Fabrication of MgO-rGO hybrid catalysts with sandwich structure for enhanced ethylbenzene dehydrogenation performance

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1. Experimental part

1.1 Synthesis of the MgO-rGO hybrid catalysts

Reduced graphene oxide (rGO, the Sixth Element Co. Ltd) was purified by concentrate hydrochloric acid (HCl) at room temperature for 12 hours under magnetic stirring, then washed with ultrapure water and dried at 120 °C in oven overnight. The purified rGO was modified with the $Mg(NO_3)_2 \bullet 6H_2O$ (98%, Alfa Aesar) ethanol solution via incipient impregnation method. Then the impregnated sample was dried at 100 °C in oven overnight and calcined at 900 °C for 10 min in argon. The obtained samples were denoted as a-MgO-rGO, and a refers to the weight percent of MgO (wt%), tuned from 1 to 30 by changing the amount of $Mg(NO_3)_2 \bullet 6H_2O$. For comparison, the 5-MgO/SBA-15 catalyst was prepared via the same procedure, the purified rGO was also annealed at 900 °C for 10 min in argon and labelled as rGO-900. In addition, to solely investigate the property of modified rGO and its effect on dehydrogenation activity, the MgO NPs in 5-MgO-rGO were removed by HCl and labelled as 5-MgO-rGO-HCl.

1.2 Characterization techniques

The morphology of rGO-900, the MgO-rGO catalysts and 5-MgO/SBA-15 were characterized by scanning electron microscopy (SEM, FEI Nova NanoSEM 450) and transmission electron microscopy (TEM, FEI Tecnai F20, 200 kV). The crystal structure of the samples were characterized by X-ray diffraction (XRD) on a D/MAX-2500 PC X-ray diffractometer with monochromatized Cu K radiation (λ=1.54 Å). Raman spectra were obtained on a LabRam HR 800 using a 632.8 nm laser. N_2 physisorption was conducted on a Micrometrics ASAP 2020 system at -196 °C. The samples were outgassed at 150 °C for 12 h prior to the isotherm measurements and the surface areas were determined according to Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) experiments were carried out on an ESCALAB 250 XPS system with a monochromatized Mg Ka X-ray source.

1.3 Catalytic tests

Dehydrogenation of ethylbenzene was carried out at 550 °C in a fix-bed quartz reactor with 50 mg of catalyst at atmospheric pressure. The catalyst was fixed between two quartz wool plugs. The system was heated to reaction temperature and

kept for 10 min in helium. The reactant (2.8% EB, total flow rate 10 ml min^{-1}, helium as balance) was then fed to the reactor from a saturator kept at 39.8 °C. The reactants were analyzed by an on-line gas chromatograph equipped with two columns: a HP-5 capillary column for the hydrocarbons and a CarboPlot capillary column for the permanent gases, coupled to FID and TCD detectors, respectively. The ethylbenzene conversion (X_{EB}) and styrene selectivity (S_{ST}) were calculated according to the following equations:

$$X_{EB} = 1 - FC_{EB, \text{outlet}} / F_0 C_{EB, \text{inlet}}$$

$$S_{ST} = C_{ST, \text{outlet}} / (C_{ST, \text{outlet}} + C_{BZ, \text{outlet}} + C_{TOL, \text{outlet}})$$

$$Y_{ST} = X_{EB} * S_{ST}$$

F and F_0 are the flow rates of the outlet and inlet. C_{EB}, C_{ST}, C_{BZ}, and C_{TOL} denote the concentrations of ethylbenzene, styrene, benzene, and toluene, respectively.
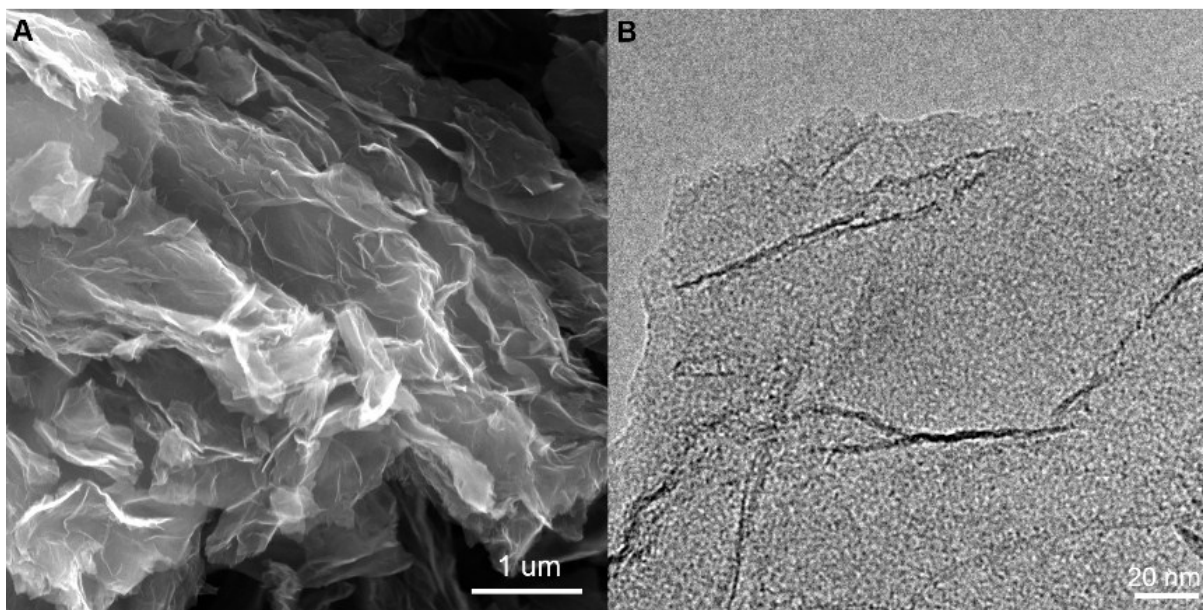
2. Figures

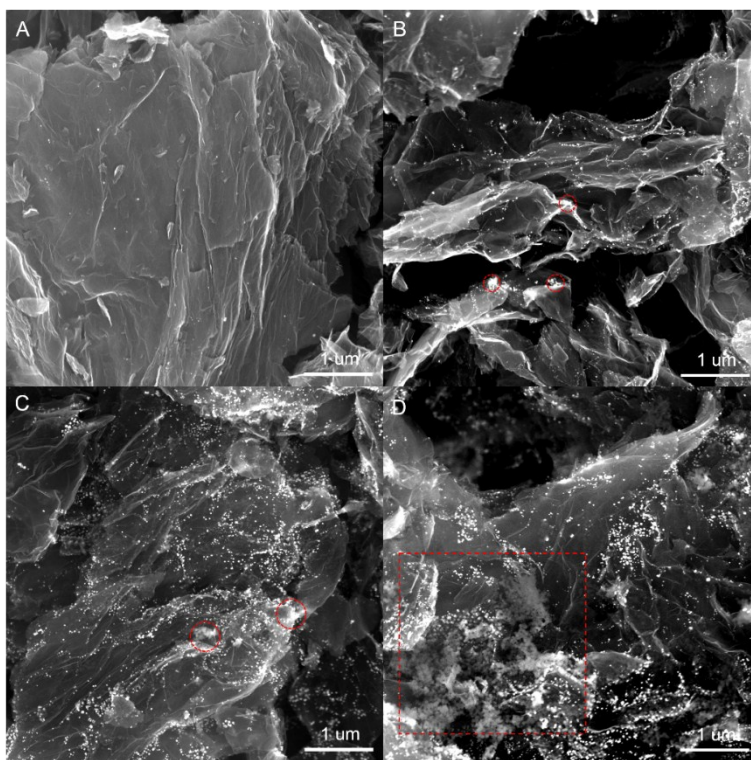Fig. S1 SEM (A) and TEM (B) images of rGO-900.

Fig. S2 SEM images of MgO-rGO hybrid catalysts with 1 wt% (A), 10 wt% (B), 20 wt% (C) and 30 wt% (D) MgO content.
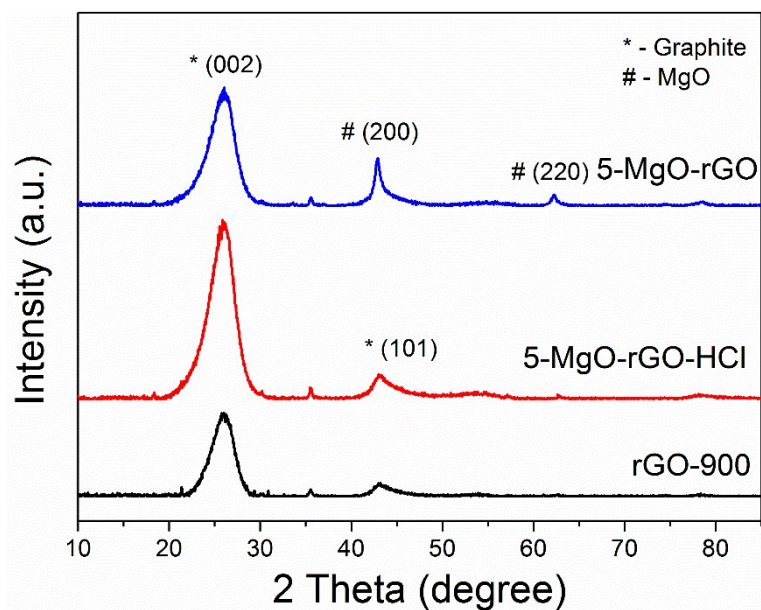
Fig. S3 The XRD pattern of 5-MgO-rGO-HCl, compared with that of 5-MgO-rGO and rGO-900.
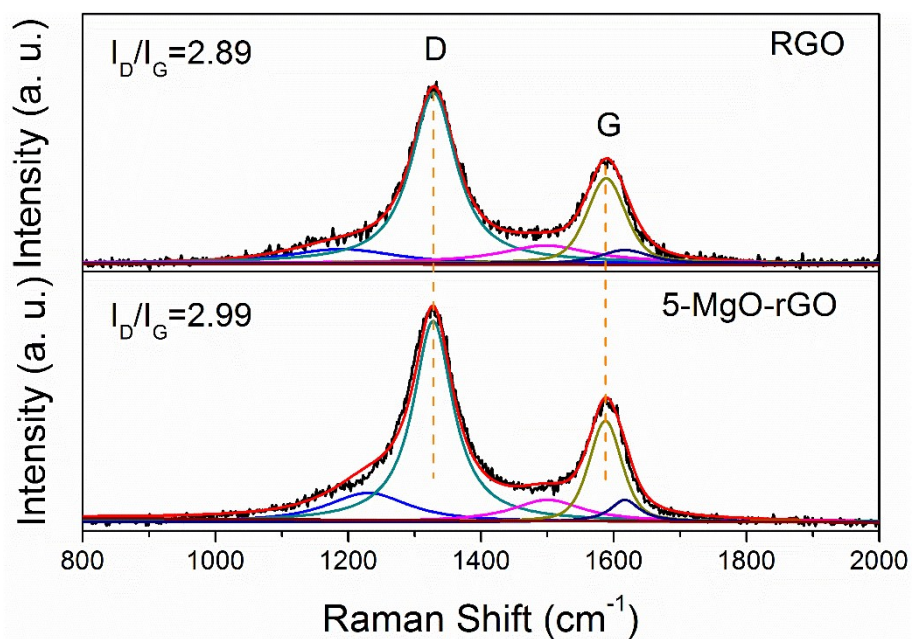

Fig. S4 Deconvolution of Raman spectra of rGO and 5-MgO-rGO. The value of I_D/I_G is calculated by the fitted area of D peak and G peak.
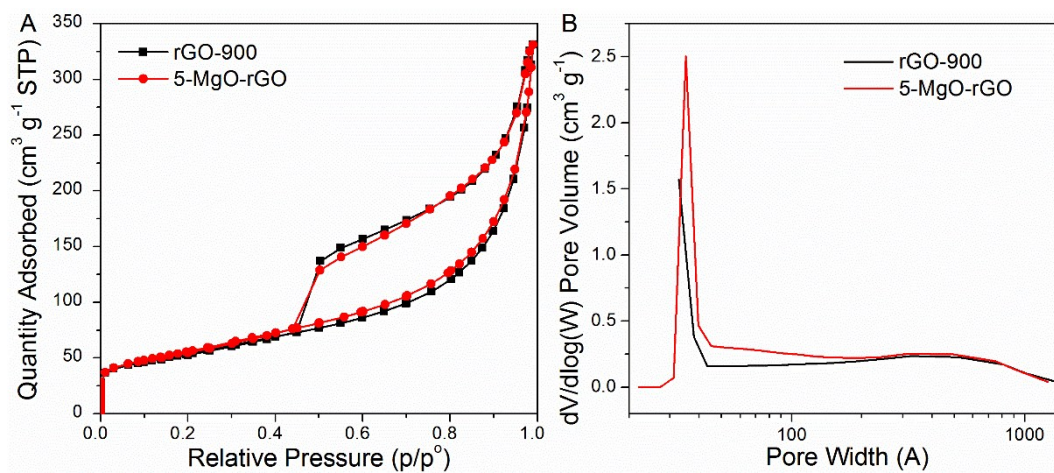
Fig. S5 N$_2$ physisorption isotherms and pore size distributions of rGO-900 and 5-MgO-rGO.
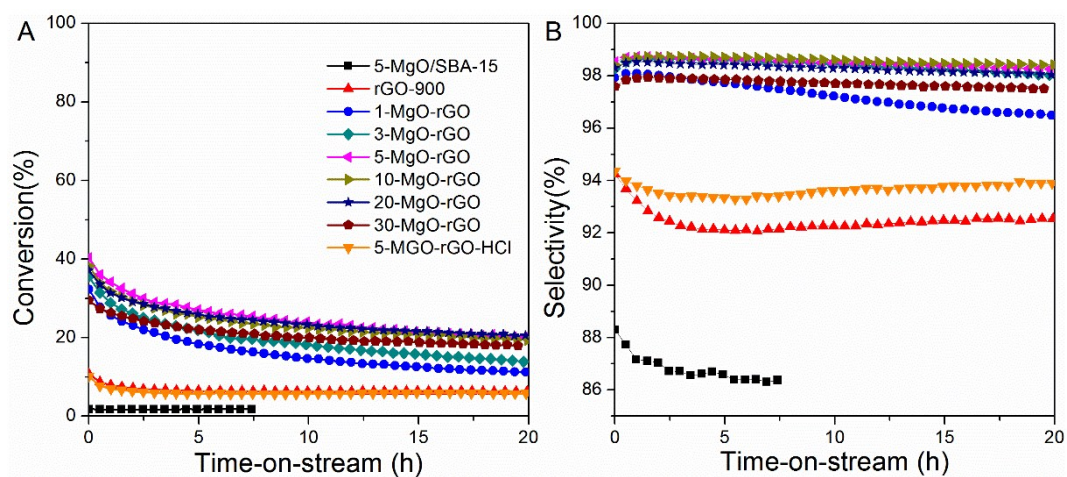

Fig. S6 Catalytic performance of 5-MgO/SBA-15, rGO and MgO-rGO hybrid catalysts. The legend in figure B is the same with figure A. Reaction conditions: 50 mg catalyst, T = 550 °C, flow rate = 10 ml min^{-1}, 2.8% ethylbenzene with He balance.
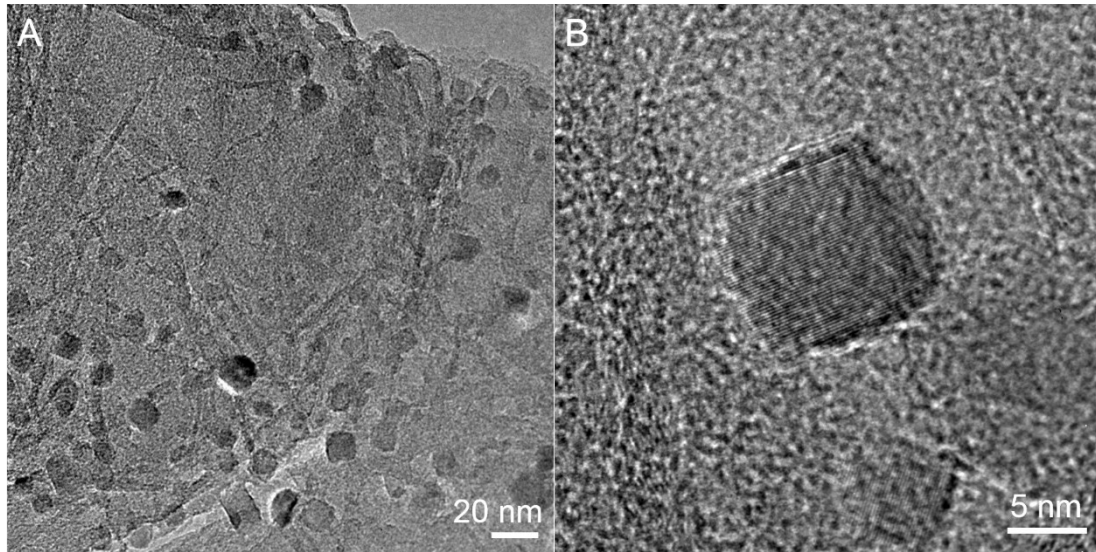
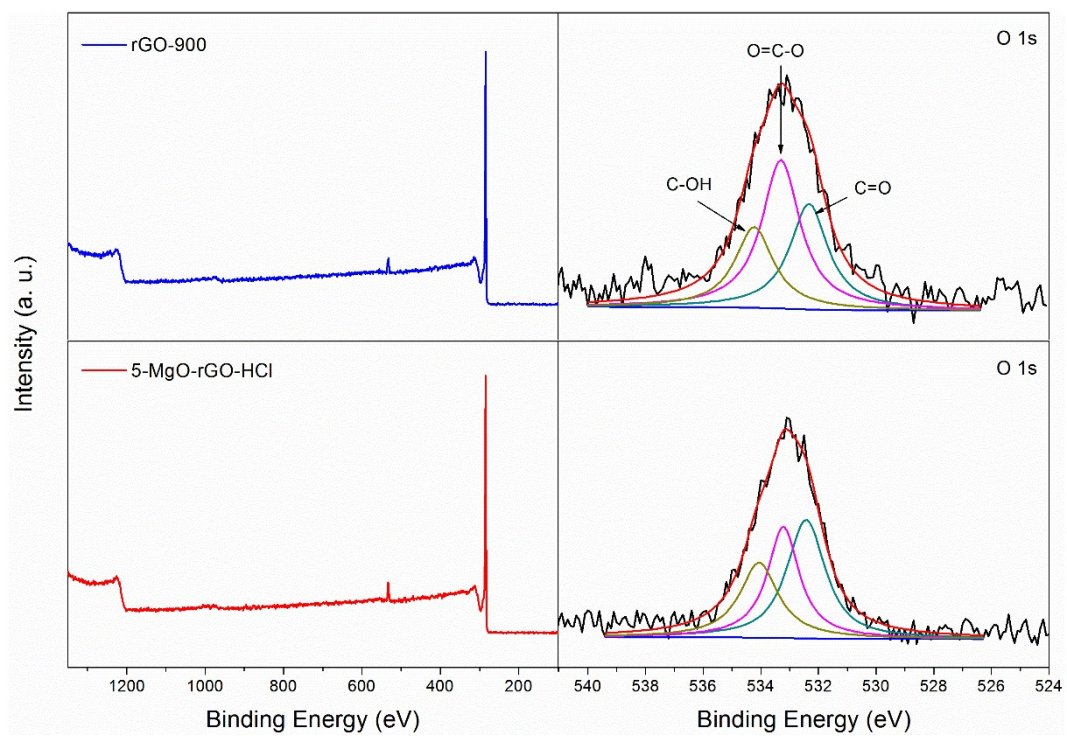Fig. S7 TEM images of the used 5-MgO-rGO catalyst.

Fig. S8 XPS spectra and O 1s peak fitting of rGO-900 (upper) and 5-MgO-rGO-HCl (lower).

Table S1 N_2 physisorption and XPS analysis of rGO-900, 5-MgO-rGO and 5-MgO-rGO-HCl.

	BET surface area/m^2 g^{-1}	XPS analysis			
		C/at%	O/at%	Mg/at%	$O_{C=O}/O_{total}$
RGO-900	189.85	96.86	3.14	—	31.5%
5-MgO-rGO	198.47	95.31	4.37	0.32	—
5-MgO-rGO-HCl	—	96.84	3.16	—	40.4%

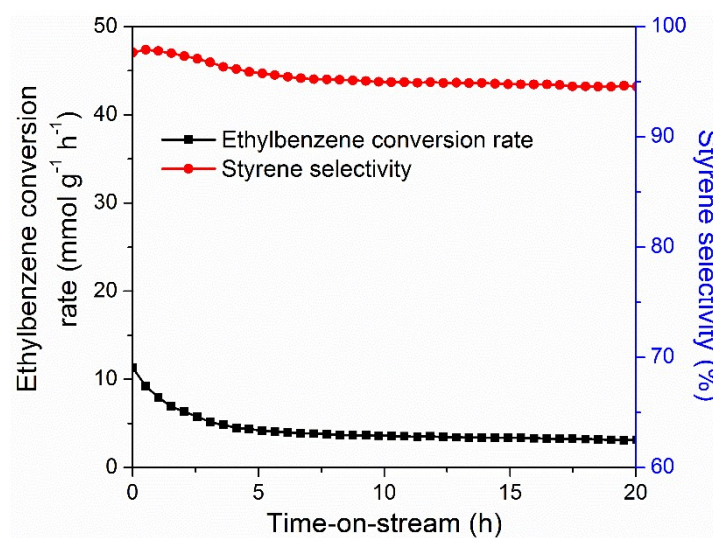Fig. S9 Catalytic performance of 5-MgO-rGO. Reaction conditions: 50 mg catalyst, T = 550 °C, flow rate = 10 ml min^{-1}, 7% ethylbenzene with He balance.