

## Supporting Information

### **Ru Nanospheres in Water Drops for Enhanced Catalytic Performances in Selective Hydrogenation**

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### *Experimental section*

#### *Preparation of Ru(0) catalyst*

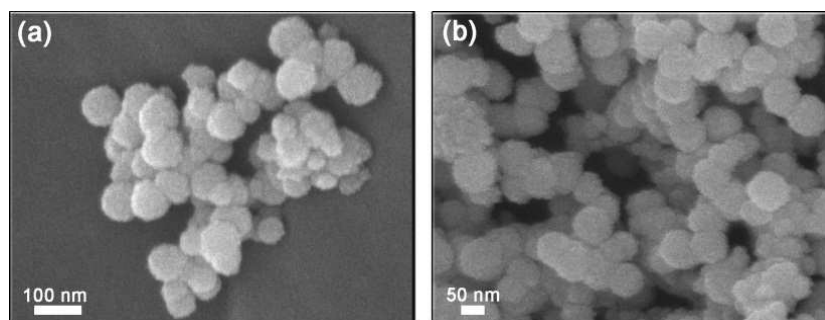
19.46 g  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was dissolved in 200 mL of  $\text{H}_2\text{O}$  with agitation. 11.12 g NaOH was dissolved in 200 mL of  $\text{H}_2\text{O}$  and then added to the above stirred solution instantaneously and the resulting mixture was agitated for an additional 30 min. The black precipitate was then transferred into a 1 L Hastelloy autoclave. Hydrogen was introduced into the autoclave to raise the total internal pressure of 5 MPa and operated at 150 °C, 800 rpm for 3 h. When the reaction mixture was cooled, the catalyst was washed with deionized water until  $\text{Cl}^-$  was undetectable, and then the desired Ru catalysts were obtained.

**Table S1.** Textural properties and crystallite size of three catalysts.

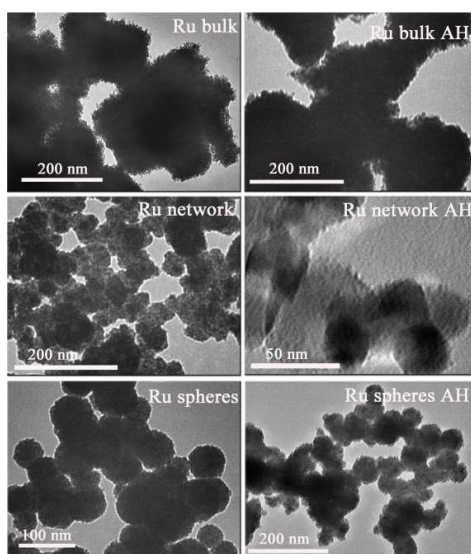
Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{Pore}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{Pore}}$	$d_{\text{M}}^{\text{a}}$
			nm	
Ru bulk	13	0.02	6.7	4.2
Ru network	15	0.03	8.9	4.3
Ru NSs	20	0.05	9.2	4.0
Ru(0) <sup>[S1]</sup>	88	0.18	4.1	4.1

<sup>a</sup> Measured by Scherrer equation.**Table S2.** The variety of Ru catalysts for benzene-selective hydrogenation.

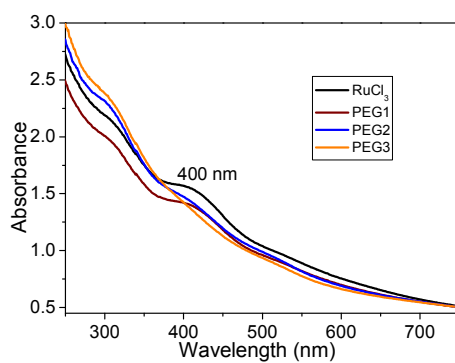
Catalysts	Benzene conv. (%)	CHE select. (%)	$Y_{\text{max}}$ (%)	Reference
Ru/La <sub>2</sub> O <sub>3</sub>	40	25	14	[1]
Ru-[bmim]BF <sub>4</sub>	49.5	34.1	17.0	[2]
Ru/BEN	59.7	44.9	26.8	[3]
Ru/Al <sub>2</sub> O <sub>3</sub>	40	13	-	[4]
Ru/ZnO-La(OH) <sub>3</sub>	48.0	50.3	29.2	[5]
Ru/ZnO-Mg(OH) <sub>2</sub>	49.8	35.2	17.5	[5]
Ru/SiO <sub>2</sub>	64.9	33.1	21.5	[6]
Ru/ZrO <sub>2</sub> -GLY	65	43	28	[7]
Ru/ZrO <sub>2</sub> -EG	58	41	24	[7]
Ru/ZrO <sub>2</sub> -PDO	84	37	31	[7]
Ru-Cd/BEN	57.4	43.1	24.8	[8]
Ru-Cu/ZnO	37.2	18.3	34.8	[9]
Ru NSs	50.0	61.9	37.5	This work



**Figure S1.** (a, b) FESEM images of Ru NSs.

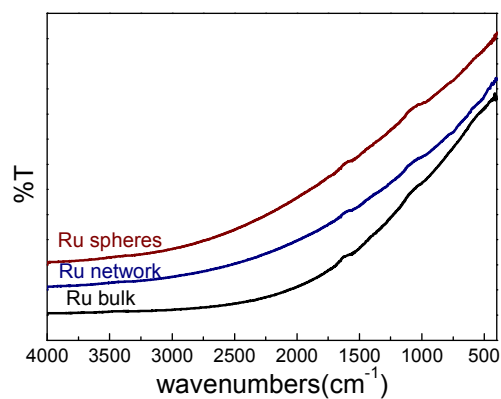


**Figure S2.** TEM images of three different morphology catalysts before and after hydrogenation (AH).

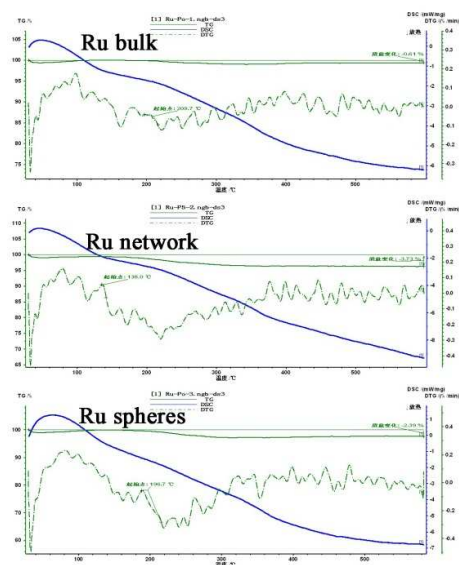


**Figure S3.** UV-Vis spectra of  $\text{Ru}^{3+}$  with different amount of  $\text{PEG}_{10000}$ .  
 PEG1:  $n(\text{Ru}^{3+}):n(\text{PEG})=2.44:1$   
 PEG2:  $n(\text{Ru}^{3+}):n(\text{PEG})=1.22:1$

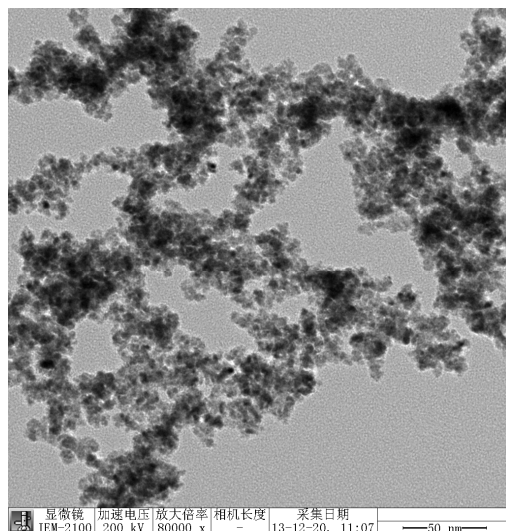
PEG3: n(Ru<sup>3+</sup>):n(PEG)=0.61:1



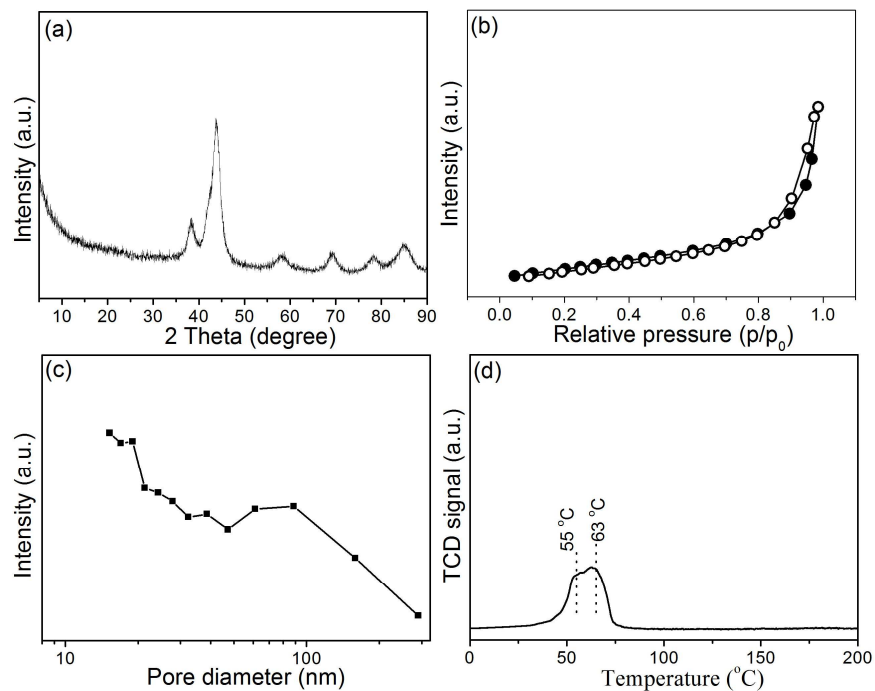
**Figure S4.** FT-IR spectra of three different morphology catalysts. Ru bulk (0.547 mg) in KBr (124.5 mg); Ru network (0.542 mg) in KBr (124.7 mg); Ru spheres( 0.548 mg) in KBr (126.3 mg).



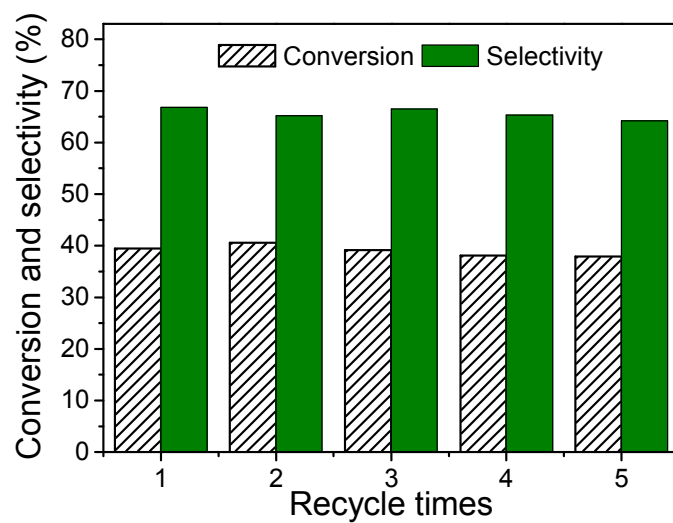
**Figure S5.** TG and DSC curves of three different morphology catalysts measured in Ar atmosphere.



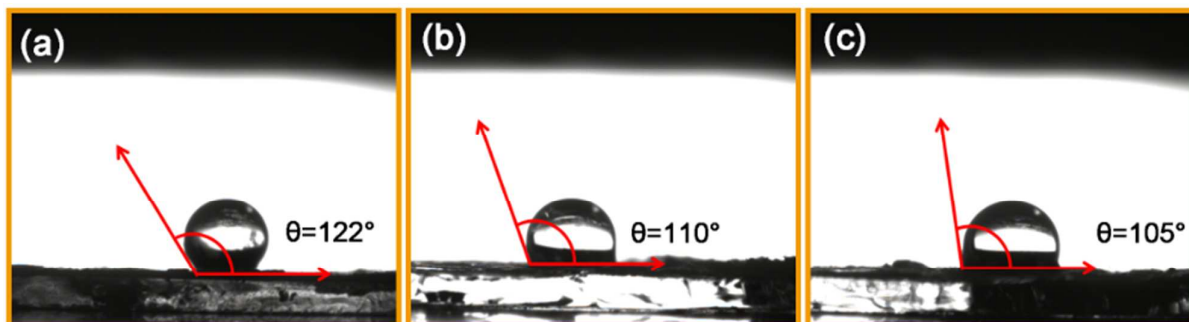
**Figure S6.** TEM image of Ru(0) prepared by coprecipitation.



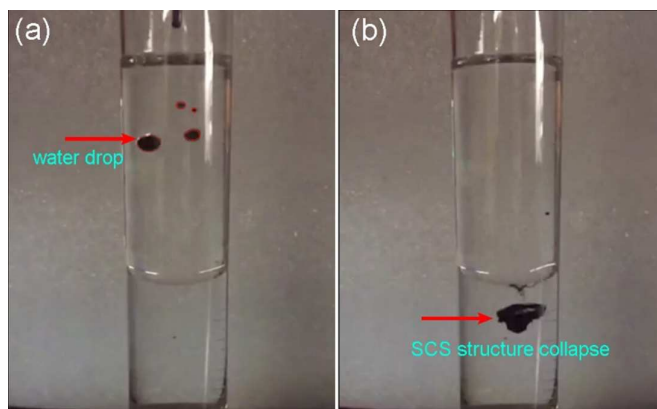
**Figure S7.** (a) XRD patterns, (b) N<sub>2</sub> adsorption (close symbol)-desorption (open symbol) isotherms, (c) pore size distribution curves, and (d) H<sub>2</sub>-TPR profiles of Ru(0) catalysts.



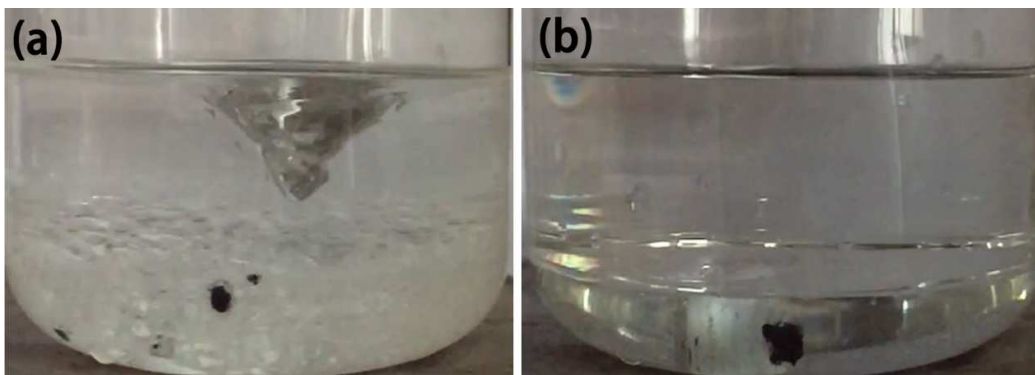
**Figure S8.** Reusability of Ru NSs for benzene-selective hydrogenation towards benzene conversion and CHE selectivity (sampling at 25 min).



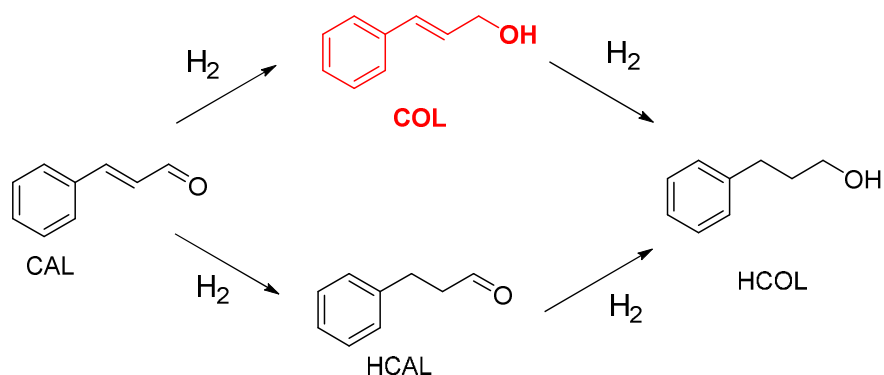
**Figure S9.** The water contact angle test for the (a) Ru bulk, (b) Ru network, and (c) Ru NSs.



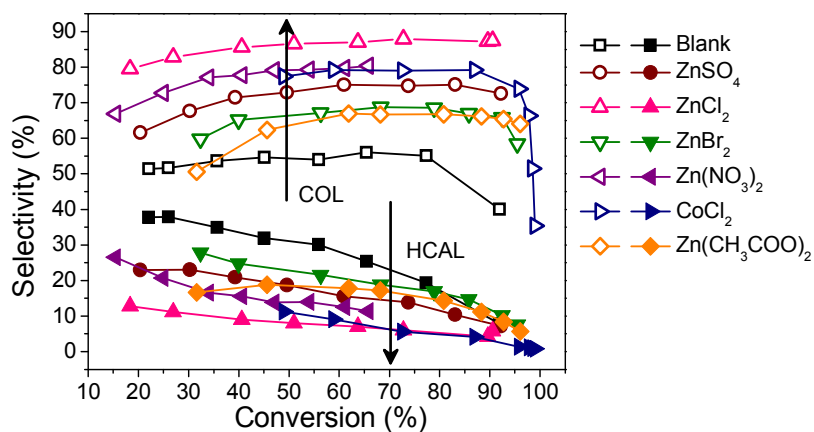
**Figure S10.** illustration of (a) the catalyst particles locating in water drops in benzene phase and (b) the SCS structure collapsing in water phase.



**Figure S11.** Illustration of the Ru SCS structure (a) under stirring and (b) stop stirring.



**Figure S12.** Hydrogenation of cinnamaldehyde (CAL) (cinnamyl alcohol (COL) is the preferred product)



**Figure S13.** The selectivity of COL and HCAL as a function of CAL conversion in the presence of variety of electrolyte solutions. Reaction condition: 0.2 g of catalyst, 48 mL of H<sub>2</sub>O, 12 mL of CAL,  $C_{\text{salt}} = 0.5 \text{ mol L}^{-1}$ , temperature of 70 °C, H<sub>2</sub> pressure of 5.0 MPa, and stirring rate of 800 rpm



## References

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