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Graphene oxide as acid catalyst for the room temperature ring opening of epoxides

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General: All reagents and starting materials were obtained commercially from Aldrich and used without any further purification unless otherwise noted. Graphene oxide was characterized by IR and Raman vibrational spectroscopy, chemical analysis, and XPS. IR spectra were recorded with a Nexus 8700 FTIR spectrometer using a DTGS detector and acquiring at 4 cm^{-1} resolution. An IR cell allowing in situ treatments in controlled atmospheres and temperatures has been connected to a vacuum system with gas and liquid dosing facility. For IR studies the samples were pressed into self-supported wafers and treated at 100 ºC under vacuum at 10^{-6} mbar. After activation, 36 mbar of methanol was adsorbed at 100ºC, and the IR spectra collected after gas phase subtraction. Methanol evacuation was done under vacuum at 100ºC. Elemental analysis was determined by a Fisons EA1108CHN-S. FT-Raman spectra were recorded with a Bio-Rad FT-Raman spectrophotometer. Nd:YAG laser was used for excitation along with a germanium detector cooled at liquid nitrogen temperature using high quality quartz tubes as cells. The percentage conversion, purity and relative yields of the final products were determined by using a Hewlett Packard 5890 series II gas chromatograph with an FID detector and high purity helium as the carrier gas. The products were identified by GC–MS by using a Hewlett Packard 6890 series spectrometer. The regioselectivity of the ring opening was determined by mass spectrometry, which shows different fragmentation pattern depending on the relative position of the nucleophilic group. In the case of 2-methoxy-2-phenylethanol, the structure was confirmed by comparison with an authentic sample.

Typical procedure for ring opening of epoxides with alcohols: A 50 mL round-bottomed flask was charged with catalyst (5 mg) in alcohol (10 mL) and substrate (8.33 mmol). The reaction mixture was stirred for the required time at room temperature. The reaction was monitored periodically by analyzing the sample with GC up to the completion of reaction. The mass balances of the recovered reaction mixture accounted for more than 95 % of the initial substrate, as confirmed by GC using nitrobenzene as the internal standard. The yields of the product were determined by using nitrobenzene as the internal standard considering the response factors unity.

Experimental procedure for reusability tests: The reusability of GO was tested for the ring opening of **1a** with methanol. At the end of the reaction, the heterogeneous mixture was submitted to centrifugation at 15,000 rpm. The recovered catalyst was dried, then, reused without further purification for a consecutive run with fresh **1a** with methanol.

Experimental procedure for the preparation of GO

Graphite flakes (3 g) was suspended in a mixture of concentrated H_2SO_4/H_3PO_4 (360:40 ml). To this mixture, $KMnO_4$ (18 g) was added by producing an exothermic reaction raising the temperature to 35-40 ºC. This reaction mixture was then heated to 50 ºC under stirring for 12 h. The reaction was cooled to room temperature and poured into 400 g of ice containing 30 % H_2O_2 (3 ml). After air cooling the suspension was filtered, washed with 1:10 HCl (37 %) solution and then further with water. The remaining solid was sonicated with 400 ml of water for 30 min and centrifuged at 4,000 rpm for 4 h. The supernatant was centrifuged at 15,000 rpm for 1 h. The solid obtained after centrifugation at 15,000 rpm was dried at 60 ºC. The obtained GO was characterized by Raman and XPS analysis.[1]

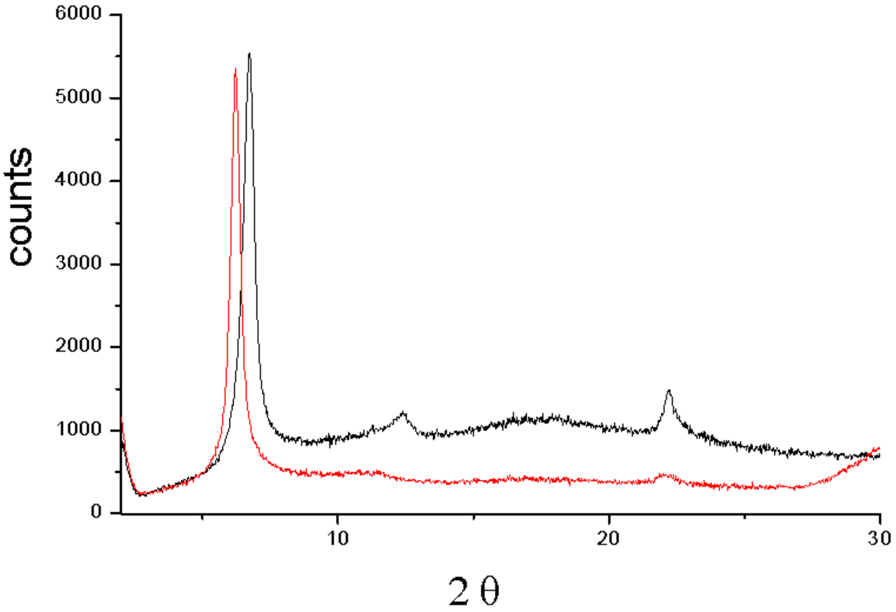

Figure S1. Powder XRD spectra of two GO obtained in two different batch (black)

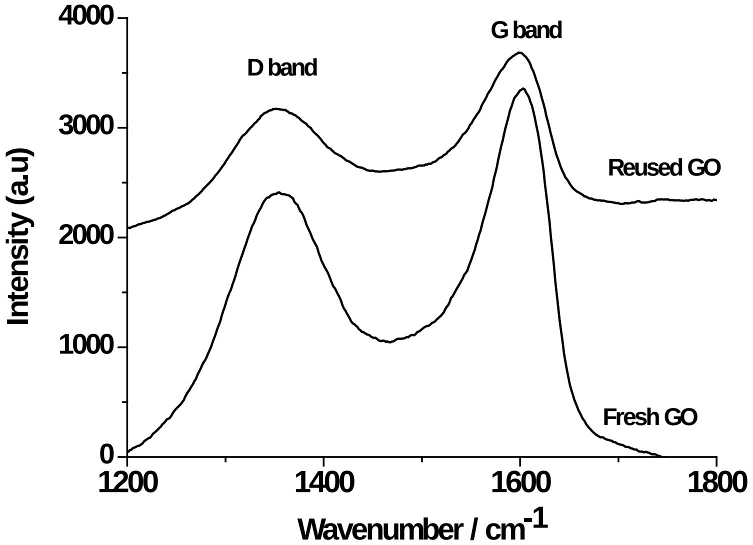

Figure S2. FT-Raman spectra of fresh and three times reused GO catalyst showing the presence of the characteristic G and D bands corresponding to GO with the same ratio intensity.

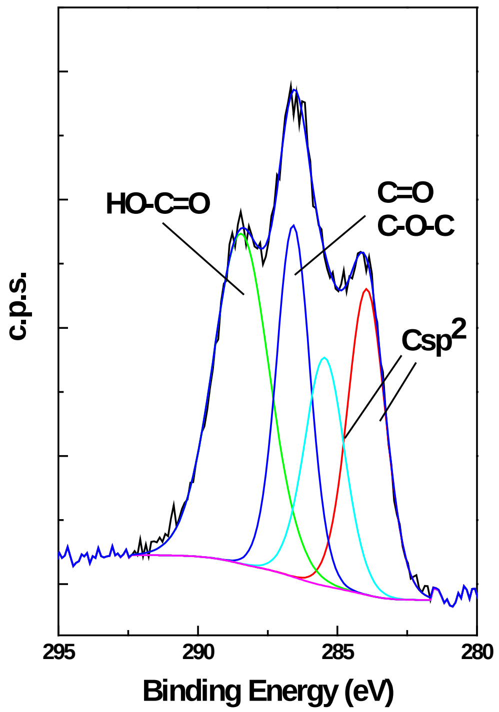

Figure S3. Expansion of C 1s peak in the XPS of GO. This Figure shows the best deconvulution of the experimental peak and the most probable assignments of the each component. The three times reused GO catalyst exhibited identical C1s peak.

Elemental Analysis

	C (%)	H (%)	S (%)	N (%)
GO	47.371	2.591	1.168	0.069
Different batch	41.919	1.972	1.652	0.00

Reference

1. M. Latorre-Sanchez, P. Atienzar, G. Abellan, M. Puche, V. Fornes, A. Ribera, and H. Garcia, *Carbon*, 2012, **50**, 518.