Supporting Information:

**First-principles study of Ti-catalyzed hydrogen chemisorption
on an Al surface: A critical first step for reversible hydrogen
storage in NaAlH₄**

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Figure S-1: Alternate view of the surface-H₂ complex HOMO showing the overlap with the H₂ σ^* orbital which ultimately causes the H-H bond to come apart.

Figure S-2: An MO diagram showing how the surface electrons are donated to the H₂ σ^* orbital of the surface-HOMO complex shown in Figure 4a. When H₂ begins to interact with the surface, the σ bonding orbital of H₂ mixes with the surface HOMO, stabilizing the “bonding” combination and destabilizing the “antibonding” combination. Meanwhile, the surface LUMO mixes with the H₂ σ^* orbital, stabilizing the “bonding” combination (shown in Fig. 4a) and destabilizing the “antibonding” combination. As the surface HOMO and LUMO are not widely separated in energy, the stabilized combination of the surface LUMO

and σ^* becomes lower in energy than the destabilized combination of the surface HOMO and σ , so the pair of electrons that was originally in the surface HOMO ends up in the stabilized combination of the surface LUMO and σ^* . The latter becomes the HOMO of the surface- H_2 adduct.

Figure S-3: The NaH(001) surface doped with one Ti atom shows chemisorption of the hydrogen molecule. This is a probable catalytic reaction, but it lacks any low-energy pathway for the diffusion of the dissociated hydrogen to the Al lattice.

Movie (AVI format, 99.6 MB): First-principles molecular dynamics simulation at 350 K.

We included 26 atoms in the MD runs – 24 from the doped surface plus the two hydrogen atoms. These were slab calculations that were periodic in 3D with a 25-30 Å layer of vacuum above the surface. The positions of subsurface Al atoms are marked with crosses for clarity.