# Electronic Supplementary Material

## Effect of noble metal nanoparticle size on C–N bond cleavage performance in hydrodenitrogenation: a study of active sites

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Table S7. The particle size of Pt/Pd sample.

**1. Calculation of transfer limitations**

The effect of reaction diffusion limitations on 1,2,3,4-THQ HDN were assessed by Weisz-Prater criterion [1] ($C_{WP}$) for internal diffusion and Mears' criterion [2] ($C_M$) for external diffusion. The detailed calculations are presented as follows:

$$C_{WP} = \frac{r_{obs}\rho_c R_p^2}{D_{eA} C_{As}} \ll 1 \tag{1}$$

$$C_M = \frac{r_{obs}\rho_b R_p n}{k_c C_{Ab}} \ll 0.15 \tag{2}$$

$$D_{eA} = \frac{D_A \varepsilon}{\tau} \tag{3}$$

$$k_c = \frac{D_A Sh}{d_p} \tag{4}$$

$$Sh = 2 + 0.6\,\mathrm{Re}^{1/2}\,Sc^{1/3} \tag{5}$$

where $r_{obs}$ is the observed reaction rate, kmol $kg_{cat}^{-1}$ $s^{-1}$; $\rho_c$ is the bulk density of solid catalyst, kg $m^{-3}$; $\rho_b$ is the bulk density of catalyst bed, kg $m^{-3}$, $\rho_b$= (1-ε) $\rho_c$, ε is the porosity, which is the product of $\rho_c$ and total pore volume $V_t$; the catalysts are assumed to be identically spherical particles, and $R_p$ is the particle radius, m; dp is the particle diameter, m; $D_{eA}$ is the effective diffusivity, $m^2$ $s^{-1}$; $D_A$ is the molecular diffusivity of 1,2,3,4-THQ, $m^2$ $s^{-1}$; $C_{As}$ is the bulk concentration of 1,2,3,4-THQ on the external surface of the catalyst, kmol $m^{-3}$; $C_{Ab}$ is the bulk concentration of 1,2,3,4-THQ, kmol $m^{-3}$; n is the reaction order; $k_c$ is the external mass transfer coefficient, m $s^{-1}$; τ is the tortuosity factor; Sh is the Sherwood number; Re is the Reynolds number; Sc is the Schmidt number.

For the 500-Ru catalyst,

$r_{obs}$=2.1×$10^{-5}$ kmol $kg^{-1}$ $s^{-1}$;

$\rho_c$=400.33 kg $m^{-3}$;

$\varepsilon=\rho_c\times V_t$= 0.25;

$\rho_b$= (1-ε) $\rho_c$=300.25 kg $m^{-3}$

$R_p=1.25\times10^{-4}$ m;

$C_{As}\approx C_{Ab}=2.61\times10^{-2}$ kmol $m^{-3}$

n=1;

$D_{eA}=3.86\times10^{-7}$

$k_c=4.81\times10^{-1}$

Based on the above values, the results are calculated as follows:

$C_{WP}=1.30\times10^{-2}\ll 1$

$C_M=6.28\times10^{-5}\ll 0.15$

The above results suggest that the effect of internal and external diffusion can be excluded.

**2. Figures and Tables**

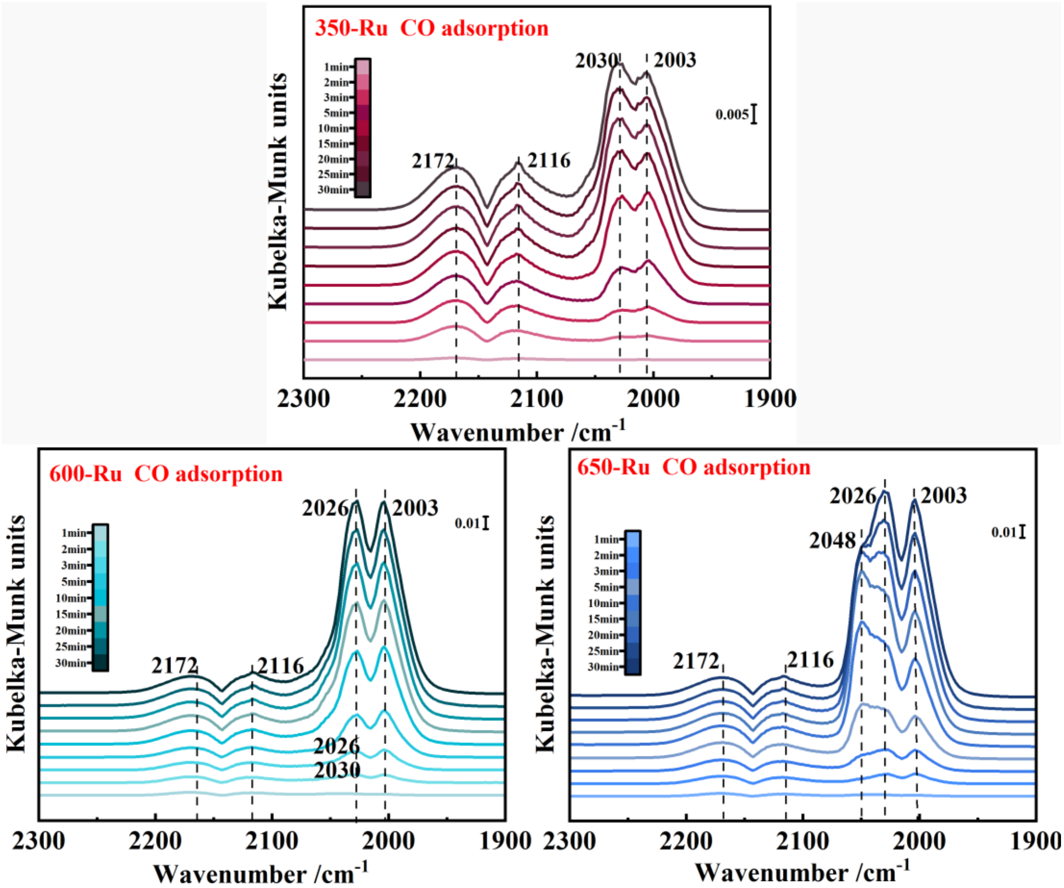


**Fig. S1** CO-DRIFTS spectra: 350-Ru CO adsorption, 600-Ru CO adsorption and 650-Ru CO adsorption.

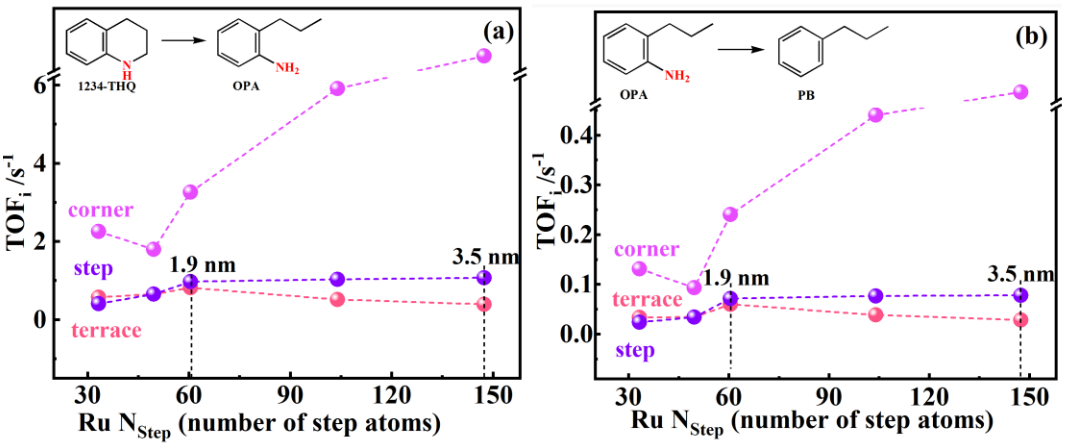


**Fig. S2** Variation of TOF values for active sites in C–N bond cleavage with Ru nanoparticle sizes (a: 1,2,3,4-THQ as the reactant, $sp^3$ C–N bond cleavage; b: OPA as the reactant, $sp^2$ C-N bond cleavage).

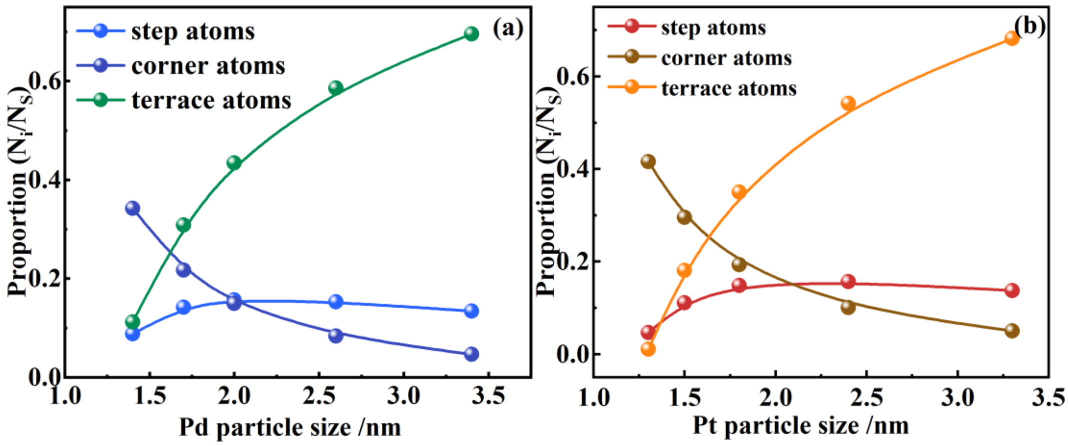


**Fig. S3** Three type of sites distribution of (a) Pd nanoparticle; (b) Pt nanoparticle.

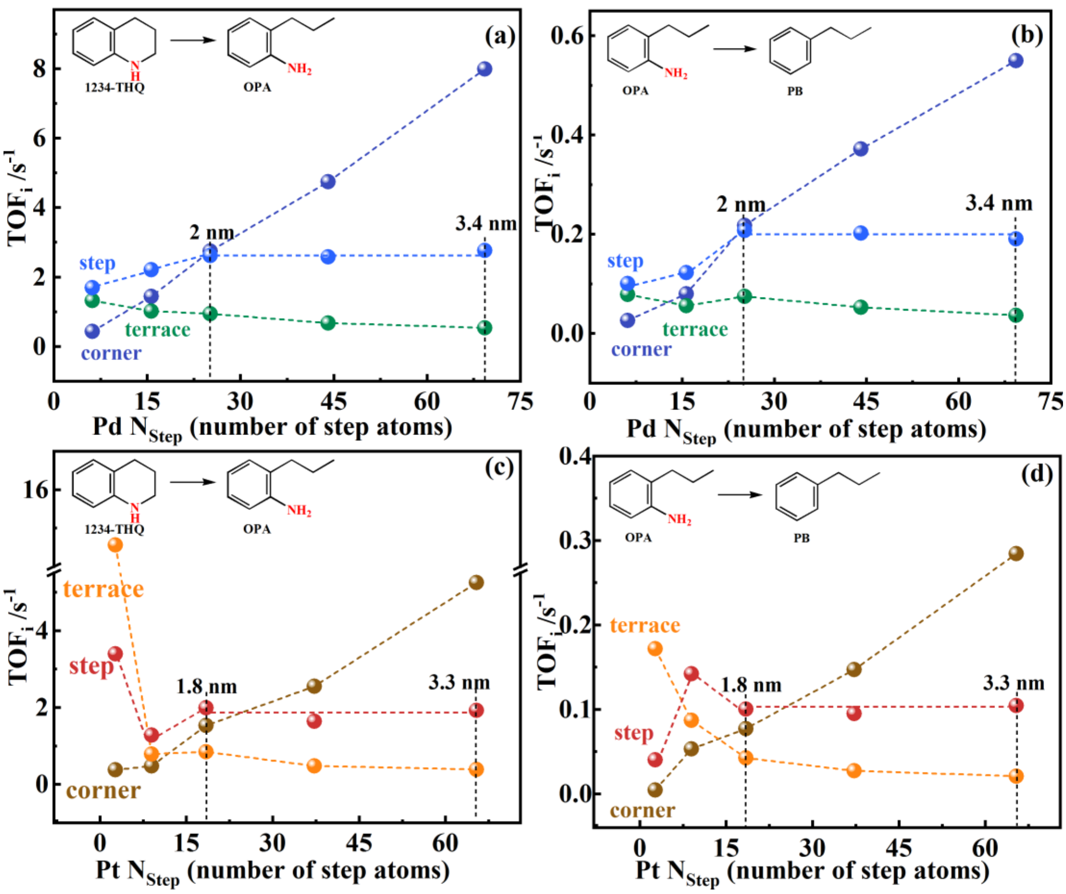


**Fig. S4** TOF values of active sites on Pt/Pd catalysts. (a, c: 1,2,3,4-THQ as the reactant, *sp*$^3$ C–N cleavage; b, d: OPA as the reactant, *sp*$^2$ C–N cleavage)

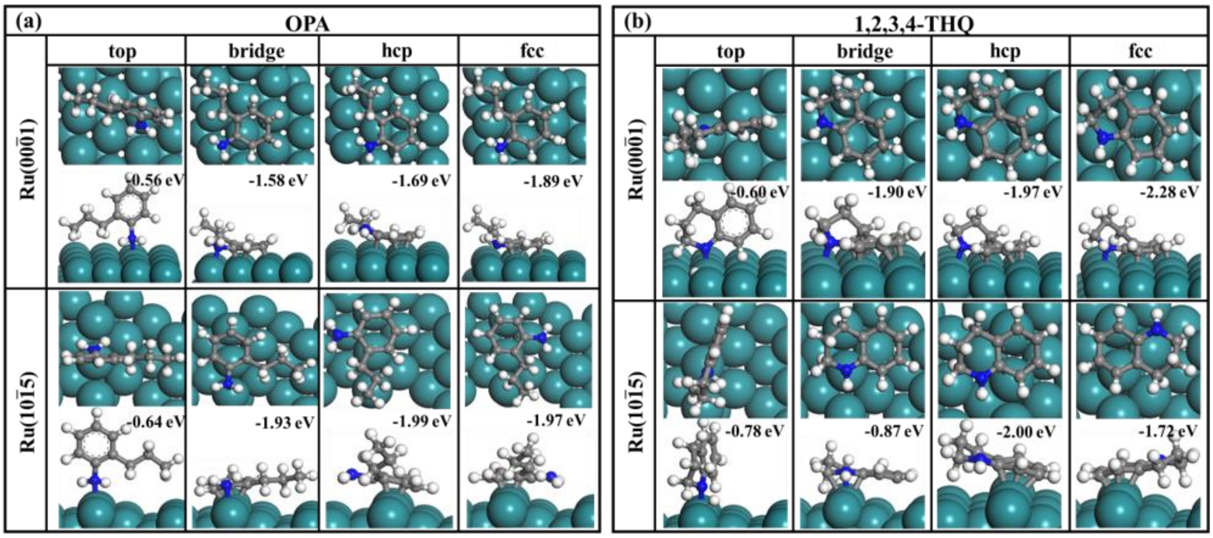


**Fig. S**5 Top and side views of the optimized adsorption configuration of OPA (a) and 12,3,4-THQ (b) on hollow (hcp or fcc), bridge, and top sites of Ru (0001) and (1015) surfaces.

Ru; C; H; N.

**Table S1** The number of atoms in different coordination environments (hcp crystal).

| | m | |
|---|---|---|
| | Even | Odd |
| $N_T$ | $\frac{1}{4}(14m^3-21m^2+14m-4)$ | $\frac{1}{4}(14m^3-21m^2+14m-3)$ |
| $N_B$ | $\frac{1}{4}(14m^3-63m^2+98m-52)$ | $\frac{1}{4}(14m^3-63m^2+98m-53)$ |
| $N_S$ | $\frac{1}{2}(21m^2-42m+24)$ | $\frac{1}{2}(21m^2-42m+25)$ |
| $N_{corner}$ | 18 | 18 |
| $N_{step}$ | 24m-54 | 24m-54 |
| $N_{terrace}$ | $\frac{21}{2}m^2-45m+48$ | $\frac{21}{2}m^2-45m+\frac{97}{2}$ |

The table is based on the model in Reference 39, where m represents the number of atoms lying on an equivalent edge(corner atoms included); $N_T$ represents the total number atoms in each nanoparticle; $N_B$ represents the number of bulk atoms; $N_S$ represents the number of surface atoms; $N_{corner}$, $N_{step}$ and $N_{terrace}$ represents the number of different active site atoms.

**Table S2** The peak red-shift time in different catalysts.

| | 2 min | 3 min | 5 min |
|---|---|---|---|
| 350-Ru | 2030 $cm^{-1}$ | 2030 $cm^{-1}$ | 2030 $cm^{-1}$ |
| 400-Ru | 2030 $cm^{-1}$ | 2030 $cm^{-1}$ | 2030 $cm^{-1}$ |
| 500-Ru | 2034 $cm^{-1}$ | 2028/2026 $cm^{-1}$ | 2026 $cm^{-1}$ |
| 600-Ru | 2030 $cm^{-1}$ | 2026 $cm^{-1}$ | |
| 650-Ru | 2026 $cm^{-1}$ | | |

**Table S3** Textural and physicochemical characteristics of $SiO_2$ support and prepared catalysts.

| Samples | $S_{BET}$ /($m^2 \cdot g^{-1}$) | $V_t$ /($cm^3 \cdot g^{-1}$) | Pore diameter /nm |
|---|---|---|---|
| $SiO_2$ | 305.1 | 0.86 | 17.2 |
| 350-Ru | 321.8 | 0.63 | 12.3 |
| 400-Ru | 326.3 | 0.64 | 12.3 |
| 500-Ru | 294.6 | 0.54 | 12.4 |
| 600-Ru | 303.7 | 0.51 | 12.3 |
| 650-Ru | 298.4 | 0.54 | 9.6 |

**Table S4** CO uptake, dispersion, particle size of the catalysts.

| Sample | CO uptake /(μmol·g −1 ) | Ru dispersion D /% | Particle size $d^a$ /nm |
|---|---|---|---|
| 350-Ru | 13.1 | 58.9 | 1.8 |
| 400-Ru | 12.3 | 55.3 | 2.0 |
| 500-Ru | 11.2 | 50.3 | 2.2 |
| 600-Ru | 8.3 | 37.4 | 2.9 |
| 650-Ru | 6.6 | 29.6 | 3.7 |

[a] Particle size obtained by dispersion.

**Table S5** Theoretical and actual measurements of the reaction rate of total surface atoms.

| Catalyst | 1,2,3,4-THQ $TOF_{surface}$ /$s^{-1}$ | | OPA $TOF_{surface}$ /$s^{-1}$ | |
|---|---|---|---|---|
| | Theoretical | Measured | Theoretical | Measured |
| 350-Ru | 0.182 | 0.208 | 0.021 | 0.024 |
| 400-Ru | 0.275 | 0.296 | 0.028 | 0.030 |
| 500-Ru | 0.388 | 0.422 | 0.029 | 0.031 |
| 600-Ru | 0.336 | 0.359 | 0.025 | 0.026 |
| 650-Ru | 0.275 | 0.309 | 0.020 | 0.022 |

**Table S6** The number of atoms in different coordination environments (fcc crystal).

| | m |
|---|---|
| $N_T$ | $16m^3-3m^2+24m-6$ |
| $N_B$ | $16m^3-63m^2+84m-38$ |
| $N_S$ | $30m^2-60m+32$ |
| $N_{corner}$ | 24 |
| $N_{step}$ | 36(m-2) |
| $N_{terrace}$ | $30m^2-96m+60$ |

**Table S7** The particle size of Pt/Pd sample.

| Temperature /°C | Pd Particle size /nm | Pt particle size /nm |
|---|---|---|
| 350 | 1.4 | 1.3 |
| 400 | 1.7 | 1.5 |
| 500 | 2.0 | 1.8 |
| 600 | 2.6 | 2.4 |
| 650 | 3.4 | 3.3 |

**References**


1. Weisz P B, Prater C D, Interpretation of measurements in experimental catalysis, in Advances in Catalysis. New York: Academic Press. 1954, 143-196.
2. Mears D E. Tests for transport limitations in experimental catalytic reactors. Industrial & Engineering Chemistry Process Design and Development, 1971, 10(4): 541-547