**Supplementary Information**

# Kinetics insights into structure sensitivity of Ru catalyzed L-alanine hydrogenation to alaninol

*Rui Song,[1] Chang Yao,[1] Wenhua Li,[1] Nihong An,[2] Yafeng Shen,[2,*] Nina Fei,[1] Xiaohu Ge,[1] Yueqiang Cao,[1,3,*] Xuezhi Duan,[1] Xinggui Zhou,[1]*

*[1]State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*

*[2]Sino-Platinum Industrial Catalyst (Yunnan) Co., Ltd., 988 Keji Road, Kunming 650106, Yunnan, China*

*[3]Engineering Research Center of Resource Utilization of Carbon-containing Waste with Carbon Neutrality, Ministry of Education, Shanghai 200237, China*

*[*] Corresponding authors: shenyf@ipm.com.cn; yqcao@ecust.edu.cn*

**Equation derivation**

The derivation process of the total activation energy formula is as follows:
The total reaction rate r is represented by the sum of the reaction rate of each type of active sites:

$$r = \sum_{1}^{n} y_i r_i \#(1)$$

where n is the number of the type of active sites, $y_i$ is the fraction of each type of active sites and $r_i$ is the reaction rate of specific active sites.
Assume that the hydrogenation reaction rate expression of L-alanine is:

$$r = k c_1^{n_1} c_2^{n_2} \#(2)$$

where k is the reaction rate constant, $c_1$ is the concentration of L-alanine and $c_2$ is the concentration of $H_2$, $n_1$ and $n_2$ are the reaction orders of L-alanine and $H_2$ respectively.
Substituting Eq. 2 to Eq. 1 gives:

$$k c_1^{n_1} c_2^{n_2} = \sum_{1}^{n} y_i k_i c_1^{n_1} c_2^{n_2} \#(3)$$

Divide both sides of the Eq. 3 by $c_1^{n_1} c_2^{n_2}$ gives:

$$k = \sum_{1}^{n} y_i k_i \#(4)$$

where $k_i$ is the reaction rate constant of each type of active sites.
The reaction rate constant is also expressed by:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \#(5)$$

where A is the pre-exponential factor, $E_a$ is the activation energy, R is the universal gas constant and T is the absolute temperature.
Substituting Eq. 5 to Eq. 4 gives:

$$A \cdot \exp\left(-\frac{E_a}{RT}\right) = \sum_{1}^{n} y_i \cdot A_i \cdot \exp\left(-\frac{E_i}{RT}\right) \#(6)$$

The logarithm of Eq. 6 gives Eq. 7:

$$\ln A + \left(-\frac{E_a}{RT}\right) = ln\left[\sum_{1}^{n} y_i \cdot A_i \cdot \exp\left(-\frac{E_i}{RT}\right)\right] \#(7)$$

Taking the derivative of Eq. 7 with respect to T gives Eq. 8:

$$\left(\frac{1}{RT^2}\right)\cdot E_a = \left(\frac{1}{RT^2}\right)\cdot\frac{\sum_1^n\left[y_i\cdot A_i\cdot\exp\left(-\frac{E_i}{RT}\right)\cdot E_i\right]}{\sum_1^n\left[y_i\cdot A_i\cdot\exp\left(-\frac{E_i}{RT}\right)\right]}\#(8)$$

The simplification of Eq. 8 gives Eq. 9:

$$E_a = \frac{\sum_1^n\left[y_i\cdot A_i\cdot\exp\left(-\frac{E_i}{RT}\right)\cdot E_i\right]}{\sum_1^n\left[y_i\cdot A_i\cdot\exp\left(-\frac{E_i}{RT}\right)\right]}\#(9)$$

**Model calculations**

The total number of Ru atoms ($N_T$) in nanoparticles can be calculated from Eq. 10:

$$d_{Ru\,paritcle} = 1.105 \times N_T^{\frac{1}{3}} \times d_{Ru} \#(10)$$

where $d_{Ru\,paritcle}$ is the statistical average particle size of Ru nanoparticles, and $d_{Ru}$ is the diameter of Ru atom. The number of atoms locating on the equivalent edge (corners included) *m* can be given by Eq. 11:

$$N_T = 0.25 \times \left(14m^3 - 21m^2 + 14m - 4\right) \#(11)$$

The number of atoms on different active sites of each Ru particle can be calculated from Eq. 12 -Eq. 15:

$$N_{corner} = 12 \#(12)$$

$$N_{edge} = 18m - 40 \#(13)$$

$$N_{(001)} = 1.5 \times (m-2)^2 \#(14)$$

$$N_{(101)} = 6m^2 - 26m + 28 \#(15)$$

The surface atom number of each Ru particle can be obtained from Eq. 16:

$$N_S = 7.5m^2 - 14m + 6 \#(16)$$

The reaction rate for L-alanine conversion or alaninol formation and apparent activation energy were calculated using Eq. 17 and Eq. 18:

$$r_{initial} = \frac{-\frac{dn_{L-alanine/Alaninol}}{dt_{initial}}}{\frac{amount \times loading_{Ru}}{M_{Ru}}} \#(17)$$

$$TOF_{app} = \frac{r_{initial}}{\frac{N_S}{N_T}} \#(18)$$

where $amount$, $loading_{Ru}$ and $M_{Ru}$ are the amount of catalyst, the loading of Ru and the molecular weight of Ru, respectively, while $n_{L-alanine}$ and $n_{Alaninol}$ are the number of moles of L-alanine and alaninol, respectively.

**Table S1.** Initial reaction rate for L-alanine conversion on Ru/CNT catalysts at different temperatures.

| Catalysts | Temperature (°C) | $R_{in}$ ($mol_{L\text{-}alanine} \cdot mol_{Ru}^{-1} \cdot min^{-1}$) |
|---|---|---|
| 1.3-Ru/CNT | 85 | 0.023 |
| | 90 | 0.035 |
| | 95 | 0.049 |
| | 100 | 0.071 |
| 1.7-Ru/CNT | 85 | 0.030 |
| | 90 | 0.045 |
| | 95 | 0.062 |
| | 100 | 0.089 |
| 2.2-Ru/CNT | 85 | 0.039 |
| | 90 | 0.049 |
| | 95 | 0.074 |
| | 100 | 0.112 |
| 2.5-Ru/CNT | 85 | 0.032 |
| | 90 | 0.044 |
| | 95 | 0.067 |
| | 100 | 0.095 |

**Table S2.** Initial rate of alaninol formation on Ru/CNT catalysts at different temperatures.

| Catalysts | Temperature (°C) | $R_{in}$ ($mol_{Alaninol} \cdot mol_{Ru}^{-1} \cdot min^{-1}$) |
|---|---|---|
| 1.3-Ru/CNT | 85 | 0.020 |
| | 90 | 0.025 |
| | 95 | 0.038 |
| | 100 | 0.051 |
| 1.7-Ru/CNT | 85 | 0.024 |
| | 90 | 0.037 |
| | 95 | 0.049 |
| | 100 | 0.077 |
| 2.2-Ru/CNT | 85 | 0.030 |
| | 90 | 0.040 |
| | 95 | 0.064 |
| | 100 | 0.086 |
| 2.5-Ru/CNT | 85 | 0.028 |
| | 90 | 0.040 |
| | 95 | 0.059 |
| | 100 | 0.072 |

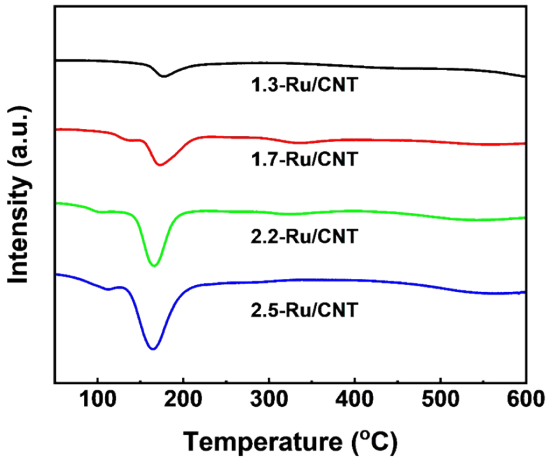


**Figure S1.** $H_2$-TPR profiles of differently sized Ru/CNT catalysts.

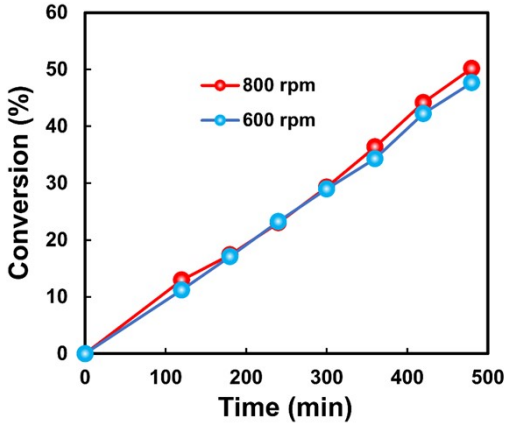


**Figure S2.** L-alanine conversion as a function of time over the 2.2-Ru/CNT catalyst at 95 ℃.

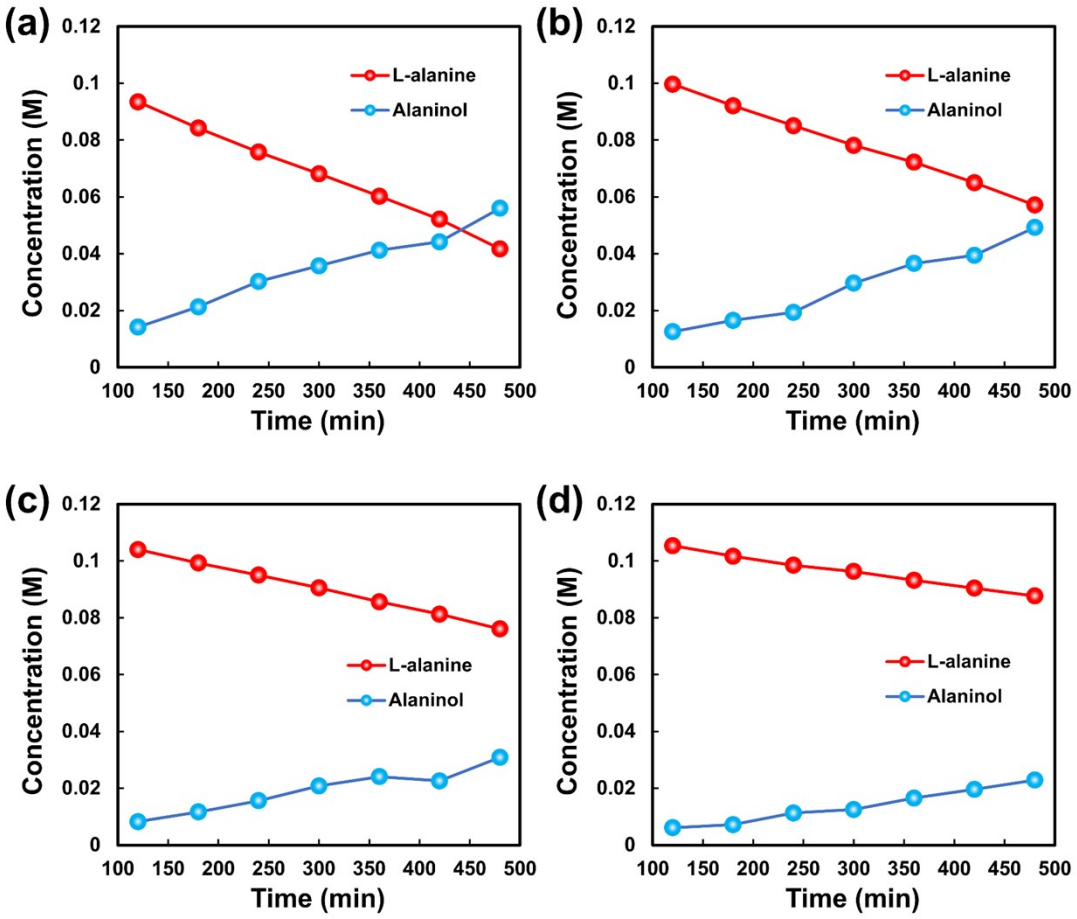


**Figure S3.** Concentrations of L-alanine and alaninol versus reaction time for L-alanine hydrogenation over the 2.5-Ru/CNT catalyst at (a) 100 ℃, (b) 95 ℃, (c) 90 ℃ and (d) 85 ℃.

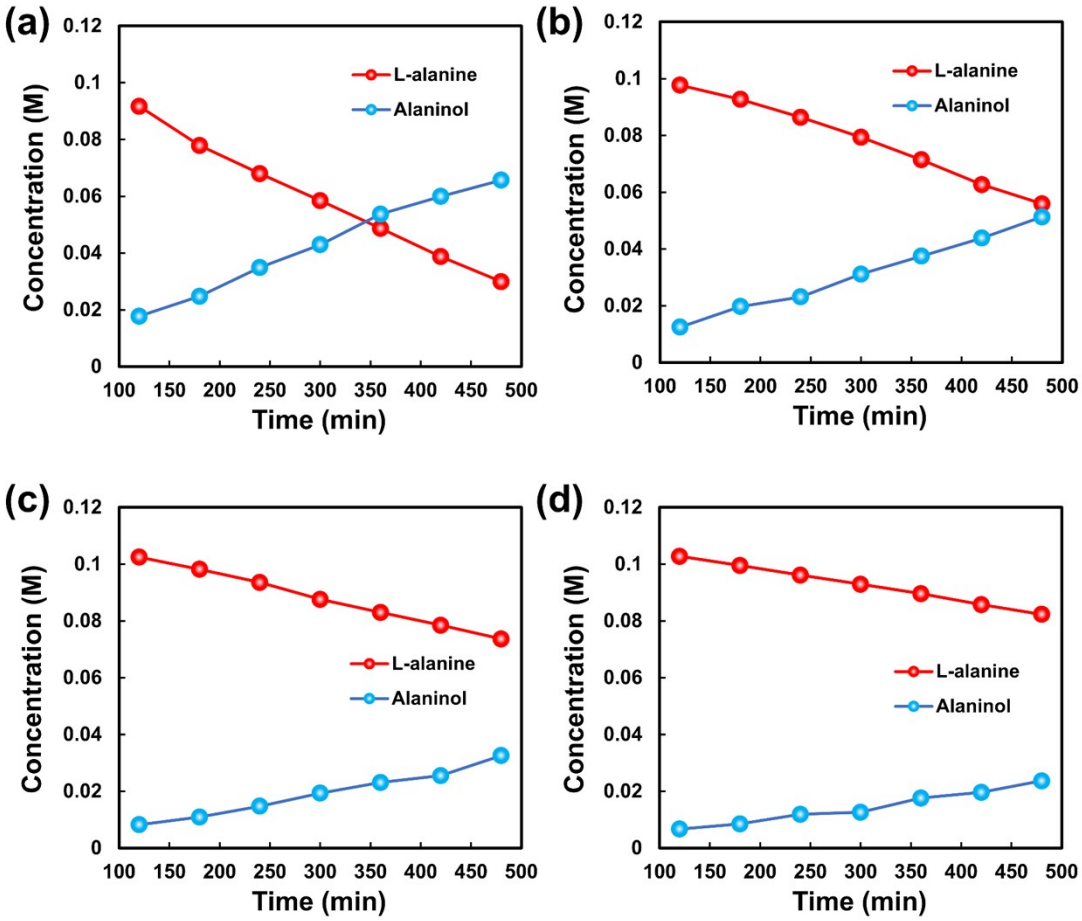


**Figure S4.** Concentrations of L-alanine and alaninol versus reaction time for L-alanine hydrogenation over the 2.2-Ru/CNT catalyst at (a) 100 ℃, (b) 95 ℃, (c) 90 ℃ and (d) 85 ℃.

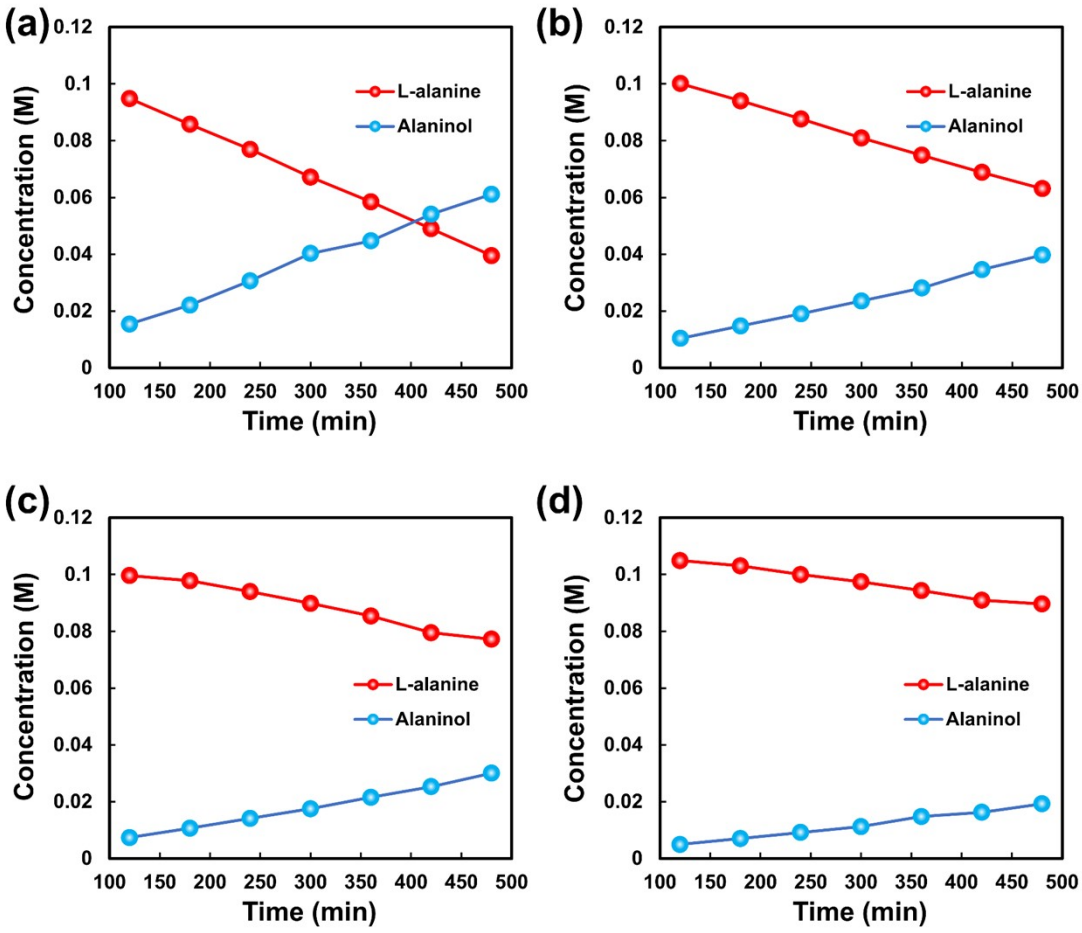


**Figure S5.** Concentrations of L-alanine and alaninol versus reaction time for L-alanine hydrogenation over the 1.7-Ru/CNT catalyst at (a) 100 ℃, (b) 95 ℃, (c) 90 ℃ and (d) 85 ℃.

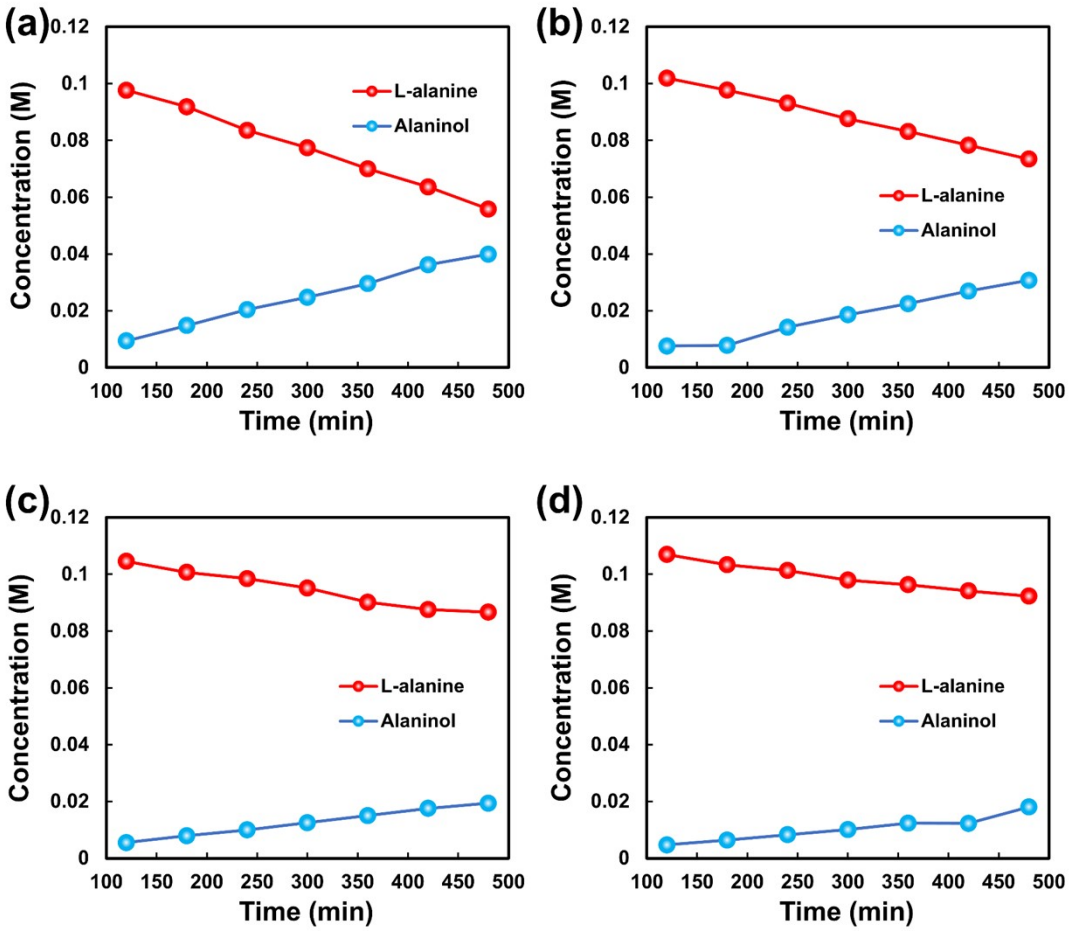


**Figure S6.** Concentrations of L-alanine and alaninol versus reaction time for L-alanine hydrogenation over the 1.3-Ru/CNT catalyst at (a) 100 ℃, (b) 95 ℃, (c) 90 ℃ and (d) 85 ℃.

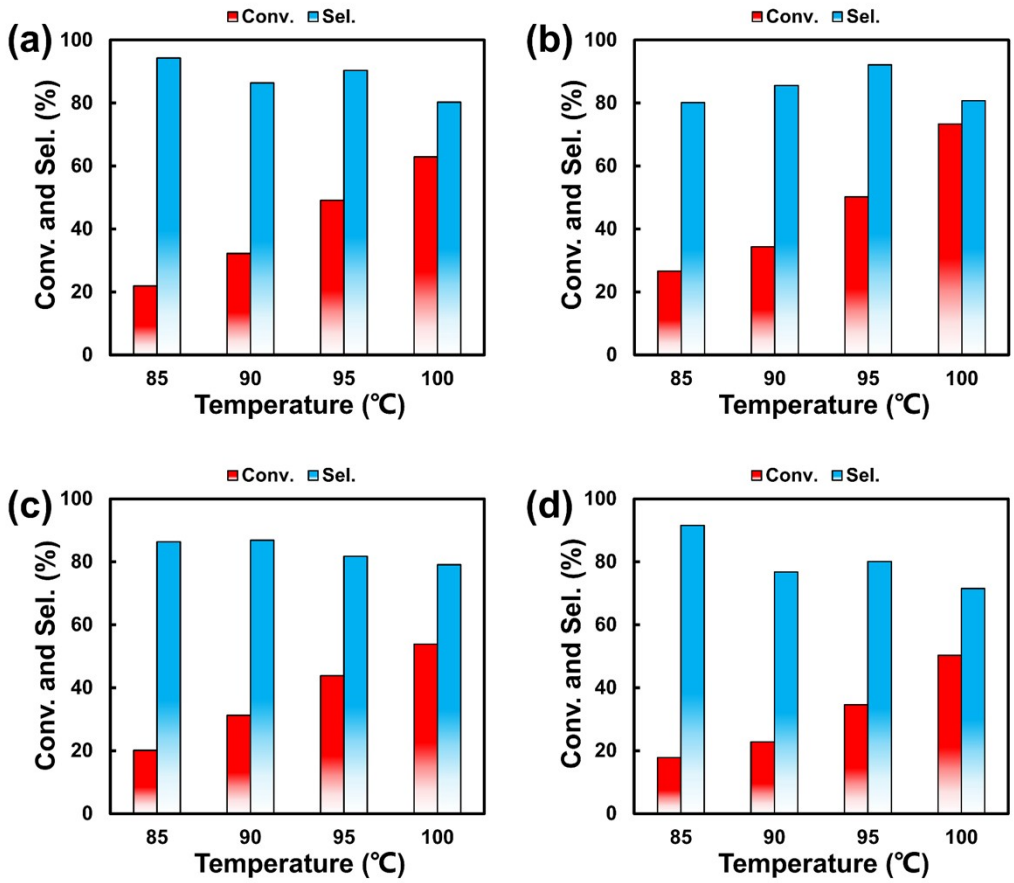


**Figure S7.** Conversion of L-alanine and selectivity to alaninol over (a) 2.5-Ru/CNT, (b) 2.2-Ru/CNT, (c) 1.7-Ru/CNT and (d) 1.3-Ru/CNT at 480 min.

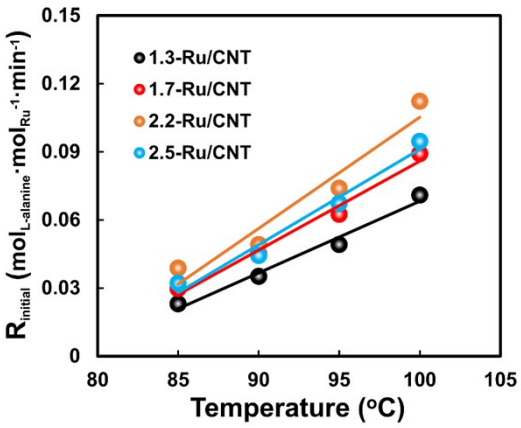


**Figure S8.** Plots of $R_{initial}$ for L-alanine conversion over differently sized Ru/CNT catalysts as a function of temperature.

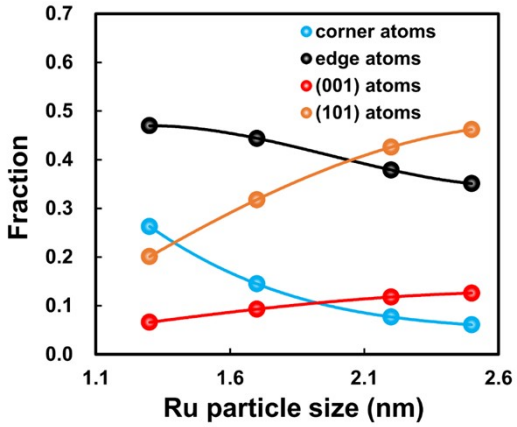


**Figure S9.** The fraction of different type of surface sites as a function of the Ru particle size.

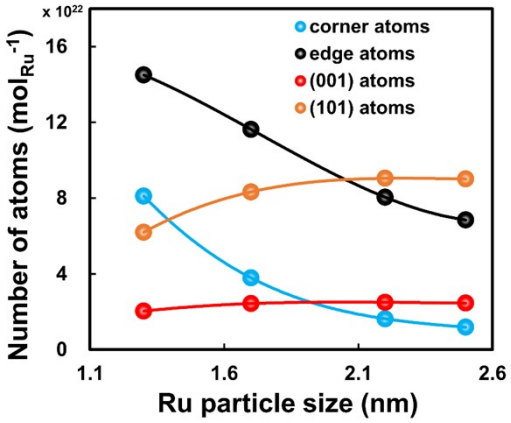


**Figure S10.** The number of each type of active site per mole of Ru as a function of the Ru particle size.

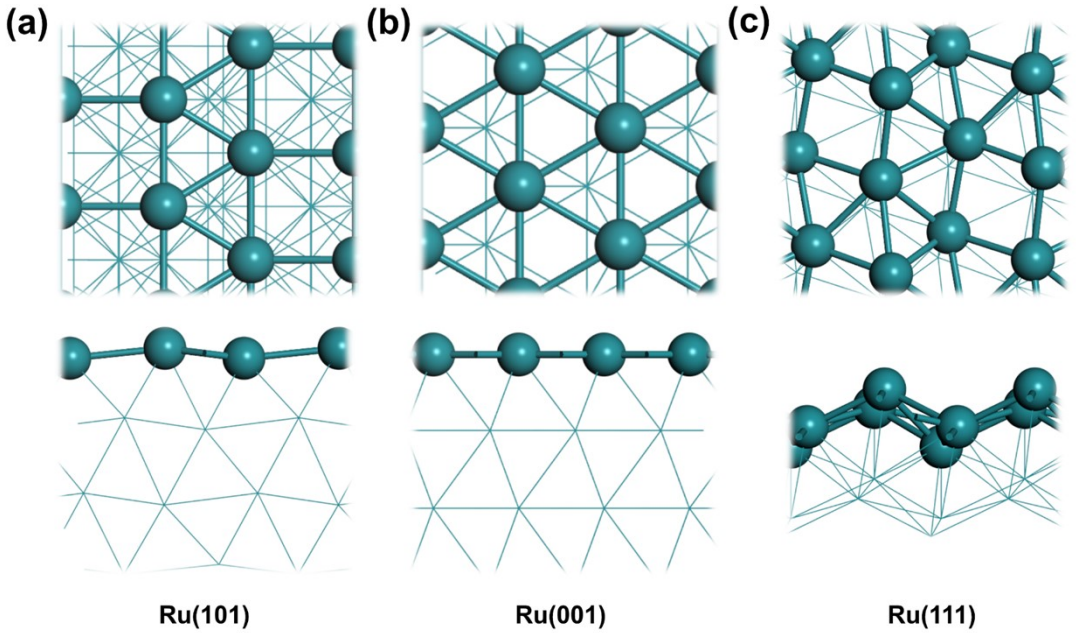


**Figure S11.** Schematic diagrams of clean (a) Ru(101), (b) Ru(001) and (c) Ru(111) surfaces.

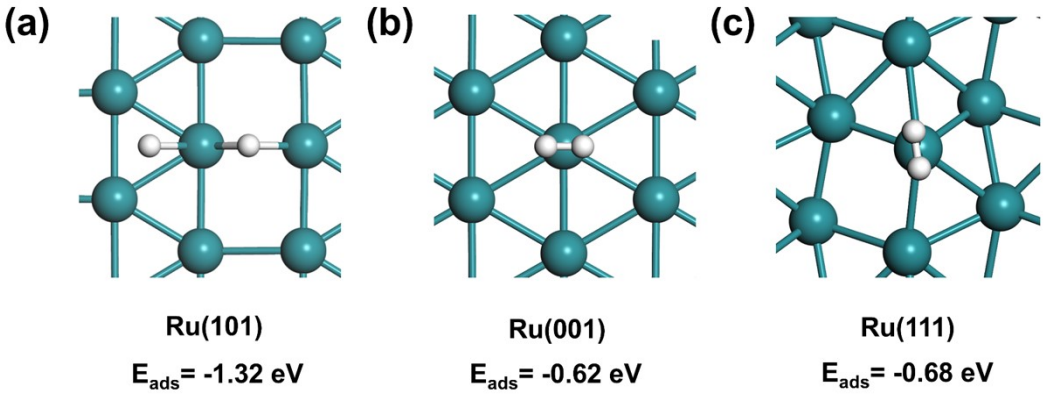


**Figure S12.** Adsorption energies and configurations of $H_2$ on the Ru(101), Ru(001) and Ru(111) surfaces.