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Catalytic effect of near-surface alloying on hydrogen interaction on the aluminum surface

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A small amount of catalyst, such as Ti, was found to greatly improve the kinetics of hydrogen reactions in the prototypical hydrogen storage compound sodium alanate ($NaAlH_4$). We propose a near-surface alloying mechanism for the rehydrogenation cycle based on a detailed analysis of available experimental data as well as first-principles calculations. The calculated results indicate that the catalyst remains at subsurface sites near the Al surface, reducing the dissociation energy barrier of H_2. The binding between Ti and Al modifies the surface charge distribution, which facilitates hydrogen adsorption and enhances hydrogen mobility on the surface.

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I. INTRODUCTION

Hydrogen is an ideal energy carrier because it is lightweight and plentiful, with an oxidation product (water) that is environmentally benign. However, storage remains a challenge. In 1997, Bogdanović and Schwickardi[1] reported ahydrogen storage system of Ti-doped sodium alanate ($NaAlH_4$) that could function under moderate temperature and pressure conditions. This breakthrough was able to lower the first decomposition temperature and also help the rehydrogenation reaction.[2,3] Since then, extensive experimental studies have been performed[4] focusing on the microstructure and reaction kinetics of these compounds, and many other possible catalysts have also been identified.[2] The critical role played by these catalysts in facilitating hydrogen cycling in the alanate has been an ongoing research topic for more than a decade and is still an unsolved mystery.[5]

In sodium alanate, hydrogen is released by a two-step process:

$$NaAlH_4(s) \leftrightarrow \tfrac{1}{3}\,Na_3AlH_6(s) + \tfrac{2}{3}\,Al(s) + H_2(g), \qquad (1)$$

$$Na_3AlH_6(s) \leftrightarrow 3\,NaH(s) + Al(s) + \tfrac{3}{2}\,H_2(g). \qquad (2)$$

Two possible scenarios exist for the catalyzed hydrogenation and dehydrogenation reactions that make alanates readily reversible. The first possibility is that the catalyst enters the bulk as a dopant and stimulates phase separation and crystal growth inside the material. The second one is that, without entering the bulk, the catalyst modifies the hydrogen release and adsorption processes near the surface. Many calculations have been performed to search for the evidence of Ti acting as a bulk dopant in sodium alanate or to confirm that the presence of Ti lowers the bulk diffusion barrier of hydrogen.[4] However, theoretical studies show that Ti on the surface of, or substituted into, $NaAlH_4$ has a higher energy than in the metal form.[6] Our calculated results agree with previous studies in that implanting Ti into the $NaAlH_4$ crystal is an endothermic process with a substantial energy cost. In addition, there is little experimental evidence to date to conclude that Ti can be incorporated into the sodium alanate lattice. Therefore, the present study will focus on the second surface mechanism. This investigation is also guided by a careful examination of relevant experimental data in the literature, as summarized below.

Experimental findings. With catalysts, reactions (1) and (2)are rapid solid-state reactions, and one expects to obtain a homogeneous mixture composed of extremely small grains of each phase. However, the *in situ* diffraction experiments found narrow peaks corresponding to relatively large crystallites (>100 nm) of Al.[7] Therefore, there must be some long-range diffusion mechanism to transport Al over a long distance (∼1000 Å). As a result, we expect a different dehydrogenation mechanism in the alanate than in traditional metal hydrides with interstitial hydrogen. The possible mobile species is likely to contain both Al and H, some type of $(AlH_3)_x$ species, in order to balance the amount of Al and H in the reaction. It was demonstrated more than 50 years ago in a study of different decay products of various alanates at room temperature[8] that the catalyst, such as Ti, affects the decomposition of AlH_3 near the surface, although the underlying mechanism is not yet known and will be the subject of future study.

Regarding the rehydrogenation process, it is well known that metallic aluminum does not readily absorb hydrogen from the gas phase unless it is under extremely high hydrogen pressure. However, atomic hydrogen reacts strongly with aluminum surfaces, producing a variety of surface alane species.[9,10] A careful surface study using complementary scanning tunneling microscopy (STM) and surface infrared (IR) measurements[10] showed that atomic H extracts aluminium atoms directly from the surface (H etching) to create mobile AlH_3 monomers, which then condense into alane oligomers. These alane oligomers, ranging in size from the monomer to 30-mers, are thermally stable on the surface at room temperature.[10] Moreover, it has been reported that the synthesis of $NaAlH_4$ directly from NaH or Na_3AlH_6 can be achieved by mixing with AlH_3 without a catalyst or hydrogen overpressure.[11–13] These aforementioned observations suggest that if atomic H is present at the Al surface in the rehydrogenation process, AlH_3 oligomers will form, and consequently the reverse reactions in (1) and (2) will take place. Therefore, the presence of Ti near the surface is likely to play a role to facilitate the dissociation of H_2 and the subsequent hydrogen diffusion on the surface. These processes can be checked by first-principles calculations, which is the focus of this study.

II. CALCULATION DETAILS

Our calculations are based on density functional theory (DFT) using the Vienna *ab initial* simulation package (VASP).[14] The generalized gradient approximation (GGA)[15] and ultrasoft pseudopotentials[16] are employed. The surfaces are modeled by periodic slabs containing ten or twelve (001) atomic layers of Al separated by a vacuum region of 23 Å. Atomic H adsorption and H_2 dissociation are studied in a 2×2 unit cell (in reference to the cubic unit cell of Al) with eight metal atoms per layer. The k-space integrals are evaluated using a 4×4 grid for the 2×2 unit cell in the DFT calculation and a 8×8 grid for evaluating the density of states (DOS). The plane-wave cutoff energy is 425.0 eV, the total-energy convergence is 10^{-5} eV, and the force convergence in structural relaxation is 0.01 eV/Å.

III. RESULTS AND DISCUSSION

A. Position of the catalyst

Recent data from the Ti K-edge extended x-ray absorption fine-structure spectroscopy (EXAFS) suggests a formal valence of zero for Ti in the "doped" $NaAlH_4$ sample.[13,17,18] A quantitative comparison of the edge fine structure further suggests that the active Ti atoms are located on or near the surface surrounded by Al, probably with a tetragonal local symmetry in the form of $TiAl_3$, and that the environment does not change with hydrogenation-dehydrogenation cycles.[13,17] $TiAl_3$ has two possible structures: cubic $L1_2$ and tetragonal $D0_{22}$.[19] We will examine Ti positions following both arrangements near an Al(001) surface. The atomic configurations considered are shown in Fig. 1, including configurations with Ti either exposed at the surface (configuration A) or covered completely by Al layers (configurations B–E). Similar to the case in bulk $TiAl_3$, the Ti coverage is 0.5 ML in each surface layer that contains Ti. The top eight layers are allowed to relax further, while the deepest four layers are fixed at bulk positions since in real systems the Ti additives at low doping levels will not significantly change the lattice constant of the Al particles. The surface-alloy configurations in Fig. 1 always have a lower energy than the pure Al layers and bulk Ti combined, indicating that mixing Ti and Al near the surface is energetically favorable.

The energy variation as a function of Ti position is shown in Fig. 1 for both $L1_2$ and $D0_{22}$ local arrangements of Ti and Al. For comparison purposes, the energy of configuration A with a $D0_{22}$-type local arrangement is used as the energy reference. Among all the configurations considered, the geometry with Ti in the topmost surface layer (configuration A) is least favored energetically. As soon as Ti goes to subsurface sites, the energy drops significantly. For configuration A, the $L1_2$ arrangement has a slightly lower energy than the $D0_{22}$ arrangement. This is consistent with previous theoretical investigations,[20,21] and has been explained from the interaction of Ti in the first and the third layers.[20] However, the $D0_{22}$ arrangement is preferred when Ti atoms go deeper into Al, consistent with the fact that the $D0_{22}$ phase is more stable for bulk $TiAl_3$. We do not find any favorable active Ti sites on the surface, as considered in previous studies.[13,22,23] The result is understandable since the Al surface has a lower surface energy than the Ti surface, so exposing Ti atoms raises the energy. A surface reconstruction induced by the presence of Ti in the topmost surface layer was proposed in Ref. 22; we find that this reconstructed structure is higher in energy than configuration B by 0.6 eV per surface unit cell.

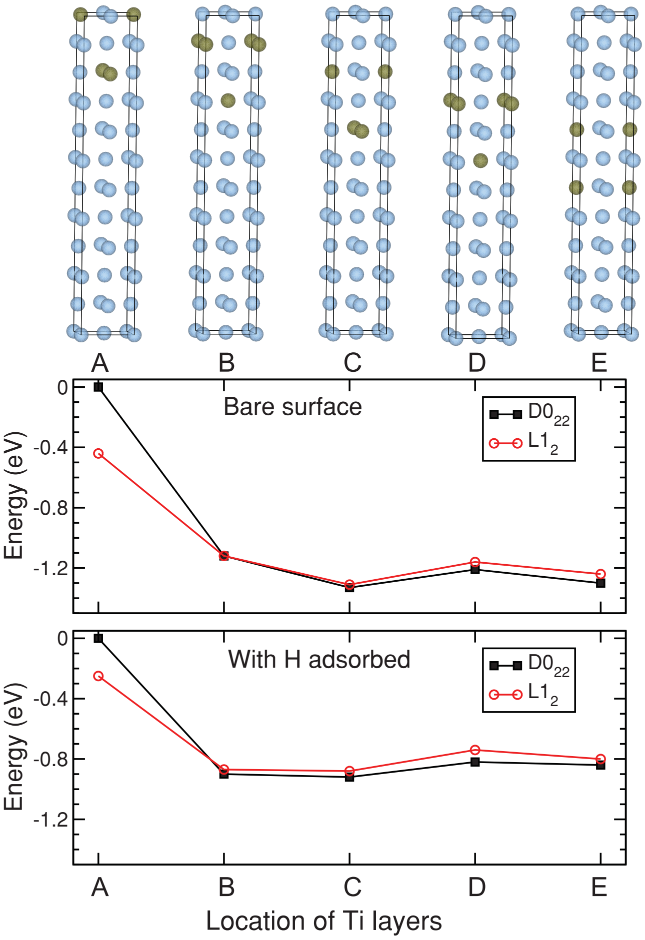

FIG. 1. (Color online) Top: Different surface slab configurations of Al(100) considered in the calculation, representing different locations of Ti (dark spheres) into the surface. Only 1×1 unit cells are shown. We illustrate the $D0_{22}$-type local $TiAl_3$ arrangement in configurations A–D, and the $L1_2$-type arrangement in configuration E. Bottom: Relative energies of modified Al(100) surfaces as the Ti position varies for both hydrogen-free and hydrogen-covered surfaces. For comparison purposes, the energy of configuration A with a $D0_{22}$ local arrangement is set to zero.

Based on our results, we conclude that Ti prefers to occupy subsurface sites. This is consistent with the measurements using ion scattering spectroscopy[24,25] and low-energy electron diffraction (LEED).[25,26] Although subsurface Ti was found favorable in a previous calculation for a 0.5 ML coverage of Ti on Al(100),[21] the single-layer geometry considered in Ref. 21 has a higher energy than the alloy configurations with a local $TiAl_3$ arrangement, as studied in the present work. Our study focuses on identifying the most energetically favorable atomic arrangements involving surface alloying between Ti and Al without exposing Ti on the surface. This conclusion does not change when hydrogen is added on the surface, as shown in the lower panel of Fig. 1, where the energies are calculated by using 1×1 surface unit cells (with one hydrogen per two surface metal atoms at the top site).

B. Hydrogen adsorption

Hydrogen adsorption is investigated in detail for different adsorption sites on the surface with subsurface Ti. These include sites on top of Al (top site T), between two Al atoms

TABLE I. Energy of a hydrogen atom (E_{ads}, in reference to that of the gas phase) at different adsorption sites (Hydrogen position) on the pure and Ti-modified Al(100) surfaces. The local arrangement of Ti is of the $D0_{22}$ type. T stands for top sites, B for bridge sites, and H for hollow sites. H1 (H2) denotes the hollow site above a second-layer Al (Ti) atom in configuration B; and T1 (T2) denotes the top site above a third-layer Al (Ti) atom in configuration C.

	Hydrogen position	E_{ads} (eV) GGA	E_{ads} (eV) LDA
Pure Al(100)	T	0.29	0.16
	B	0.08	−0.04
	H	0.50	
Ti at second surface layer (configuration B)	T	−0.12	−0.22
	B	−0.05	−0.18
	H1	0.31	
	H2	0.55	
Ti at third surface layer (configuration C)	T1	0.20	
	T2	0.27	
	B	0.04	
	H	0.42	

(bridge site B), and between four surface atoms (hollow site H). With a 2 × 2 unit cell, the separation between two H atoms is 8.0 Å, so the interaction between hydrogen adsorbed in adjacent cells is negligible. The vertical position of hydrogen is optimized, and the calculated hydrogen energies, in reference to that in the molecule, are listed in Table I, together with the results for the pure Al(100) surface where adsorbed H prefers the bridge site.[27] Some results using the local-density approximation (LDA) are also shown in Table I for comparison. GGA and LDA results agree well on the energy difference between different adsorption sites or between pure and Ti-modified surfaces, although LDA gives ∼0.1 eV lower hydrogen energy than GGA. Therefore, all of the following conclusions based on relative energies are not expected to depend on the specific choice of the exchange-correlation functional. We will focus on the GGA results in the following analysis. The most energetically favorable geometry for H is found to be at the top site with subsurface Ti in configuration B with the $D0_{22}$ local arrangement. With full relaxation, the distance between Al and the top-site H is about 1.6 Å, with Al slightly lifted above the surface by 0.2 Å. Compared with the pure Al surface, the energy of adsorbed H on this Ti-modified surface is lowered by 0.2 eV. We will therefore focus our study below on this energetically favorable Ti-modified surface.

An examination of the electronic structure reveals that the presence of subsurface Ti induces changes in the p states of surface Al atoms, thus affecting their interaction with top-site H. No direct interaction is found between the subsurface Ti and adsorbed H. Therefore, the subsurface Ti modifies the properties of the Al surface layer, enhancing the binding of adsorbed H on the surface.

C. Hydrogen diffusion

Another interesting result shown in Table I is that the energy difference between the top and bridge sites for the Ti-modified surface is only 0.07 eV, indicating that hydrogen may diffuse easily on the surface. In Fig. 2, the circles and triangles represent the calculated energy values, with respect to the gas phase for adsorbed H along the path between the bridge and top sites, on the pure Al and Ti-modified surfaces, respectively.The diffusion barrier of 220 meV on the pure Al(100) surface is greatly reduced to 90 meV on the Ti-modified surface.

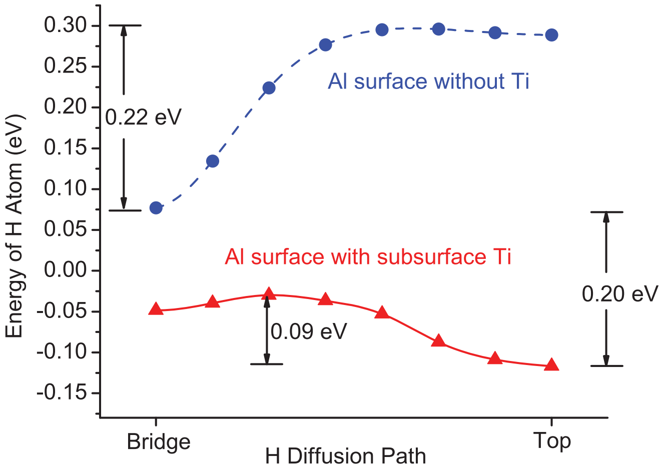

FIG. 2. (Color online) Energy of H along a diffusion path connecting the bridge and top sites on the pure Al(100) surface and on the Ti-modified surface of configuration B in Fig. 1. The solid and dashed lines are interpolated curves through the calculated values with and without subsurface Ti, respectively. The energy is in reference to that of the gas phase.

D. H_2 dissociation

We have also examined the effect of subsurface Ti on the H_2 dissociation process on the Al surface. Figure 3(a) shows the energy of an H_2 unit as a function of the H-H separation along the dissociation path for both pure and Ti-modified surfaces. The dissociation path is derived from a complete 2D potential-energy surface constructed by sampling the energy of the H_2 unit in a plane perpendicular to the Al surface and containing the final adsorption sites: two close-by bridge sites for the pure Al(100) surface and two close-by top sites for the Ti-modified surface. A similar method has been used to study the interaction between the H_2 and Al(110) surface.[28] The calculated activation barrier for the dissociative adsorption of H_2 on pure Al(100) is 0.9 eV, which is close to the results of previous calculations.[21,23] When Ti is located at the subsurface, this value is reduced to 0.7 eV, which compares favorably with the experimentally observed energy barrier of 0.58–0.64 eV for the H_2 uptake in the Ti-catalyzed $NaAlH_4$ hydrogen storage system.[29] In a previous calculation with only 0.5 ML of Ti at the second layer, the dissociation barrier was found to be 0.63 eV,[21] which is also close to our result. This indicates that Ti at the fourth layer in configuration B, although helpful in stabilizing the surface alloy, does not interact strongly with the hydrogen at the surface. The 0.2-eV reduction in the activation barrier significantly accelerates the dissociation process by an Arrhenius factor ($e^{\Delta E/kT}$) of $\sim 10^3$ at a typical reaction temperature of 100 °C. It was proposed previously[13] that Ti exposed at the top surface layer is able to reduce the dissociation barrier by a larger amount. However, these top-layer

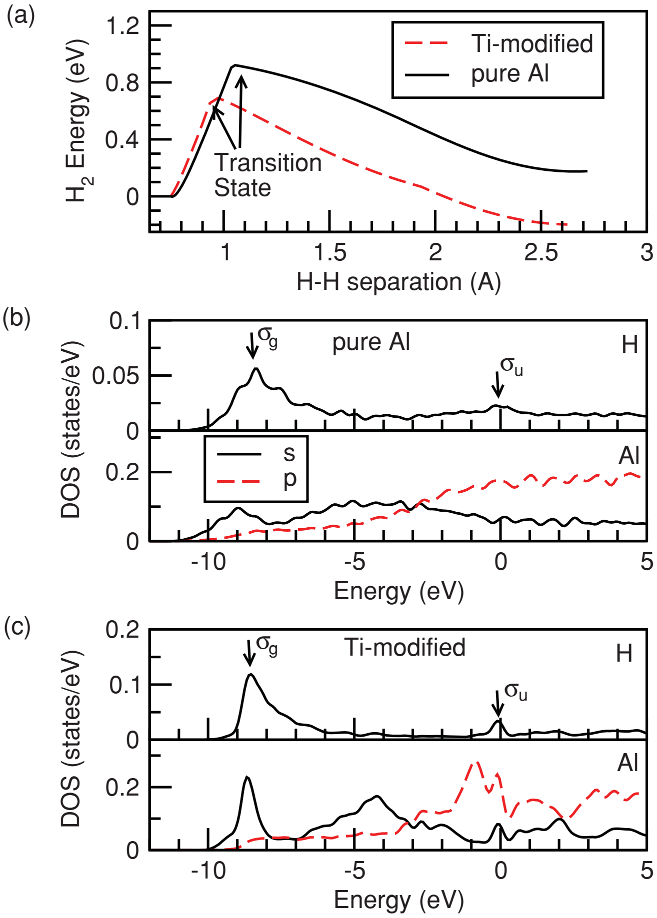

FIG. 3. (Color online) (a) Energy variation of an H_2 unit (in reference to the energy of an H_2 molecule in the gas phase) as a function of the H-H separation along the dissociation path. Projected DOS of H and surface Al that is closest to the H_2 unit at the transition state for (b) pure and (c) Ti-modified (configuration B) Al surfaces. σ_g and σ_u denote the H-H bonding and antibonding states, respectively.

Ti configurations are energetically unfavorable (see Fig. 1), so the total activation energy, including the energy cost to transfer Ti from the subsurface to the top layer, will be much higher.

To understand the influence of subsurface Ti on the electronic structure of the surface system, we plot in Figs. 3(b) and 3(c) the projected density of states (DOS) of H and surface Al at the transition state during the dissociation process for the pure and Ti-modified surfaces, respectively. The transition state is characterized by the onset of the occupation of the H-H antibonding state (σ_u). One can see clearly the effect of Ti in enhancing the interaction between the H-H bonding (σ_g) and Al-s states, in moving more Al-p states below the Fermi, and in promoting the interaction of σ_u and Al-p states. This stronger H_2-surface interaction with subsurface Ti at the transition state effectively reduces the activation barrier by 0.2 eV.

E. Role of the catalyst

Our calculated results indicate that subsurface Ti significantly changes the binding characteristics of H on the Al surface, promotes H adsorption, enhances H mobility, and reduces the H_2 dissociation barrier. These greatly help the rehydrogenation reaction. The major results are independent of the number of Ti layers included in the calculation. Therefore, only a small amount of the catalyst is needed to facilitate the reactions.[1] Putting all the pieces provided by both experimental and theoretical studies together, we propose a mechanism for the catalyst-assisted rehydrogenation reactions associated with $NaAlH_4$: the catalyst facilitates hydrogen dissociation and adsorption on the Al surface. Based on the results in Ref. 10, atomic H then extracts Al atoms directly from the surface (H etching) to create mobile AlH_3 monomers. They can subsequently condense into mobile alane oligomers that diffuse to the NaH or Na_3AlH_6 region. A recent inelastic neutron-scattering measurement has confirmed the formation of a volatile molecular aluminum hydride, possibly AlH_3 and oligomers, during the early stage of H_2 regeneration of a depleted, catalyst-doped sodium aluminum hydride.[30] In a sense, this picture describes a process of storing AlH_3 in NaH in the form of alanates. It is noted that recent experimental studies of the regeneration of AlH_3 using complexing agents (such as amine and ether) to form stabilized alane complexes have been performed by direct hydrogenation of catalyzed Al.[31]

The "catalyst" Ti stays below the surface and affects the reaction by modifying the properties of the Al surface. We expect that any working catalyst has to be able to "mix" well with Al. As a matter of fact, Ref. 2 reported quite a few elements that could act as catalysts for $NaAlH_4$, including Ti, Zr, V, Fe, Ni, Nb, and rare earths such as Y, La, Ce, Pr, Nd, and Sm. These elements all form stable alloys with Al. The current calculation concludes that near-surface alloying with Ti can have favorable effects on the rehydrogenation reaction on the Al surface for $NaAlH_4$.

For the dehydrogenation cycle, hydrogen-deuterium exchange experiments during the decomposition of $NaAlH_4$ have been performed to identify the rate-limiting diffusing species.[5,32] It was suggested that atomic hydrogen is not the rate-controlling unit, but the AlH_3 unit would be a good possibility.[32] This points to a decomposition reaction of $NaAlH_4$ via the formation of AlH_3 vacancies at the surface which subsequently migrate into the bulk. This mechanism involving the diffusion of AlH_3 vacancies was supported by hydrogen-deuterium exchange experiments[5] and a recent NMR study.[33] A recent molecular dynamics calculation has also shown that the Al mass-transport process possibly involves diffusion of AlH_3 vacancies.[34] Therefore, the catalyst is expected to kinetically facilitate the release and decomposition of AlH_3 from the solid-state alanate and the nucleation of the Al phase without entering the $NaAlH_4$ bulk. The verification of this part of the reaction will be the subject of future investigation.

IV. CONCLUSION

In summary, we have studied H adsorption and diffusion, and H_2 dissociation, on the Ti-modified Al(100) surface using first-principles calculations. These results point to a mechanism of near-surface alloying for the catalytic effect associated with rehydrogenation reactions on the aluminum surface in connection with hydrogen storage in $NaAlH_4$: the "catalyst" modifies the properties of the Al surface and promotes the reactions.

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