

Electronic Supplementary Information

Microcalorimetric adsorption and infrared spectroscopic studies of supported Pd, Ru and Pd-Ru catalysts for the hydrogenation of aromatic rings with carboxyl groups

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1. Determination of Pd/Ru ratio for the bimetallic catalyst

We once used a powder of activated carbon (AC) as the support to prepare Pd/AC and Ru/AC catalysts (5%wt) by the liquid phase reduction method, which were then tested for the hydrogenation of BA (Table S1). It was found that the Ru/AC showed the high conversion of BA with the relatively low selectivity to CCA because of the side reactions related to the -COOH group. In contrast, the conversion of BA was significantly lower on the Pd/AC than on the Ru/AC, while the selectivity to CCA was significantly higher on the Pd/AC than on the Ru/AC. Then, the two catalysts were mechanically mixed with different mass ratios and the mixed catalysts exhibited the better activity than the Pd/AC and the better selectivity than the Ru/AC. In particular, the mixed catalyst with the mass ratio of 3:1 showed the similar activity to the Ru/AC and the similar selectivity to the Pd/AC. Accordingly, we prepared the Pd-Ru bimetallic catalyst with the mass ratio of 3:1 in this work and found that it also worked very well for the hydrogenation of BA to CCA.

Table S1 Results for the hydrogenation of benzoic acid on different mass mixing ratios blending Pd/AC with Ru/AC catalysts.

| Mass mixing ratio | P (MPa) | WHSV (h ⁻¹) | T (K) | Conversion (%) | Selectivity (%) |
|-------------------|------------|----------------------------|----------|-------------------|--------------------|
| Ru/AC | 2 | 0.7 | 403 | 99 | 92 |
| 1: 1 | 2 | 0.7 | 403 | 99 | 95 |
| 3: 1 | 2 | 0.7 | 403 | 99 | 99 |
| 7: 1 | 2 | 0.7 | 403 | 49 | 100 |
| Pd/AC | 2 | 0.7 | 403 | 47 | 100 |

2. Calculation of diffusions

The diffusion rates of molecules in pores of catalysts can be calculated by the Knudsen diffusion equation S1 and the other equations S2, S3 and S4,

$$\frac{dN}{dt}_{\text{single}} = -\pi r^2 \times \frac{2r}{3} \times \sqrt{8kT / \pi m} \times \frac{dC}{dx} \quad (\text{Eq. S1})$$

$$\frac{dC}{dx} = \frac{\rho \times N_A}{M \times L} \quad (\text{Eq. S2})$$

$$L = \frac{1.414 \times d}{6} \quad (\text{Eq. S3})$$

$$\frac{dN}{dt}_{\text{total}} = \frac{dN}{dt}_{\text{single}} \times V_{\text{pore}} \times m_{\text{cat.}} \div V_{\text{single}} \quad (\text{Eq. S4})$$

where dN/dt_{single} is the diffusion rate of a reactant in a single pore, k the Boltzmann constant (1.38×10^{-23} J/K), dC/dx the concentration gradient in molecules/(mL·cm), N_A the Avogadro constant (6.023×10^{23}), L the average pore length in cm, d the particle diameter in cm, r the pore radius in cm, m the mass of a molecule in kg/molecule, ρ the density of a liquid reactant, M the molar mass of a reactant, dN/dt_{total} the diffusion rate of molecules in all the pores, V_{single} the volume of a single pore, V_{pore} the total pore volume in a catalyst and $m_{\text{cat.}}$ mass of the catalyst.

Based on the above equations, the diffusion rates were calculated and compared with the conversion rates for the hydrogenation of benzoic acid (BA) and toluene (Tables S2 and S3).

Table S2 Comparison of diffusion and conversion rates for the hydrogenation of BA at 383 K over the catalysts.

| Catalyst | Ru/SiO ₂ | Pd/SiO ₂ | Pd-Ru/SiO ₂ |
|---|-----------------------|-----------------------|------------------------|
| WHSV (h ⁻¹) | 0.5 | 0.5 | 0.5 |
| Conversion (%) | 96 | 22 | 100 |
| Pore size (nm) ^a | 4.1 | 3.4 | 3.7 |
| V _{pore} (cm ³ /g) ^b | 0.81 | 0.46 | 0.54 |
| BA converted (molecules/s) | 2.63×10 ¹⁷ | 6.03×10 ¹⁶ | 2.74×10 ¹⁷ |
| dN/dt _{total} (molecules/s) | 1.27×10 ²² | 6×10 ²¹ | 7.66×10 ²¹ |

^a BJH desorption average pore size and ^b total pore volume.

Table S3 Comparison of diffusion and conversion rates for the hydrogenation of toluene at 403 K over the catalysts.

| Catalyst | Ru/SiO ₂ | Pd/SiO ₂ | Pd-Ru/SiO ₂ |
|---|-----------------------|-----------------------|------------------------|
| WHSV (h ⁻¹) | 10 | 10 | 10 |
| Conversion (%) | 38 | 13 | 30 |
| Pore size (nm) ^a | 4.1 | 3.4 | 3.7 |
| V _{pore} (cm ³ /g) ^b | 0.81 | 0.46 | 0.54 |
| Toluene converted (molecules/s) | 2.76×10 ¹⁸ | 9.46×10 ¹⁷ | 2.18×10 ¹⁸ |
| dN/dt _{total} (molecules/s) | 1.91×10 ²² | 8.97×10 ²¹ | 1.15×10 ²² |

^a BJH desorption average pore size and ^b total pore volume.

The particles of a catalyst were in the range of 20-40 meshes, so that the maximum particle size of a catalyst was 0.85 mm, which was used to estimate the

average pore length. The data in above tables showed that the diffusion rates in pores were much faster than the conversion rates for the hydrogenation of BA and toluene, i. e., the diffusion limits could be excluded for the reactions studied in this work.

3. Stability of catalyst

Fig. S1 shows the results for the hydrogenation of BA over the Pd-Ru/SiO₂ catalyst for extended time. It is seen that the conversion of BA was nearly 100% with about 99% selectivity to CCA for at least 170 h on-stream.

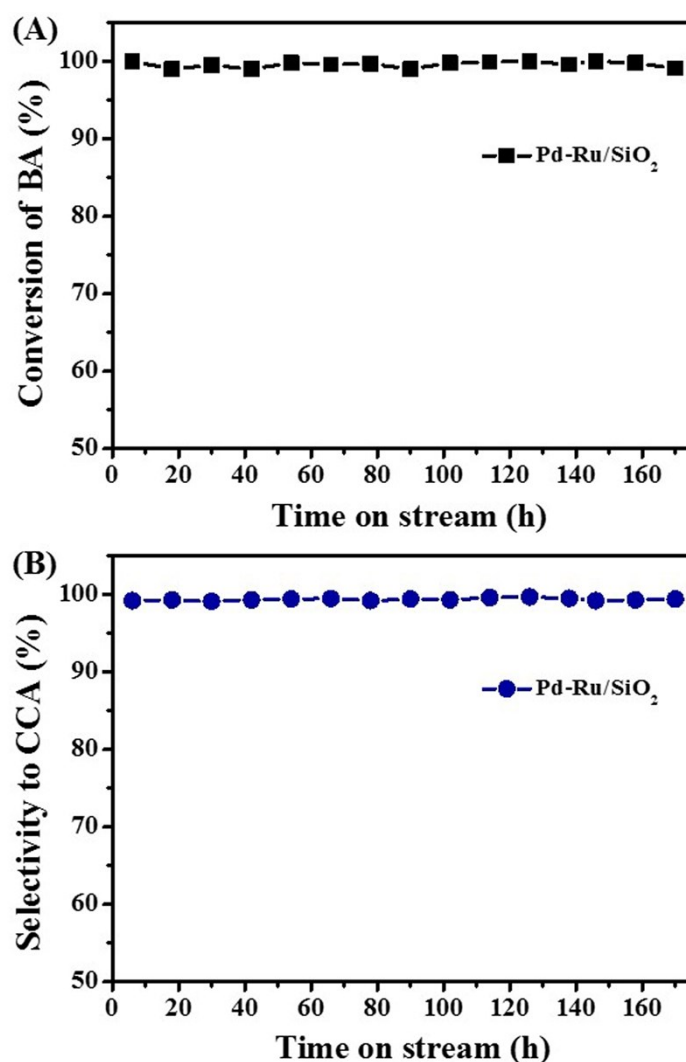


Fig. S1 Hydrogenation of BA over the Pd-Ru/SiO₂ catalyst for extended time. Reaction conditions: T= 383 K, WHSV= 0.5 h⁻¹, P= 2 MPa, H₂/BA= 10 (mol/mol) and 10%wt BA in THF.