

Supplementary Information for

Active Sites and Their Individual Turnover Frequencies for Ethylene Hydrogenation on Reduced Graphene Aerogel

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Figure S1. Representative image of GO paper.

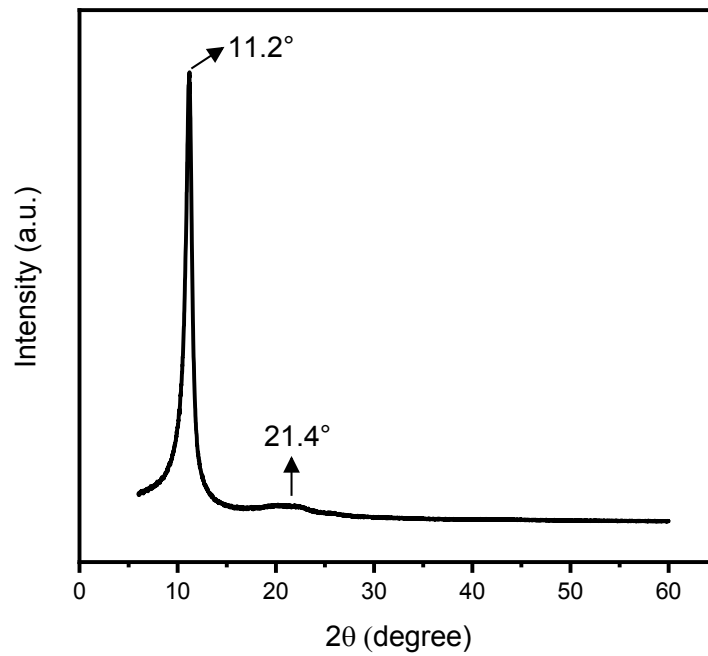


Figure S2. XRD pattern of GO thin layer demonstrating multiple peaks associated with the turbostratic disorder.

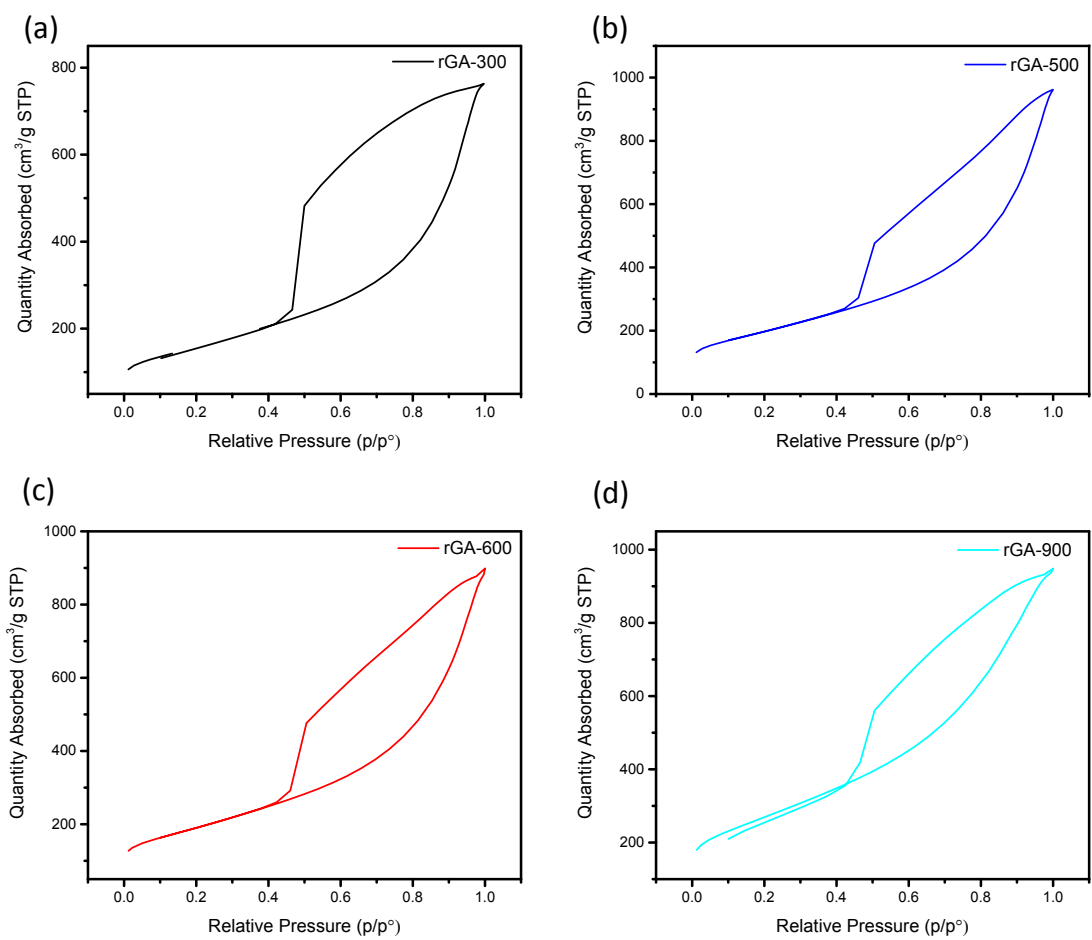


Figure S3. N_2 adsorption-desorption isotherms measured for a) rGA-300, b) rGA-500, c) rGA-600, d) rGA-900.

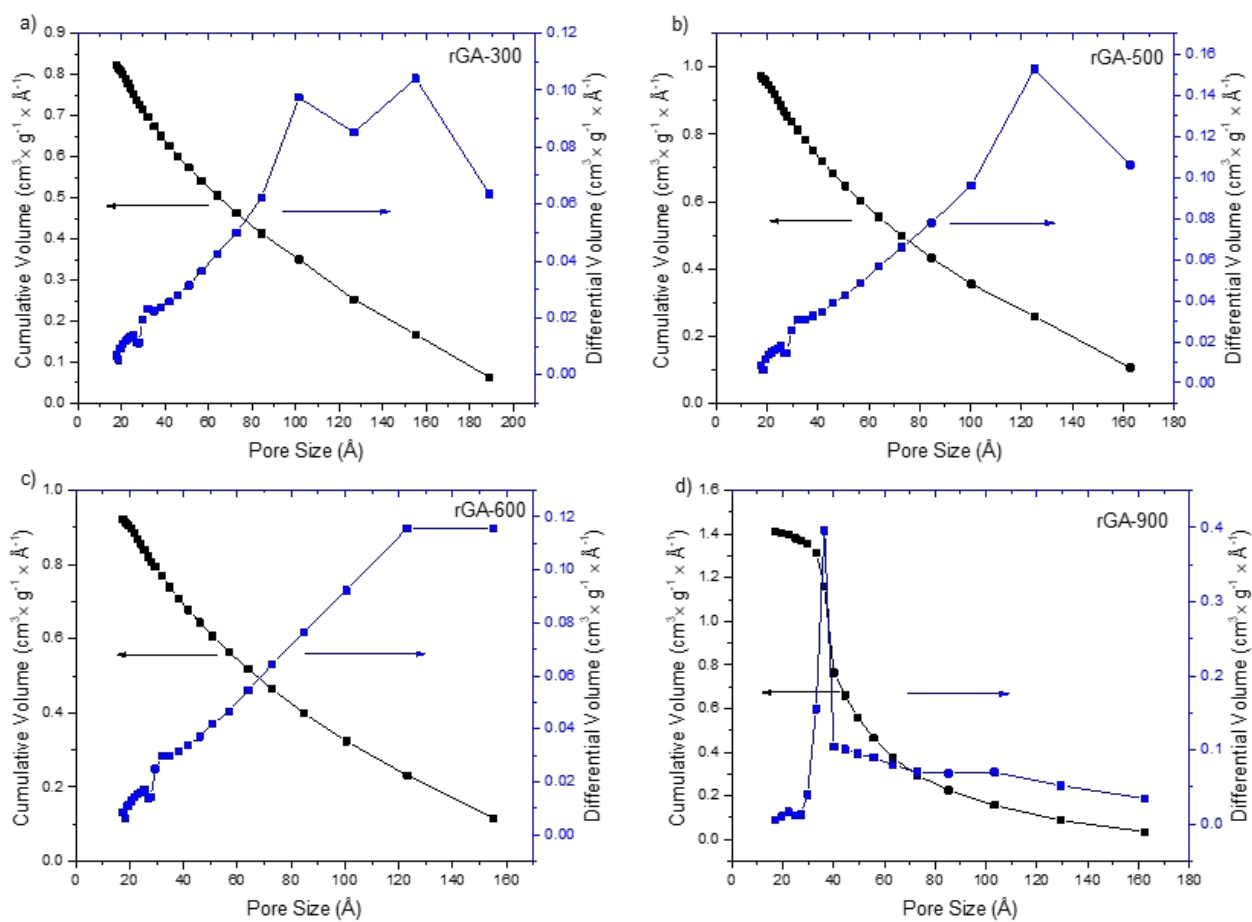


Figure S4. Pore size distribution and cumulative volume of the samples determined by Barrett-Joyner-Halenda method; a) rGA-300, b) rGA-500, c) rGA-600, d) rGA-900.

Table S1. Atomic percentages of C–C/C=C/C–H, C–O, C=O, π – π^* groups obtained from X-ray photoelectron spectroscopy for rGA-300, rGA-500, rGA-600, rGA-700, and rGA-900.

| Sample | C–C/C=C/C–H | C–O | C=O | π – π^* |
|---------|-------------|-------|-------|-----------------|
| rGA-300 | 60.16 | 17.99 | 12.59 | 9.26 |
| rGA-500 | 63.02 | 16.06 | 10.98 | 9.94 |
| rGA-600 | 63.92 | 15.43 | 10.21 | 10.44 |
| rGA-700 | 66.22 | 14.11 | 9.41 | 10.27 |
| rGA-900 | 66.85 | 12.45 | 9.06 | 11.64 |

Table S2. Relative peak intensities and positions calculated from fitted Raman Spectra with deconvoluting 5 peaks of *G*, *D*, *D'*, *D''*, and *D**.

| Sample | <i>D</i> (cm ⁻¹) | <i>G</i> (cm ⁻¹) | <i>D*</i> (cm ⁻¹) | <i>D''</i> (cm ⁻¹) | <i>D'</i> (cm ⁻¹) | <i>I_{D*}/I_G</i> | <i>I_D/I_G</i> | <i>I_{D'}/I_G</i> | <i>I_{D''}/I_G</i> |
|---------|------------------------------|------------------------------|-------------------------------|--------------------------------|-------------------------------|-------------------------------------|------------------------------------|-------------------------------------|--------------------------------------|
| rGA-300 | 1351 | 1597 | 1182 | 1526 | 1619 | 0.06 | 1.24 | 0.23 | 0.4 |
| rGA-500 | 1351 | 1595 | 1185 | 1537 | 1620 | 0.11 | 1.35 | 0.31 | 0.47 |
| rGA-600 | 1350 | 1593 | 1243 | 1531 | 1617 | 0.19 | 1.46 | 0.37 | 0.65 |
| rGA-700 | 1350 | 1589 | 1220 | 1530 | 1616 | 0.31 | 1.93 | 0.5 | 1.11 |
| rGA-900 | 1346 | 1586 | 1215 | 1526 | 1589 | 0.56 | 3.42 | 0.63 | 2.21 |

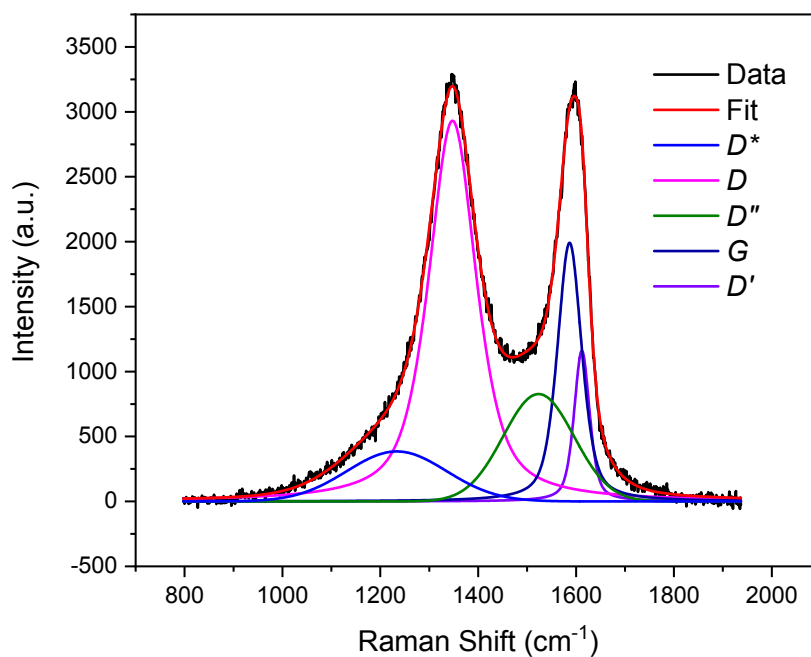


Figure S5. Fitted Raman spectrum of rGA600 prepared in an *in-situ* cell. Data was measured under a flow of Ar without exposing the sample to air.

Table S3. Relative peak intensities calculated from fitted Raman Spectra in Figure S5 with deconvoluting 5 peaks of *G*, *D*, *D'*, *D''*, and *D** and its comparison with air-exposed rGA600.

| Sample | I_{D^*}/I_G | I_D/I_G | $I_{D''}/I_G$ | $I_{D'}/I_G$ |
|--|---------------|-----------|---------------|--------------|
| rGA-600 (measured under a flow of Ar, without exposing to air) | 0.19 | 1.47 | 0.41 | 0.58 |
| rGA-600 (air exposed)* | 0.19 | 1.46 | 0.37 | 0.65 |

*The air exposed sample's information is taken from the main manuscript from Table 2.

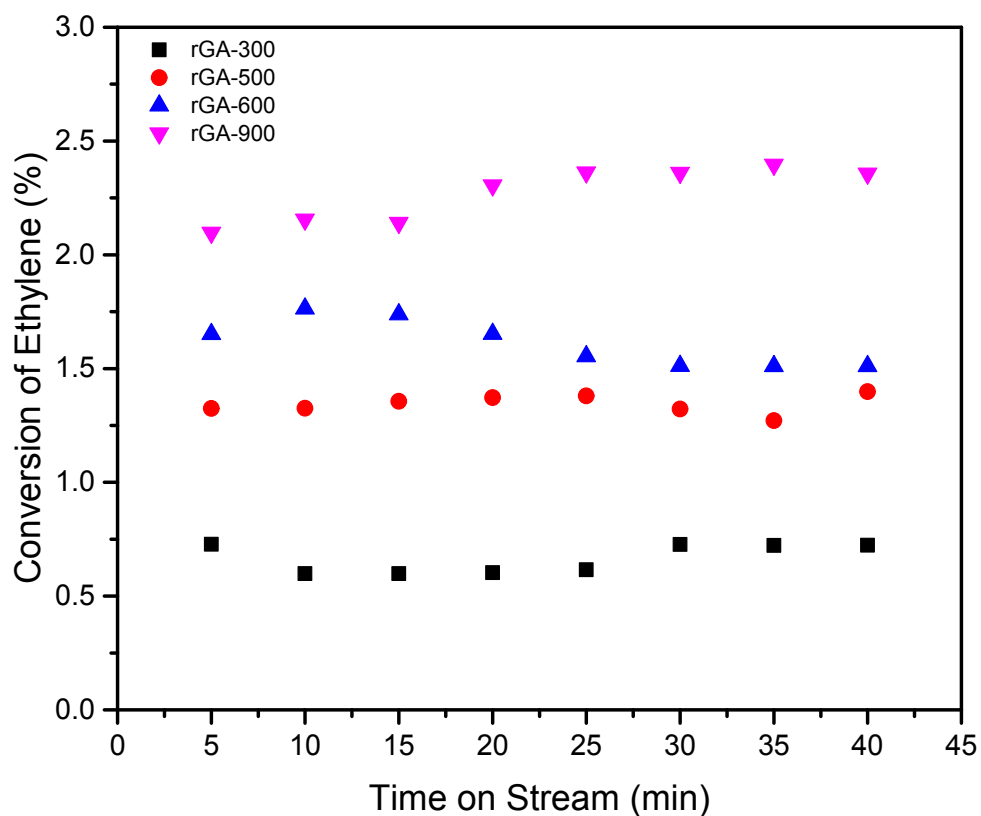


Figure S6. Variation of ethylene conversion over time for the samples of rGA-300, rGA-500, rGA-600, and rGA-900. Reaction conditions: 50 vol% ethylene, 50 vol% H₂, Gas hourly space velocity (GHSV)= 4600 mL ethylene × g_{cat}⁻¹ × h⁻¹; at 1 bar and 200 °C.

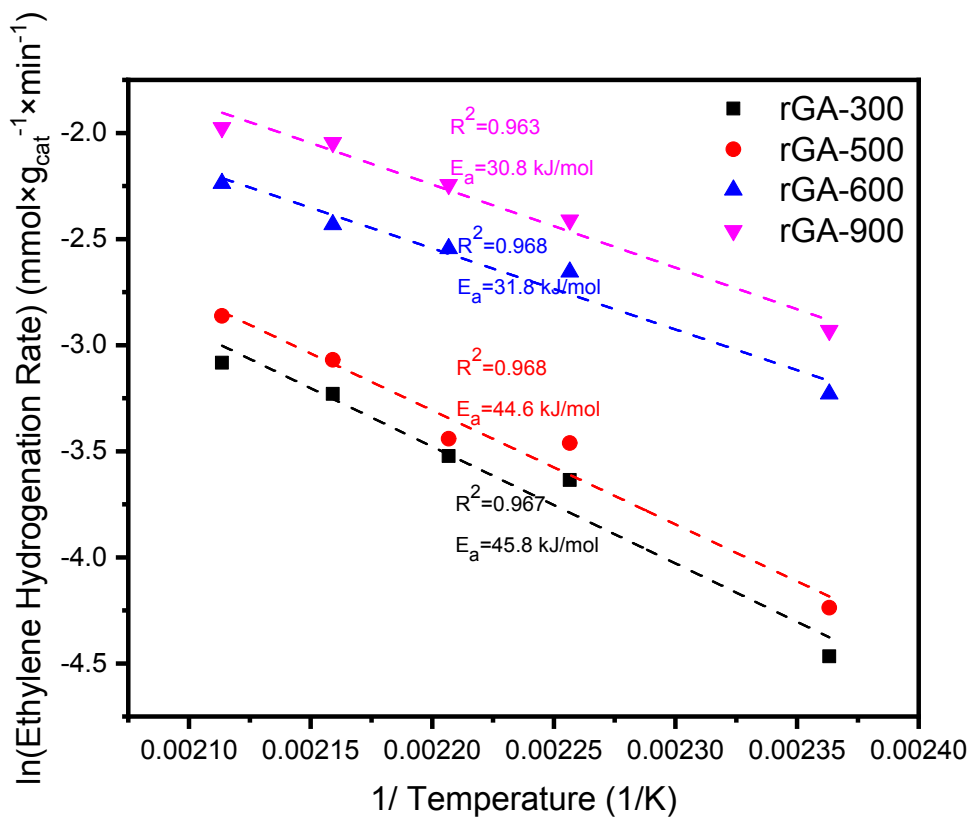


Figure S7. Arrhenius plots for rGA-300, rGA-500, rGA-600 and rGA-900 under differential conversion (between 0.2% and 2.5%). Reaction conditions: 50 vol% ethylene, 50 vol% H₂, GHSV= 4600 mL ethylene × g_{cat}⁻¹ × h⁻¹; at 1 bar and 150, 170, 180, 190, and 200 °C.

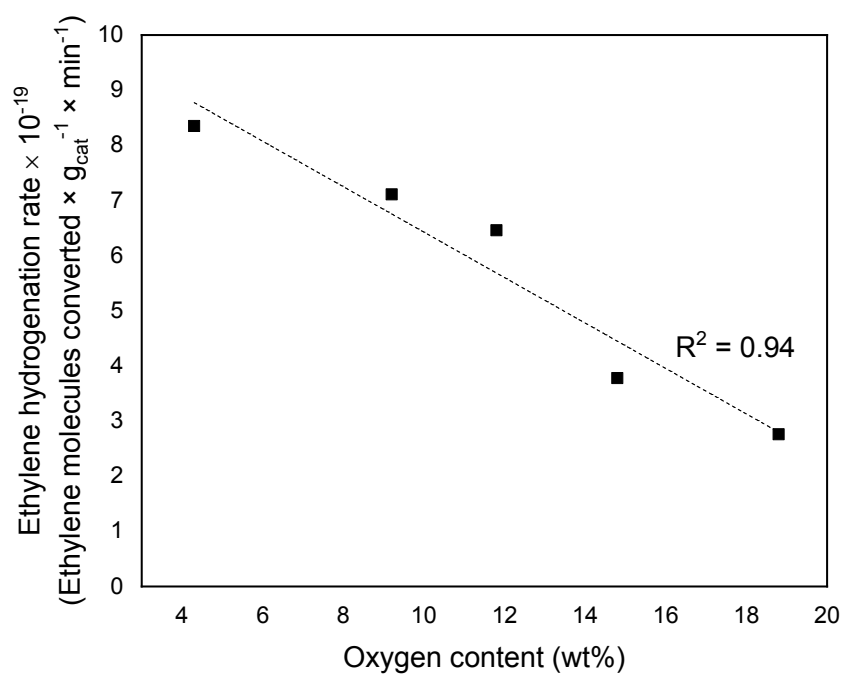


Figure S8. The variation of per gram ethylene hydrogenation rate with the oxygen content obtained by CHSN-O analysis for rGA300, rGA500, rGA600, rGA700, and rGA900.

$$I. \quad 2.76 \times 10^{19} = 8.26 \times 10^{20} \times TOF D^* + 1.71 \times 10^{22} \times TOF D + 3.17 \times 10^{21} \times TOF D'' + 5.51 \times 10^{21} \times TOF D'$$

$$\begin{aligned}
 \text{II.} \quad & 3.78 \times 10^{19} = 1.43 \times 10^{21} \times TOF D^* + 1.76 \times 10^{22} \times TOF D + 4.05 \times 10^{21} \\
 & \times TOF D'' + 6.14 \times 10^{21} \times TOF D' \\
 \text{III.} \quad & 6.46 \times 10^{19} = 2.27 \times 10^{21} \times TOF D^* + 1.74 \times 10^{22} \times TOF D + 4.42 \times 10^{21} \\
 & \times TOF D'' + 7.77 \times 10^{21} \times TOF D' \\
 \text{IV.} \quad & 8.35 \times 10^{19} = 3.40 \times 10^{21} \times TOF D^* + 2.08 \times 10^{22} \times TOF D + 3.83 \times 10^{21} \\
 & \times TOF D'' + 1.34 \times 10^{22} \times TOF D'
 \end{aligned}$$

Equation Set S1. Reaction rate equations for I) rGA-300, II) rGA-500, III) rGA-600, IV) rGA-900 derived by Equation 1 given in the main text where the rate is defined in “Ethylene Molecules converted $\times g_{cat}^{-1} \times min^{-1}$ ”.

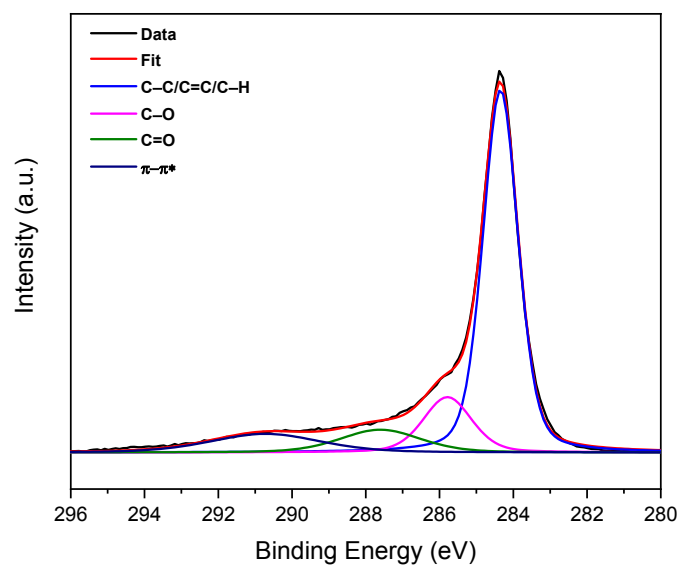


Figure S9. C 1s XP spectra of rGA-700.

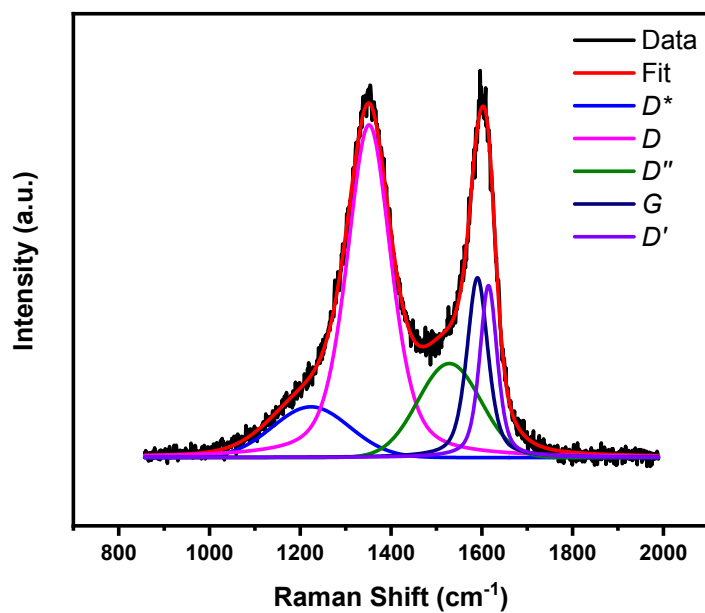


Figure S10. Deconvoluted Raman spectrum of rGA-700 sample identifying the peaks of G , D , D' , D'' and D^* .

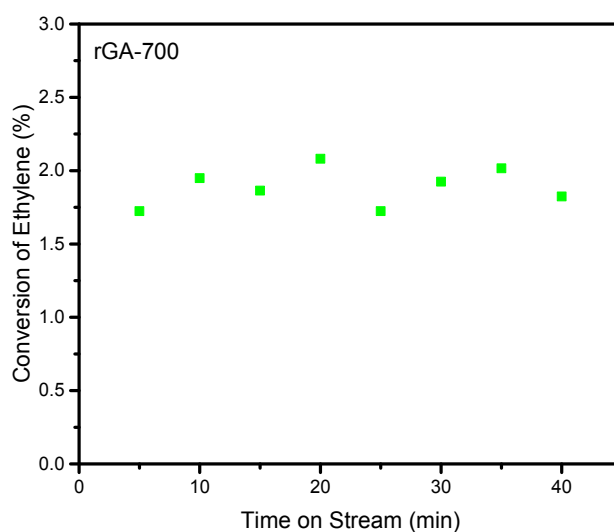


Figure S11. Ethylene conversion over time on stream. Reaction conditions: 50 vol% ethylene, 50 vol% H₂, GHSV= 4600 mL ethylene × g_{cat}⁻¹ × h⁻¹; at 1 bar and 200 °C.

Table S4. CHSN-O elemental analysis results of rGA-700.

| Sample | Weight percentages (wt.%) | | |
|---------|---------------------------|-----|-----|
| | C | O | H |
| rGA-700 | 90.0 | 9.2 | 0.8 |

Table S5. Quantification of *D*, *D'*, *D''*, and *D** defect sites for rGA-700 and glassy carbon. For rGA-700, the ethylene hydrogenation rate was collected at 50 vol% ethylene, 50 vol% H₂, GHSV= 4 600 mL ethylene × g_{cat}⁻¹ × h⁻¹; at 1 bar and 200 °C for rGA-700. For glassy carbon a GHSV of 4 000 mL ethylene × g_{cat}⁻¹ × h⁻¹ was used.

| Sample | Number of Defected Sites in Gram of Sample | | | | Initial ethylene hydrogenation rate (Ethylene Molecules converted × g _{cat} ⁻¹ × min ⁻¹) |
|---------------|--|-----------------------|-----------------------|-----------------------|---|
| | <i>D*</i> | <i>D</i> | <i>D''</i> | <i>D'</i> | |
| rGA-700 | 2.88×10 ²¹ | 1.79×10 ²² | 4.64×10 ²¹ | 1.03×10 ²² | 7.11×10 ¹⁹ |
| Glassy carbon | 8.21×10 ²⁰ | 2.67×10 ²² | 1.44×10 ²¹ | 5.19×10 ²⁰ | 2.08×10 ¹⁹ |

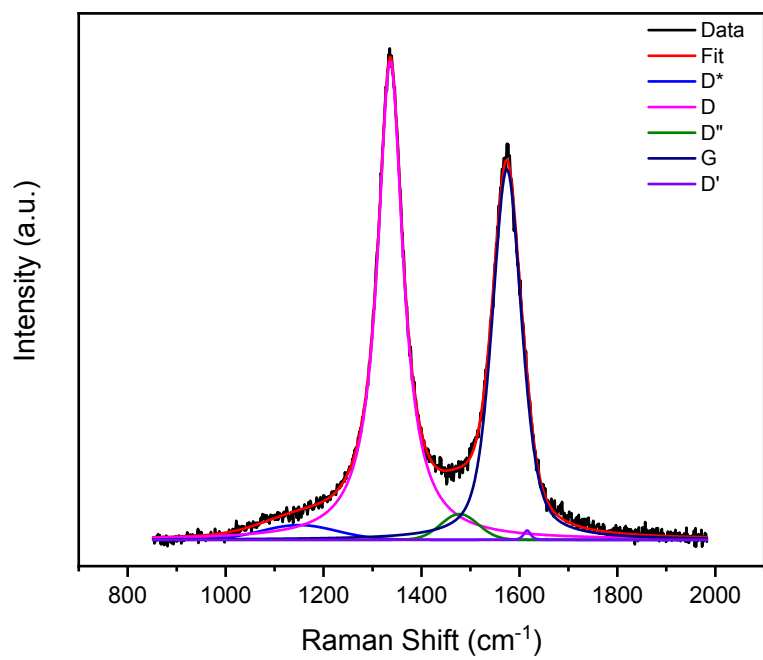


Figure S12. Deconvoluted Raman spectrum of glassy carbon identifying the peaks of *G*, *D*, *D'*, *D''*, and *D**.