**Electronic Supplementary Information (ESI) for**

# Surface engineering on a nanocatalyst: basic zinc salt nanoclusters improve catalytic performances of Ru nanoparticles

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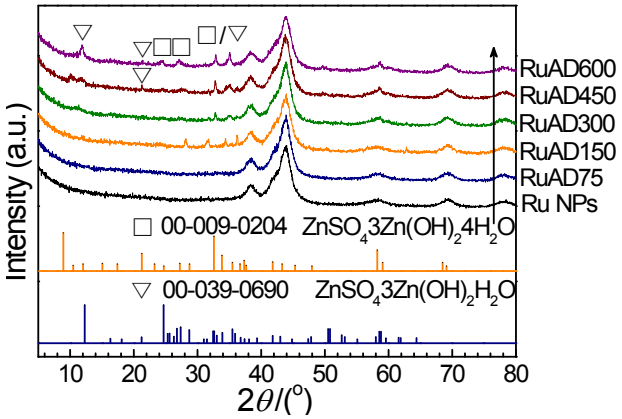


**Fig. S1** The XRD patterns of Ru NPs and RuADX.

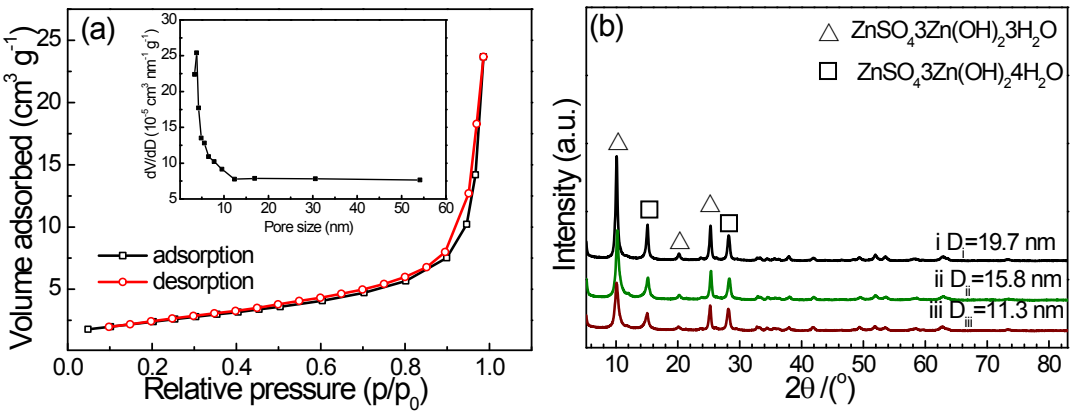


**Fig. S2** (a) $N_2$ adsorption-desorption isotherms of BZSS, inset is the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curves. (b) XRD patterns of BZSS with different crystallite size prepared by (i) adding NaOH dropwise, (ii) adding NaOH dropwise, $ZnSO_4$ excess 50%, (iii) adding NaOH dropwise, $ZnSO_4$ excess 100%. The crystallite size calculation is according to the Scherrer equation.

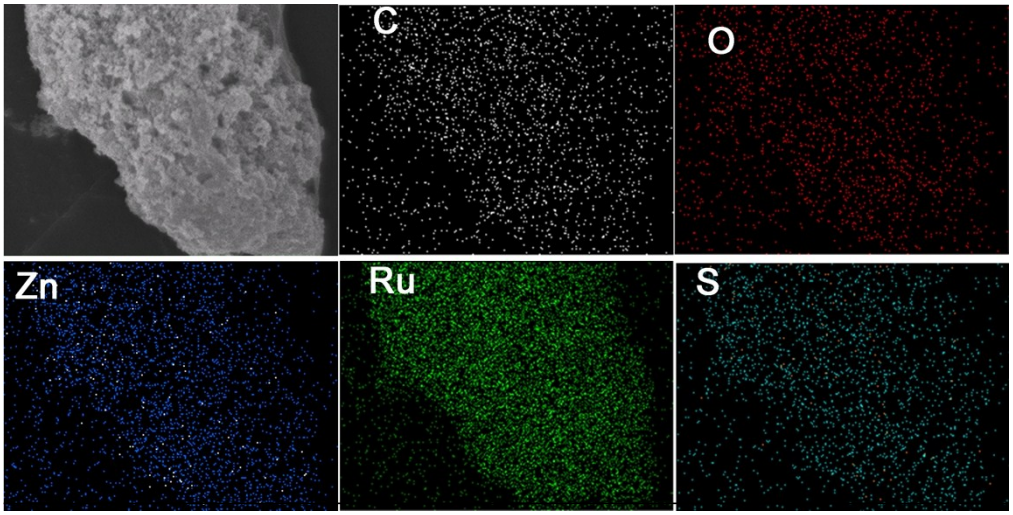


**Fig. S3** FESEM image of RuAD600 and corresponding EDS surface scanning images.

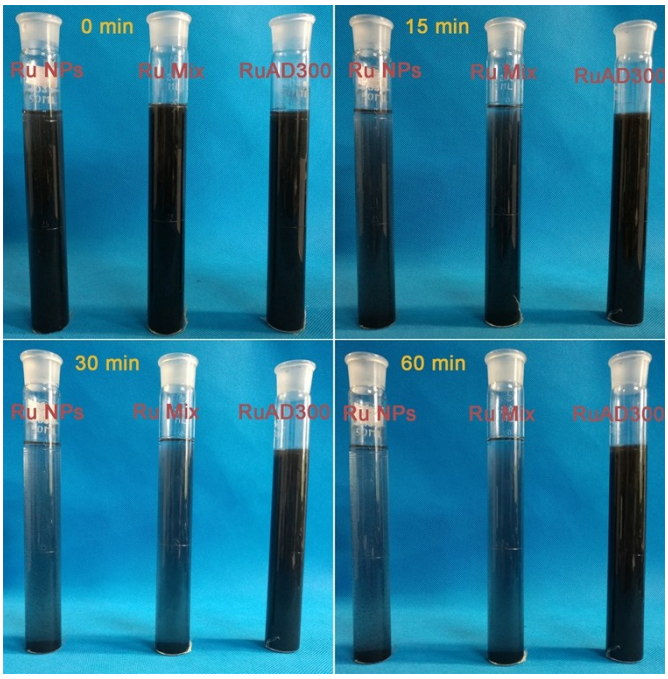


**Fig. S4** The settlement in deionized water for samples of Ru NPs, Ru Mix, and RuAD300 at different times.

The pure Ru NPs, mechanical mixture of Ru NPs and BZSS (denoted as Ru Mix), and RuAD300 are used to observe their settlement in deionized water (Fig. S4). Ru NPs sample is settling fast due to the high density and hydrophobic surface of Ru NPs. Ru Mix is settling fast due to no strong interaction between Ru NPs and BZSS. But the RuAD300 sample is almost not settling within 1h. The hydrophilicity of RuAD-based catalysts is improved. This demonstrates BZSS nanoclusters are not simple mechanical mixed with Ru NPs, but a structural reconstruction caused by the interaction between them under the chemisorption condition ($ZnSO_4$ solution, 50 °C). The interactions lead to the transformation of BZSS from lamellar structure to nanoclusters structure, and make the BZSS nanoclusters adsorbed and distributed on Ru NPs.

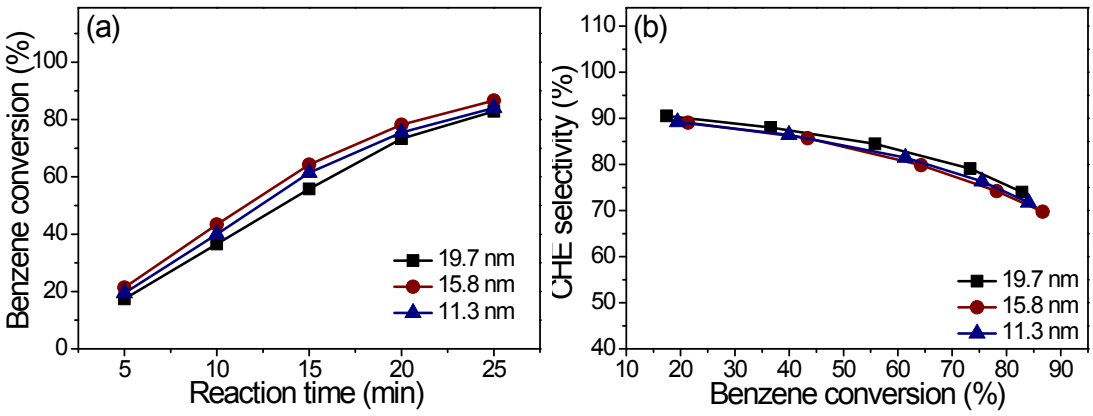


**Fig. S5** Plots of the (a) benzene conversion versus the reaction time and (b) CHE selectivity versus the benzene conversion over different crystallite size of BZSS (300 mg) chemisorbed on Ru NPs.

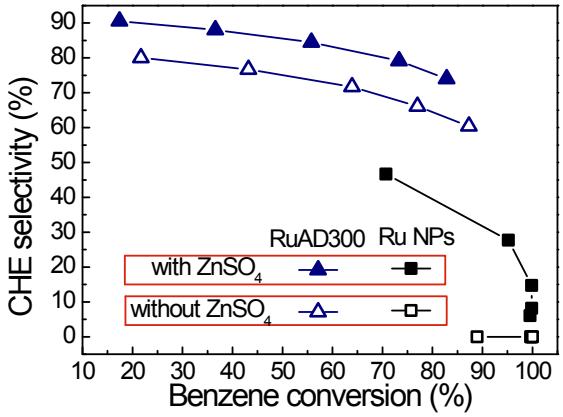


**Fig. S6** Plots of the selectivity of CHE versus the conversion of benzene over Ru NPs and RuAD300 with and without $ZnSO_4$.

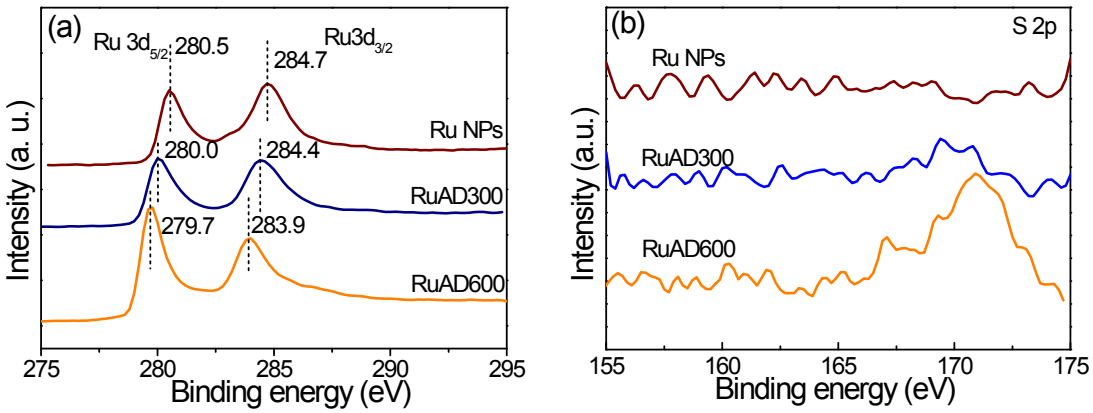


**Fig. S7** Ru 3d and S 2p XPS spectra of (a) Ru NPs, (b) RuAD300, (c) RuAD600.

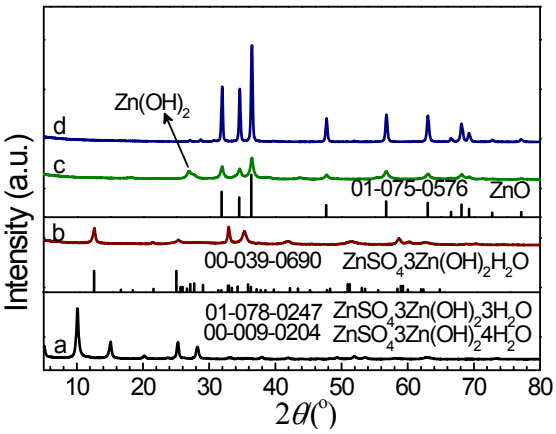


**Fig. S8** XRD patterns of (a) BZSS, and samples calcinated at (b) 200 °C, (c) 300 °C, and (d) 700 °C under $N_2$ atmosphere.

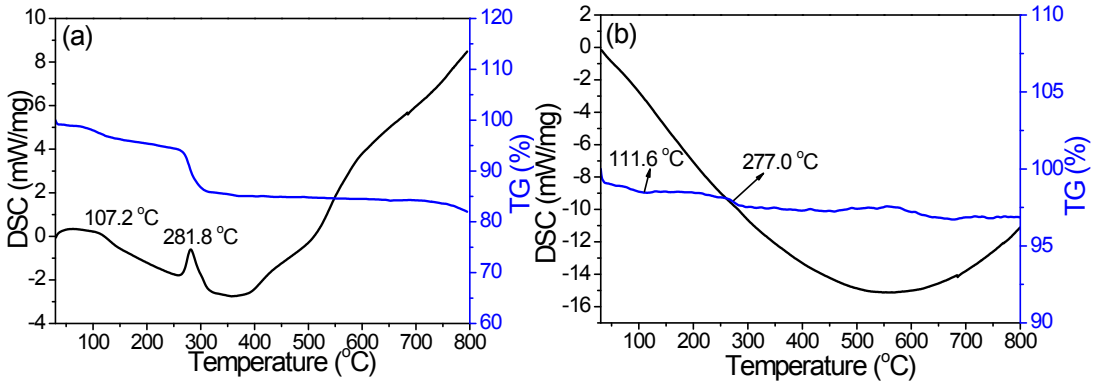


**Fig. S9** TG/DSC curves of (a) BZSS, and (b) RuAD300.

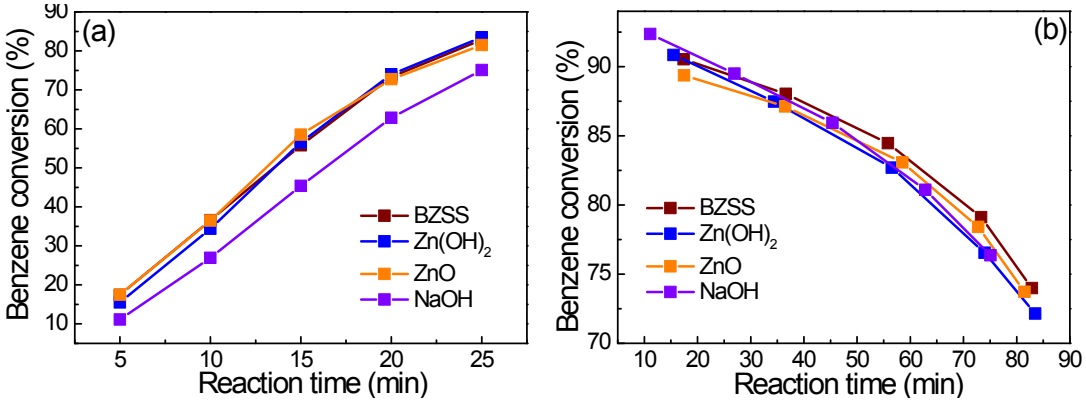


**Fig. S10** Comparisons of the catalytic performance of benzene-selective hydrogenation by chemisorbing of 300 mg BZSS, 196 mg $Zn(OH)_2$, 160 mg ZnO, and by adding 158 mg NaOH.

**Table S1.** The comparison of 30ml of BZSS suspension taken 6 times in parallel.

| Number | Mass of BZSS (mg)[a] | Standard deviation (mg) |
|---|---|---|
| 1 | 199 | 1.97 |
| 2 | 198 | |
| 3 | 195 | |
| 4 | 195 | |
| 5 | 199 | |
| 6 | 199 | |

[a] The mass of BZSS after centrifugal washing and vacuum drying.

**Table S2.** The measured and design values of Zn content of Ru NPs and RuADX.

| Sample | Measure (Zn wt.%)[a] | Design (Zn wt.%)[b] |
|---|---|---|
| BZSS | 54.5 | - |
| RuAD150 | 3.5 | 3.8 |
| RuAD300 | 6.9 | 7.1 |
| RuAD600 | 12.5 | 12.6 |

[a] Measured by XRF.

[b] According to the measured value (Zn wt.%) of BZSS.

**Table S3.** Physicochemical properties of Ru NPs and RuADX.

| catalyst | $S_{BET}$ ($m^2/g$) | $V_{Pore}$ ($cm^3/g$) | $D_{Pore}$ (nm) | $d_M$ (nm) | Dispersion (%) |
|---|---|---|---|---|---|
| Ru NPs | 59 | 0.16 | 6.4 | 3.4 | 6.8 |
| RuAD150 | 60 | 0.16 | 5.4 | 3.7 | 6.9 |
| RuAD300 | 58 | 0.13 | 4.5 | 3.6 | 7.5 |
| RuAD450 | 55 | 0.11 | 4.8 | 3.4 | 7.6 |
| RuAD600 | 54 | 0.12 | 4.4 | 3.4 | 7.8 |

**Table S4.** Activity and selectivity of pure BZSS for hydrogenation of benzene and CHE.

| *t*/min | Benzene-selective hydrogenation | | CHE hydrogenation | |
|---|---|---|---|---|
| | Benzene/% | CHE/% | CHA/% | CHE/% |
| 25 | 99.91 | 0.09 | 0.55 | 99.45 |

Slurry composition: 2.0 g of BZSS, 280 mL of $H_2O$, 45.7 g of $ZnSO_4 \cdot 7H_2O$.

Hydrogenation conditions: 140 mL of benzene ($C_6H_6$) or CHE ($C_6H_{10}$), 5MPa of $H_2$ pressure, 150 °C, 1400 *rpm*.

**Table S5.** Activity and selectivity of the Ru NPs.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 70.69 | 46.65 | 32.98 |
| 10 | 95.20 | 27.73 | 26.40 |
| 15 | 99.83 | 14.7 | 14.68 |
| 20 | 99.85 | 8.15 | 8.14 |
| 25 | 99.53 | 6.03 | 6.00 |

**Table S6.** Activity and selectivity of the RuAD150.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 37.98 | 82.36 | 31.28 |
| 10 | 66.37 | 74.93 | 49.73 |
| 15 | 85.05 | 68.28 | 58.07 |
| 20 | 91.13 | 61.26 | 55.83 |
| 25 | 100 | 55.83 | 55.83 |

**Table S7.** Activity and selectivity of the RuAD300.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 17.41 | 90.53 | 15.76 |
| 10 | 36.59 | 88.03 | 32.21 |
| 15 | 55.8 | 84.47 | 47.13 |
| 20 | 73.32 | 79.12 | 58.01 |
| 25 | 82.85 | 73.99 | 61.30 |

**Table S8.** Activity and selectivity of the RuAD450.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 10.97 | 91.25 | 10.01 |
| 10 | 23.41 | 90.86 | 21.27 |
| 15 | 40.36 | 87.51 | 35.32 |
| 20 | 54.78 | 83.35 | 45.66 |
| 25 | 66.37 | 79.75 | 52.93 |

**Table S9.** Activity and selectivity of the RuAD600.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 5.28 | 92.8 | 4.90 |
| 10 | 11.09 | 92.06 | 10.21 |
| 15 | 20.9 | 91.63 | 19.15 |
| 20 | 31.51 | 89.75 | 28.28 |
| 25 | 43.49 | 87.08 | 37.87 |

Tables S5-9: Slurry composition: 2.0 g of catalyst, 280 mL of $H_2O$, 45.7 g of $ZnSO_4 \cdot 7H_2O$. Hydrogenation conditions: 140 mL of $C_6H_6$, 5MPa of $H_2$ pressure, 150 °C, 1400 *rpm*.

**Table S10.** Activity and selectivity of the Ru NPs(0.2g).

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 7.85 | 46.62 | 3.66 |
| 10 | 14.74 | 49.05 | 7.23 |
| 15 | 21.52 | 49.02 | 10.55 |
| 20 | 28.66 | 48.19 | 13.81 |
| 25 | 36.60 | 46.31 | 16.95 |
| 40 | 55.96 | 42.10 | 23.56 |
| 50 | 65.33 | 38.67 | 25.26 |
| 60 | 73.29 | 35.95 | 26.35 |

Slurry composition: 0.2 g of catalyst, 280 mL of $H_2O$, 45.7 g of $ZnSO_4 \cdot 7H_2O$.
Hydrogenation conditions: 140 mL of $C_6H_6$, 5MPa of $H_2$ pressure, 150 °C, 1400 *rpm*.

**Table S11.** Activity and selectivity of the Ru NPs with 196mg $Zn(OH)_2$.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 15.51 | 90.84 | 14.09 |
| 10 | 34.39 | 87.47 | 30.08 |
| 15 | 56.55 | 82.69 | 46.76 |
| 20 | 73.99 | 76.55 | 56.64 |
| 25 | 83.48 | 72.15 | 60.23 |

**Table S12.** Activity and selectivity of the Ru NPs with 160mg ZnO.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 17.49 | 89.37 | 15.63 |
| 10 | 36.49 | 87.12 | 31.79 |
| 15 | 58.50 | 83.08 | 48.60 |
| 20 | 72.76 | 78.41 | 57.05 |
| 25 | 81.48 | 73.72 | 60.07 |

**Table S13.** Activity and selectivity of the Ru NPs with 158 mg NaOH.

| *t*/min | $C_{BZ}$/% | $S_{HE}$/% | $Y_{HE}$/% |
|---|---|---|---|
| 5 | 11.12 | 92.36 | 10.27 |
| 10 | 26.93 | 89.49 | 24.10 |
| 15 | 45.39 | 85.94 | 39.01 |
| 20 | 62.82 | 81.10 | 50.95 |
| 25 | 75.08 | 76.36 | 57.33 |

Slurry composition: 2.0 g of catalyst, 280 mL of $H_2O$, 45.7 g of $ZnSO_4 \cdot 7H_2O$.
Hydrogenation conditions: 140 mL of $C_6H_6$, 5MPa of $H_2$ pressure, 150 °C, 1400 *rpm*.

**Table S14.** The quantitative amount of $OH^-$ for the corresponding amount of BZSS, $Zn(OH)_2$, ZnO, and NaOH.

| | 300 mg BZSS | 196 mg $Zn(OH)_2$ | 160 mg ZnO | 158 mg NaOH. |
|---|---|---|---|---|
| $n_{OH-}$ (mmol) | 3.93 | 3.94 | 3.94 | 3.95 |

The quantitative methods is based on the amount of $OH^-$. $Zn(OH)_2$, ZnO, and NaOH are considered to react according to the equation (1)-(3) in the presence of $ZnSO_4$ solution.

$$3Zn(OH)_2 + ZnSO_4 + xH_2O \rightarrow ZnSO_4(Zn(OH_2))_3 \cdot xH_2O \quad (1)$$

$$3ZnO + ZnSO_4 + (x+3)H_2O \rightarrow ZnSO_4(Zn(OH_2))_3 \cdot xH_2O \quad (2)$$

$$6NaOH + 4ZnSO_4 + xH_2O \rightarrow ZnSO_4(Zn(OH_2))_3 \cdot xH_2O + 3Na_2SO_4 \quad (3)$$