

# Electronic Supplementary Material

## Diffusion process in enzyme-metal hybrid catalysts

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**Table S1** Parameters used to calculate the internal diffusion limitations of Pd/C when catalyzing the racemization reaction in toluene.

Symbol	Description	Value	Unit	Reference
$\rho_c$	Particle density	0.21	$\text{g}\cdot\text{cm}^{-1}$	[1]
$R$	Particle size	$110\times 10^{-4}$	cm	[1]
$\theta$	Porosity of the catalysts	0.4	1	[2]
$\tau$	Tortuosity of the catalysts	3	1	[2]
$r_e$	Average pore size	$2.40\times 10^{-7}$	cm	[3]
$r'(\text{obs})$	Observed reaction rate	$2.60\times 10^{-7}$	$\text{mol}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$	[4]
$C_s$	Reactant concentration	$0.20\times 10^{-3}$	$\text{mol}\cdot\text{cm}^{-3}$	[4]
$X$	Associating coefficient of the solvent	1	1	[4]
$\mu$	Viscosity of the solvent	0.006	P	[4]
$M$	Relative molecular weight of the solute	121.18	$\text{g}\cdot\text{mol}^{-1}$	[4]
$V_b$	Molar volume of the solute	128.91	$\text{cm}^3\cdot\text{mol}^{-1}$	[4]

**Table S2** Parameters used to calculate the internal diffusion limitations of Pd/C when catalyzing the *Sonogashira* reaction in water.

Symbol	Description	Value	Unit	Reference
$\rho_c$	Particle density	0.21	$\text{g}\cdot\text{cm}^{-1}$	[1]
$R$	Particle size	$110\times 10^{-4}$	cm	[1]
$\theta$	Porosity of the catalysts	0.4	1	[2]
$\tau$	Tortuosity of the catalysts	3	1	[2]
$r_e$	Average pore size	$2.40\times 10^{-7}$	cm	[3]
$r'(\text{obs})$	Observed reaction rate	$2.06\times 10^{-7}$	$\text{mol}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$	[4]
$C_s$	Reactant concentration	$0.40\times 10^{-3}$	$\text{mol}\cdot\text{cm}^{-3}$	[4]
$X$	Associating coefficient of the solvent	2.6	1	[4]
$\mu$	Viscosity of the solvent	0.0055	P	[4]

$M$	Relative molecular weight of the solute	204.01	$\text{g}\cdot\text{mol}^{-1}$	[4]
$V_b$	Molar volume of the solute	111.91	$\text{cm}^3\cdot\text{mol}^{-1}$	[4]

**Table S3** Estimated values of kinetic parameters in the DKR reaction model.

Catalyst	$k_1$	$k_2$
Pd/C + Novozyme 435	0.01	5.76
Pd/CALB-P	0.14	9.11

**Supplementary equations:**

When assuming the reaction order of CALB to substrates is 1, the rate equation can be written as:

$$\frac{d[R]}{dt} = -k_2[R] \quad (\text{S1})$$

where the integral form of Eq. (S1) is:

$$\ln \frac{[R]_0}{[R]_t} = k_2 t \quad (\text{S2})$$

The conversion rate of reactions can be defined as follows:

$$X = \frac{[R]_0 - [R]_t}{[R]_0} \quad (\text{S3})$$

Therefore, Eq. (S2) can be written as follows:

$$\ln\left(\frac{1}{1-X}\right) = k_2 t \quad (\text{S4})$$

where  $\ln(1/(1-X))$  is proportional to  $t$ .

Similarly, when assuming that the reaction order of CALB to substrates is 2, the rate

equations are written as follows:

$$\frac{d[R]}{dt} = -k_2[R]^2 \quad (S5)$$

$$\frac{1}{[R]_t} - \frac{1}{[R]_0} = k_2 t \quad (S6)$$

$$\frac{X}{1-X} = k_2 [R]_0 t \quad (S7)$$

where  $X/(1-X)$  is linearly dependent on time.

### Supplementary methods:

Here, Pd/lipase-Pluronic conjugate was selected as the model for hybrid catalysts, in comparison with the combination of immobilized lipase (Novozyme 435) and Pd/C. Pd/C refers to palladium nanoparticles (NPs) loaded on activated carbon, which was purchased from Sigma-Aldrich (St. Louis, MO, USA), labeled “10 wt.% loading, matrix carbon, dry support”. Immobilized lipase (Novozyme®435) was provided by Novozymes. Lipase used in this study was *Candida Antarctic* lipase B (CALB,  $\geq 5000$  LU/G of liquid).

Pd/CALB-Pluronic was first synthesized according to a previous study [5]. In a typical process, palladium acetate was dissolved at different concentrations in methanol (2 mL) and added to the CALB-Pluronic aqueous solution (phosphate buffer, 8 mL, 50 mM, pH 7.0) under magnetic stirring at 25 °C. Thereafter, the reaction solution was stirred for 20 h followed by dialysis against phosphate buffer (10 mM, pH 7.0) at 4 °C overnight. The powder of the nanohybrids was finally obtained by lyophilization and stored in a desiccator. Prior to characterization and utilization, the dry powder of the Pd/CALB-P nanohybrids (30 mg) was resuspended in toluene (3 mL) and reduced using  $\text{NaBH}_4$  (31.7  $\mu\text{mol}$ ) under magnetic stirring at 25 °C for 3 h. The precipitated nanohybrids were then collected by centrifugation and washed with toluene three times. The powder of the Pd/CALB-P nanohybrids was obtained by drying under vacuum at 35 °C overnight and then stored in a vacuum oven.

The size of Pd NPs was characterized by transmission electron microscopy (TEM) and was confirmed to be affected by the concentrations of palladium acetate

and CALB-Pluronic used in synthesis. According to Li's work [5], Pd NPs with a size of 0.8 nm were observed to exhibit a higher activity in experiments and thus being selected for further study. The 0.8 nm Pd/CALB-Pluronic was synthesized using 0.6 mg/ mL palladium acetate and 16.7 mg/ mL CALB-Pluronic. In addition, the average size of the Pd NPs in Pd/C was characterized to be 4.2 nm by TEM [4].

### Supplementary characterizations:

Several characterization techniques were conducted to further check the structure of materials studied in this study.

In terms of Pd/C, TEM, Brunauer-Emmett-Teller (BET) test and X-ray photoelectron spectroscopy (XPS) were applied to observe the morphology, pore structure and valence of Pd, respectively. Figure S1 shows the TEM image of Pd/C and the size distribution of the Pd NPs, where Pd particles are uniformly distributed on the carbon substrate with a mean size of 4.1 nm.

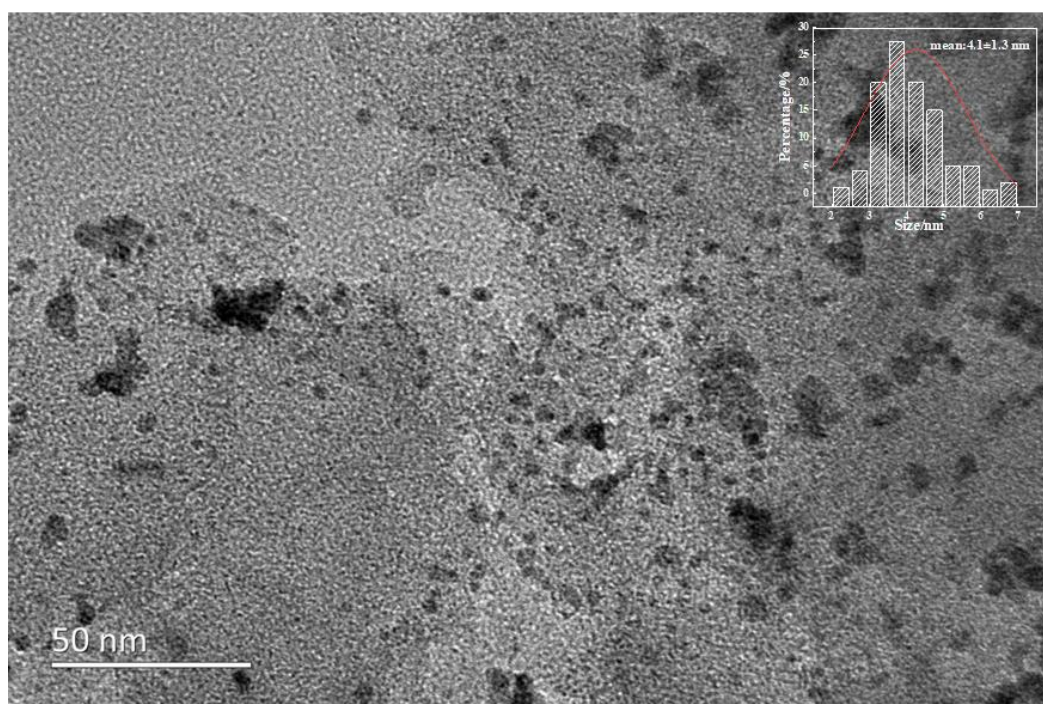


Fig. S1 TEM image and size distribution of Pd particles in Pd/C.

Pore size distribution is an important factor in diffusion process, particularly the internal diffusion. Therefore, the BET test was applied to study the pore structures of Pd/C (Fig. S2). Results indicate that the BET specific surface area of Pd/C is 786.6

$\text{m}^2 \text{g}^{-1}$  and the pore volume and average pore width are  $0.489 \text{ cm}^3 \text{ g}^{-1}$  and  $2.8 \text{ nm}$  respectively based on the density functional theory (DFT) method, which are consistent with the data reported in previous study ( $0.56 \text{ cm}^3 \text{ g}^{-1}$  of the pore volume and  $2.4 \text{ nm}$  of the average pore width) [3]. Therefore, when calculating the Weisz-Prater parameters, the average pore size of Pd/C was valued as  $2.4 \text{ nm}$  as the literature reported [3].

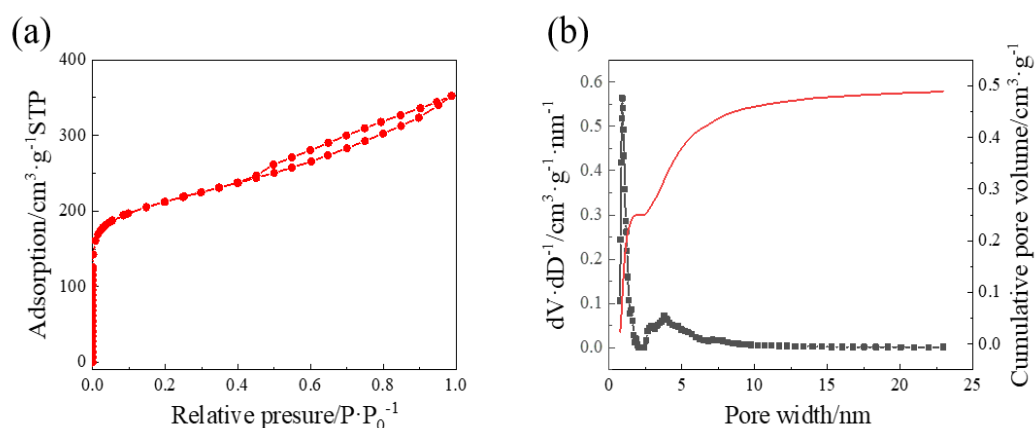


Fig. S2 BET test of Pd/C with (a) nitrogen adsorption curve and (b) DFT distribution of pore width.

XPS was conducted to investigate the valence state of Pd existing in Pd/C. As shown in Fig. S3, two peaks are observed which are resulted from the spin splitting of 3d orbitals in Pd ( $3d_{5/2}$  and  $3d_{3/2}$ ) with a distance of  $5.25 \text{ eV}$  between these peaks, where the  $3d_{5/2}$  peak is contributed by Pd(0) and Pd(+2), with the characteristic peaks located at  $335.8$  and  $337.7 \text{ eV}$ , respectively. This result indicates that there are two valence states of Pd in Pd/C which are Pd(0) and Pd(+2), similar to that in Pd/CALB-Pluronic [5]. The detailed characterization of Pd/CALB-Pluronic is available in Li's work [4, 5].

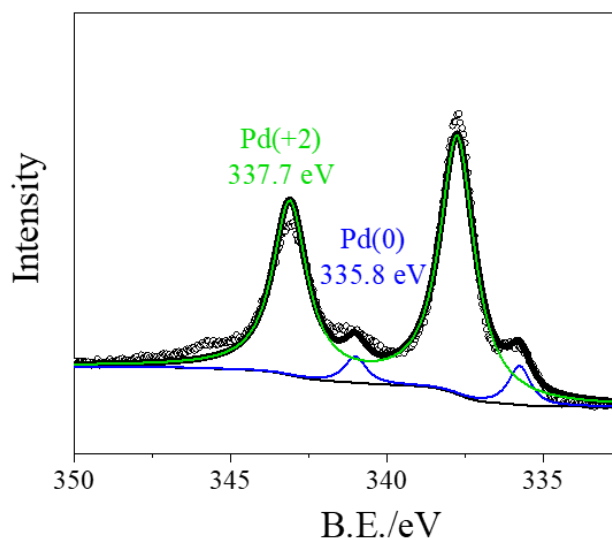


Fig. S3 XPS spectra of Pd in Pd/C.

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