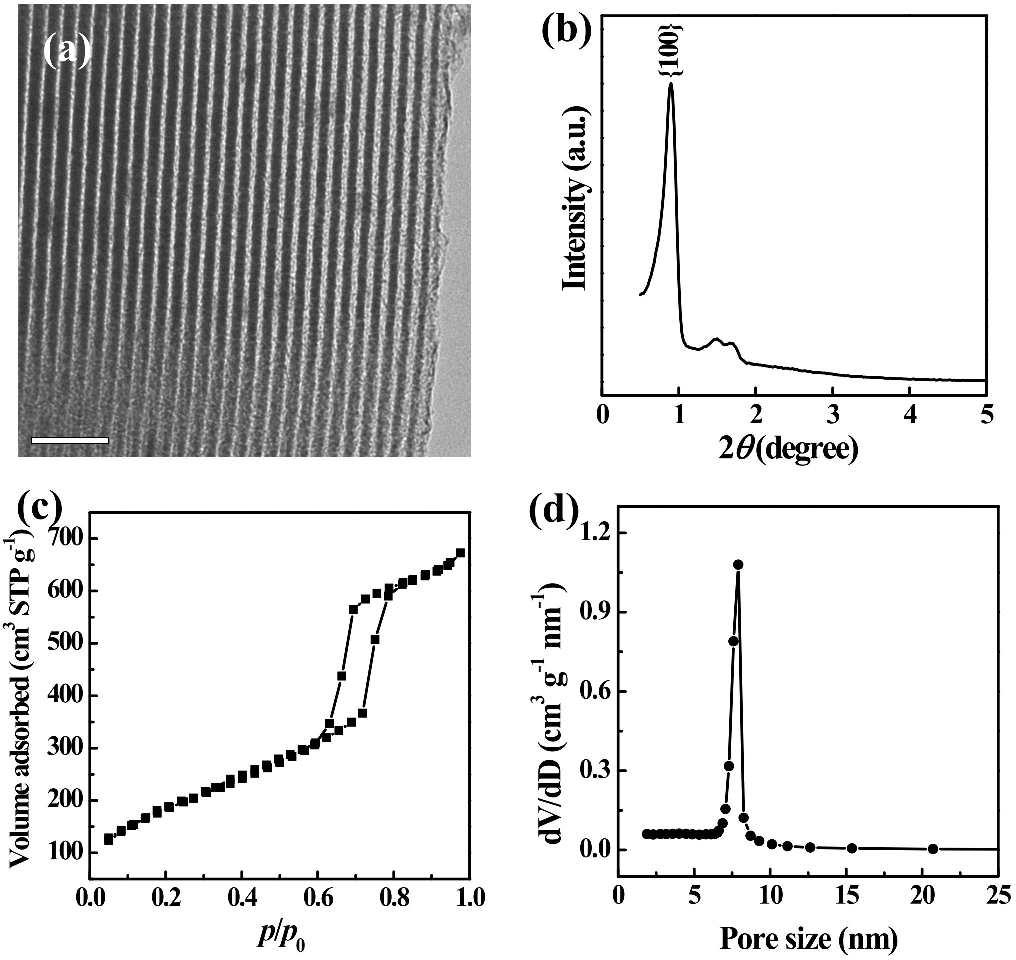


Fig. S2 (a) TEM image, (b) low-angle XRD pattern, (c) N_2 adsorption-desorption isotherms, and (d) pore size distribution of SBA-15.

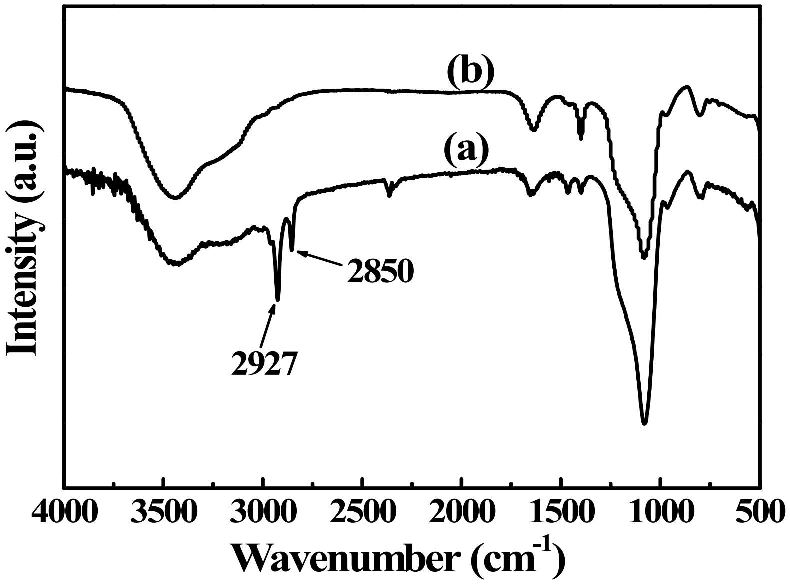
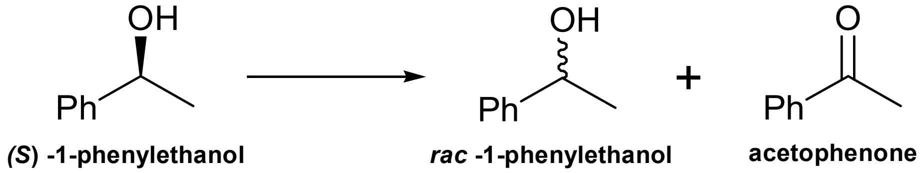


Fig. S3 FTIR spectra of Pd@SBA-15 (a) before and (b) after being washed with acetic acid.

Supporting Tables

Table S1 Pd@SBA-15-catalyzed racemization of (*S*)-1-phenylethanol[a]

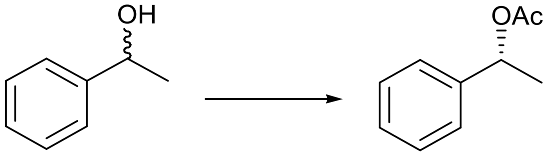


Entry	T (℃)	P_{H2} (MPa)	Solvent	t (h)	*rac*/ketone	*ee* (%)
1	60	0.03	*n*-hexane	12	97/3	30
2	70	0.03	*n*-hexane	12	96/4	4
3	80	0.03	*n*-hexane	12	94/6	3
4	90	0.03	*n*-hexane	12	92/8	3
5	70	0.01	*n*-hexane	12	78/22	2
6	70	0.02	*n*-hexane	12	92/8	3
7	70	0.04	*n*-hexane	12	98/2	33
8	70	0.03	Toluene	12	94/6	29
9	70	0.03	DMF	12	90/10	13
10	70	0.03	*i*-PrOH	12	100/0	83
11	70	0.03	*n*-hexane	15	99/1	0
12[b]	70	0.03	*n*-hexane	2	99/1	6
13[b]	70	0.03	*n*-hexane	4	100/0	0

[a] Reaction conditions: a catalyst containing 2 mg of Pd, 0.5 mmol of (*S*)-1-phenylethanol, 4 mL of solvent.

[b] Microwave heating conditions.

Table S2 Novozym® 435-catalyzed kinetic resolution of racemic 1-phenylethanol[a]

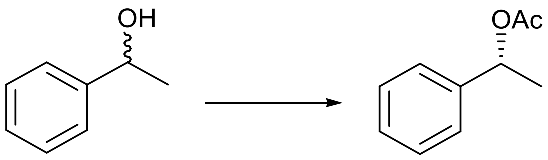


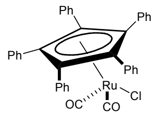
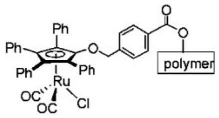
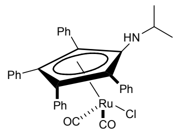
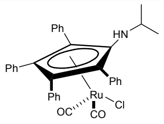
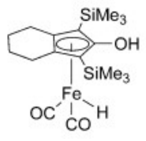
Entry	T (℃)	P_{H2} (MPa)	Solvent	t (h)	Conversion (%)	*ee* (%)
1	70	0.03	*n*-hexane	2	49	99
2[b]	70	0.03	*n*-hexane	2	49	99
3[b]	70	0.03	*n*-hexane	4	50	99

[a] Reaction conditions: a catalyst containing 100 mg of Novozym® 435, 0.5 mmol of *rac*-1-phenylethanol, 1.5 mmol of vinyl acetate, 4 mL of *n*-hexane.

[b] Microwave heating conditions.

Table S3 Comparison of the performances of different catalysts for DKR of racemic 1-phenylethanol



Cat.	*T* (℃)	*t* (h)	Yield (%)	*ee* (%)	Recycling number	Reference
 + CALB	25	3	95	99	1	1. *Angew. Chem. Int. Ed.*, 2004, **43**, 6535 2. *J. Am. Chem. Soc.*, 2005, **127**, 8817
 + Novozym® 435	25	20	99	99	3	*Org. Lett.*, 2005, 7, 4523
 + Novozym® 435	25	30	97	99	1	*Angew. Chem. Int. Ed.*, 2002, **41**, 2373
 + Surfactant-treated subtilisin	25	72	98	89	1	*J. Am. Chem. Soc.*, 2003, **125**, 11494
$AlMe_3$/binol + Novozym® 435	25	3	96	96	1	*Angew. Chem. Int. Ed.*, 2006, **45**, 6567
 + Novozym® 435	60	24	81	99	1	*Angew. Chem. Int. Ed.*, 2016, **55**, 13602
H-Beta-zeolite + Novozym® 435	60	8	90	99	2	*Chem. Commun.*, 2003, 1928

Zr-beta-zeolite + Novozym® 435	60	24 48	79 82	84.8 83.1	-	*Chem. Eur. J.*, 2007, **13**, 541
$VOSO_4$ + CALB	80	3.5	93	99	1	*Green Chem.*, 2007, **9**, 1104
$Ru(OH)_3/Al_2O_3$[a] + lipase AK on Celite	40	5	90	92	1	*ChemCatChem*, 2010, **2**, 1615
Pd@SBA-15 + Novozym® 435	70	2 4	80 89	99 99	- 6	This work

[a] DKR of *rac*-2-hydroxy-1-indanone.