

Orbital landscapes for reductive $2e^-$ activation of dihydrogen molecule

Wojciech Grochala

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Abstract The various spatial arrangements of frontier orbitals that may lead to facile reductive splitting of the H_2 molecule at mono- or binuclear catalysts containing s, p, d or f-block metals, and on surfaces of solids are briefly reviewed. The postulation is also made that binuclear divalent titanium (Ti^{II}) and mononuclear silicon (Si^{II}) species might serve as active sites for the H_2 attachment reaction for hydridoalanates doped with Ti salts and hydridoborates doped with SiO_2 , respectively.

Keywords Catalysis · Density functional theory · Hydrogen · Redox reactions

Introduction

Activation of the H_2 molecule and subsequent facile transfer of hydrogen constitute two fundamental chemical processes of importance for charging of chemical stores of hydrogen fuel. The reverse process—that of evolving H_2 —may also be realised from protonic sources of hydrogen, such as water; this process is of great importance for photo-electrochemical generation of H_2 [1]. Therefore, developing

fast and efficient methods for splitting H_2 , utilising cheap catalysts, has far-reaching implications for the forthcoming H_2 economy [2]. The most important classes of H_2 storage materials include (1) hydrides and destabilised hydrides [3, 4], (2) protonic–hydridic materials [5], (3) solely protonic systems [6] and (4) sources with covalently bound H [7]. In addition, efforts are underway to regenerate selected discharged stores of H_2 via chemical pathways [8].

The reductive $2e^-$ activation of the dihydrogen molecule:



is now one of the most important ways of splitting H_2 because majority of lightweight storage materials are composed of metals (Mg, Al, Li, Na) or their alloys, alone or mixed with other types of chemical compounds (for example, hydrogenation of a mixture of Al and sodium hydride yields $NaAlH_4$).

In this contribution, I aim to summarise possible spatial arrangements of frontier orbitals that often lead to facile reductive splitting of H_2 at mono- or bi-nuclear catalysts containing s, p, d or f-block metals, and on surfaces of solids containing these elements.

Methods

Calculations

We used either MP2 or the density functional theory (DFT) calculations as implemented in Gaussian '03 [9] code. For DFT, the B3LYP [10, 11] functional was used for approximation of the exchange–correlation energy. The 6-311++G** basis set was used for light elements (H, C, O, N, Si), and 6-31G** for Ti, Fe, Ni. Core electrons for heavy elements (W, Pd, Xe) were described by SDD pseudopo-

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W. Grochala (✉)
Department of Chemistry, Warsaw University,
Pasteur 1, 02093 Warsaw, Poland
e-mail: wg22@cornell.edu

W. Grochala
ICM, Warsaw University,
Pawińskiego 5a,
02106 Warsaw, Poland

tentials [see 12, and subsequent contributions from this group], followed by a standard double dzeta basis set for valence electrons. Note, the f electrons were explicitly represented in our calculations, as required for fair description of species containing lanthanides.

Quantum mechanical calculations here serve only to illustrate concepts and show the molecular orbital ordering, rather than to quantitatively reproduce any particular microscopic feature of the species studied. Therefore, for the sake of simplicity, complex ligands have usually been substituted in our calculations by simple neutral species such as Xe atom (weak Lewis base, isoelectronic with the Γ anion) and CO (σ donor and π acceptor ligand). Note: no geometry optimisation was performed if not explicitly mentioned. Our calculations are for $T=0$ K. None of these calculations has been previously published.

Selected quantitative results (MP2 and DFT values of the energy of hydrogenation of Ti^{II} embedded in the oxide environment, and optimised geometries of these species) may be found in the Electronic supplementary material (ESM) that accompanies this paper.

Results

Two electrons are required for the reaction described by Eq. 1 to occur. Therefore, reductive splitting of H_2 may occur either at one atomic reaction center equipped with two spare electrons, or at two atomic reaction centers in close spatial proximity (each with one electron), or at even a more complex moiety. The most important cases of activation of H_2 at mononuclear or binuclear reaction centers are discussed in more detail in the following sections.

H_2 activation at *one* metal center via a $2e^-$ process

Reductive activation of dihydrogen by necessity involves its σ^* molecular orbital. For an isolated H_2 molecule this orbital is at rather high energy, slightly above the energy of a free electron in vacuum (the conventional zero energy level). The H–H bond is very strong (4.52 eV per molecule), and so must be the bonding and antibonding orbital effects. Consequently, and despite the substantial affinity of isolated H atoms to an electron attachment (-0.75 eV), the activation of a dihydrogen molecule (in vacuum) described by Eq. 1 is not favoured thermodynamically by ~ 3 eV per H_2 [2]. Therefore, strong electron reducing agents with their filled HOMO (donor) orbital at pretty high energies must be used in order to overcome this daunting energy effect of Eq. 1. Indeed, such agents are mainly electropositive elemental metals or their alloys, and compounds of low-valent metals (electron-rich cations), which effectively activate H_2 . Unfortunately, thinking of Eq. 1,

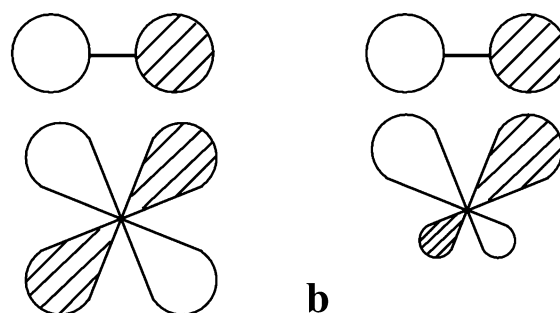


Fig. 1 Two important orbital landscapes for $2e^-$ reductive splitting of H_2 at a mononuclear reaction center. Activation of σ^* of H_2 via a doubly filled d orbital (**a**) or via two sp^3 hybrids with an electron count of two (**b**)

chemists cannot learn too much from Nature. In contrast to bacterial hydrogenases, which utilise the reversible process, proceeding in aqueous solutions at mild conditions:



living organisms do not survive in the extremely reducing environment typical of hydride anions (H^-).

Sufficient thermodynamic driving force is not enough for activation of H_2 to occur rapidly and at mild H_2 pressures. There must also be an efficient overlap between two molecular orbitals (MOs): the σ^* (H_2) and that of the HOMO in a two-electron donor. Two orbital arrangements that allow for such effective mixing are depicted in Fig. 1.

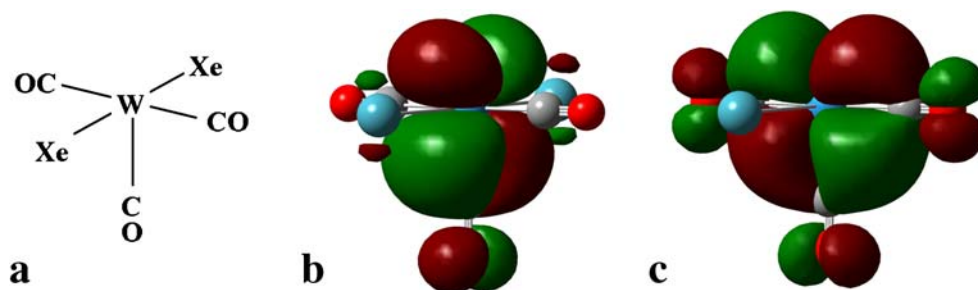
The σ^* of H_2 achieves good overlap with selected diffuse d orbitals (Fig. 1a) or with two sp^3 hybrids at one reaction center (Fig. 1b). The following sections discuss several important cases.

Kubas complex and the d^6 isoelectronic series

Since the discovery in 1984 of the first complex of molecular dihydrogen [13], now called the Kubas complex¹, the chemistry of such species has been beautifully advanced. It is now understood that a low-valent low-spin transition metal centre coming from the isoelectronic d^6 series with one unsaturated coordination site (usually pentacoordinated) is needed to activate H_2 (the reader is referred to early accounts on the activation of H_2 and of CH_4 by molecular complexes with various electron counts, and by selected surfaces of metals [14, 15]). The list of elements easily forming dihydrogen complexes (and/or completely splitting H_2 to $2H^-$) encompasses mainly the heavy $5d^6$ systems (W^0 [13, 16] (overlap between the occupied σ orbital of H_2 and empty orbitals of the metal

¹ This complex had in fact been prepared as early as 1979, but its structure was determined for the first time in late 1983. Kubas et al. [13] has now received nearly 500 citations. The forthcoming references list only selected examples of similar complexes.

Fig. 2 Two important MOs of the model pentacoordinate d^0 complex: $W[(CO)_2Xe_2](CO)$ (a). **b** HOMO. **c** HOMO-2. HOMO is used to activate the H_2 molecule



centre is important, but not crucial for the reaction described by Eq. 1 to proceed efficiently, see also [17]), Re^I [18–20]², Os^{II} [21] and Ir^{III} [22, 23]—here, the reaction proceeds directly to hydride of Ir^V , and the dihydrogen complex cannot be isolated as a transient state), and their lighter congeners ($4d^6$: Mo^0 [16, 17], Tc^I [24], Ru^I [18, 25], and $3d^6$: Cr^0 [26], Mn^I [27], Fe^{II} [28]—here, coordination of small Fe^{II} is close to tetrahedral). For some of these systems two isomers can be isolated, one corresponding to an η^2-H_2 complex and the other to a dihydride (product of the redox reaction), but for some species only one isomer can be detected (or a dynamic equilibrium exists over a broad temperature range). In all cases, initial formation of a η^2-H_2 complex—as a real minimum on the potential energy surface or at least as a transition state—seems to be a prerequisite for the subsequent low-barrier dihydride formation in the majority of similar systems [29].

Let us take a closer look at the well-known molecular orbital diagram for the interaction of H_2 with the Kubas complex-type species using a hypothetical $W^0[(CO)_2Xe_2](CO)$ (CO) as a model of the pentacoordinate $M(d^6)X_2Y_2Z$ complex with neutral ligands. In real complexes synthesised in the laboratory, phosphine, amine ligands and halide anions are frequently utilised as X, Y, Z. Figure 2 illustrates two important MOs of the $W^0[(CO)_2Xe_2](CO)$ complex (Fig. 2a): HOMO (Fig. 2b) and HOMO-2 (Fig. 2c).

Zerovalent W is coordinated by two CO and two Xe ligands (coplanar), and by one axial CO ligand. Both MOs shown in Fig. 2 have similar shape [they would in fact be degenerate for the $W^0(CO)_5$ complex], but the bonding combination of the W(d) orbital with π^* orbitals of two in-plane CO ligands (HOMO-2) is of course stabilised with respect to an analogous bonding combination of the W(d) orbital with p orbitals of a poor Lewis base, Xe (HOMO). This particular feature of HOMO and HOMO-2 should result in the attachment of H_2 in a coplanar fashion rather than being perpendicular to the $[WXe_2]$ moiety.

HOMO of $W^0[(CO)_2Xe_2](CO)$ has significant contribution from the π^* MO of an axial CO ligand. It may be therefore be postulated that use of a strong π donor at the

axial site will result in increased energy of the HOMO of the entire complex, and in its more diffuse character. This would allow for the better spatial exposure of the d orbital lobes towards the approaching H_2 molecule and, consequently, for the easier reduction of H_2 . Indeed, the importance of the ‘trans effect’ for the {dihydrogen complex \leftrightarrow dihydride} transformation, has been pointed out previously [30–32].

Facile activation of H_2 by Kubas complex-like species has encouraged some researchers to search for efficient hydrogen storage in “generalised Kubas complexes” with light metal elements (such as Be or B) [33] as well as in more complex systems [34].

d^8 Systems

The d^8 transition metal systems show less propensity for homolytic H_2 activation than the above-mentioned d^6 systems. However, selected complexes of monovalent cations of the Group 9 elements (Co^I , Rh^I , Ir^I) and of isoelectronic Fe^0 show reversible H_2 uptake [35–38]. In addition, Pt^{II} (isoelectronic with Ir^I) may be oxidised by H_2 to a hexahydride complex of Pt^{IV} (M_2PtH_6 , $M = Rb, Cs$); however, this requires extremely harsh conditions [39].

Metal centres usually adopt a butterfly-like coordination ($CN = 4$) in complexes of Co^I , Rh^I , Ir^I , and Fe^0 capable of H_2 activation. But why does H_2 bind to these species? Analysis of MOs will provide the answer.

In Fig. 3 we show HOMO and HOMO-1 of the hypothetical model system Fe^0Xe_4 , where Fe is tetraordinated in a butterfly fashion.

HOMO-1 has the correct symmetry to interact with σ^* of H_2 , but the interaction between HOMO and σ of H_2 is

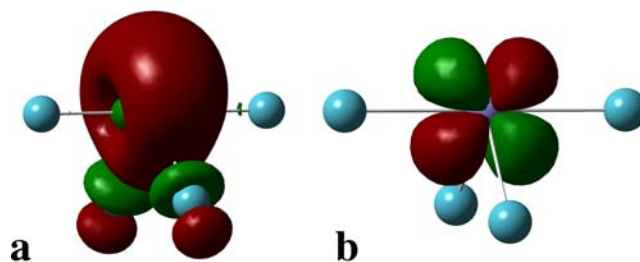
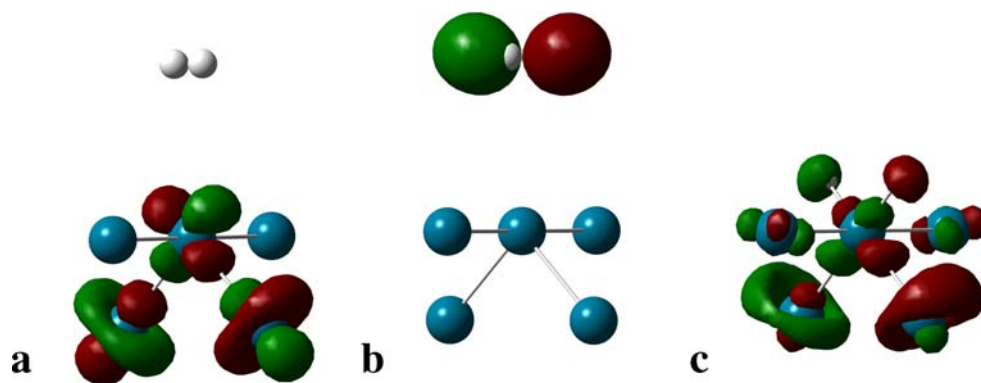


Fig. 3 **a** HOMO and **b** HOMO-1 of the model d^8 complex, $FeXe_4$, with a tetraordinate metal center in a butterfly coordination

² Fair electronic description assumes presence of the NO^+ ligand

Fig. 4 **a** HOMO of the model d^{10} complex, $\text{Pd}^0(\text{Pd}^0)_4$ with the tetra-coordinate Pd^0 metal center (a butterfly coordination with four other Pd atoms), and the H_2 molecule far distant. **b** LUMO of H_2 . **c** LUMO+1 of the dihydride complex of the Pd_5 cluster, $(\text{H}^-)_2\text{Pd}^{\text{II}}(\text{Pd}^0)_4$



repulsive. This probably explains why d^8 species activate H_2 less readily than the d^6 species described above. Substitution of two Xe atoms by CO molecules (within the *linear* XeFeXe moiety) and/or two Xe atoms by strong σ -electron acceptors (within the *bent* XeFeXe moiety) should result in stabilisation of HOMO and in destabilisation of HOMO-1. This should lead to better exposure of the HOMO-1 orbital towards the σ^* of H_2 , and to a significant reduction in the energy barrier for the H_2 splitting reaction.

Elemental palladium and the entire d^{10} family

Palladium is the oldest known material for hydrogen storage, and is the prototypical system capable of splitting H_2 on its surface. Nickel and platinum have also long been utilised in many hydrogenation/dehydrogenation reactions in organic chemistry as surface-active H_2 transfer catalysts. The detailed mechanism of H_2 splitting on the surface of Pd is still under dispute. For example, it has been postulated relatively recently that dissociation of H_2 requires three or more vacancies on the (111) surface [40], in contrast to older mechanisms, which suggested the presence of two vacancies would suffice [41].

There is still much scope for the proposal of new mechanisms of virtually barrier-less H_2 splitting on surface defects of the d^{10} metals Ni^0 , Pd^0 , Pt^0 , at their clusters [42], and at their zerovalent complexes with an unsaturated coordination site [43]³. Specifically, I would like to propose that a tetra-coordinate Pd^0 metal center in a butterfly coordination should be capable of efficient splitting of H_2 .

Figure 4a,b shows selected MOs of a model d^{10} complex, PdPd_4 , where a central Pd center is coordinated by another four Pd atoms serving here as electron-rich ligands. Figure 4c shows LUMO+1 of a dihydride complex of the Pd_5 cluster.

³ Note, some tri-coordinated complexes of Pd^0 are also capable of heterolytic activation of H_2 . Possibly, two such moieties in spatial proximity would also be capable of a homolytic H_2 split via a mechanism similar to that discussed in the section “ H_2 activation at two half-filled or entirely filled d orbitals”.

HOMO of the Pd_5 cluster (Fig. 4a) has a significant contribution from the central Pd atom, with the d orbital loops pointing towards the LUMO of the approaching H_2 molecule (Fig. 4b). In consequence, H_2 splitting should be kinetically easy. Significant overlap of the HOMO of Pd_5 and the LUMO of H_2 helps to transform these MOs into their bonding and antibonding combinations, which would now serve as the σ and σ^* orbitals of the dihydride reaction product, respectively. The bonding combination at low binding energy is of course occupied, while the antibonding combination constitutes LUMO+1 of the dihydride complex (Fig. 4c). Therefore, the reaction of a homolytic dissociation of H_2 at Pd^0Pd_4 cluster can be approximated as:



with the concomitant transformation of the central Pd atom into the cationic d^8 species.

The presence of the unsaturated coordination site and the proper electron count at the metal centre has again resulted in an efficient attachment of H_2 . A bonding situation such as that depicted in Fig. 4 is not a purely theoretical creation, and might indeed occur at kinks, steps and surface defects on various surfaces of elemental Pd, Pt, Ni and their alloys.

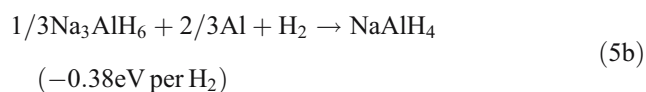
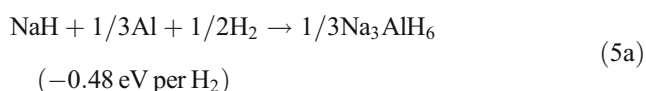
d^2 Systems as H_2 transfer catalysts?

Since the 1997 paper by Bogdanović and Schwickardi [44], the role of titanium compounds for catalysis of H_2 absorption and desorption in hydridoalanates (i.e. alkali metal aluminium hydrides) has been very much disputed. Efficient catalysis in these important systems may be achieved by a small addition of TiO_2 , $\text{Ti}(\text{OR})_4$ where R is an alkyl group, or TiX_4 and TiX_3 halides, where X = F, Cl (note that, under experiment conditions, these compounds become reduced by alanates to low valent Ti species and to elemental Ti). Nanoclusters of Ti [45], surfaces of the TiAl_3 alloy [46, 47, and references therein] and, more recently, TiH_2 [48, 49] have been held responsible for the catalytic effect, to list only the most important candidates. Efficient catalysis was also found in systems where the hydrogen storage material was doped with ZrO_2 , VCl_3 , or Nb_2O_5 .

It is the opinion of this reviewer that it is rather improbable that any chemical moieties containing zerovalent Ti (such as Ti nanocluster or TiAl_3) would be catalytically active in the hydrogenation/dehydrogenation processes. The reasons for this view are based on fundamental thermodynamics, since the process



is very exothermic (-1.5 eV per H_2 under standard conditions [50]). This means that, once chemically attached to a Ti^0 -like surface site, H_2 cannot be further transferred to materials with relatively small negative enthalpy of formation, such as alanates [51, 52; numerical data are taken from 51]:



It can be anticipated that a completely different redox process must be responsible for H_2 transfer catalysis. One interesting possibility is associated with the process



while three others, which involve *two* adjacent Ti sites, will be described below.

We feel that the process described by Eq. 6—although it might have a nearly neutral thermodynamic (see *ESM*)—cannot be responsible for catalysis, for two important reasons:

- (1) Ti^{II} should have two electrons available for donation from one d orbital, i.e. adopt the low-spin state; however, Ti^{II} is found in the high-spin (triplet) state in the majority of known chemical compounds of Ti^{II} , even if very strong Lewis bases (such as H^-) are present;
- (2) in addition to (1), the above-mentioned d orbital should be exposed towards the approaching H_2 molecule; such a situation occurs for low-spin Ti^{II} species only if very strong π -electron acceptors (such as CO) are present (see Fig. 5); this is not the case in doped alanates, where only the hydride, halide and possibly also hydroxide/oxide anions (due to traces of water and oxygen) are present [53].

It can be concluded that isolated surface sites containing Ti^{II} , Zr^{II} , or isoelectronic V^{III} and Nb^{III} [54, 55] are unlikely to catalyze H_2 splitting⁴. Binuclear moieties involving these

⁴ Note, Nb^{III} is a reasonable candidate for splitting H_2 since Nb^{V} is a poor oxidizer. Indeed, quite stable hydride compounds of Nb^{V} are known, which eliminate H_2

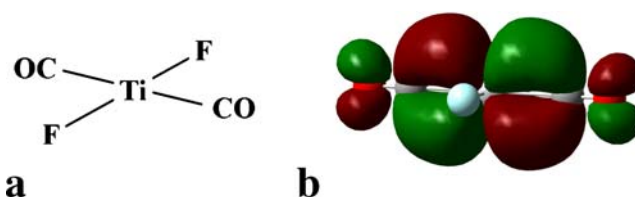


Fig. 5 One of the few atomic arrangements that may lead to exposure of the donor d orbital of the Ti^{II} species towards the approaching H_2 molecule. **a** Formula of low-spin $\text{Ti}^{\text{II}}\text{F}_2(\text{CO})_2$, with coordination of Ti^{II} close to square planar, and **b** its HOMO

d^2 species are discussed in a later section of this review. Here, we end the discussion of these catalysts and catalyst candidates of H_2 cleavage, which act through their single d orbital exposed towards σ^* of H_2 , as shown in Fig. 1a. We now proceed to catalysts containing s- and p-block elements.

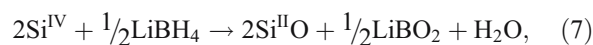
s- and p-block elements

The metallic elements of the s- and p-block and their cations are very seldom considered to act as genuine catalysts of H_2 cleavage. The relative ease of formation of selected binary hydrides from this group (LiH , NaH , CaH_2) can rather be attributed—via Hammond’s rule—to their significant thermodynamic stability, which facilitates fast H_2 uptake. In fact, kinetics of H_2 sorption of many lightweight s- and p-block elements and of their compounds (Mg , Na , $\text{Al} + \text{NaH}$, etc.) can be improved by the use of appropriate catalysts.

There are several known cases where s- or p-block elements act as H_2 transfer catalysts. For example, an experimental report on the thermal decomposition of digallane, Ga_2H_6 , autocatalyzed by metallic Ga exists (A.J. Downs, personal communication; for gallane, see e.g. [56]). In addition, the remarkable potential of SiO_2 to accelerate the hydrogenation/dehydrogenation of LiBH_4 has been demonstrated experimentally [57, 58]. The nature of the catalytically active phase remains unknown.

Let us concentrate on the important $\text{LiBH}_4/\text{SiO}_2$ system. Catalysis of H_2 splitting at a single site p-block species requires, as depicted in Fig. 1b, the presence of two sp^{2+3} hybrids, each occupied by one electron. For Si, such a situation might occur if two conditions are simultaneously fulfilled:

- (1) Si^{IV} is partially reduced by LiBH_4 on the surface of SiO_2 , in an idealised process:

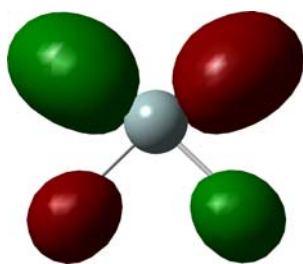


and

- (2) a divalent silicon (Si^{II}) species acts as a H_2 transfer catalyst, with the $\text{Si}^{\text{II}}/\text{Si}^{\text{IV}}$ redox pair involved:



Fig. 6 LUMO+2 of optimised $^1\text{SiH}_2$ molecule (H atoms are at the bottom). Population of this orbital with two electrons generates good conditions for facile homolytic splitting of H_2



Divalent Si^{II} is found in several chemical compounds, including solid SiO , and in many gaseous species, such as, for example, SiH_2 . It is a prototypical $(\text{sp})^2$ system (the valence electron count is 2), which, if in a low-energy ground singlet state, often exposes a lone pair [59], similar to the known isoelectronic entities (Sn^{II} , As^{III}). Therefore, to be catalytically active, Si^{II} should be excited to the biradical-like excited singlet state (Fig. 6). Such a process requires a lot of energy, but it is not completely impossible under the conditions of experiments performed by Züttel and co-workers [57, 58]; thermal generation of small amounts of Si^{III} might indeed take place at elevated temperatures of 200–300 °C [57, 58].

In conclusion, Si^{II} , and possibly also the isoelectronic Al^{I} , Ge^{II} , Ga^{I} species, might serve as H_2 transfer catalysts if they are in this excited state, in which a combination of two sp^{2+3} hybrids is occupied by two electrons.

f Elements

Many pure f metals, i.e. lanthanides and actinides, chemisorb and absorb H_2 with great ease, while forming di- (Yb, Eu), tri- (remaining lanthanides, actinium, uranium) or even tetra- (thorium) hydrides; the reaction products are most often nonstoichiometric. One might link facile activation of H_2 by selected lanthanides with the shape and energy of f orbitals exposed at the surfaces of solid phases. Unfortunately, as far as we know, no systematic screening has been performed for a broad selection of f metals to gain detailed insight into the kinetics aspects of H_2 chemisorption. In addition, lanthanides and actinides are beyond the area of interest of modern H_2 storage technologies, due to their detrimental large atomic mass, and therefore these elements are omitted from this review. One exception is the interesting sandwich complexes of low-valent f elements, known from experiment; these will be mentioned in the section below on H_2 activation at two half-filled or entirely filled f orbitals.

H_2 activation at two metal centers via two concerted $1e^-$ processes

Another important scenario for the reductive activation of H_2 is provided by two concerted $1e^-$ reactions, which occur at a complex reaction site built of two one-electron donors

in close spatial proximity. Obviously, this route requires that both active sites are at an adequate distance from each other, i.e. at a distance suitable for reaching the loops of the LUMO of H_2 (σ^*) with their orbitals. This fortunate situation sometimes occurs at selected surfaces of solids. In the majority of cases, a molecular binuclear complex must be precisely crafted, so that the separation of both centres is engineered with great accuracy.

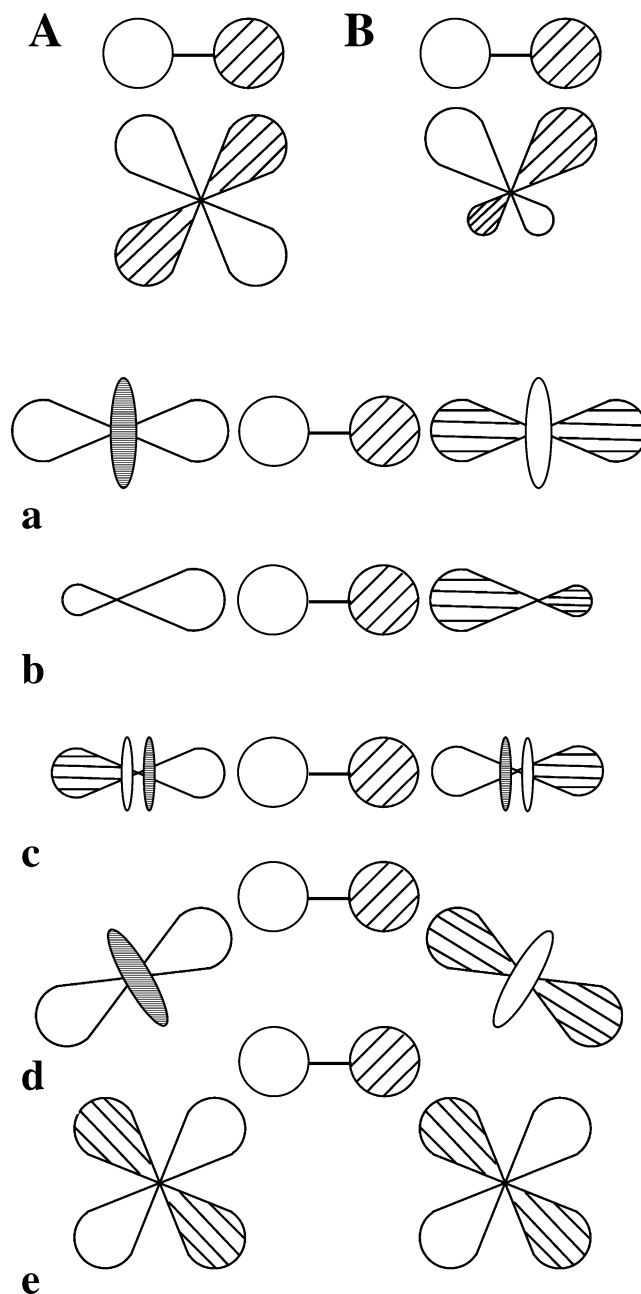


Fig. 7 Several important orbital landscapes for reductive splitting of H_2 at two neighboring reaction centres via two concerted $1e^-$ reactions. Activation of σ^* of H_2 via **a** two half-filled d orbitals; **b** two half-filled sp hybrids; **c** two half-filled f orbitals; **d**, **e** two mutually inclined d orbitals coming from adjacent surface sites or from a carefully engineered molecular complex

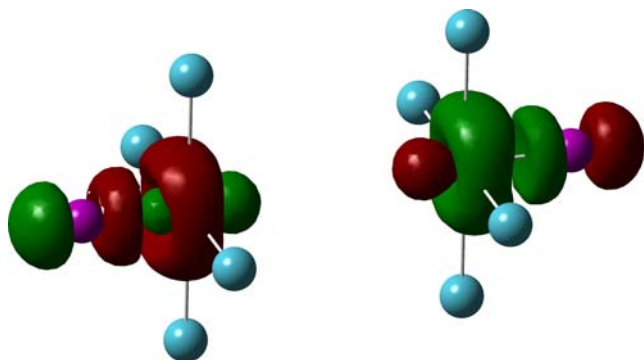


Fig. 8 HOMO of the model binuclear complex $[\text{Ni}^{\text{I}}\text{FXe}_4]_2$ with Ni^{I} in a square pyramidal coordination

Figure 7 shows several generalised cases in which σ^* of H_2 achieves good overlap with loops of two half-occupied orbitals on two adjacent atomic centres⁵. Activation of H_2 might be realised at a sandwich complex with two d elements (Fig. 7a), two p elements (Fig. 7b), two f elements (Fig. 7c), or at two neighbouring surface sites with mutually inclined orbitals, for example d orbitals (Fig. 7d,e). This list covers a selection of important scenarios but is not exhaustive. Other possibilities, such as asymmetric insertion of H_2 into the $\sigma(\text{sp-sp})$ orbital of singlet M_2 molecules ($\text{M} = \text{Al}, \text{Ga}$), will be described briefly. Each of these cases will now be discussed separately.

H₂ activation at two half-filled d_{z^2} orbitals

Activation of H_2 in the scenario depicted in Fig. 7a,d could, for example, be realised at a binuclear complex containing d^9 species: Co^0 , Ni^{I} , and their heavier congeners Rh^0 , Pd^{I} , Ir^0 , Pt^{I} (Cu^{II} , Ag^{II} , and Au^{II} are excluded, because these cations and their oxidised forms are too strong oxidisers and cannot withstand the presence of H^- anions).

It has been shown by DFT calculations that the reaction:



might indeed be close to thermodynamic equilibrium, when Ni^{I} is powerfully complexed by cyclic tetramine ligands [60]. Figure 8 shows the HOMO of a model binuclear complex of the kind $[\text{Ni}^{\text{I}}\text{FXe}_4]_2$ (singlet state) with Ni^{I} in a square pyramidal coordination.

Indeed, the most important donor orbital of the binuclear complex of d^9 Ni^{I} has the correct symmetry to interact with the σ^* of H_2 . The presence of strong axial σ donor ligands is required for good exposure of the $d(z^2)$ loops. It might be expected that a similar situation may take place also for two d^{10} species (for example Ni^0), if their oxidised d^9 analogues were not susceptible to subsequent chemical reactions.

⁵ For transition elements, these two orbitals may also be fully occupied, the redox reaction decreasing their occupation by one-half.

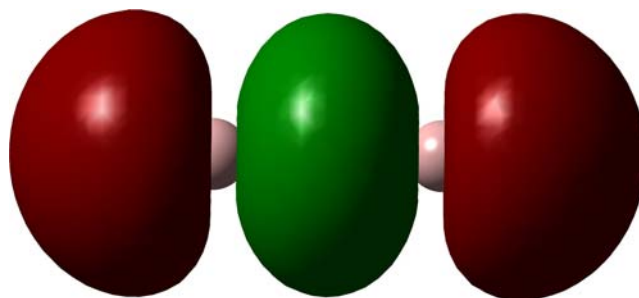


Fig. 9 HOMO of the optimised Ga_2 molecule. H_2 must approach Ga_2 at one selected Ga atom to facilitate activation of the H–H bond

H₂ activation at two half-filled (sp) hybrids

The situation shown in Fig. 7b is very rare due to inherent instability of odd-electron (radical) species of elements belonging to the p block. However, an interesting related case is known, where H_2 activation proceeds with a very low barrier despite the fact that the two sp hybrids have now formed the σ bond. This example is provided by singlet M_2 dimers [61, 62]:



This reaction may be extended up to M_2H_6 composition, but larger barriers are encountered for the subsequent stages of hydrogenation [63].

The activation of H_2 is spontaneous and occurs even at very low temperatures in noble gas matrixes, provided that ground state triplet M_2 dimer is excited to the low-lying singlet state [64–68].

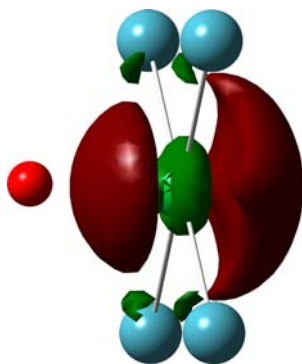
Figure 9 shows the HOMO of singlet Ga_2 . Note that H_2 must be inserted in an asymmetric orientation if its σ^* is to interact with HOMO of Ga_2 ; indeed, formation of the $[\text{Ga-H-Ga-H}]$ isomer has been observed experimentally [64–68] and confirmed by theory [61–63].

H₂ activation at two half-filled or entirely filled f orbitals

Two lanthanide cations open an interesting possibility for facile activation of H_2 : these are Yb^{II} and Sm^{II} . The divalent state is easily accessible for four lanthanide metals, Eu, Yb, Sm and Tm, the corresponding standard redox potentials for the $\text{Ln}^{\text{III}}/\text{Ln}^{\text{II}}$ couples being: -0.35 V, -1.05 V, -1.55 V, and -2.30 V. Therefore, the divalent state is very stable for Eu (f^7), and indeed the trihydride of this element has never been obtained. Yb is a borderline case, its divalent state (f^{14}) having moderate stability; genuine YbH_3 is unknown⁶, but the limiting composition $\text{YbH}_{2.67}$ corresponds to the mixed-valence $\text{Yb}^{\text{II}}(\text{Yb}^{\text{III}}\text{H}_4)_2$

⁶ The equilibrium (plateau) H_2 pressure for the stoichiometric YbH_3 must be extremely large at room temperature, and synthesis of this binary compound will meet with difficulties unless diamond anvil cells are used.

Fig. 10 HOMO of the model YbOXe₄ complex, composed mainly of the combination of the f and p orbitals of Yb. A sandwich complex built of two such species might be able to reversibly reduce H₂



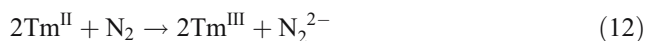
[69]. Other compounds of Yb^{III} like Cs₃YbH₆ might also possibly exist [70]. Finally, the divalent states of Sm and Tm become easily oxidized to the trivalent states, which in turn are relatively stable in the hydride environment.

Following this beautiful chemistry of lanthanides, we anticipate that the reversible reaction:



might occur for carefully crafted binuclear complexes of Yb^{II}, which contain strong Lewis bases (Figs. 7c and 10).

The reaction described by Eq. 11 would thus be analogous to the known reaction of N₂ activation [71]:



which also occurs for other lanthanides [72]. An analogous reaction involving selected low-valence actinides, such as U^{III}, has also been reported [see, for example, 73–75].

The reaction proposed in Eq. 11 is not purely a theoretical concept; indeed, formation of the analogous [(Cp)₂Sm^{III}(H⁻)₂Sm^{III}(Cp)₂] sandwich structure (Cp = cyclopentadienyl anion) was reported in early 1980s [76]. Note that organosamarium (II) species are catalyst precursors for hydrogenation of alkanes [77]. This reaction may also be extended to the derivatives of ytterbium, with the concomitant benefit of thermodynamic reversibility under ambient conditions, and thus with the possible appearance of catalytic activity for hydrogenation reactions.

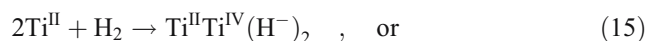
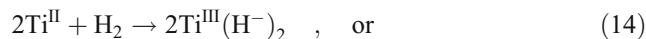
H₂ activation at two half-filled or entirely filled d orbitals

An interesting scenario of H₂ activation on the reconstructed (001) surface of Al metal, where two next-nearest-neighbour Al atoms have been substituted by two Ti atoms, has been proposed [78]. The mechanism involves formation of the surface hydride species, with both hydride anions bridging between Ti^I centers and between (only slightly oxidized) Al⁰ centers:



The energy barrier of this reaction has not been calculated, but the overall computed reaction energy is -0.59 eV [78]. If this number is to be treated seriously as an approximate of reaction enthalpy, then the chemisorbed hydrogen could not be further transferred to the (Al + NaH) mixture, to form Na₃AlH₆ and subsequently NaAlH₄, since these two reactions have smaller reaction enthalpies (compare Eqs. 5a and 5b). Nevertheless, the twin-Ti⁰ site of the relaxed (001) surface of Al metal has an interesting electronic structure, with loops of two d(xy)-like orbitals pointing towards the LUMO of H₂ (see Fig. 4 in [78] and compare to our Fig. 7e). Such an orbital landscape originates from the ligand field on Ti⁰ (d⁴) provided by a hexagon of surrounding Al atoms, and by four additional Al atoms in the sub-surface layer; it should indeed promote facile splitting of H₂. More precise calculations, including zero-point vibrational corrections, are definitely needed to properly assess the real importance of this scenario.

An alternative reasonable mechanism for H₂ activation might involve two adjacent Ti^{II} (d²) or Ti^{III} (d³) surface sites on the surfaces of TiH₂, TiO, or on partially reduced surfaces of TiO₂:

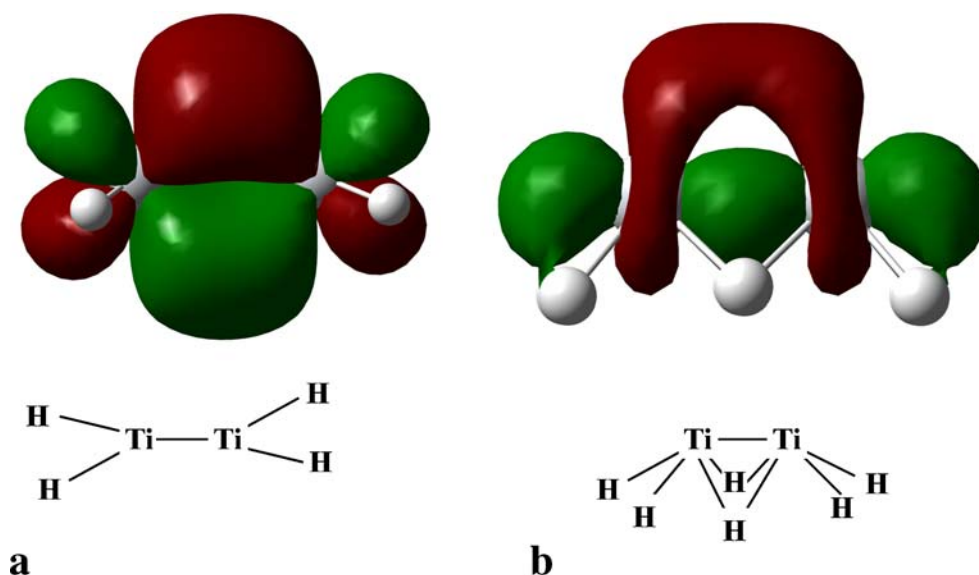


Remembering that Ti^{II} is a prototypical d² system, which rather easily undergoes the 1e⁻ oxidation, the standard redox potential of the Ti^{III}₂O₃/Ti^{II}O couple being as negative as -1.95 V in basic aqueous solutions. The corresponding redox potential for the Ti^{IV}O₂/Ti^{III}₂O₃ pair is still very negative at -1.58 V [<http://www.webelements.com>]. These values mean that H₂ could become reduced by two ligated Ti^{II} cations, and possibly even by two Ti^{III} cations, at least from the thermodynamic point of view. But what about the orbital match and the reaction kinetics?

Let us first consider a reaction involving two Ti^{II} sites. Figure 11a shows the HOMO of one possible model of the binuclear Ti site: the planar singlet (TiH₂)₂ dimer with a Ti=Ti bond. The π(Ti–Ti) orbital constitutes the uppermost donor orbital of this species. It could interact with the LUMO of H₂ only if H₂ approached the Ti=Ti bond in such way as to form the asymmetric H–Ti...H...Ti structure. In this way, the case shown in Fig. 11a is similar to the case of H₂ activation by a Ga₂ dimer (see above).

The surface Ti^{II} center could also expose its two d electrons in other bonding environments, thus facilitating the kinetics of H₂ cleavage. Indeed, recent theoretical

Fig. 11 **a** HOMO of the model two-center $[\text{Ti}^{\text{II}}\text{H}_2]_2$ complex in the singlet state. **b** HOMO of the model two-center $[\text{Ti}^{\text{III}}\text{H}_3]_2$ in the singlet state. Note the possibility of good overlap of both HOMO orbitals with the LUMO of H_2 under formation of asymmetric insertion ($\text{H}-\text{Ti}\dots\text{H}\dots\text{Ti}$)



studies by Gryciuk and Górecki [79, 80]⁷—without any apparent relation to the pioneering work on catalytic enhancement of H_2 discharge in alanates [44]—have shown that the energy of H_2 adsorption on the unreconstructed (100) surface of TiH_2 (at $T = 0$ K) is close to -0.416 eV per H_2 molecule. We note that this number is very close to the entropy factor for H_2 at 298 K ($+0.404$ eV), and also to the enthalpies of formation reactions for Na_3AlH_6 (-0.48 eV) and NaAlH_4 (-0.38 eV, Eqs. 5a, 5b). In addition, the only experimental study of H_2 adsorption on random selection of surfaces of TiH_2 [81] has shown that the barrier for H_2 cleavage is as low as 0.19 eV per molecule; the TiH_2 surface thus seem to be the ‘dream catalyst’ of H_2 splitting. Our working hypothesis that twin Ti^{II} sites might be responsible for reversible cleavage of H_2 also finds support in various experimental studies on TiH_2 -doped alanates [48].

What of binuclear species containing Ti^{III} ? Figure 11b shows the HOMO of one possible model of such a site: the Ti_2H_6 species in the singlet state. As in the case of $(\text{TiH}_2)_2$ and Ga_2 , H_2 splitting might be facilitated if it leads to the addition of one terminal and one bridging hydride anion. And again, several other interesting scenarios involving binuclear $\text{Ti}^{\text{III}}-\text{Ti}^{\text{III}}$ clusters can be envisaged.

We conclude this section with a statement that the mechanism of H_2 activation by Ti species (Eqs. 6, 13, 14 and 15, or yet another different pathway?) cannot be unequivocally assessed at present; we certainly need many more very careful theoretical and experimental studies to reach an understanding

of this process. However, the mechanisms described by Eqs. 13–15 should at least be considered as serious candidates.

Summary

This review provides a brief survey of various frontier orbital landscapes that facilitate reductive splitting of the H_2 molecule at mono- or binuclear catalysts containing s, p, d or f-block elements, and on the surfaces of solids. It has been postulated that a binuclear cluster containing two divalent or two trivalent titanium (Ti^{II} , Ti^{III}) sites is active in homolytic split of H_2 for hydridoalanates doped with Ti salts. It was also argued that a mononuclear species containing electronically excited divalent silicon (Si^{II}) might be capable of catalytic charging/discharging of hydridoborates doped with SiO_2 . Finally, the proposal that binuclear molecular catalysts containing selected divalent lanthanides (Yb, Sm) could be prepared and tested for their capability to reversibly split H_2 has been advanced. These results may be useful for understanding catalytic action in doped hydrogen storage materials, and for identifying and preparation of new H_2 transfer catalysts⁸.

This mini-review is not exhaustive due to space restrictions; therefore, only the most important orbital landscapes for low-barrier reductive splitting of H_2 are covered in this contribution (heterolytic splitting of H_2 —similar to that which occurs for the Ti-Si and Ti-C compounds—are discussed elsewhere [82–84]).

⁷ Note, these studies use many approximations, for example: (1) a very thin three-layer TiH_2 slab is used in calculations; (2) this slab has a large dipole moment, which influences the final results; and (3) the surface is not allowed to relax.

⁸ It should be realised that, although H_2 transfer is an extremely important constituent of the charging/discharging processes of various hydrogen storage materials, the nucleation and growth of the particles of reaction products may often be the rate-limiting step.

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