

Supporting information

Porous Graphene-based Material as an Efficient Metal Free Catalyst for the Oxidative Dehydrogenation of Ethylbenzene to Styrene

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Experimental Section

Carbon materials:

The graphene materials we used were bought from the Sixth Element Company (Changzhou, China). The graphite powder branded Acheson was produced by Henkel company (Germany). The multiwalled carbon nanotubes (CNT) were bought from Dazhan Nanomaterial company (Zouping, China). All the catalysts were used as-received except CNT. The general production route of rPGO was as follows: first, graphite oxide powder (GO) made from natural graphite by modified Hummers' method was irradiated in a microwave oven. The as-prepared microwave exfoliated graphite oxide powder was then placed in KOH solution at a specific ratio to go through an activation process, after several filtration, drying, annealing and washing procedures, partially reduced graphene oxide (rPGO) with high specific surface area and abundant pores was made. Oxidized carbon nanotubes were prepared by refluxing CNT in concentrated nitric acid at 120 °C for 2 h, the obtained product was designated as oCNT.

Characterization:

X-ray diffraction (XRD) patterns of the samples were obtained using a D/MAX-2500 PC X-ray diffractometer with monochromatized Cu K α radiation ($\lambda=1.54 \text{ \AA}$). Scanning electron microscopy (SEM) images were collected on a FEI Nova NanoSEM 450 microscope, Transmission electron microscopy (TEM) images were collected on a FEI Tecnai F20 electron microscope with an accelerating voltage at 200 kV. Raman spectra were obtained on a LabRam HR 800 using a 632.8 nm laser. N₂ physisorption was conducted on a Micrometrics ASAP 2020 system. TG-MS experiments were conducted on a Netzsch-STA 449 F3 instrument connected with a Pfeiffer-Balzer Omnistar instrument. X-ray photoelectron spectroscopy (XPS) experiments were carried out on an ESCALAB 250 XPS system with a monochromatized Mg K α X-ray source.

Activity test:

The catalytic measurements were carried out in a fix-bed quartz reactor at atmospheric pressure. The catalysts were fixed between two quartz wool plugs. The mass of all the catalysts were a typical 50 mg and the reaction condition (Temperature, O₂/EB ratio) was optimized at 400 °C and O₂/EB at 1. The reactants and products were analyzed by an online gas chromatography (Agilent 7890) using a HP-5 capillary column connected to FID and a CarboPlot capillary column connected to TCD. EB conversion of blank experiment was only 0.12 % which can be ignored.

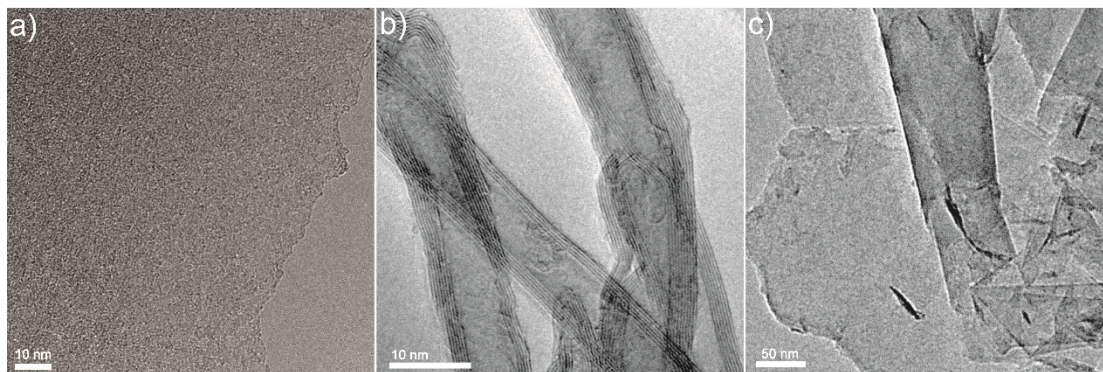


Fig. S1 TEM images of different carbon materials: A) rGO; B) oCNT; C) GP.

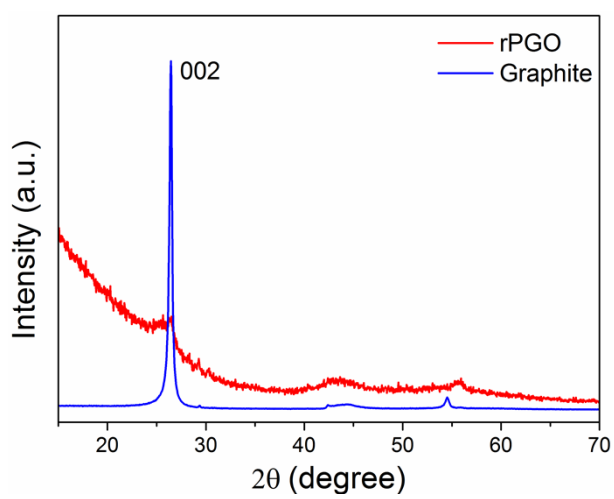


Fig. S2 XRD patterns of the rPGO (red line) and the natural graphite (blue line).

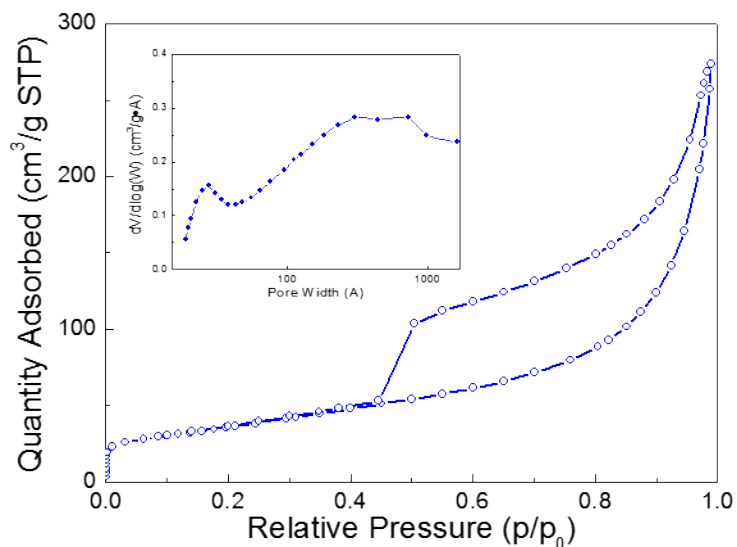


Fig. S3 N₂ adsorption-desorption isotherms of the routinely reduced graphene oxide (rGO). The specific surface area is about 127 m²/g calculated according to Brunauer-Emmett-Teller (BET) method. The cumulative pore volume and average pore width calculated from the desorption branch according to Barrett-Joyner-Halenda (BJH) model is about 0.43 cm³/g and 6.9 nm, respectively.

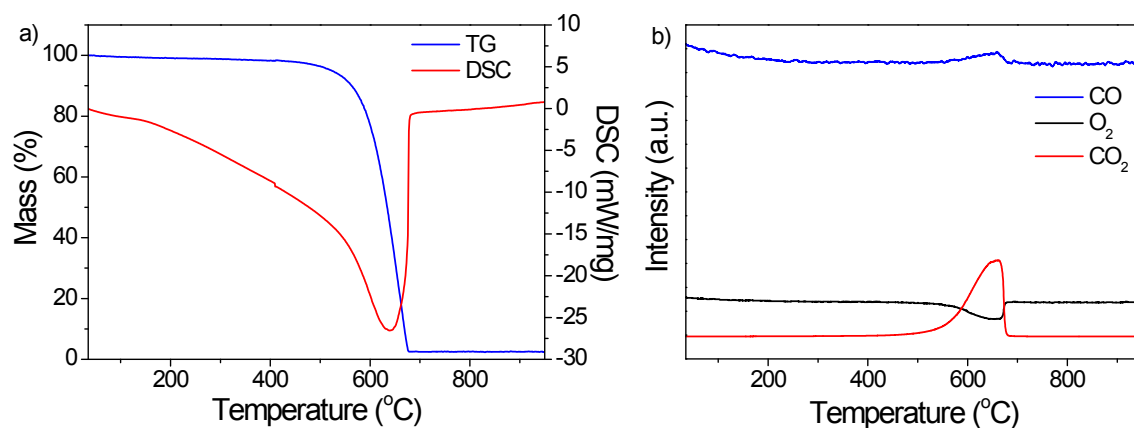


Fig. S4 TG-MS results of the fresh rPGO. Conditions: 5 % O₂/Ar, 5 K/min.

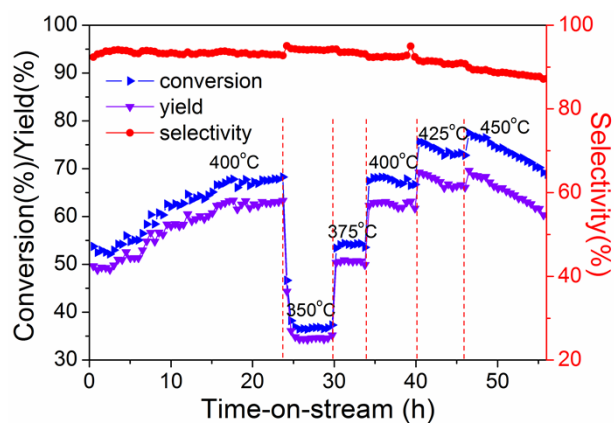


Fig. S5 Effect of temperature on the catalytic performance of the rPGO. Reaction condition: 50 mg catalyst, 3 % EB with He balance, $O_2/EB = 1$, total flow rate= 10 ml/min.

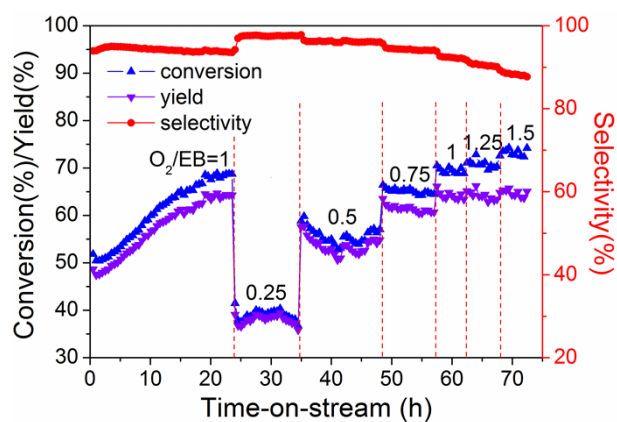


Fig. S6 Effect of O_2/EB ratio on the catalytic performance of the rPGO. Reaction condition: 50 mg catalyst, 3 % EB with He balance, total flow rate = 10 ml/min, $T = 400\text{ }^\circ\text{C}$.

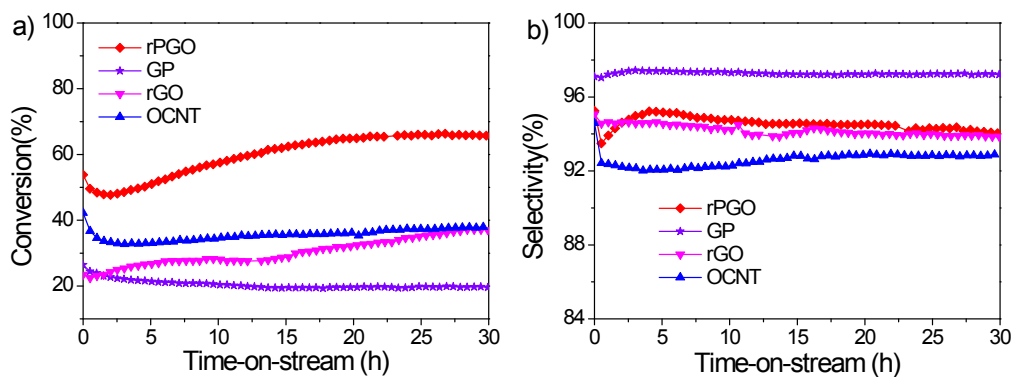


Fig. S7 The catalytic performance over different carbon materials on ODH of EB. Reaction condition: 50 mg catalyst, 3 % EB with He balance, $O_2/EB = 1$, total flow rate= 10 ml/min, $T = 400\text{ }^\circ\text{C}$.

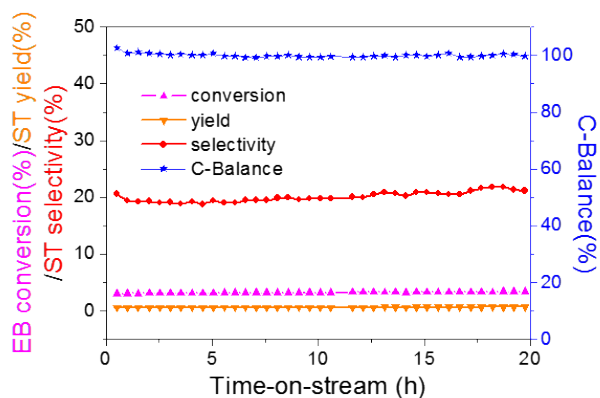


Fig. S8 Catalytic activity of the commercial iron oxide catalyst on ODH of EB. Reaction condition: 50 mg catalyst, 3 % EB with He balance, $O_2/EB = 1$, total flow rate = 10 ml/min, $T = 400\text{ }^\circ\text{C}$.

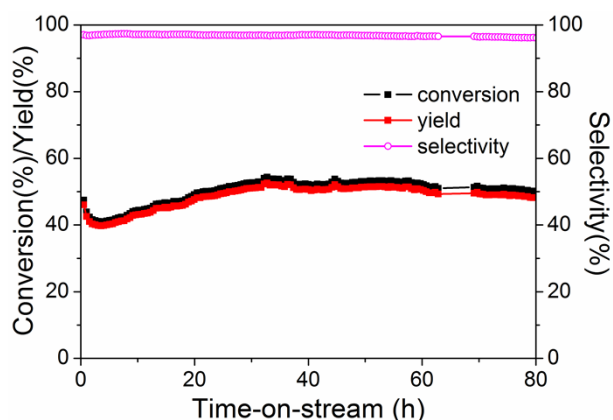


Fig. S9 The long time behavior of the rPGO on ODH of EB. Reaction condition: 50 mg catalyst, 3 % EB with He balance, $O_2/EB = 0.5$, total flow rate= 10 ml/min, $T = 400\text{ }^\circ\text{C}$.

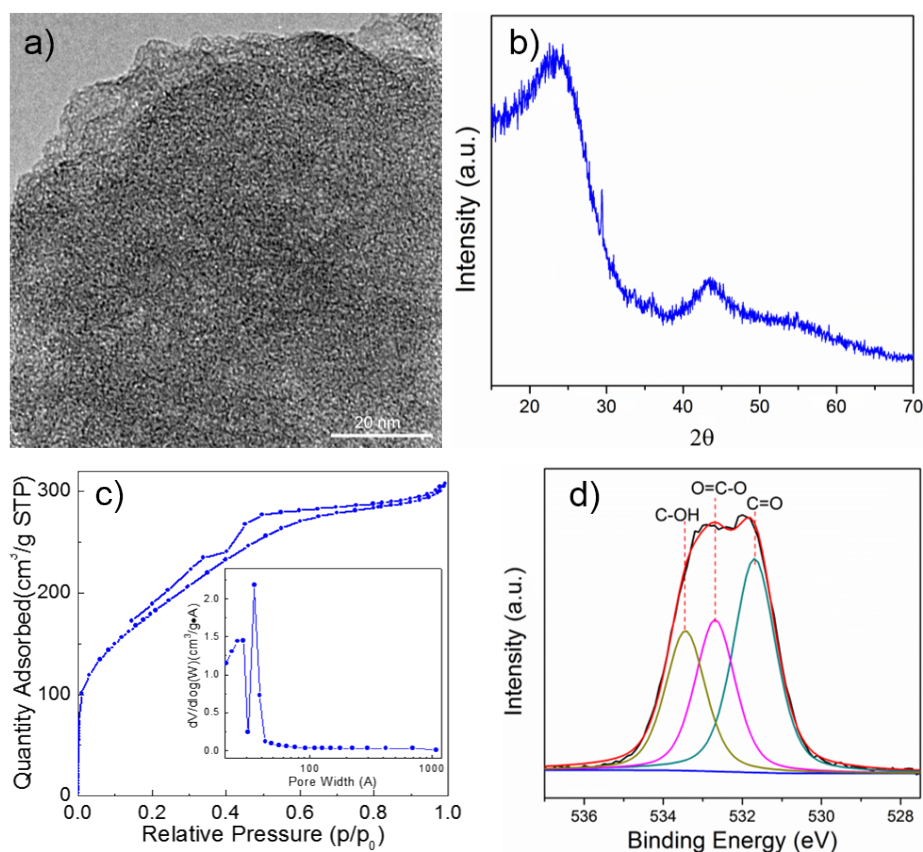


Fig. S10 Characterizations of the used rPGO after 30 h on stream. A) TEM; b) XRD pattern; c) N_2 adsorption-desorption isotherms and corresponding pore size distribution (inset); d) O1s peak fitting of the XPS spectrum.

Table S1 Comparison of the catalytic performance of the rPGO with the reported carbon materials

Catalyst	Mass (mg)	T (°C)	O ₂ /EB	Conv. (%)	Select. (%)	ST production rate (mmol•g ⁻¹ •h ⁻¹)	Ref.
rPGO	50	400	1	65	93	9.27	—
CNT monolith	100	400	2.5	48	90	3.36	1
HPC	60	325	2.5	43	75	3.8	2
OMC	60	400	2.5	69	76	6.09	3
UDD	40	515	1	85	45	5.53	4
OLC	40	515	1	92	68	9.05	4

Table S2 XPS analysis of different carbon materials.

sample	Total (at.%)			O _{group} /Oxygen (%)			Total O _{C=O} (at.%)
	C	N	O	C-OH	O=C-O	C=O	
rPGO	84.58	0.15	15.27	31.07	28.13	40.80	6.23
rPGO-used	82.31	0.05	17.64	27.10	29.39	43.51	7.68
rGO	95.77	0.01	4.22	31.71	49.51	18.78	0.79
GP	97.03	0.44	2.53	29.98	40.43	29.59	0.65
oCNT	96.39	0.23	3.38	43.17	35.63	21.20	0.72

Reference

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