

Supporting Information

Targeted-regulating the selectivity of cascade synthesis towards imines/secondary amines by carbon-coated Co-based catalysts

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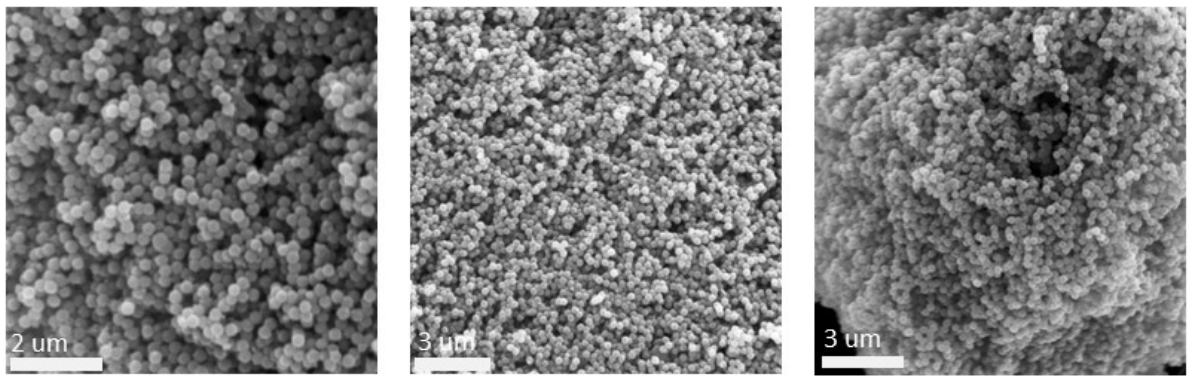


Figure S1. Representative SEM images of PtCo/SiO₂@CN

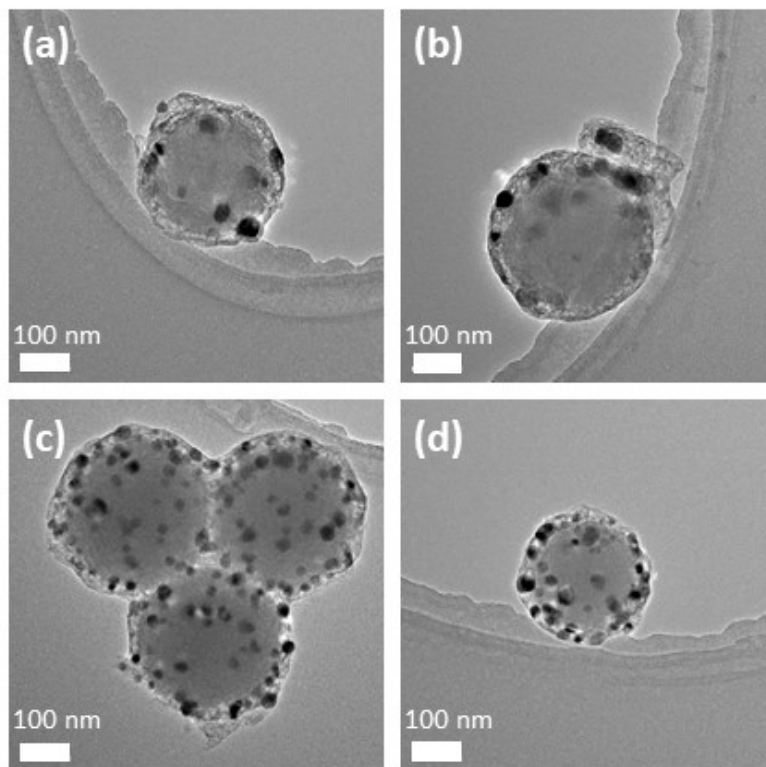


Figure S2. TEM images of the effect of ethanol, water and ammonia water on the morphology of SiO₂ balls and the degree of metal dispersion when the ratio of ethanol, water and ammonia water was 12.5 : 1.65 : 0.5. a, b) Co/SiO₂@CN; c, d) PtCo/SiO₂@CN.

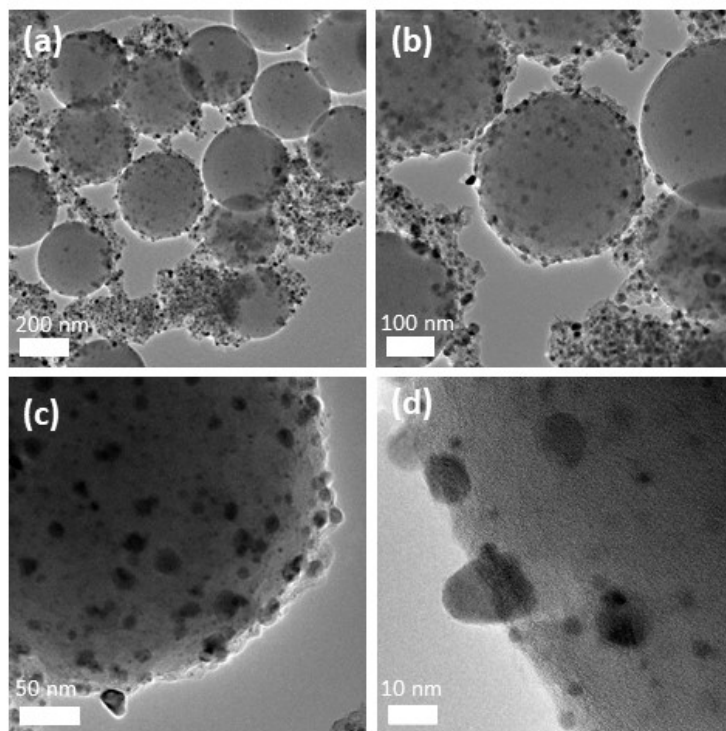


Figure S3. TEM images of the effect of ethanol, water and ammonia water on the morphology of SiO₂ balls and the degree of metal dispersion when the ratio of ethanol, water and ammonia water was 24 : 80 : 1. a, b, c, d) PtCo/SiO₂@CN.

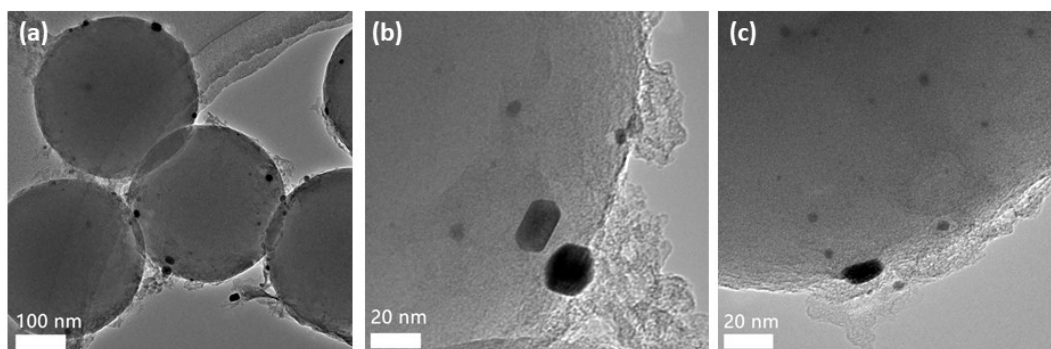


Figure S4. a,b,c) Representative TEM images of Pt/SiO₂@CN.

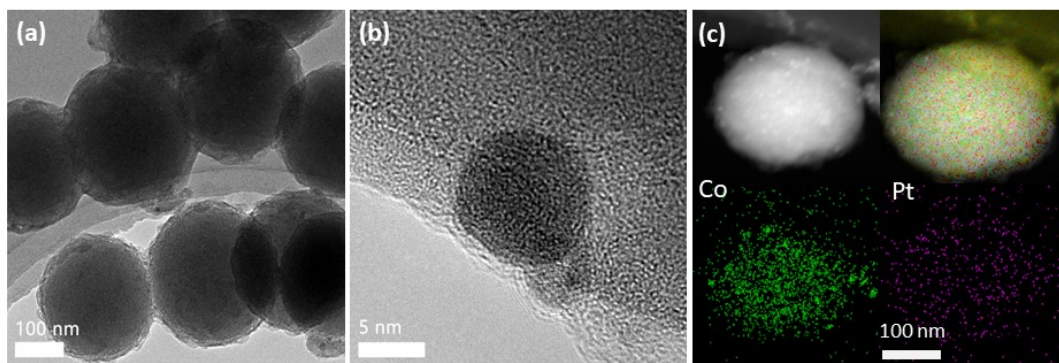


Figure S5. a,b,c) Representative TEM and HRTEM images of PtCo/SiO₂@CN-HCl-21day and the corresponding EDS elemental mapping of Co and Pt.

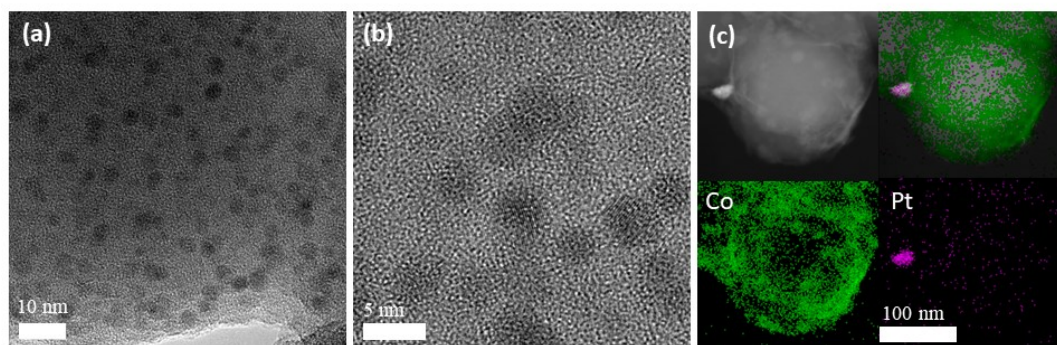


Figure S6. a,b,c) Representative TEM and HRTEM images of PtCo/SiO₂-NaBH₄ and the corresponding EDS elemental mapping of Co and Pt.

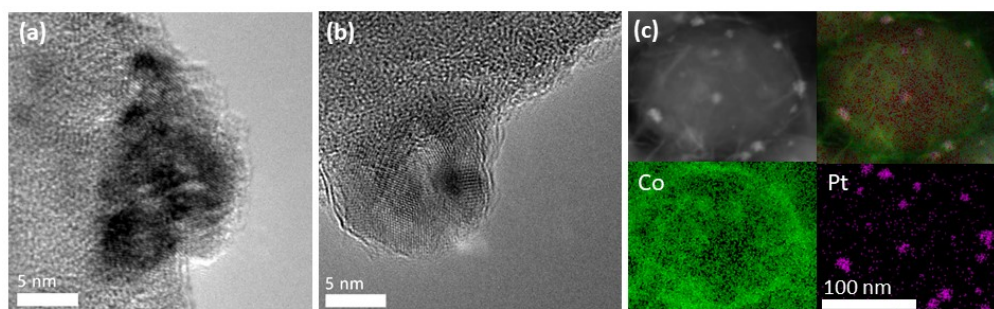


Figure S7. a,b,c) Representative HRTEM images of Co/SiO₂@CN-Pt and the corresponding EDS elemental mapping of Co and Pt.

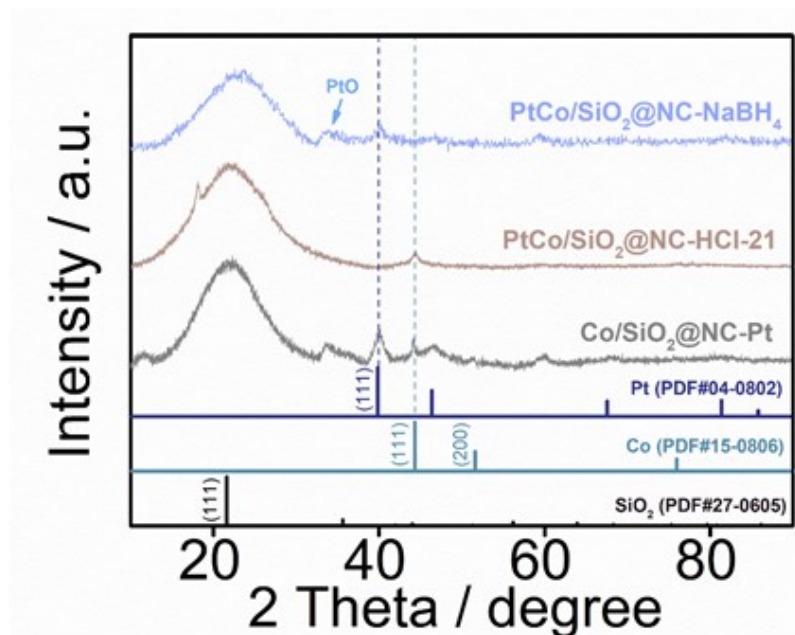


Figure S8. XRD images of Co/SiO₂@CN-Pt, PtCo/SiO₂@CN-HCl-21day and PtCo/SiO₂-NaBH₄.

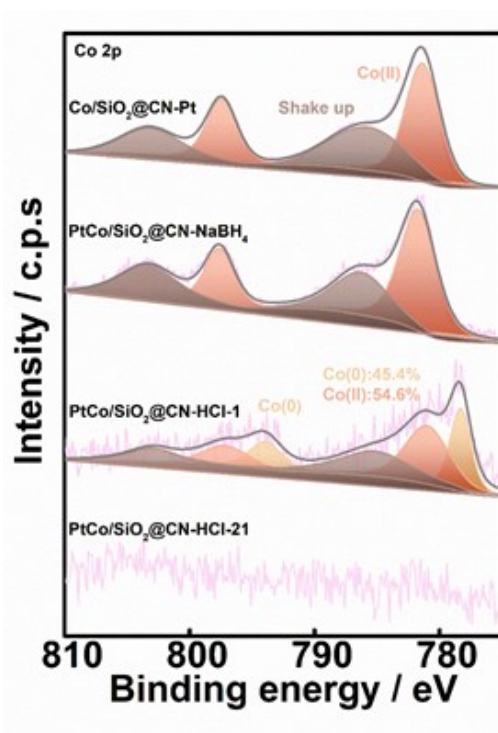


Figure S9. Co 2p XPS spectrum images of Co/SiO₂@CN-Pt, PtCo/SiO₂@CN-HCl-1day, PtCo/SiO₂@CN-HCl-21day and PtCo/SiO₂-NaBH₄.

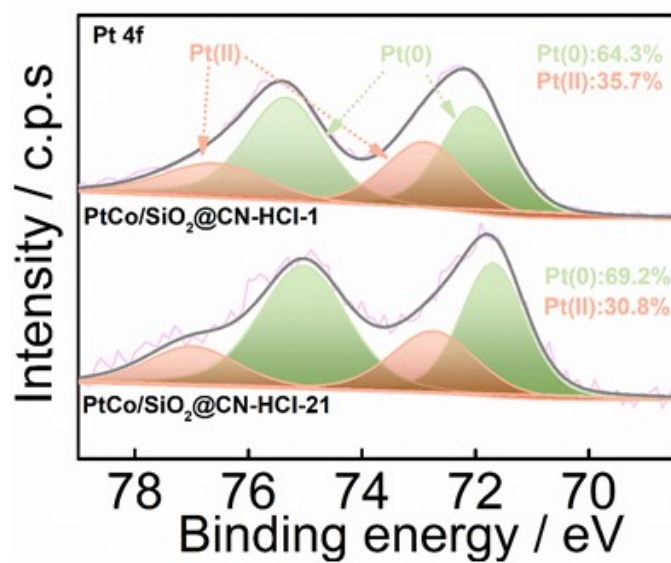


Figure S10. Pt 4f XPS spectrum images of PtCo/SiO₂@CN-HCl-1day, PtCo/SiO₂@CN-HCl-21day.

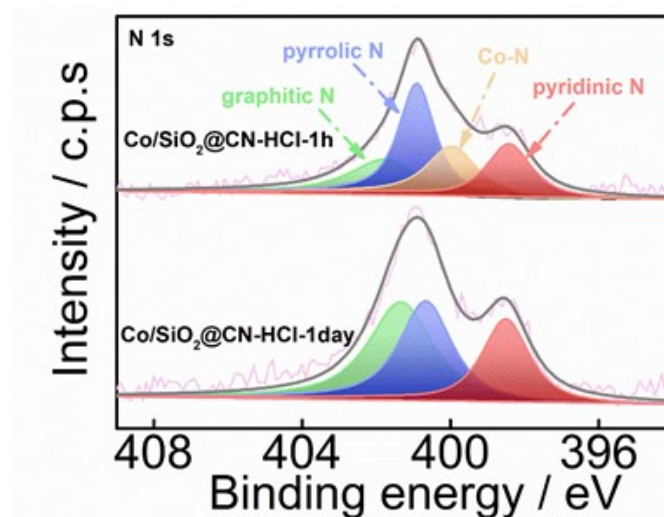


Figure S11. N 1s XPS spectrum images of Co/SiO₂@CN-HCl-1h and Co/SiO₂@CN-HCl-1day.

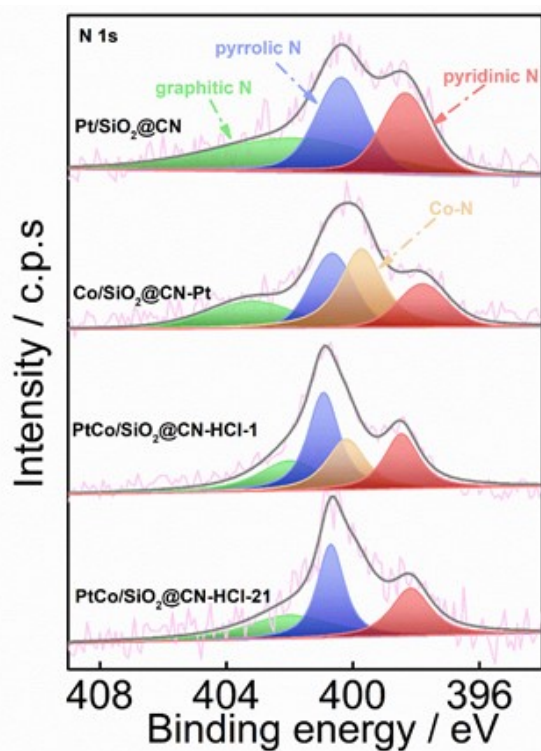


Figure S12. N 1s XPS spectrum images of Pt/SiO₂@CN, Co/SiO₂@CN-Pt, PtCo/SiO₂@CN-HCl-1day and PtCo/SiO₂@CN-HCl-21day.

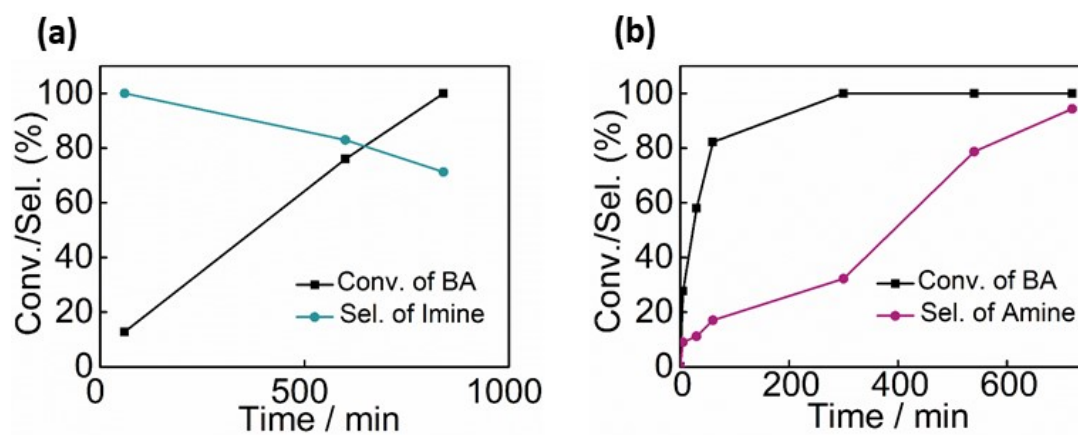


Figure S13. Activity test of PtCo/SiO₂@CN at different temperatures a) room temperature, b) 50 °C.

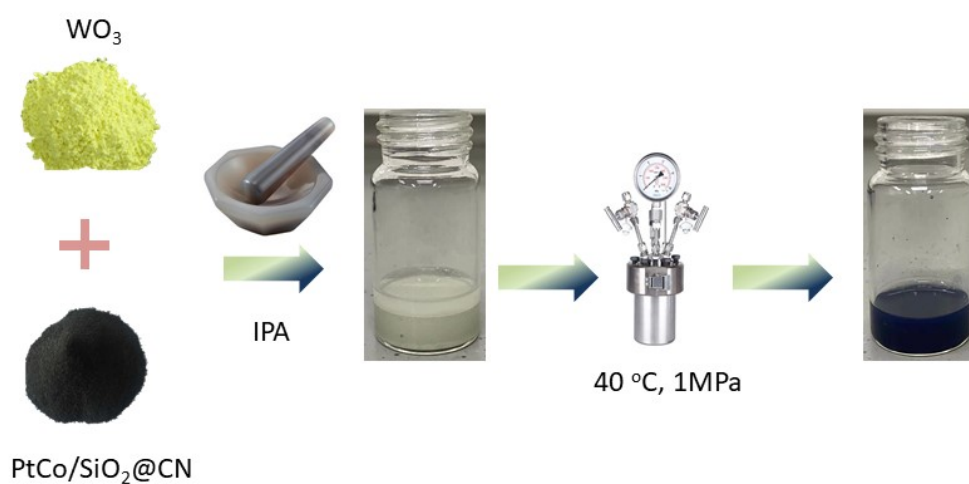


Figure S14. Physical mixed solution of PtCo/SiO₂@CN and WO₃ before and after the reaction. Reaction conditions: 1.02 g mixture catalyst (PtCo/SiO₂@CN : WO₃=1:50), 600 r/min, 5 mL solvent, 1 h, 1 Mpa H₂.

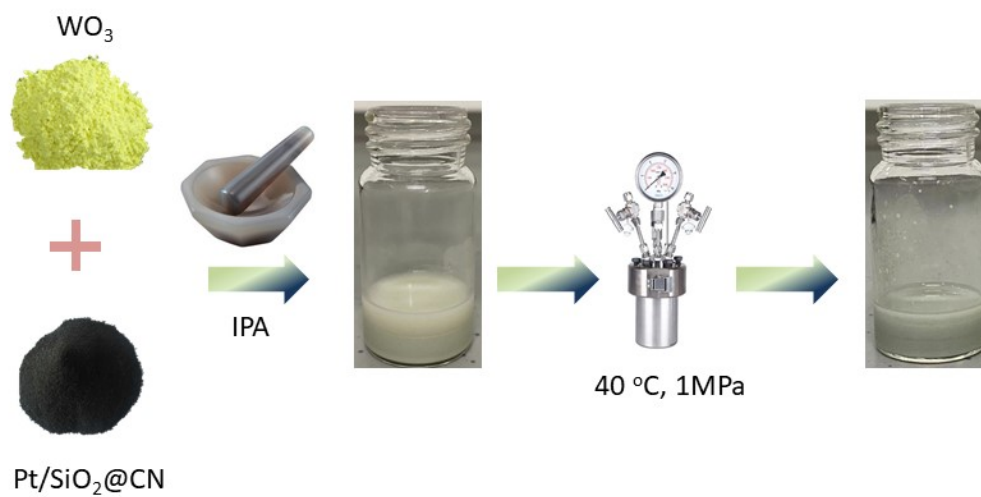


Figure S15. Physical mixed solution of Pt/SiO₂@CN and WO₃ before and after the reaction. Reaction conditions: 1.02 g mixture catalyst (PtCo/SiO₂@CN : WO₃=1:50), 600 r/min, 5 mL solvent, 1 h, 1 Mpa H₂.

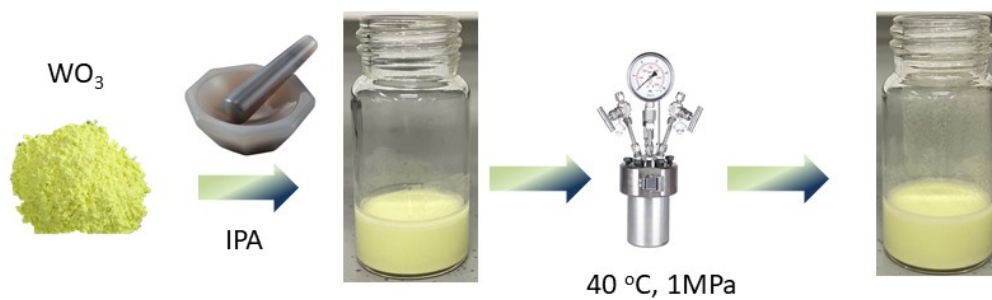


Figure S16. Solution of WO_3 before and after the reaction. Reaction conditions: 1 g WO_3 , 600 r/min, 5 mL solvent, 4 h, 1 MPa H_2 .

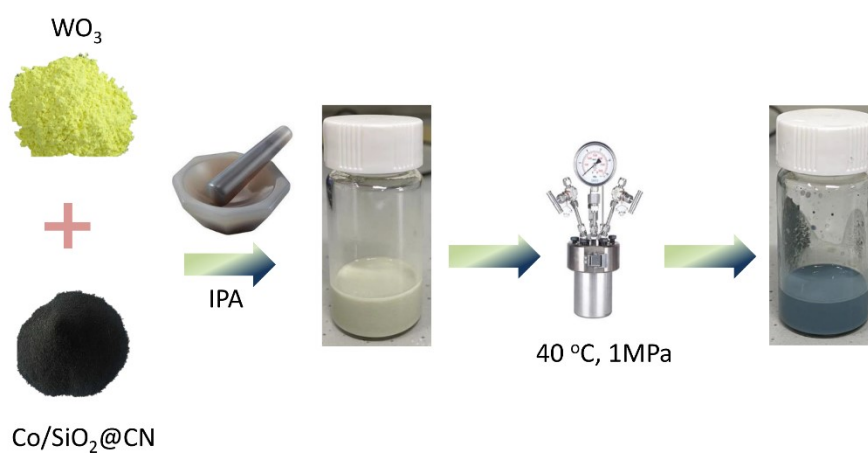


Figure S17. Physical mixed solution of $\text{Co/SiO}_2@\text{CN}$ and WO_3 before and after the reaction. Reaction conditions: 1.02 g mixture catalyst ($\text{Co/SiO}_2@\text{CN} : \text{WO}_3 = 1:50$), 600 r/min, 5 mL solvent, 4.5 h, 1 MPa H_2 .

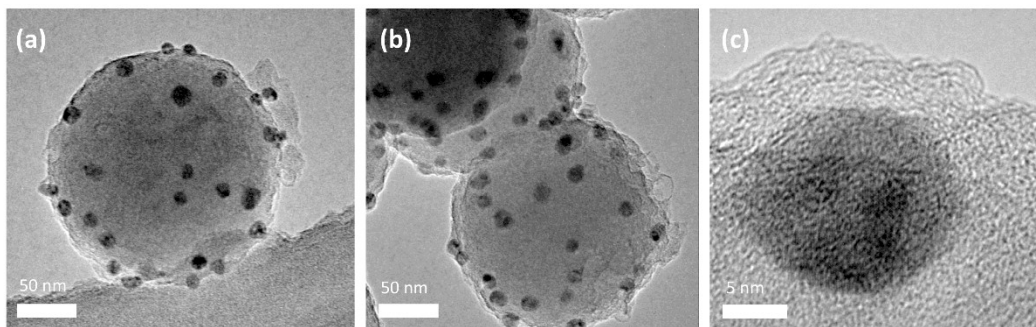


Figure S18. a, b, c) Representative TEM and HRTEM images of the used Co/SiO₂@CN.

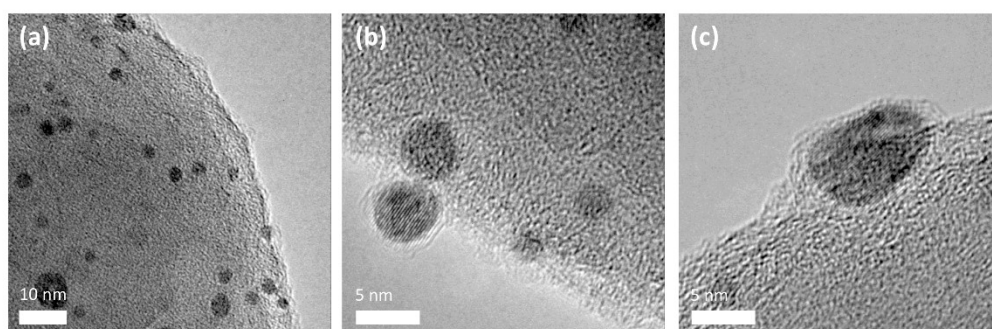


Figure S19. a, b, c) Representative TEM and HRTEM images of the used PtCo/SiO₂@CN.

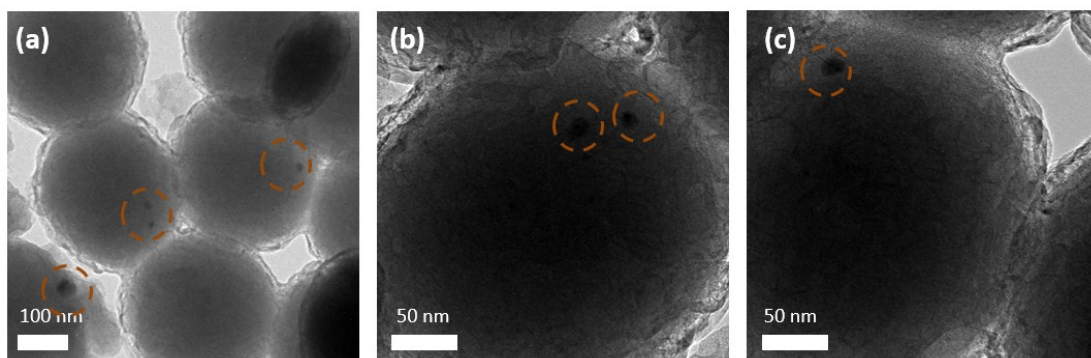


Figure S20. a, b, c) Representative TEM images of the Co/SiO₂@CN-HCl-1day.

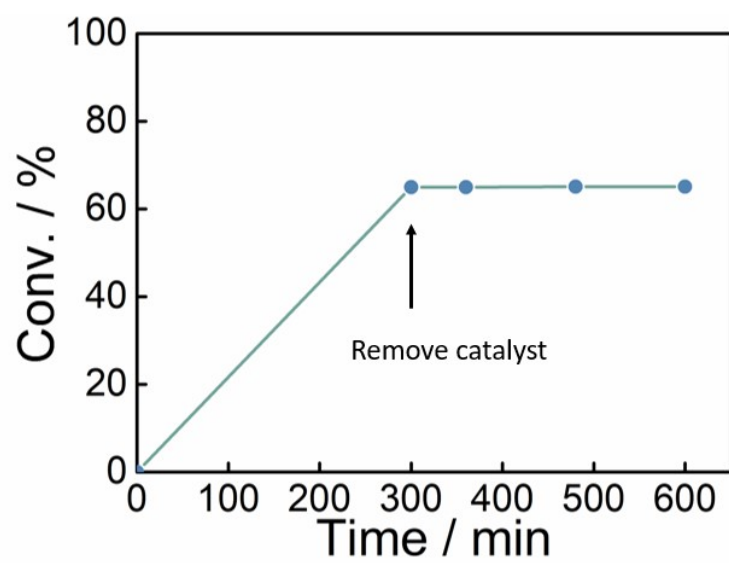


Figure S21. Hot filtration experiments of Co/SiO₂@CN.

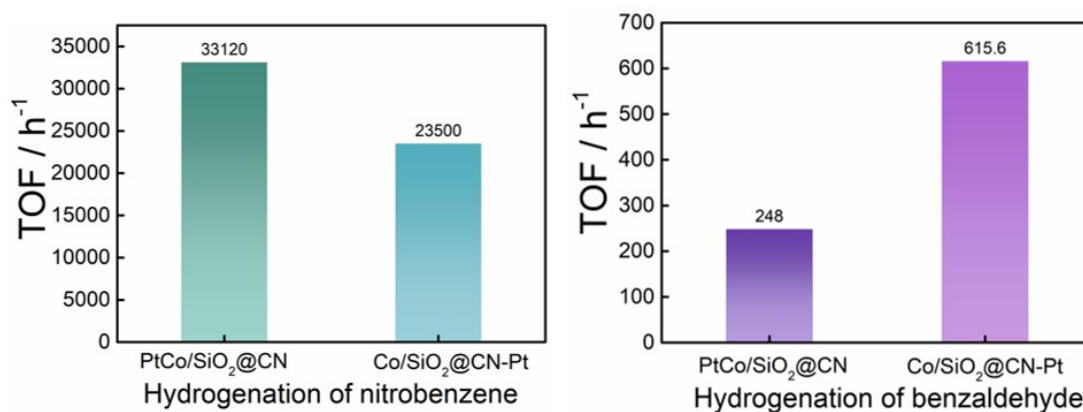


Figure S22. Effect of Pt in and out of carbon layer on reaction rate. a) hydrogenation of nitrobenzene, b) hydrogenation of benzaldehyde.

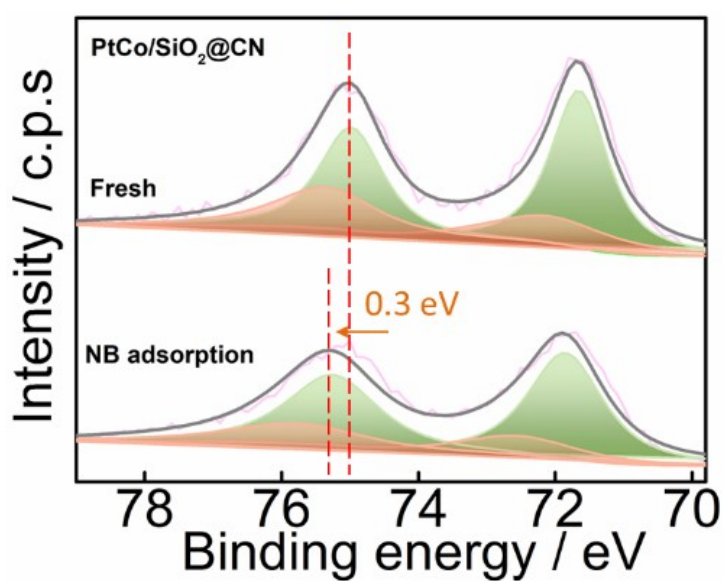


Figure S23. Pt 4f XPS spectra of PtCo/SiO₂@CN before and after NB adsorption.

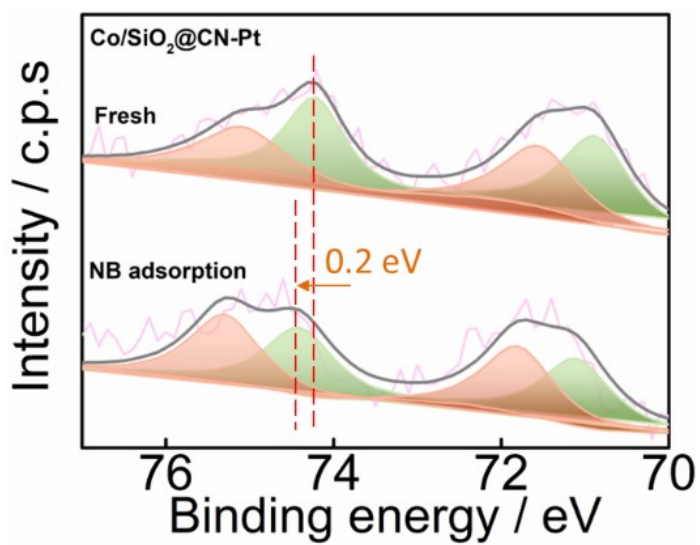


Figure S24. Pt 4f XPS spectra of Co/SiO₂@CN-Pt before and after NB adsorption.

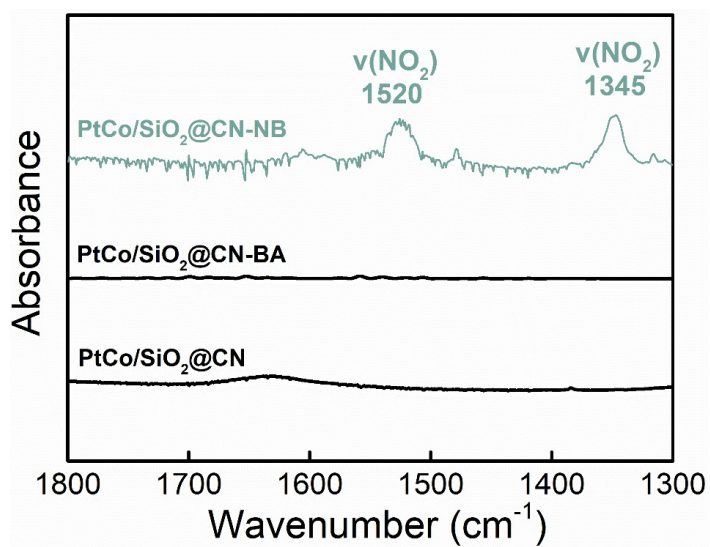


Figure S25. FT-IR spectra of PtCo/SiO₂@CN after treatment with BA and NB.

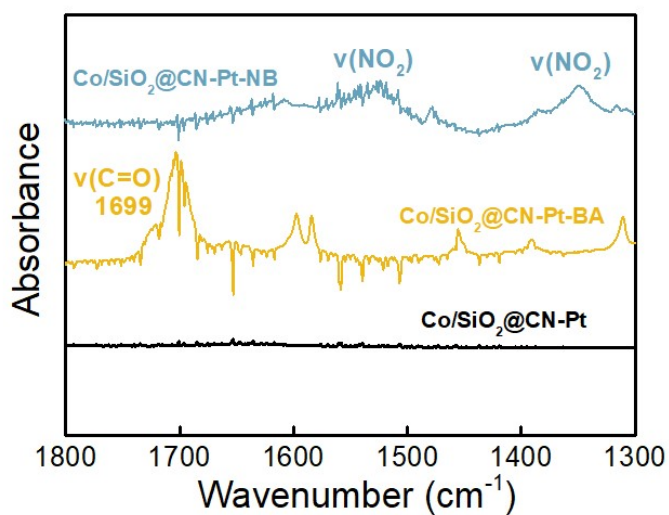


Figure S26. FT-IR spectra of $\text{Co/SiO}_2\text{@CN-Pt}$ after treatment with BA and NB.

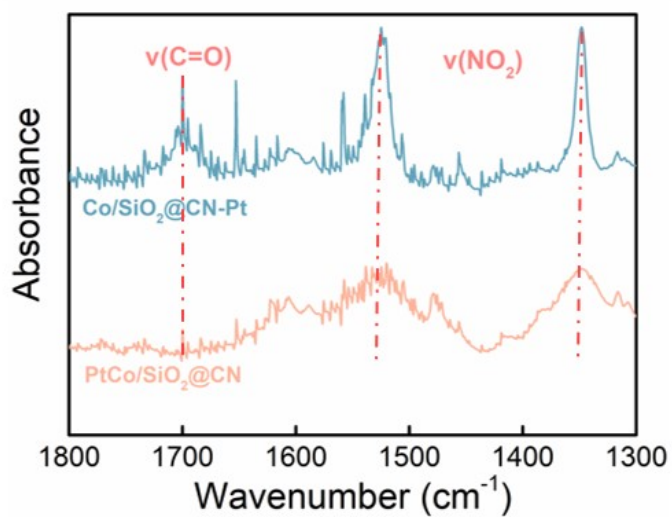


Figure S27. FT-IR spectra of $\text{PtCo/SiO}_2\text{@CN}$ and $\text{Co/SiO}_2\text{@CN-Pt}$ after treatment with the mixture of BA and NB.

Table S1. ICP testing of each catalyst

| Sample | Metal loading | |
|--|---------------|-----------|
| | Pt (wt.%) | Co (wt.%) |
| PtCo/SiO ₂ @CN | 0.8 | 8.4 |
| Co/SiO ₂ @CN-Pt | 1.4 | 10.2 |
| PtCo/SiO ₂ -NaBH ₄ | 1.1 | 10.8 |
| Co/SiO ₂ @CN | / | 9.0 |
| Pt/SiO ₂ @CN | 0.8 | / |

Table S2. Comparison of the catalytic performance of PtCo/SiO₂@CN and Co/SiO₂@CN with other catalytic system in references

| Entry | Catalyst | T [°C] | Pre. [MPa] | TOF[h ⁻¹] | Selectivity[%] | | Ref. |
|-------|---|-----------|---------------|-----------------------|----------------|--|-----------|
| | | | | | Imine | Amine | |
| 1 | Co/SiO ₂ @CN | 60 | 1 | 64 | 98.0 | | This work |
| 2 | PtCo/SiO ₂ @CN | 60 | 1 | 296 | | 100 | This work |
| 3 | CAT-450 | 120 | 2 | - | 0.7 | 85.2 | [1] |
| 4 | Pd ₃ /γ-Al ₂ O ₃ | 80 | 2 | 9.2 | 94.5 | | [2] |
| 5 | CoOx@NC-800 | 110 | 5 | - | 100 | | [3] |
| 6 | CoS ₂ @MoS ₂ -180-0.75 | 60 | 1.5 | - | 93 | 3.8 | [4] |
| 7 | Ni ₃ Sn ₂ /TiO ₂ | 150 | 1 | 2.2 | 100 | | [5] |
| 8 | NiCo ₅ | 90 | 1 | 10.0 | 83 | | [6] |
| 9 | Co/mCN-900 | 120 | 1 | 12.3 | 0.2 | 99.8 | [7] |
| 10 | Pd ₁ Ag ₁ @MIL-101 | r.t. | 0.2 | 20.2 | 3 | 90 | [8] |
| 11 | AuPd-Fe ₃ O ₄ | r.t. | 0.1 | 93.3 | | 93 | [9] |
| 12 | GA-Pd | r.t. | 0.1 | - | | 88 | [10] |
| 13 | Fe ₂ O ₃ /NGr@C | 120 | 5 | 1.48 | | 89 | [11] |
| 14 | CoOx@NCNTs | 110 | 3 | 8.3 | 100 , | Hydrogenation of nitrobenzene | [12] |
| 15 | Co-SiCN | 110 | 5 | 1.4 | 82 | | [13] |
| 16 | Ni/C | 140 | 1 | 6.3 | 86.6 , | hydrogenation of o-chloronitrobenzenes | [14] |
| 17 | Ni-W ₂ C/mpg-CN _x | 220 | 2.5 | 28.1 | 100 , | Hydrogenation of nitrobenzene | [15] |
| 18 | Co/NC-600 | 170 | 4 | - | | 99.4 | [16] |

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