Supporting Information for

Preparation of hydrophobic reduced graphene oxide supported Ni-B-P-O and Co-B-P-O catalysts and their high hydrodeoxygenation activities

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Experimental Details

Preparation of catalysts The Ni(Co)-B-P-O unsupported catalyst is prepared by chemical reduction methods. $NiCl_2$ or $CoCl_2$ (5 mmol), NaH_2PO_2 (30 mmol) were dissolved in 20 mL of ultra-pure water, and then placed into a 250 mL three-necked flask. 20 mL aqueous solution of $NaBH_4$ (30 mmol) was added dropwise to the three necked flask under vigorous stirring at 0 °C. After reaction for 1 h, the black precipitate was collected and washed with ultra-pure water and ethanol for several times, and finally dried under vacuum at 50 °C for 4 h. The resultant catalyst was marked as Ni-B-P-O or Co-B-P-O.

The graphene supported Ni(Co)-B-P-O catalyst were prepared by in situ reduction method. In a typical experiment, 20 mg graphene oxide (GO) was dispersed in 20 ml ultra-pure water under ultrasonic environment. $NiCl_2$ or $CoCl_2$ (5 mmol) and NaH_2PO_2 (30 mmol) were added and dissolved into the above solution. Consequently, 20 mL solution containing 30 mmol $NaBH_4$ was added slowly at 0 °C under vigorous stirring. The reaction was proceeded for 10 h to ensure the reduction of GO to reduced grapheme oxide (RGO). The black solution was separated and washed with ultra-pure water and ethanol for several times, and then dried in vacuum at 50 °C for 4 h. The resultant catalyst was marked as Ni-B-P-O/RGO or Co-B-P-O/RGO.

Catalyst characterization The specific surface area was measured by a Quantachrome's NOVA-2100e Surface Area instrument by physisorption of nitrogen at -196 °C. The samples were dehydrated at 150 °C using vaccum degassing for 12 h before experiments. X-ray diffraction (XRD) measurements were carried on a D/max2550 18KW Rotating anode X-Ray Diffractometer with monochromatic Cu Kα radiation (λ= 1.5418Å) radiation at voltage and current of 40 kV and 300 mA. The 2θ was scanned over the range of 5-90° at a rate of 10°/min. The scanning electronic microscopy (SEM) images of the catalysts were obtained on a JEOL JSM-6360 electron microscopy. The surface composition and surface electronic state were analyzed by X-ray Photoelectron Spectroscopy (XPS) using Kratos Axis Ultra DLD instrument at 160eV pass energy. Al Kα radiation was used to excited photoelectrons. The binding energy value of each element was corrected using C_{1s} = 284.6 eV as a reference. The XP spectra of each element was deconvoluted using a Gaussian-Lorentz curve-fitting program.

Catalyst activity measurement The HDO activity tests were carried out in a 100-mL sealed autoclave. The prepared catalyst (0.1 g) without any further treatment, p-cresol (4.8 g) and dodecane (28.5 g) were placed into the autoclave. Air in the autoclave was evacuated by pressurization-depressurization cycles with nitrogen and subsequently with hydrogen. The system was heated to 225 °C, then pressurized with hydrogen to 4.0 MPa and adjusted the stirring speed to 900 rpm. During the reaction, liquid samples were withdrawn from the reactor and analysed by Agilent 6890/5973N GC-MS and 7890 gas chromatography using a flame ionization detector with a 30 m AT-5 capillary column. To separate the reaction products, the temperature in the GC oven was heated from 40 °C to 85 °C with the ramp of 20 °C/min, held at 85 °C for 4.0 min, then heated to 200 °C at a rate of 20 °C/min and kept at 200 °C for 5.0 min. Duplicate or triplicate experiments were performed and the average of these tests was reported here. The errors for conversion values were typically within plus/minus 5.0 mol%. Deoxygenation degree (D. D., wt %) is defined as [1-oxygen content in the final organic compounds / total oxygen content in the initial material] × 100%. Carbon balance is better than 96 ± 3 % in this work.

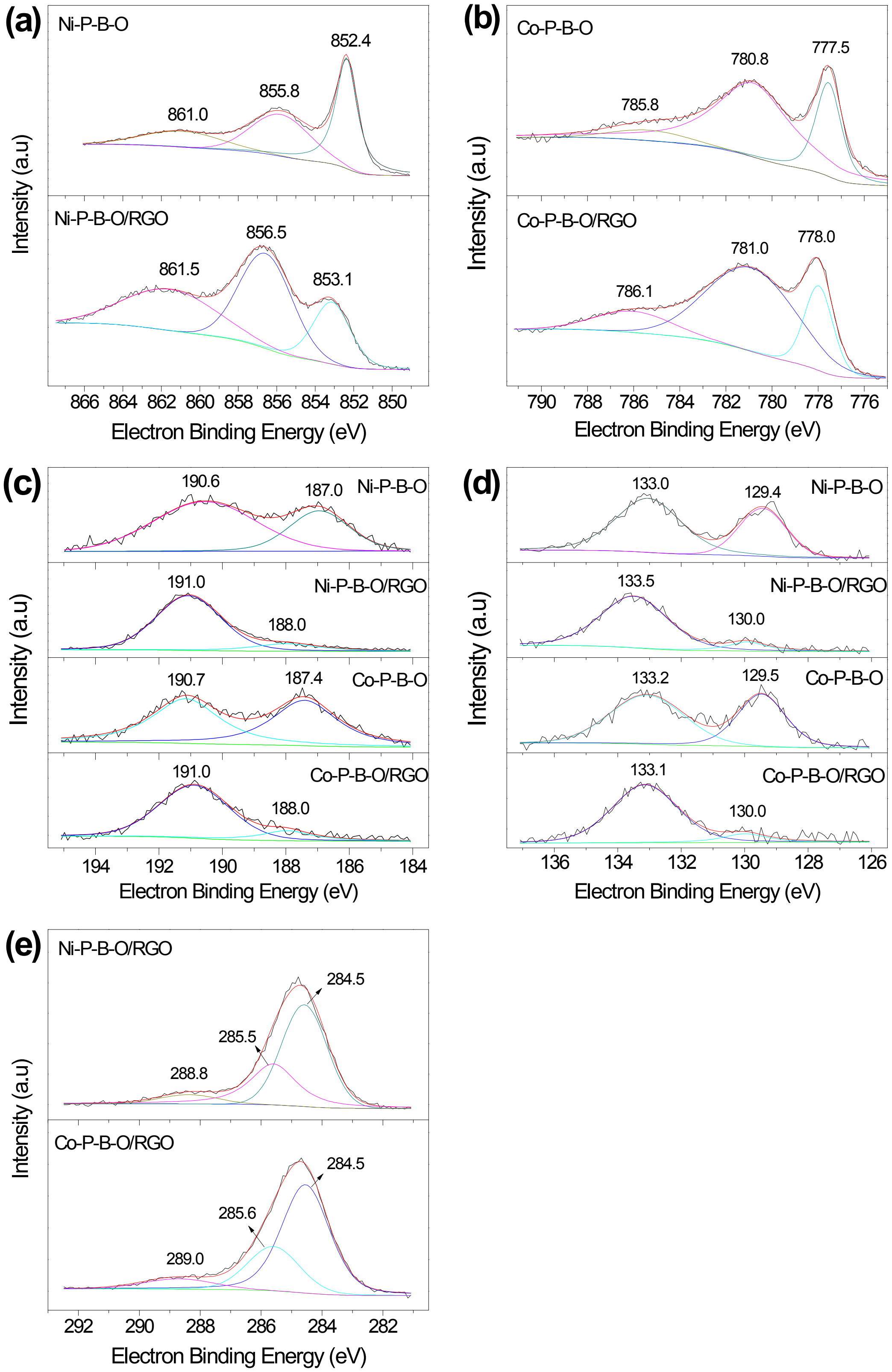

Fig. S1 XP spectra of (a) Ni 2p, (b) Co 2p, (c) B 1s, (d) P 2p and (e) C 1s levels of Ni-B-P-O, Ni-B-P-O/RGO, Co-B-P-O and Co-B-P-O/RGO catalysts

Fig. S1 (a) presented three deconvolution peaks at 852.7–853.1 eV, 855.5–856.5 eV and 860.2–861.5 eV, matching to Ni^0, Ni oxide and Ni hydroxide, respectively. Similarly as Ni 2p level, Co in Co-B-P-O and Co-B-P-O/RGO catalysts existed in three forms, Co^0, Co oxide and Co hydroxide. In comparison with the standard binding energies (BE) of Ni^0 (853.1 eV), Co^0 (778.0 eV), B^0 (187.1 eV) and P^0 (130.0 eV), the binding energy of Ni^0 or Co^0 and P^0 shifted negatively but the binding energy of B^0 changed positively in Ni-B-P-O and Co-B-P-O, indicating that B^0 donated part of its electrons to metallic Ni or Co and P^0 accepted electrons from these metals. The deconvoluted C 1s XPS spectrum (Figure S1e) of Ni-B-P-O/RGO and Co-B-P-O/RGO showed three fitted peaks at around 284.5, 285.5 and 288.8 eV, assigned to C-C/C−C, C−O(epoxy/hydroxyls) and O=C-OH functional groups, respectively. Compared with the C1s XPS spectrum of GO in previous studies, the peak at 287.6 to C=O was not observed, but there still presented some oxygen-containing groups, indicating that GO had been partially reduced by the BH_4^- reduction treatment.

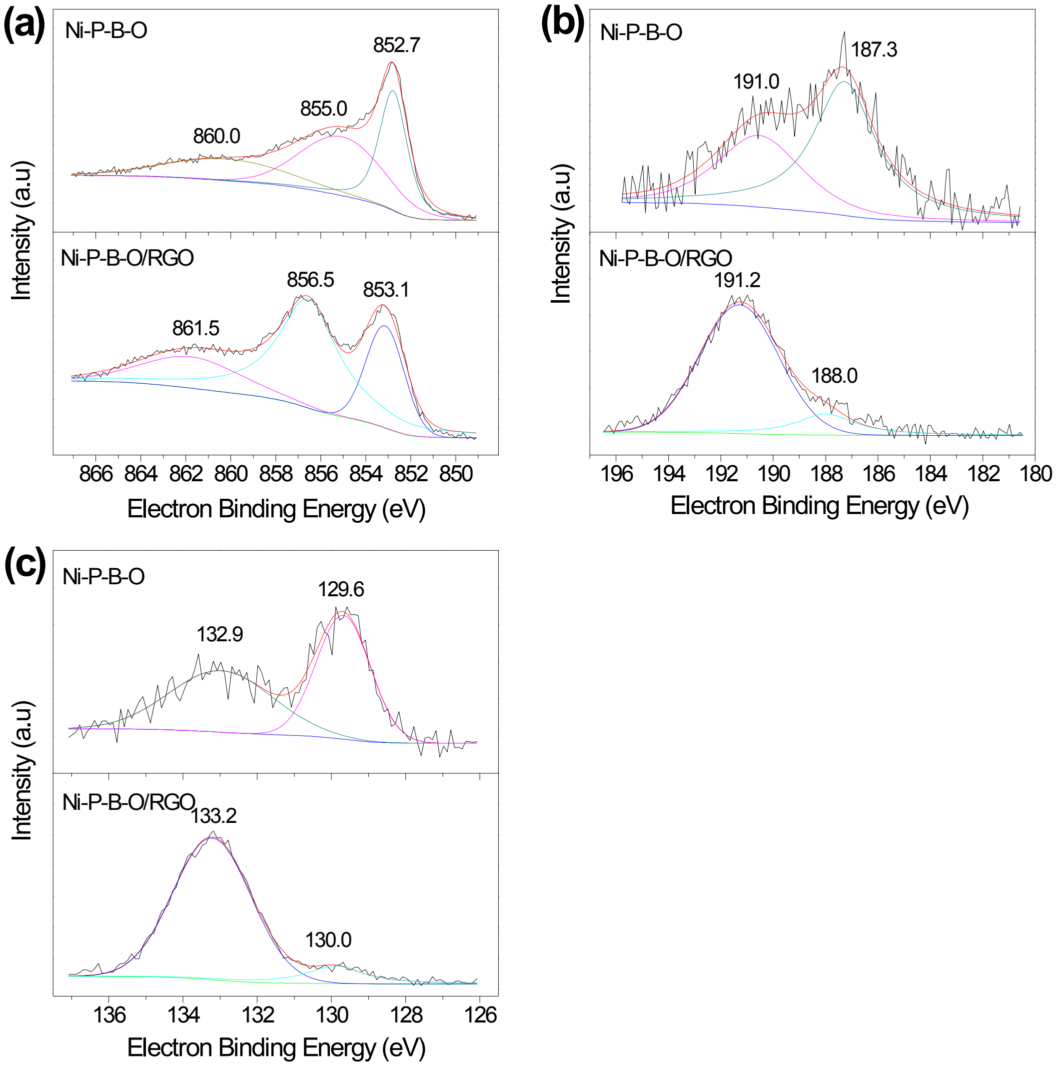

Fig. S2 XP spectra of (a) Ni 2p, (b) B 1s and (c) P 2p levels of the used Ni-B-P-O and Ni-B-P-O/RGO catalysts

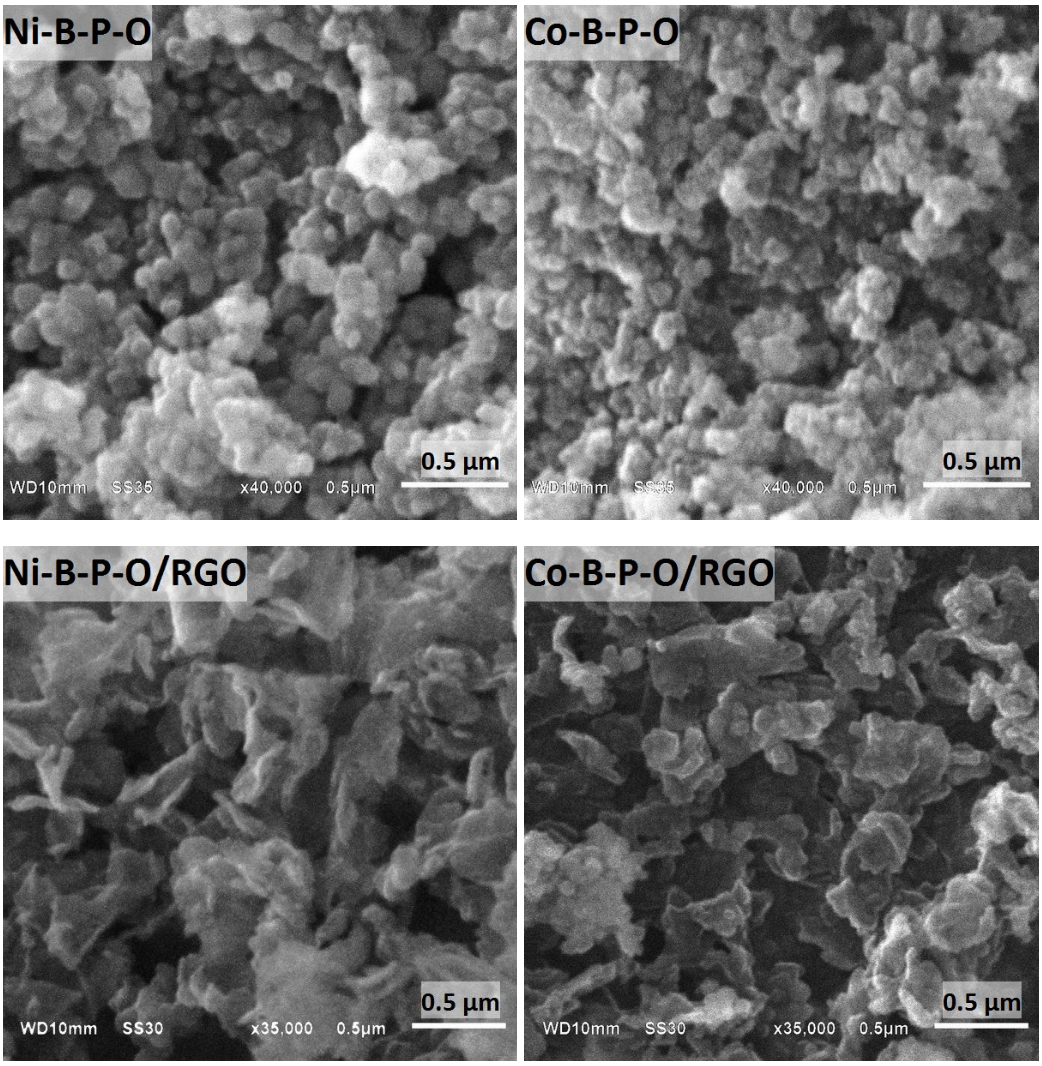

Fig. S3 SEM images of Ni-B-P-O, Co-B-P-O, Ni-B-P-O/RGO and Co-B-P-O/RGO catalysts

Table S1 Comparison of element valence state compositions of fresh and used Ni-B-P-O and Ni-B-P-O/RGO catalysts

Catalysts	Ni (%)		B (%)		P (%)	
	Ni^{0}	Ni^{2+}	B^{0}	B^{3+}	P^{0}	P^{n+}
Ni-B-P-O	46.8	53.2	33.9	66. 1	36. 4	63.6
Ni-B-P-O-Used	35.7	64.3	62.4	37.6	51.3	48.7
Ni-B-P-O/RGO-Fresh	22.8	77.2	15.2	84.8	11.6	88.4
Ni-B-P-O/RGO-Used	22.6	77.4	15.5	84.5	11.9	88.1

Table S2. Comparison of atomic ratios on the surface of fresh and used Ni-B-P-O and Ni-B-P-O/RGO catalysts

Ratio	Ni-B-P-O-Fresh	Ni-B-P-O-Used	Ni-B-P-O/RGO-Fresh	Ni-B-P-O/RGO-Used
P:Ni	0.53	0.30	0.67	0.71
B:Ni	1.05	0.69	1.54	1.56
O:Ni	1.65	1.39	2.49	2.27