Supporting Information

Graphene as an adsorption template for studying double bond activation in catalysis

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S1. Pristine Graphene for O₂ and H₂/C₂H₄ experiments.

a) C 1s spectrum measured on the graphene film used for the O₂ experiments (figure 2). Spectra measured after exposing the surface to CO, the lack of CO adsorbed signal confirms the film’s full coverage. b) C 1s spectrum measured on the graphene film used for the H₂ and C₂H₄ experiments (figure 3), also after CO exposure. The lack of CO adsorbed signal confirms the film’s full coverage. c) Survey spectra measured after graphene growth in both cases. Only iridium and carbon can be clearly distinguished. Note that the red spectrum shows oscillations at the high-binding energy side (500 - 800 eV). Those are due to instabilities of the beamline during the measurement.
S2a. Direct comparison: H-Gr exposed to O₂, H₂ and C₂H₄

Direct comparison of the C 1s curve fitting after graphene growth, after hydrogenation and after the following exposures: i) 60 s, 1.0 mbar O₂, ii) 60 s, 1.0 mbar H₂, and iii) 60 s, 1.0 mbar C₂H₄. Exposure to O₂ and C₂H₄ results in the complete removal of H dimers (component Cₙ), while exposure to H₂ leads to no change to the C 1s spectrum. The slightly different relative size of Cₙ component is caused by the use of different hydrogen sources at different beamtimes (see the experimental section in the main article).
S2b. Direct comparison: H-Gr exposed to O\textsubscript{2}, H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}

Accumulative plots representing the intensity of each C 1s component after graphene growth, after hydrogenation, and after i) 60 s O\textsubscript{2} exposure at 1.0 mbar, ii) 60 s H\textsubscript{2} exposure at 1.0 mbar, and iii) 60 s C\textsubscript{2}H\textsubscript{4} exposure at 1.0 mbar. The values are stated next to each plot. All fits are shown in figure S2a.
S3. Discussion of H clusters and interaction with the substrate with the analysis of Ir 4f\textsubscript{7/2}

In the main text we have shown how the exposure to molecular oxygen of a H saturated Gr film results in the selective removal of the most weakly adsorbed H structures (the H dimers). We observed, however, that some of the more strongly adsorbed H atoms (which form H clusters in the FCC and HCP regions of the moiré) are also removed. While the removal of dimers is not reflected in the Ir4f\textsubscript{7/2} spectra, the partial removal of H clusters is reflected by the relative intensities of the iridium components.

The Ir 4f\textsubscript{7/2} spectra in figure S3 are fitted with three components: bulk iridium (I\textsubscript{bulk} at 60.8 eV), surface iridium (I\textsubscript{surf} at 60.3 eV), and surface iridium atoms binding to C atoms from the graphene film atop (I\textsubscript{c} at 60.7 eV). For the fit, we have assumed that the total surface area (I\textsubscript{surf} + I\textsubscript{c}) is maintained, and only the relative intensities of I\textsubscript{surf} and I\textsubscript{c} change.

After the graphene growth, in panel a, we only observe the bulk and surface components, due to the weak interaction between the Ir surface and the graphene film. After hydrogenation, the presence of hydrogen clusters in both FCC and HCP regions of the moiré unit cell increases the interaction of graphene with the substrate. This is reflected in the Ir 4f\textsubscript{7/2} spectra (left spectrum in panels b, c and d), where now approximately 80 % of the I\textsubscript{surf} intensity becomes I\textsubscript{c}, meaning that 80 % of the Ir surface is now binding to C-atoms. This coverage is in agreement with the H-saturated Gr surface described in the main text, where most of the HCP and FCC regions in the moiré unit cells are occupied by H clusters, and the rest of the Gr surface is covered by weakly adsorbed H dimers (figure 2b in the main text). These changes in the Ir 4f\textsubscript{7/2} spectra are also in good agreement with previous studies\textsuperscript{1}.

After oxygen exposure (right spectrum in figure S3b), the I\textsubscript{surf} component recovers to 55 %, meaning that only 45 % of the iridium surface atoms remain binding to C-atoms from the graphene atop. This is in agreement with the reduction of the cluster-related C 1s components (C\textsubscript{b} and C\textsubscript{d}), which decrease from 55% to 36% of the total C 1s intensity. Note that for every C-H bond breaking from the graphene-like clusters, 1 to 3 Ir surface atoms unbind to C atoms (assuming that H atoms at the edges of the H clusters are the ones being removed).

Similar observations can be done for the Ir 4f\textsubscript{7/2} spectra measured before and after exposure to other gases (figure S3c for molecular hydrogen and figure S3d for ethylene). After hydrogen exposure, where no change can be observed in the H coverage (see figure 3a, or S2a and S2b above), the I\textsubscript{c} and I\textsubscript{surf}...
components maintain almost the same intensity ratios after exposure. After ethylene, on the other hand, which is capable of removing the H dimers but much less efficient than oxygen at affecting the H clusters coverage (see figure 3b or S2a, panel (iii)), we observe a slight recover of the I$_{surf}$ component (from 20% to 35%), which can be directly linked to the 5% diminishing of the C$_b$ and C$_d$ components in the C 1s spectra shown in figure S2b, panel (iii).

Overall, the analysis of the Ir 4f$_{7/2}$ confirms the conclusions drawn in the main text: Exposure to oxygen results in the complete removal of H-dimers and reduction of graphane-like H-clusters, while exposure to molecular hydrogen does not affect the system, and exposure to ethylene results in the removal of H-dimers alone.
Additional STM images for the O\textsubscript{2} exposure experiment (figure 2)

i) Pristine graphene

ii) After hydrogenation

iii) After oxygen exposure

Additional STM images measured on i) pristine graphene, ii) after hydrogenation (H-Gr/Ir(111)), and after exposure to oxygen flow (1.0 mbar, 60 s). Size and scanning parameters: i) (left to right) 40×40 nm\textsuperscript{2}, V\textsubscript{t} = 0.15 V, I\textsubscript{t} = 3 nA, 20×20 nm\textsuperscript{2}, V\textsubscript{t} = 0.60 V, I\textsubscript{t} = 2 nA, 70×70 nm\textsuperscript{2}, V\textsubscript{t} = 0.15 V, I\textsubscript{t} = 3 nA. ii) (left to right) 50×50 nm\textsuperscript{2}, V\textsubscript{t} = -0.95 V, I\textsubscript{t} = 1 nA, 40×40 nm\textsuperscript{2}, V\textsubscript{t} = 1.00 V, I\textsubscript{t} = 2.5 nA, 50×50 nm\textsuperscript{2}, V\textsubscript{t} = -0.95 V, I\textsubscript{t} = 1 nA. iii) (left to right) 30×30 nm\textsuperscript{2}, V\textsubscript{t} = -0.15 V, I\textsubscript{t} = 1.5 nA, 50×50 nm\textsuperscript{2}, V\textsubscript{t} = -0.15 V, I\textsubscript{t} = 1.5 nA. The bright protrusions in the center images of i and ii correspond to impurities on the sample.
S5. Graphene supercell and adsorption sites used for the DFT calculations

The picture above shows a 6×6 graphene sheet with adsorption sites highlighted in brown color. The annotations are the indices of C atoms onto which adsorption is considered (the others are not used in the calculations). In the following figures S6 - S10, the different investigated adsorption configurations are illustrated with the indices of the adsorption sites and corresponding adsorption strength sorted after the most stable configuration found. The title of each configuration points out where the adsorbates are located in the initial guess structure. Upon DFT relaxation, we filter out all failed structures, e.g. structures which relax into another configuration that is already covered in our systematic testing of adsorption configurations.
S6. Configurations of co-adsorbed 2H and 2O (Para H dimer)

DeltaE = -2.083 eV

DeltaE = -1.632 eV

DeltaE = -1.542 eV

DeltaE = -1.526 eV

DeltaE = -1.521 eV

DeltaE = -1.338 eV

DeltaE = -1.082 eV

DeltaE = -1.024 eV
S7. Configurations of co-adsorbed 2H and 2O (Ortho H dimer)
S8. Configurations of co-adsorbed H, O, and OH
S9. Configurations of co-adsorbed OH and OH

![Diagram of configurations with energy differences](image)

S10. Configurations of co-adsorbed OOH

![Diagram of configurations with energy differences](image)
S11. Structures of transition states identified for the reaction network in Figure 3

S12. Additional geometric details of state 2d (top and side views)
S13. Reaction path 1b to 2c

The structures (top and side views) along the reaction path of 1b => 2c are shown below with some concrete geometry information labeled. Starting from a physisorbed $O_2$ molecule together with H dimer on the graphene, we observe that $O_2$ approaches the H dimer and picks up two hydrogen atoms sequentially during the reaction. Specifically, the O=O bond is weakened, as evidenced by the O-O bond length increase to 1.38 and 1.55 Å, respectively, for the first and second hydrogenation steps. Finally, we end up with a H-O-H angle equal to 105.3°, which is very similar to its counterpart in a water molecule (104.5°).
S14. Stability of various O* adsorption sites in vicinity of H dimer

Stability of various O* adsorption sites referenced to the most stable one (site 41-42 marked in red) in the vicinity of an H dimer. Meta-stable structures are marked in orange. For bonding of O* next to the graphene-like clusters we expect even higher stability due to the sp³-like bonding geometry here.

T1. Calculated diffusion barriers for O and H atoms on graphene

Calculated diffusion barriers with various supercell sizes and k-point densities for O and H atoms adsorbed on freestanding graphene.

| Graphene size | K-points | $\Delta E_{(Hbri - Htop)}$ | $\Delta E_{(Obri - Otop)}$ |
|---------------|----------|---------------------------|---------------------------|
| 3x3           | 9x8      | 1.18                      | -0.82                     |
| 4x4           | 9x6      | 1.14                      | -0.87                     |
| 5x5           | 9x5      | 1.15                      | -0.86                     |
| 6x6           | 4x4      | 1.06                      | -0.71                     |
| 7x7           | 3x3      | 1.04                      | -0.62                     |
| 8x8           | 3x3      | 1.09                      | -0.64                     |
| 9x8           | 9x6      | 1.09                      |                           |
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