# Supporting Information

## 3D Charged Grid Induces a High Performance Catalyst: Ruthenium Clusters Enclosed in X-zeolite for Hydrogenation of Phenol to Cyclohexanone

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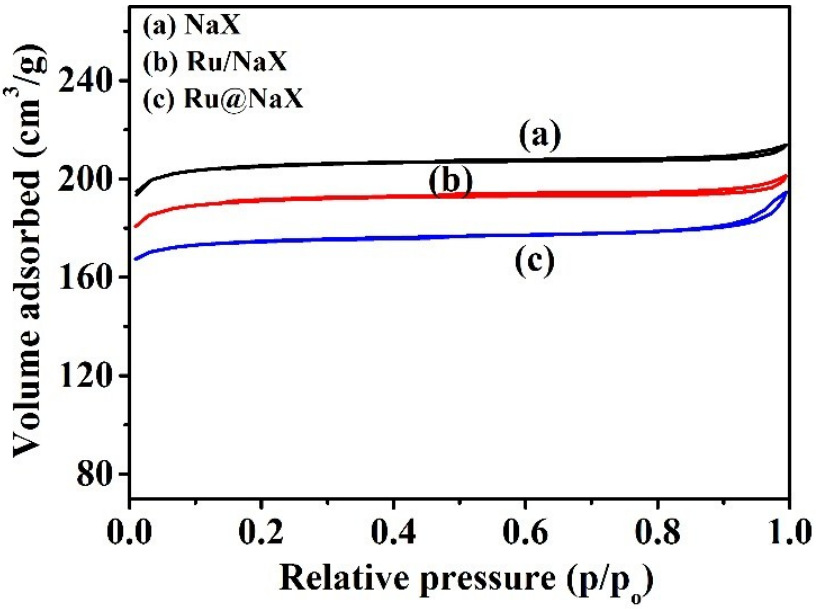


**Figure S1.** The $N_2$ adsorption/desorption isotherms of different samples.

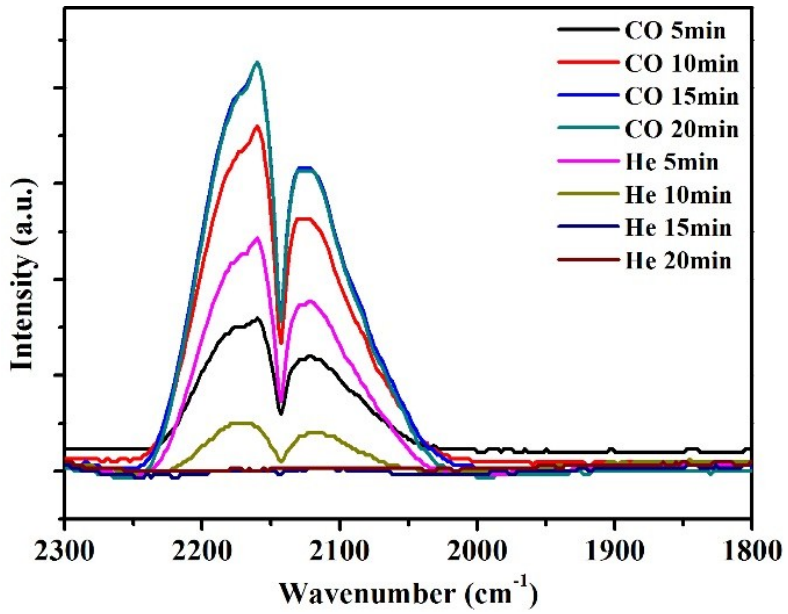


**Figure S2.** The in-situ DRIFTS of CO adsorption on NaX zeolite. (There are two CO bands located at 2173 $cm^{-1}$ and 2118 $cm^{-1}$, associated respectively with the formation of OH-CO adducts and gas phase CO.)

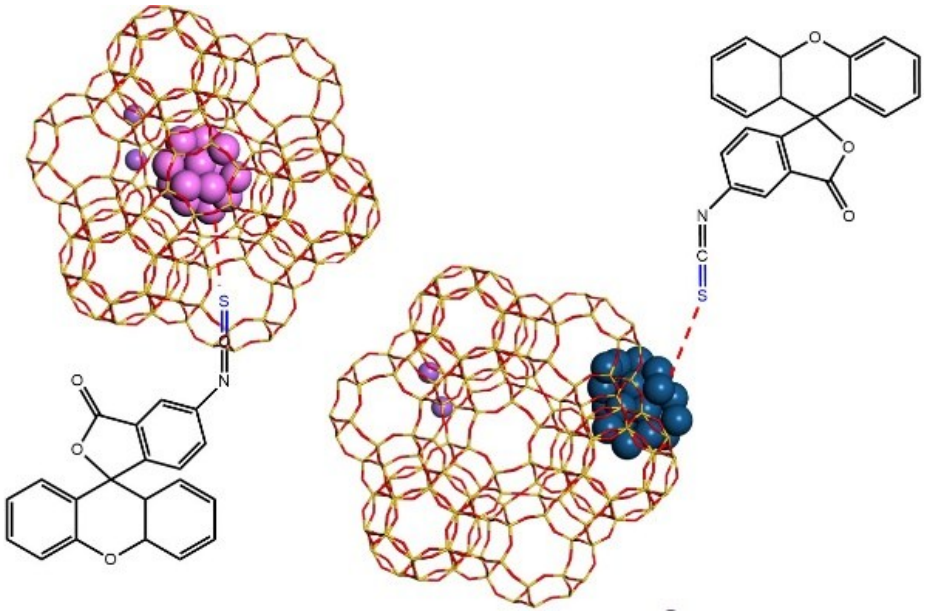

**Figure S3.** The adsorption model of FITC over the Ru@NaX and Ru/NaX.

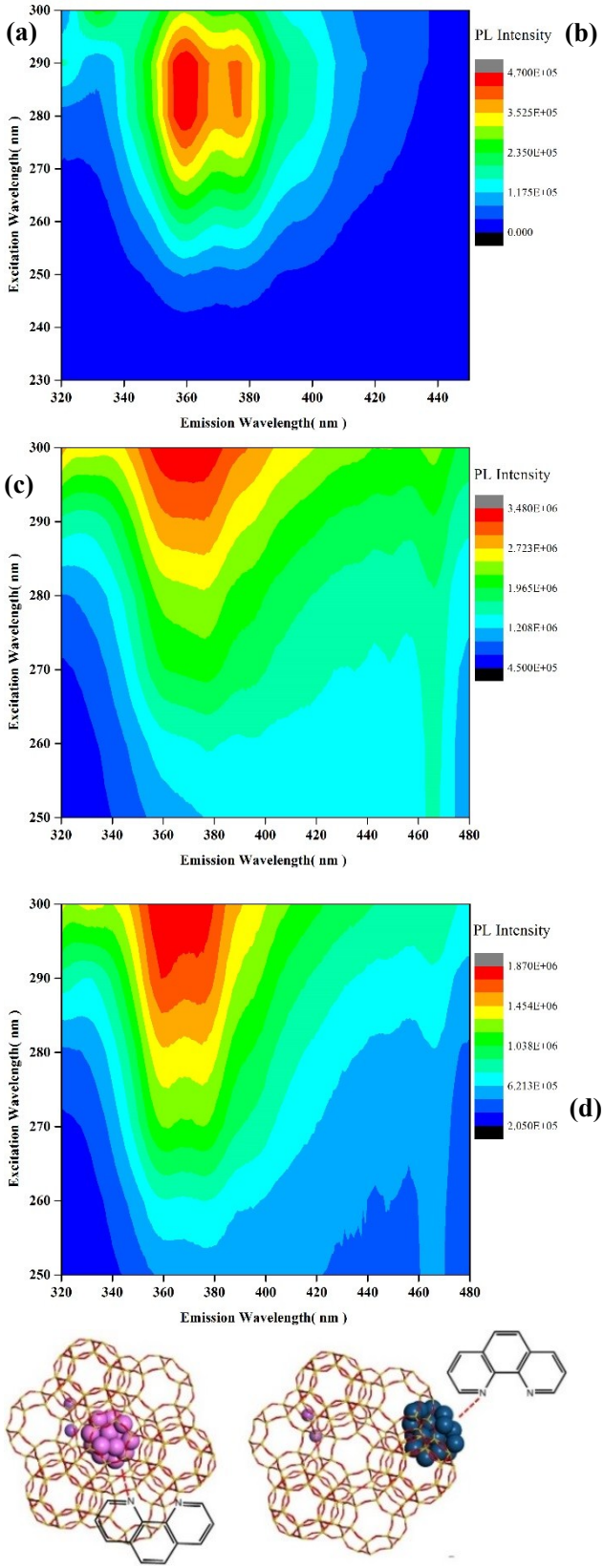


**Figure S4.** The three-dimensional fluorescence spectrum of (a) 1,10-phenanthrolinemonohydrate (PM); (b) PM/Ru@NaX; (c) PM/Ru/NaX; (d) The adsorption model of PM over the Ru@NaX and Ru/NaX.

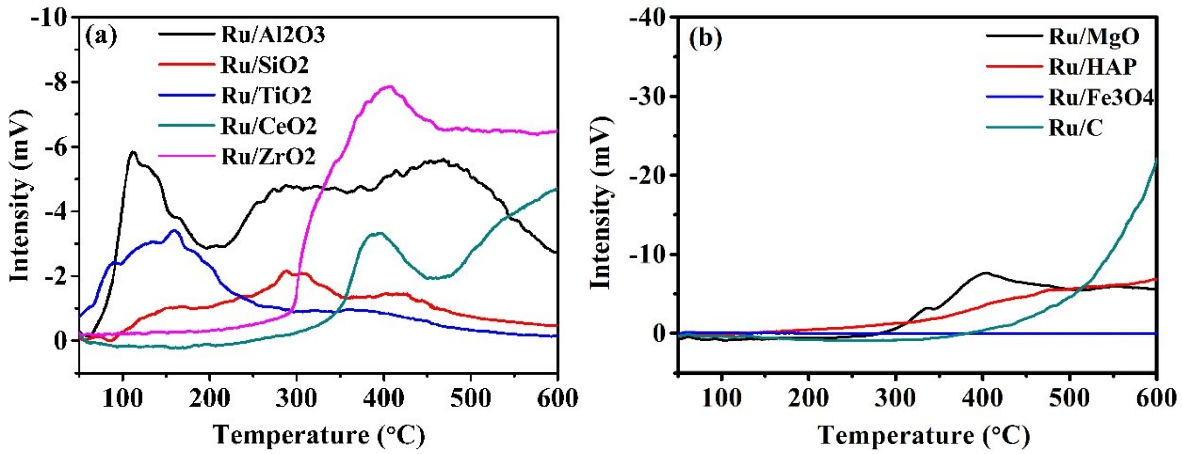


**Figure S5.** The $H_2$-TPD experimental curves for different samples.

**Table S1.** The catalytic performance of phenol selective hydrogenation for ruthenium catalysts in literatures

| Catalyst | Loading (%) | Reaction conditions | | | | Catalytic performance | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | Temperature (K) | Pressure (MPa) | Time (h) | Solvent | Conversion (%) | Selectivity (%) | |
| Ru/γ-$Al_2O_3$ | 5.0 | 433 | 5.0 | 2 | water | 81.5 | 87.0 | 1 |
| Ru/MIL-101 | 5.0 | 323 | 0.5 | 4 | water | 90.0 | 90.0 | 2 |
| Ru/MSN | 2.1 | 323 | 1.0 | 1 | $CH_2Cl_2$ | 1.1 | 64.9 | 3 |
| Ru/K-10 | ~ | 298 | 0.4 | 3 | water | 23.0 | 38.5 | 4 |
| Ru/γ-$Al_2O_3$ | ~ | 433 | 5.0 | 2 | cyclohexane | 88.0 | 83.0 | 5 |
| Ru/C | 5.0 | 328 | 10.0 | 2 | $CO_2$ | 30.0 | 5.0 | 6 |
| Ru@NDCs | 3.0 | 313 | 0.5 | 2 | water | 52.0 | 2.0 | 7 |
| Ru@C | 5.0 | 328 | 10 | 2 | water | 30.0 | 5.0 | 8 |

**Table S2.** The catalytic performance of phenol selective hydrogenation for different catalysts in literatures

| Catalyst | Loading (%) | Reaction conditions | | | | Catalytic performance | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | Temperature (K) | Pressure (MPa) | Time (h) | Solvent | Conversion (%) | Selectivity (%) | |
| Pd@sMMT-1 | 1.5 | 308 | 0.1 | 15 | water | 99.0 | 98.0 | 9 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $Pd/CeO_2$ | 1.0 | 298 | 0.1 | 4 | water | 86.2 | 96.3 | 10 |
| Pd@CN | ~ | 318 | 0.1 | 4 | water | 100.0 | 99.0 | 11 |
| $Pd/C\text{-}AlCl_3$ | 5.0 | 303 | 1.0 | 12 | water | 99.9 | 99.9 | 12 |
| Pd/FDU-N | 5.0 | 373 | 0.1 | 1 | water | 80.0 | 99.0 | 13 |
| Pd/UHT | 2.0 | 453 | 0.1 | 4 | vapour-phase | 95.0 | 85.0 | 14 |
| $Pd/TiO_2\text{-}C$ | 1.1 | 373 | 0.5 | ~ | water | 99.0 | 98.0 | 15 |
| Pd-NPs | 2.0 | 363 | 0.1 | 16 | water | 99.7 | 99.5 | 16 |
| Pd/MIL-101 | 4.9 | 323 | 0.5 | 2 | water | 90.0 | 98.6 | 17 |
| $Pd/Al_2O_3$ | ~ | 490 | no | ~ | $CH_3OH/H_2O$ | 82.5 | 77.1 | 18 |
| Pd-La-B | | 393 | 1.0 | 4 | water | 79.0 | 38.0 | 19 |
| Pd@mpg-C3N4 | 5.0 | 373 | 0.1 | 1 | water | 99.0 | 99.0 | 20 |

**Table S3.** Textural properties and Ru content (%) of different samples.

| Entry | Sample | $S_{BET}$[a] ($m^2g^{-1}$) | PV[b] ($cm^3g^{-1}$) | PS[c] (nm) | Ru Content (%, ICP-AES) |
|---|---|---|---|---|---|
| 1 | NaX | 682.2 | 0.14 | 2.07 | 0 |
| 2 | Ru/NaX | 632.3 | 0.18 | 2.14 | 0.57 |
| 3 | Ru@NaX | 584.5 | 0.19 | 2.01 | 0.58 |
| 4 | $Ru/Al_2O_3$ | 134.3 | 0.45 | 11.43 | 0.59 |
| 5 | $Ru/TiO_2$ | 60.8 | 0.14 | 3.45 | 0.57 |
| 6 | $Ru/SiO_2$ | 387.3 | 0.87 | 2.56 | 0.59 |
| 7 | $Ru/CeO_2$ | 92.2 | 0.17 | 3.8 | 0.64 |
| 8 | Ru/HAP | 105.0 | 0.44 | 12.8 | 0.56 |
| 9 | $Ru/ZrO_2$ | 72.9 | 0.09 | 3.6 | 0.63 |
| 10 | Ru/C | 1510.9 | 0.98 | 0.75 | 0.57 |
| 11 | $Ru/Fe_3O_4$ | 49.5 | 0.67 | 10.5 | 0.55 |

| | | | | | |
|---|---|---|---|---|---|
| 12 | Ru/MgO | 55.6 | 0.54 | 3.2 | 0.61 |

[a] BET surface area, [b] Pore volume, [c] Pore size.

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