

## Supporting Information

### **Aldehydes trapping by self-propagating atom-exchange reactions on a Gallium Nitride Monolayer: Role of the molecule complexity**

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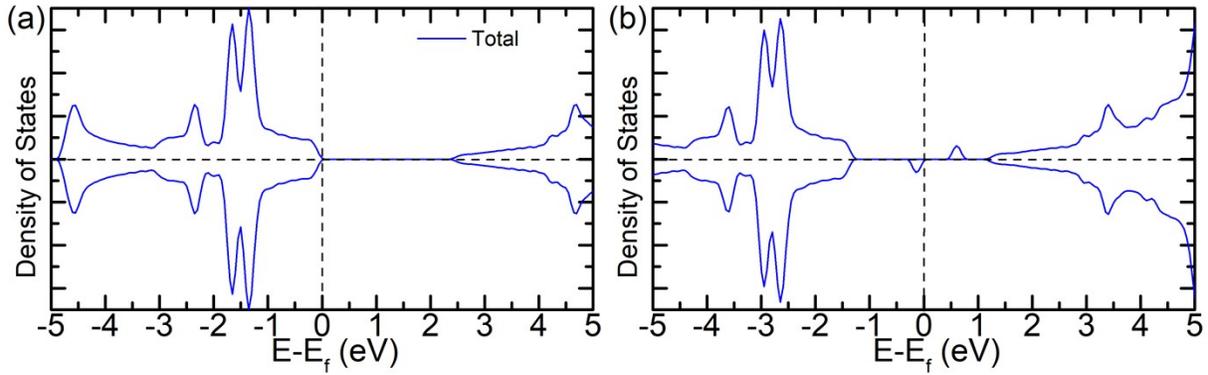
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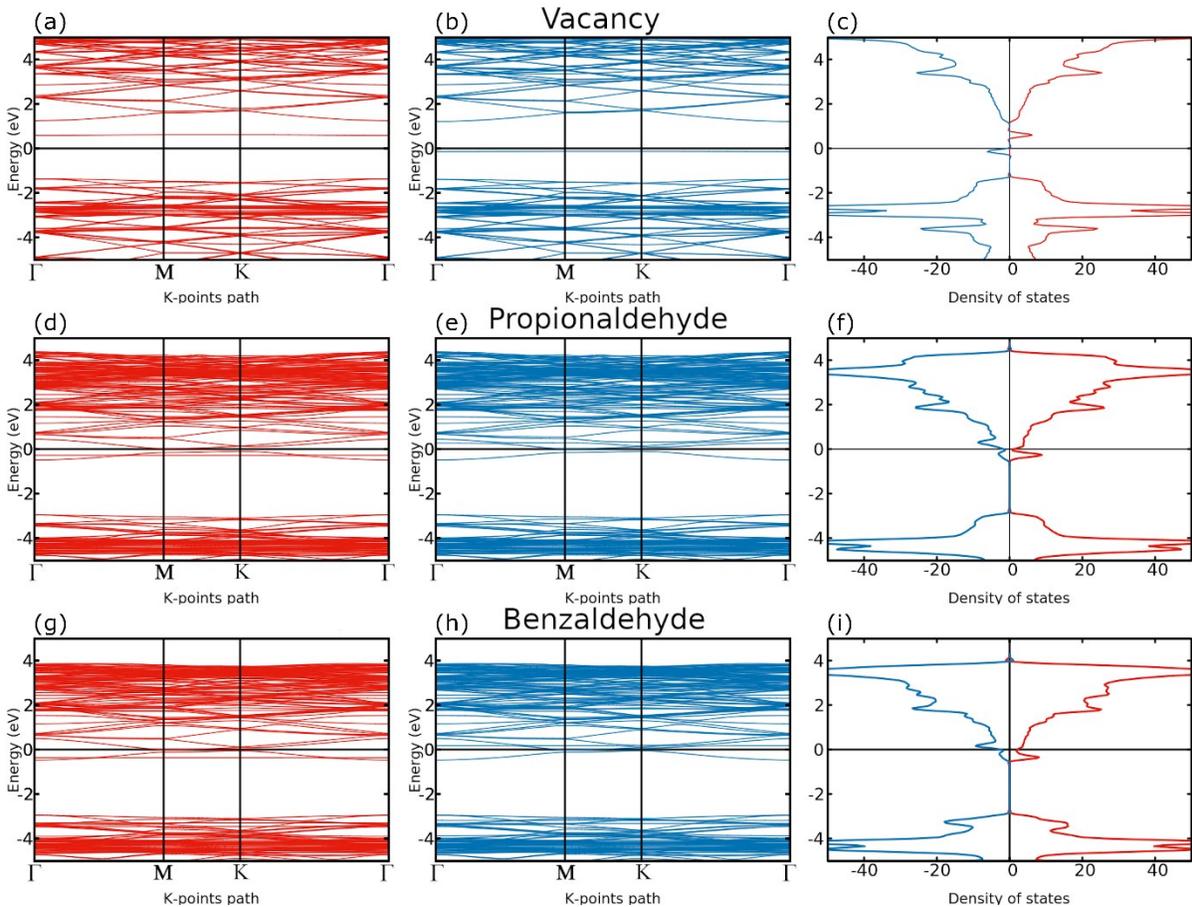
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## Density of States for the Substrate.



**Figure S1.** Electronic density of states of (a) H-GaN monolayer, and (b) H-GaN monolayer with a H vacancy. The H-GaN depicts a band gap of 2.40 eV, while in the H vacancy, electronic states are introduced in the band gap. The highest occupied states correspond to a spin-down peak, while the lowest unoccupied states correspond to a spin-up peak. This is a characteristic effect caused by the appearance of a dangling bond. The spin-down contribution is mainly composed by the electronic orbitals from the Ga with the missing H. This means that the Ga with the H vacancy is a local reactive point on the system.

## Electronic Band structures



**Figure S2.** The Spin-up and spin-down electronic band structures, along the  $\Gamma$ -M-K- $\Gamma$  path on the Brillouin zone, and the density of states for (a-c) the H-GaN with H vacancy, (d-f) the IS for propionaldehyde and (g-i) for benzaldehyde. Red lines denote spin up, while blue lines denote spin down.

The spin-up, and spin-down band structure for the H-GaN monolayer with the H vacancy are very similar. However, an extra flat conduction band is seen at 0.5 eV in the spin-up dispersion, while the spin-down shows a flat valence band close to zero energy. For the IS of propionaldehyde, and benzaldehyde, the highest valence bands are in contact with the conduction bands, independently of the spin, and becoming metallic. For both cases, the spin-up, and spin-down band structure are also very similar. However, since the system has an odd number of electrons, the spin-up band structure shows one more valence band than the spin-down, while the spin-down dispersion shows an extra conduction band. The highest occupied spin-down peak on the DOS corresponds to the last valence band of spin-down. Meanwhile, the spin-up peak is composed by two spin-up valence bands, therefore there is a larger intensity of the spin-up peak.

### Nudged Elastic Band, Climbing Image (NEB-CI) calculations.

The calculate MEPs are shown in Fig. S3. the reference energy is the one of ZS. The first and last image

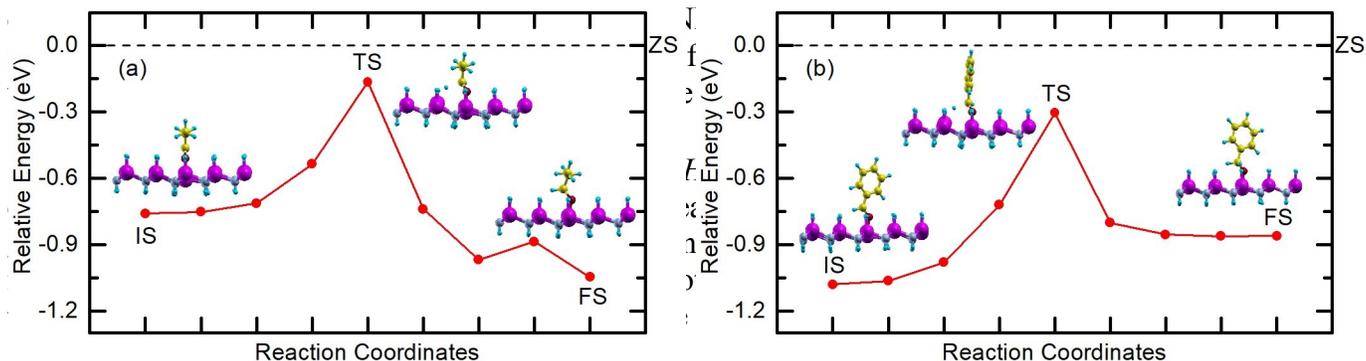


Figure S3: MEP of the reaction of  $C_3H_6O$  on H-GaN. MEP of the reaction of  $C_7H_6O$  on H-GaN.

### Atomic configuration of the transition States.

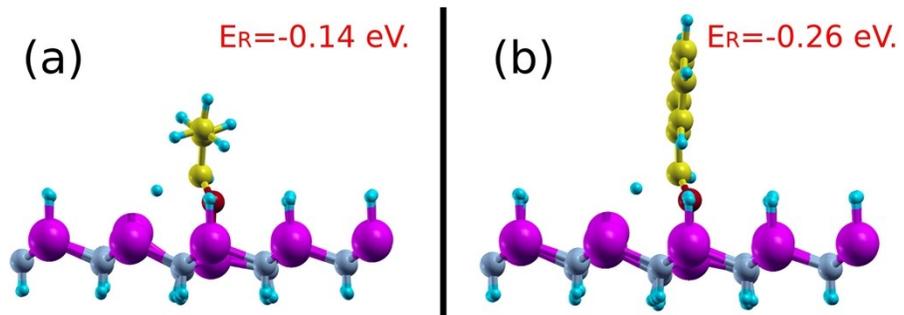


Figure S4: Transition states for (a)  $C_3H_6O$  and (b)  $C_7H_6O$ .

**Density of States.**

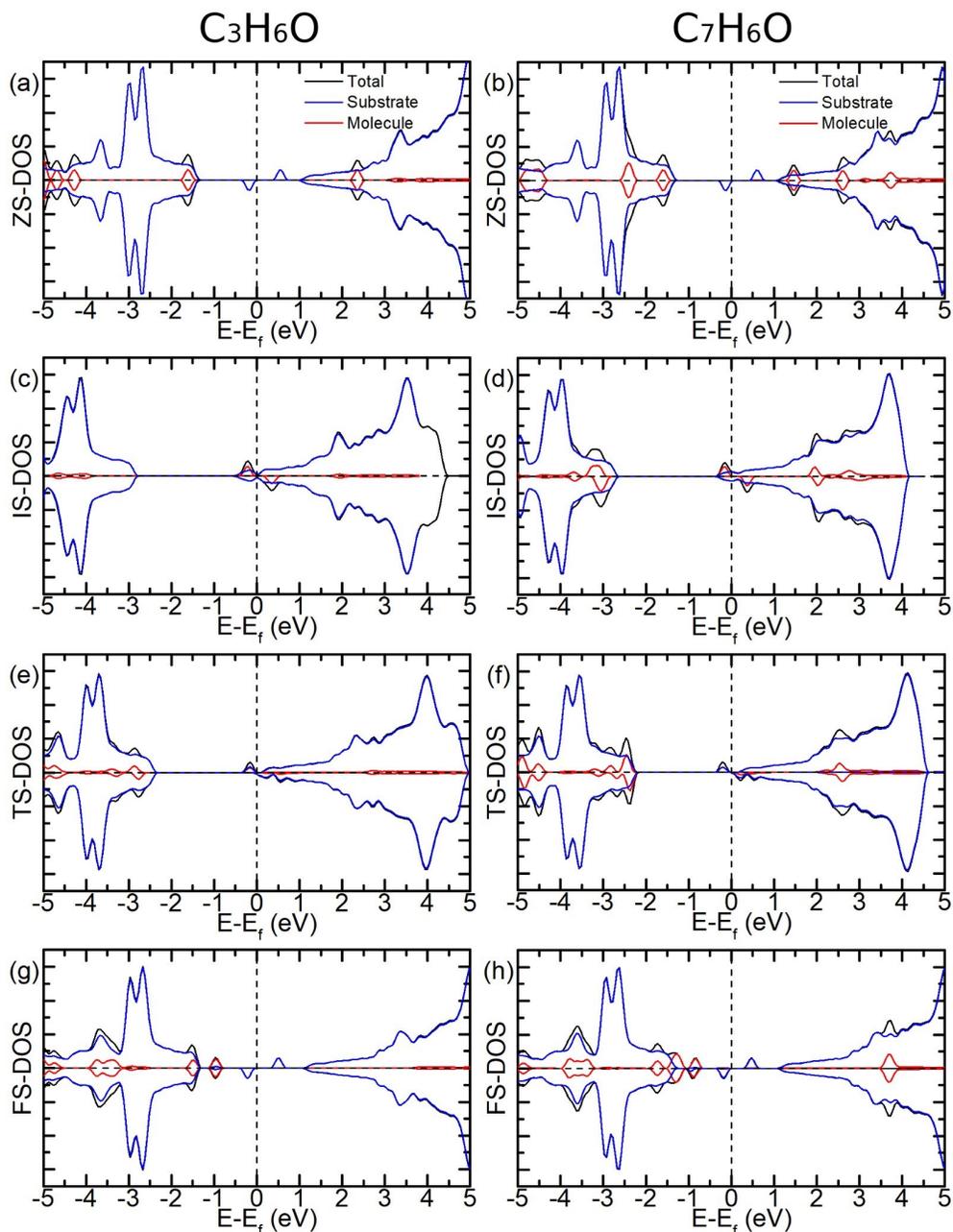


Figure S5: Density of States. (a-b) ZS, (c-d) IS, (e-f) TS, and (g-h) FS.  
Left column for  $C_3H_6O$  and right column for  $C_7H_6O$ .

The total, substrate, and molecule density of states (DOS) are plotted with the black, blue, and red line, respectively. The zero corresponds to the energy of the highest occupied state. The ZS for  $C_3H_6O$ , and  $C_7H_6O$  are shown in Fig. S5(a-b), respectively (the substrate DOS is the same on both plots). The blue peaks at -0.5 eV and 0.55 eV are due to the Ga dangling bond. It shows contributions to both occupied spin-down states and unoccupied spin-up states. The density of states of both molecules show similar behaviors, since both present peaks around the same energy levels. However, the DOS of  $C_7H_6O$  shows peaks of higher intensity, and in a wider energy range due the extra states coming from the larger molecule.

Each molecule presents their respective spin-down and spin-up DOS at the same energy level and intensity. The highest occupied states of the  $C_3H_6O$  are localized at -1.50 eV, while the lowest unoccupied

states are around 2.50 eV (Fig S5a). On the other hand, the  $C_7H_6O$  highest occupied and lowest unoccupied states are localize at -1.50 eV and 1.50 eV, respectively. The  $C_7H_6O$  presents a lower electronic bandgap.

The IS DOS for the  $C_3H_6O$  and  $C_7H_6O$  are shown in Fig. S5(c-d), respectively. The dangling bond peaks of the substrate disappear, because of the formation of the Ga-O bond on both cases. Therefore, the spin-down and spin-up states of the monolayer are identical (see blue line on Fig. S5(c-d)). Meanwhile, the molecules' DOS are no longer equivalent, a spin-up peak around -0.25 eV, and a spin-down peak around 0.34 eV emerges, showing the unpaired electron in the molecules, specifically around the C atom (this is also evident in the increase of the C-O bond length. Also, for  $C_7H_6O$ , peaks appear around -3.1 eV and 2 eV, different to  $C_3H_6O$  where the peaks appear only around the Fermi level.

The TS DOS are shown on Fig. S5(e-f). It can be noted the formation of dangling bond in the substrate, by the appearance of peaks at -0.25 eV and 0.25 eV, confirming that the H is not longer bonded to the substrate. On the other hand, the peak due to the unpaired electron in the molecules decreases.

The FS DOS are plotted in Fig. S5(g-h). The substrate peaks reaper at -0.5 eV and 0.55 eV confirming the new dangling bond. The  $C_3H_7O$  introduce electronic states at -1.0 eV (see Fig. S5e), while the  $C_7H_8O$  produces electronic states at -1.5 eV and -1.0 eV (see Fig. S5f).

## Spin Isosurfaces.

During the proposed reaction, a continuous charge redistribution is being carried out, and there is also a spin density (SD) redistribution as the reaction takes place. The spin density isosurfaces for the ZS, IS, TS, and FS are shown in Fig. S6, where blue and red lobules denote the spin-down and spin-up isosurfaces, respectively. In the ZS (for both cases) a high symmetry blue lobule is mainly centered in the Ga atom with the H-vacancy due to the presence of the dangling bond (in agreement with the high occupied states described in the previous section), and in a smaller proportion blue lobules are around the first neighboring N atoms (Fig. S6(a,e)). For the IS (Fig. S6(b,f)), the majority spin density isosurface are high symmetric red lobules surrounding the molecules, due to the unpaired electrons. On the TS (Fig. S6(c,g)), the spin isosurface is shared between the molecule, the substrate, and the H atom that is moving to the molecule. On the TS, Ga has a red lobule, in agreement with the DOS analysis. The final state SD is shown in Fig. S6(d,h), where, once again, a predominant blue lobe is shown on the Ga atom with the H-vacancy.

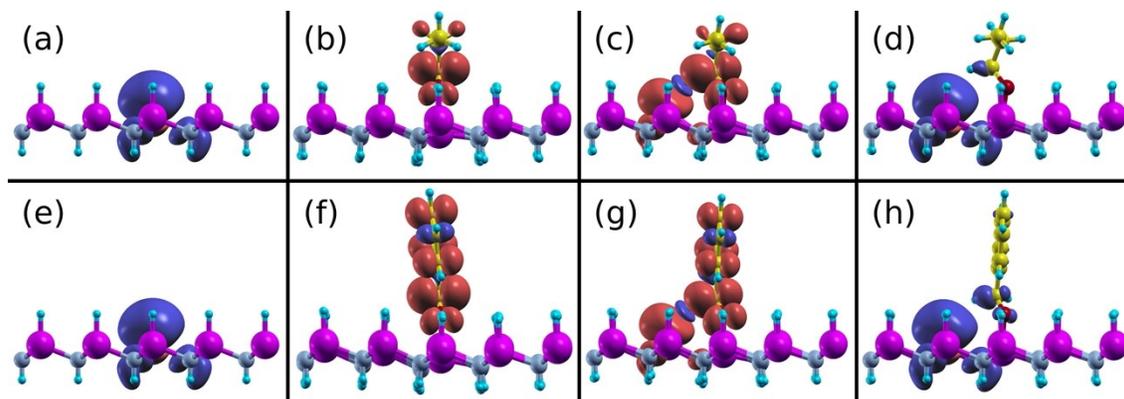


Figure S6:  $C_3H_6O$  Spin Isosurfaces for (a) ZS, (b) IS, (c) TS and (d) FS,  $C_7H_6O$  Spin Isosurfaces for (e) ZS, (f) IS, (g) TS and (h) FS. An isovalue of 0.001 was used.