# **Supplementary Information**

### Core-shell Structured Cobalt-oxide Nanoparticles and Single Co Atoms Supported on Graphene for Selective Hydrodeoxygenation of Syringol to Cyclohexanol

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#### Preparation of GO and rGO

Graphene oxide (GO) used in this research was prepared following the modified Hummers' method. In brief, the flake graphite was first mixed with NaNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mixture in an ice-water bath. Then the mixture was gradually added with KMnO<sub>4</sub> and underwent oxidation reaction at 35 °C for 2 h. Next, the mixture was diluted by water (twice the volume of H<sub>2</sub>SO<sub>4</sub>) and heated at 90 °C–98 °C for 15 min. Then, the reaction mixture was gradually added with sufficient water (about six times the volume of H<sub>2</sub>SO<sub>4</sub>) under vigorous stirring with the temperature decreased to 50 °C–60 °C and added with H<sub>2</sub>O<sub>2</sub> (30 %). Finally, the mixture was allowed to stay at room temperature for 24 h. The as-prepared GO was purified by repeated centrifugation and washing. Reduced graphene oxide (rGO) was obtained following the previously reported method.<sup>39</sup> In brief, the obtained GO was suspended in water by ultrasound, added with ammonia, and reduced with hydrazine hydrate (80% in water) at 90 °C–98 °C, followed by filtering and washing with hot deionized water. The filter cake was dried with the freeze-drying method to obtain rGO. N was incorporated into the rGO network via the hydrothermal reduction of GO by using N<sub>2</sub>H<sub>4</sub> and ammonia as reducing reagents.

#### Table

Catalyst	Element mass fraction (%)				$S_{\text{BET}}$ (m <sup>2</sup> •g <sup>-1</sup> )
_	С	Н	0	Ν	-
rGO	83.6	1.7	10.2	4.5	489
Gr	98.7	0.3	-	-	191
Co <sub>2.5</sub> /rGO					385
Co <sub>1.0</sub> /Gr					167

Table S1 Property description of the supports and the corresponding catalysts.

## Figures



Fig. S1 Electron microscope images of the fresh Co<sub>2.5</sub>/rGO catalyst: (a) TEM image and particle size distribution;(b) HRTEM image; (c) HAADF-STEM image of a core-shell structured nanoparticle



Fig. S2 HAADF-STEM image of single Co atoms of the  $Co_{2.5}$ /rGO catalyst



Fig. S3 Electron microscope images of the  $Co_{2.5}/Gr$  catalyst: (a) TEM image and particle size distribution; (b) HRTEM image and corresponding fast Fourier transform (FFT) of a nanoparticle from the green square area in (a); (c) HAADF-STEM image of single Co atoms in the  $Co_{2.5}/Gr$  catalyst



Fig. S4 XRD patterns of the fresh and spent Co<sub>2.5</sub>/rGO catalysts



Fig. S5 Raman diagrams of Co<sub>2.5</sub>/rGO and Co<sub>2.5</sub>/Gr.



Fig. S6 N<sub>2</sub>-sorption characterizations of the catalysts