

Supporting Information.

Interplay among Hydrogen Chemisorption, Intercalation and Bulk Diffusion at the Graphene covered Ni(111) Crystal.

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Analysis of the C1s spectra measured during the exposure of Gr/Ni(111) to H atoms as a function of temperature.

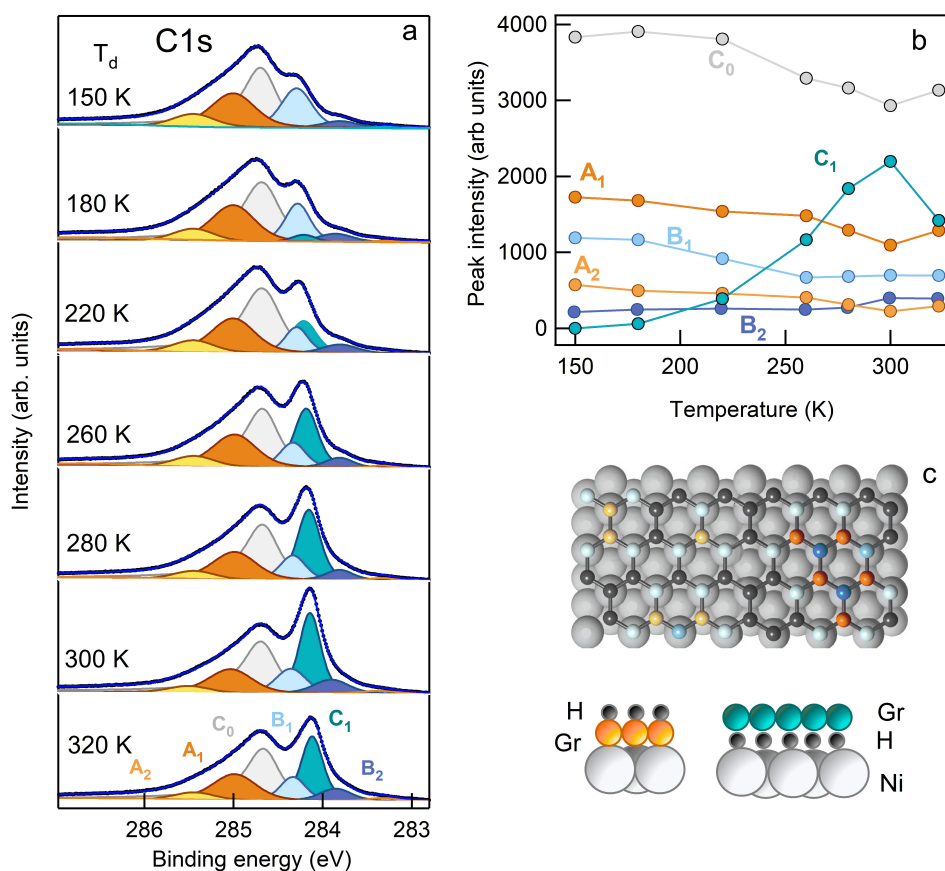


Figure S1: a) High resolution C1s spectra measured at photon energy of 400 eV on the Gr/Ni(111) surface exposed to 5 kL of hydrogen at different dosing temperatures in the range 150-320 K. Spectra were best fitted with Doniach-Šunjić functions convoluted with Gaussians, and a linear background. The spectral components were assigned to C atoms in different configurations, as illustrated in c), by following the DFT calculations reported in Ref.¹ : unhydrogenated C atoms (dark grey atoms) are represented by C₀ (284.68 eV); C atoms directly bonded to H contribute to A₂ (285.44 eV) (H monomers and dimers, yellow atoms) and to A₁ (285.05 eV) (dimers, but mainly H trimers or larger clusters, orange atoms); graphene sites first neighbours of the C-H bonds originate B₁ (284.28 eV) (neighbours of one and two C-H bonds, light blue atoms) and B₂ (283.84 eV) (neighbours of three C-H bonds, blue atoms); Gr regions decoupled from the Ni substrate [dark green atoms in the drawing at bottom of c)] by the intercalated H atoms are represented by the C₁ peak. b) Integrated intensities of the C1s spectral components obtained from the analysis shown in a), plotted as a function of the dosing temperature.

Isothermal desorption from hydrogenated Gr/Ni(111)

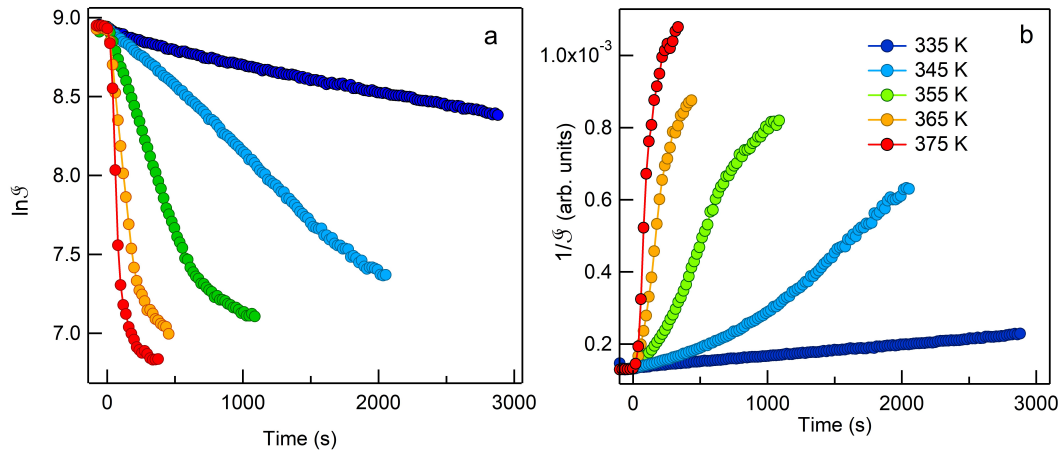


Figure S2: Analysis of the isothermal desorption curves measured for the Gr/Ni(111) sample heavily hydrogenated at room temperature. For prolonged exposure to atomic hydrogen, intercalation of the H atoms below graphene occurs and the graphene regions decoupled from the substrate originate the component C_1 in the C1s spectrum. The integrated C_1 intensity, \mathcal{J} , is proportional to the intercalated H coverage. As reported in the main text, for a first or second order desorption process $\ln \mathcal{J}(t)$ or $1/\mathcal{J}(t)$, respectively, should show a linear trend as a function of the desorption time. Panel a) and b) show the experimental $\ln \mathcal{J}(t)$ or $1/\mathcal{J}(t)$ curves measured at the different desorption temperatures between 335 and 375 K, plotted vs. time. At least during the first extended part of the desorption all curves show a linear trend in a) but not in b), indicating that the desorption initiates as a first order process and that, when the surface coverage has strongly decreased, possibly switches to a second order process.

Stability of the Gr coverage during Gr/Ni(111) hydrogenation.

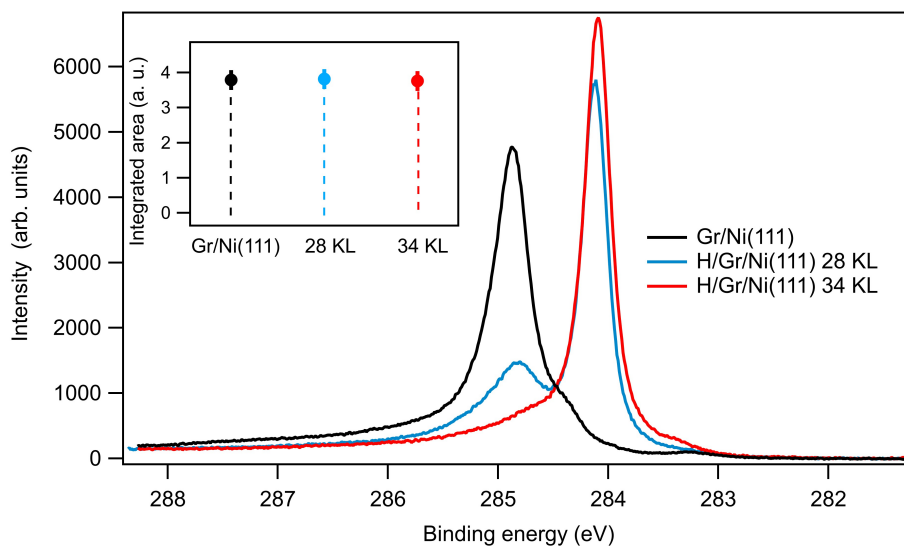


Figure S3: C1s core level spectra measured on the Gr/Ni(111) surface pristine and dosed at room temperature with 28 and 34 kL of hydrogen. The inset compares the integrated area of the three C1s spectra: after the exposure to 34 KL, which corresponds to the complete lifting of the Gr layer due to H intercalation, the C1s integrated area decreases by $\sim 2\%$ with respect to the value measured on the pristine sample, which is anyhow within the error bar.

References

- (1) Lizzit, D.; Trioni, M. I.; Bignardi, L.; Lacovig, P.; Lizzit, S.; Martinazzo, R.; Larciprete, R. Dual-Route Hydrogenation of the Graphene/Ni Interface. *ACS Nano* **2019**, *13*, 1828–1838.