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Chemisorption of gas atoms on one-dimensional transition-metal halides



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ABSTRACT

We study computationally the bonding of hydrogen and oxygen to one-dimensional materials with the formula XY_3 , where X represents Ti, Zr, or Hf and Y represents a halogen atom Cl, Br, or I. The materials consist of chains of transition metal atoms surrounded by halogen atoms with a three-fold rotation symmetry. The chemisorption leads to a reduction in the number of d-electrons in the materials accompanied by significant changes in Fermi energy. The chemisorption energies are seen to correlate with the work functions of the clean systems supporting the view that electron transfer plays a major role in the bonding.

1. Introduction

The growing energy demand and environmental issues world-wide make the transition to more sustainable production of energy, fuel, and chemicals necessary. A key technology in this area is heterogeneous (electro-)catalysis, which promotes chemical processes. Much progress has been made in this field for several decades, but it is still essential to develop new, efficient catalysts for key processes like CO_2 reduction or electrochemical production of ammonia [1].

The understanding of chemical processes at metal and semiconductor surfaces has been developed and refined in a close interplay between experimental, theoretical, and computational investigations. Theoretical models for particular classes of processes have been developed, like the so-called d-band model for reactions at transition metal (TM) surfaces [2]. Furthermore, new concepts like the linear scaling relations [3], which describe the correlation between binding energies and energy barriers for different processes, have been established, and atomic level descriptors [4] that characterize catalyst activity have been identified. The scaling relations have turned out to be a doubleedged sword in the sense that they enable fast, computational screening studies, [5,6] but at the same time pinpoint how the correlations limit the potential activity of the class of materials considered. This has led to the search for new catalyst materials, which can "break" the scaling relations and thereby enhance the catalytic activity [7].

It is well-established that for many catalytic processes, the atomiclevel active sites are related to low-dimensional structures or defects. For example, it has been demonstrated that the dissociation of N_2 on Ru(0001) takes place at step edges [8], and that the desulfurization process at MoS_2 is primarily occurring at the one-dimensional edges of the two-dimensional layers in the material [9,10]. The quest for materials, which break the scaling relations, therefore focus on new and different types of active sites including ones with different geometries, which might occur at low-dimensional materials. Many studies have investigated the catalytic properties of two-dimensional materials [11], and recently supported zero-dimensional single- or few-atom catalysts have attracted attention [12]. One-dimensional materials have been considered much less particularly at the atomic scale [13], which we think is at least partly due to the much more limited knowledge about this class of materials and their stability. One-dimensional material catalysts would provide optimal use of the active elements, and they can at the same time be conductive. This means that they are a promising starting point for discovering high surface area, unsupported, conductive catalysts [14].

Recently, we have established a computational database of atomiclevel one-dimensional materials ("C1DB") [15]. The database provides an overview of already experimentally synthesized materials and their stability, and it includes furthermore a large number of new, potentially stable, one-dimensional compounds. The studies presented here focuses on the chemisorption of hydrogen and oxygen on one of the largest groups of materials in C1DB.

This work provides fundamental insight into the adsorption on one-dimensional transition-metal halides and thereby a step towards understanding how the adsorptions can be affected and designed for catalysis. The effects found for these materials are very different from

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Fig. 1. A flow chart illustrating the steps in the DFT calculations.

the important electronic effects found on metallic surface. Adsorption on these materials have more in common with adsorption on semiconducting oxides.

2. Theoretical methods

All electronic calculations in this work are performed with DFT. More specifically, we apply the GPAW code [16,17], which uses the projector-augmented-wave method (PAW) [18]. We use a plane-wave cutoff of 800 eV throughout the calculations. The atomic simulation recipes (ASR) is a recently created set of Python modules to carry out and control standard atomic-scale computational tasks [19,20] and we apply this for all DFT calculations. For all systems (i.e. XY₃ chains in the β -TiCl₃-structure with and without chemisorbed atoms) we perform the following steps, which each correspond to a recipe in ASR (Fig. 1). The chain structures are downloaded from C1DB and for the chemisorption studies gas atoms are added to the system. The unit cell has large dimensions perpendicular to the chains so that the periodic images do not interact. A given system is then relaxed, i.e. the atomic positions are optimized to minimize the total energy. In the case of PBE, the unit cell parameter along the chain is also optimized. This step uses a Monkhorst-Pack k-point grid with a linear sample density of 6.0 Å and the optimization is terminated when the maximal force acting on the nuclei is less than 0.01 eV/Å, and the stress components acting on the unit cell are less than 0.002 $eV/Å^3$. Unless otherwise stated, the calculations are performed with the BEEF-vdW exchangecorrelation functional, which includes van der Waals interactions, and which is generally well-suited for surface chemistry studies [21]. It has been shown to be superior to for example HSE in determining chemisorption energies of atoms and small molecules on transition metal surfaces [22]. After this a ground state calculation is performed with a finer k-point sampling density of 12.0 Å.

The band structure of the Kohn–Sham energy levels is calculated non-self-consistently using the electron density from the ground-state calculation. The one-dimensional Brillouin zone is sampled with 400 points. In some cases we also calculate atomic-orbital-projected band structures and densities of states. These are obtained by projecting onto the atomic partial waves defined in the PAW formalism, which can be done using the PAW-projector functions. Please see Ref. [23] for details.

3. Results and discussion

3.1. One-dimensional model materials

We consider the compounds XY₃, where X is one of Ti, Zr or Hf, and Y is Cl, Br, or I as our model one-dimensional systems. We shall investigate the compounds in the structure of the one-dimensional components of the so-called β -TiCl₃ phase. The structure consists of chains of face-sharing octahedra with the transition-metal (TM) atoms in the centers of the polyhedra. The structure is shown in Fig. 2.

One reason to focus on this particular structure is that it is the most common one in the computational database of one-dimensional materials C1DB [15,24]. C1DB contains experimentally identified onedimensional materials from ICSD [25] and COD [26]. These forms the so-called core of the database. The database also contains materials obtained by chemical element substitution in the core materials (the "shell" materials). A clustering analysis of the one-dimensional components of the core materials – based on the root-mean-square-distance



Fig. 2. Upper: the atomic configuration of the one-dimensional chains of the β -TiCl₃structure. The configuration is computationally embedded in periodic unit cells with infinitely long chains separated by at least 16 Å of vacuum to avoid cross-chain interactions. Lower: the band structure of TiCl₃ using the BEEF-vdW functional. The colors indicate the projection onto atomic states.

between the atoms in the different materials – identifies groups of structurally similar materials [27]. The group with the most materials (11 materials) is the one with structures similar to the chain of the β -TiCl₃ phase. Because of the chemical element substitutions all of the nine materials considered here are present in C1DB in the β -TiCl₃ phase and have been studied with density-functional theory (DFT) using the PBE [28] and PBE-D3 [29] exchange–correlation functionals.

Experimentally, TiCl₃ and TiBr₃ are known as catalyst components for the polymerization of olefins. TiCl₃ appears in Nature in several other phases than the β -TiCl₃ phase including an α -TiCl₃ phase, which is a layered structure with edge-sharing octahedra [30]. TiBr₃ appears in the α -TiCl₃ phase and with the structure type EuAs₃, which is another layered phase with edge-sharing octahedra [31]. TiI₃ appears in the β -TiCl₃ phase as well as in a different structure with the same chains of face-sharing octahedra but with an alternative stacking of the chains. Furthermore, the material undergoes a phase transition with a dimerization of the Ti-atom chains at low temperatures [32]. The dimerization is also seen in the DFT ground state calculations of C1DB, where there is a short Ti–Ti bonding distance of 2.91 Å and a longer one of 3.54 Å. The zirconium halides ZrCl₃, ZrBr₃, and ZrI₃ all exhibit chains of face-sharing octahedra of the same kind as in β -TiCl₃ [33]. For

Table 1

Calculated energies above the convex hull for the XY_3 materials in the β -TiCl₃-chain structure. The data are from C1DB [15] and calculated with the PBE-D3 exchange–correlation functional. Units are in eV/atom.

X Y X	Cl	Br	Ι
Ti	0.09	0.11	0.14
Zr	0.10	0.11	0.14
Hf	0.11	0.12	0.14

the hafnium halides, HfI₃ appears in the β -TiCl₃ structure [34], while HfCl and HfBr have not been structurally characterized in the XY₃ stoichiometry. Interestingly, hafnium chloride has been studied in the HfCl₄ composition, which exhibits edge-sharing octahedra, but in this structure some of the chlorine atoms are bound to only one hafnium atom [35].

In conclusion, most but not all of the nine materials have been experimentally observed in structures with chains like the ones in β -TiCl₃. However, according to the DFT calculations of C1DB all of the nine materials are fairly stable in this structure. They are all locally stable as indicated by the calculations in C1DB of the phonon spectra at the center and boundary of the Brillouin zone. The database also contains calculations of the energy above the convex hull calculated with PBE-D3. This is the energy difference between isolated chains of the β -TiCl₃ structure and the lowest-energy combination of known bulk phases. The D3-correction is included to account for the van der Waals bonding between the one-dimensional chains (for details please see Ref. [24]). The data are shown in Table 1, where it can be seen that in all cases the energy is below 0.2 eV/atom, which is commonly taken as a criterion for meta-stability [36].

3.2. Clean one-dimensional materials

The band structure of the clean Ti2Cl6 system calculated with BEEFvdW is shown in Fig. 2. A projection of the states on atomically centered PAW-projectors is performed, and the colors in the circles indicate, how large a fraction that belongs to each state. As can be clearly seen all the states around the Fermi level are almost exclusively Ti d-states. The central part of the band structure can thus be understood from a model of just a string of titanium atoms. Due to the cylindrical symmetry the bands can be classified by the quantum number *m* corresponding to the angular momentum around the z-axis in the direction of the string. This leads to a non-degenerate $(m = 0) \sigma$ -band and doubly degenerate $(m = \pm 1) \pi$ -, and $(m = \pm 2) \delta$ -bands. These degeneracies are maintained also if the full point group of D_{3d} is considered in form of the non-degenerate A_1 and the doubly degenerate E_g irreducible representations. However, since the doubly degenerate bands belong to the same irreducible representation some mixing between the π - and δ -bands can take place. Note, that the bands are for a unit cell with two Ti atoms and six Cl atoms, so the bands are folded once compared to the bands of an atomic chain with four atoms per unit cell. The Fermi level is positioned so that the lower branch of the σ -band is filled as expected from one *d*-electron per titanium atom. Only a small band gap of about 0.2 eV is observed.

The calculated dispersions can be compared with tight-binding parameters suggested in the classic book by Harrison [37]. He suggests a hopping matrix element of *d*-states of the form $V_m = \eta_m \hbar^2 r_d^3 / (m_e d^5)$, where m_e is the electron mass, r_d is a characteristic length for the atomic orbital ($r_d = 1.08$ Å in the case of Ti), and *d* is the interatomic distance, which in our case is d = 2.86 Å. The dimensionless coefficients are taken to be $\eta_\sigma = -16.2$, $\eta_\pi = 8.75$, and $\eta_\delta = 0$. The estimated band



Fig. 3. The electronic band structure for Ti_2CI_6 , Ti_2Br_6 and Ti_2I_6 using BEEF-vdW, PBE, and HSE06 functionals, respectively. The gray curves are from calculations without spin–orbit coupling.

widths $2V_m$ thus becomes 1.6 eV, 0.9 eV, and 0 eV for the σ , π , and δ -band, respectively, in semi-quantitative agreement with the calculated bands.

As explained above we use the BEEF-vdW functional because it is well-established for chemisorption studies. To investigate if there should be any qualitative differences between different functionals, we compare in Fig. 3 the band structures for the TiY_3 materials calculated with BEEF-vdW, PBE, and HSE06 [38] The HSE06 calculations are done non-self-consistently based on the PBE wave functions. In all cases, the ground state turns out to be anti-ferromagnetic (AFM) with small energy differences of less than 0.2 eV between the AFM and the ferromagnetic states. The band structures are quite similar, but the



Fig. 4. The one-dimensional electronic band structure for the nine different XY₃ materials using the BEEF-vdW functional. The gray lines show calculations without spin–orbit coupling.

HSE06 is seen to shift the δ -bands up in energy leading to an increased band gap. This could be expected because of the improved description of more localized states with the hybrid functional. Calculations with other hybrid functionals confirm the d¹ electronic configuration [39]. Calculations without spin–orbit coupling are shown with gray curves The spin–orbit effect is very small for chlorine, and bromine, and gives rise to small shifts of up to 0.3 eV for the heavier iodine. The DFT calculations cannot be expected to provide an accurate value for the band gap. However, as we shall see in the chemisorption studies, the most important mechanism is the transfer of electrons from the lower branch of the σ -band, which does not directly involve the band gap.

The band structures of all nine XY₃ materials calculated with BEEFvdW are compared in Fig. 4. In contrast to the Ti-systems the Zr- and Hf-systems are not magnetic in their ground states as might be expected because of the less localized 4d and 5d-states. Apart from this, the band structures are quite similar with a 4–5 eV broad and half-filled σ -band and with a more localized but empty band just above the Fermi level. The different materials can therefore also be expected to behave fairly similarly when gas atoms are adsorbed, as we shall discuss in the next section.

3.3. Bonding of gas atoms to the 1D materials

We will now study the chemisorption energetics of atomic hydrogen and oxygen on the nine 1D materials. The gas atoms are added to the material at three different initial sites, and the systems are afterwards relaxed, and the one with lowest energy is selected. The three initial configurations are (1) the gas atom is positioned in a bridge position between to TM atoms and also bridging two halogen atoms, (2) the gas atom is positioned in a bridge position between two TM atoms, but in the vicinity of one halogen atom, and (3) the gas atom is positioned so that it coordinates to one TM atom and three halogen atoms. Because of the long distances between the gas atom and the halogen atoms, configuration (3) was only applied to oxygen. The chemisorption energy, ΔE , is calculated per gas atom and relative to the clean one-dimensional materials and the gas dimer. In the case of a single hydrogen atom added in the X_2Y_6 unit cell we have

$$\Delta E = E(X_2Y_6H) - E(X_2Y_6) - \frac{1}{2}E(H_2).$$
(1)

We shall describe the coverage relative to the number of TM atoms, so in the above equation the hydrogen coverage is one half.

3.3.1. Hydrogen chemisorption

The preferred chemisorption site for hydrogen at coverage one half is shown in Fig. 5. The hydrogen atom is seen to be positioned in a bridge site between two TM atoms without any coupling to the halogens. This is the preferred site for all nine materials.

The character of the bonding can be understood from the band structures in Fig. 5. The band structures are for most of the systems (except TiBr₃ and TiI₃) essentially unchanged, but the Fermi level is shifted down, so that one electron has been removed from the lowest d-band. When hydrogen is chemisorbed to a simple metal surface the 1s-state is usually well below the Fermi level and is furthermore shifted down because of the potential from the metal. The state will hybridize with available states in the metal and become doubly occupied. In case of the extended metal surfaces any electron transfer will only have a negligible effect on the Fermi level because of the large reservoir of electrons. However, for the one-dimensional materials much fewer electrons are available, and the shift in Fermi level is therefore substantial in order to accommodate the available electrons. The systems (as calculated with BEEF-vdW) are metallic or semiconductors with low band gaps before chemisorption. The shift of the Fermi level because of the electron reduction makes the systems clearly metallic. The two materials TiBr₃ and TiI₃ are exceptions, because here the removal of an electron from the d-states leads to a ferromagnetic state with a splitting of the lower d-band. As described above, the clean titanium materials are in fact anti-ferromagnetic so this may come at no surprise.



Fig. 5. Upper: the electronic band structure for the nine materials with one hydrogen atom chemisorbed. The purple and yellow bands indicate spin-up and spin-down bands, while the blue bands have no spin. Lower left: the minimum energy structure of the $ZrBr_3$ material with one hydrogen atom per unit cell (coverage one half). Lower right: the chemisorption energy of hydrogen at a coverage of 1/2 (solid lines; left scale) and the calculated work functions of the clean XY₃ materials (dashed lines; right scale).

The calculated chemisorption energies are shown in the lower right panel of Fig. 5. The energies are seen to vary considerably as a function of the TM atom, while the dependence on the halogen atom is somewhat weaker. This could be expected from the fact that the hydrogen atoms bond directly to the TM atoms. We saw above that the bonding is associated with an electron transfer away from the TM metal atom, and it is therefore of interest to compare the binding energies with the energy required to remove an electron from the clean material, *i.e.* the work function. In Fig. 5 the calculated work functions are shown with dashed lines. Except for a constant shift the chemisorption energies are seen to follow closely the work functions providing a simple explanation for the variation.

The considerable shift in Fermi level associated with the chemisorption indicates that the chemisorption energy could be strongly dependent on coverage. This is indeed the case as can be seen in Fig. 6, where the binding energy is shown for coverages 1/2, 1/4 and 1/8.



Fig. 6. The hydrogen chemisorption energy as a function of coverage. Coverage 1/2 corresponds to one hydrogen atom per two TM atoms.



Fig. 7. The projected band structure for different coverages of hydrogen on $TiCl_3$. The left panel has coverage 1/2, the middle panel coverage 1/4, and the right panel coverage 1/8.

The chemisorption energies for the lower coverages is calculated by expanding the unit cell along the chain so that coverage 1/4 has 4 TM atoms in the unit cell, and coverage 1/8 has 8 TM atoms. The chemisorption is clearly stronger at lower coverages indicating an effective repulsive interaction between the hydrogen atoms.

The chemisorption of one hydrogen atom at coverage 1/2 was accompanied by a removal of one electron from the TM d-bands. The same mechanism is at play for chemisorption at lower coverages. Fig. 7 shows the band structure at different coverages. In the cases of coverage 1/4 and 1/8 the unit cell is twice and four times as long, respectively. This results in a reduction of the Brillouin zone and a folding of the bands. As can be seen on the figure, the Fermi level is in all cases positioned so that one electron has been removed per hydrogen atom. In the limit of low coverage the Fermi level will of course be unchanged.

The transfer of electrons to the hydrogen atoms is confirmed by the charge density plot for hydrogen chemisorption on $ZrBr_3$ shown in Fig. 8a. The red areas around the hydrogen atoms indicate an increased electron density, while the green areas indicate a depletion of the electron density around the Zr atoms. The shape of the depletion agrees with the electrons being removed from the Zr $d\sigma$ -bonds.

The electron transfer leads to the formation of electric dipoles perpendicular to the chain. The one-dimensional character of the system means that the screening is low, and it is therefore reasonable to suggest that an important contribution to the energy variation with coverage could be dipole–dipole interactions along the chain.

3.3.2. Oxygen chemisorption

We now turn to chemisorption of oxygen atoms to the one-dimensional systems. Like hydrogen, oxygen also binds in a bridge position coordinating to two TM atoms. However, $TiCl_3$ is an exception to this, where the oxygen atom binds to a single TM atom. The bridge structure for ZrBr₃ is shown in Fig. 9. In contrast to hydrogen, oxygen is seen to significantly change the structure of the chain. Repulsion between the negatively charged halogen atoms and oxygen leads to a distortion of the halogen triangles around the TM atomic chain. Furthermore, the chain is not straight any more but buckled.

Since oxygen is divalent one might expect the transfer of two electrons from the one-dimensional material. This is indeed the case as shown by the band structure of $ZrBr_3$ with oxygen chemisorption in Fig. 10. At the coverage 1/4 only one d-band is occupied corresponding to the removal of two electrons and an associated lowering of the Fermi level. At the higher coverage of 1/2 all d-states become empty corresponding to the removal of four electrons — two per oxygen atom in the unit cell. The transfer of electrons to the chemisorbed atoms is also confirmed by the charge density plot in Fig. 8b.

The distortion around the oxygen atoms at coverages 1/4 and 1/2 are rather similar as can be seen in the publicly available database. The distortion includes an increase in the Zr–Zr bond length from 3.1 Å in the clean case to 3.4 Å in the bond, where oxygen participates, and furthermore two Br atoms do no longer bridge between the Zr atoms. This elongation leads to flattening of the bands as seen in Fig. 10.

The main trend is the strong dependence of the chemisorption energy on the type of TM atom, which again roughly follows the work function. Considering the case with a coverage of 1/4, the change in chemisorption energy from $TiBr_3$ to $ZrBr_3$ is -1.2 eV and from $ZrBr_3$ to $HfBr_3$ it is -0.6 eV. For comparison, the work function changes for the clean systems are -0.8 eV and -0.5 eV, respectively.

The calculated results depend on the choice of functional — in our case the BEEF-vdW functional. As discussed in the method section, we use this functional because it generally works well for chemisorption energies. However, in order to check functional dependence of the results, we also performed HSE06 calculations for the chemisorption energies on $ZrBr_3$ using the structures determined with BEEF-vdW. The values obtained with HSE06 for hydrogen are identical to the ones with BEEF-vdW within 10 meV, while HSE06 binds oxygen more strongly by 0.3–0.4 eV. The shift in chemisorption energies is rather independent of coverage, so the trend is unchanged. The energy shift is consistent with the results of Sharada et al. where they find an overbinding of HSE06 for atoms and small molecules of about on average 0.2 eV relative to both BEEF-vdW and experiments. (The mean standard error is only -0.03 eV for BEEF-vdW relative to experiment).

4. Conclusion

The present study shows that one-dimensional materials exhibit chemisorption characteristics of both molecular and extended systems. The limited reservoir of electrons available at finite coverage leads to significant changes of the Fermi level and the system may change phase from a semiconductor or insulator to a metallic state. Such fundamental changes in electronic transport properties could be useful in gas detection [40]. The hydrogen and oxygen atoms are seen to bind directly to the TM atoms of the 1D structures, and the chemisorption energies vary significantly depending on the TM element roughly following the work function of the clean material. The variation of the chemisorption energies for different halogen atom is much weaker opening up the possibility of tuning the binding energy by mixing halogen atoms. Some of us recently used machine learning to generate a large number of one-dimensional materials [41], and among the stable materials we do in fact find halogen-mixed compounds as for example Hf₂BrI₅ and



Fig. 8. Charge density difference plots for (a) hydrogen and (b) oxygen chemisorption on ZrBr₃. The plots show the difference between the charge density of the chemisorption system and the sum of the densities for clean ZrBr₃ and the free atom. For both hydrogen and oxygen, electrons are seen to be transferred to the chemisorbed atoms.



Fig. 9. Left: the lowest-energy structure of oxygen chemisorbed to $ZrBr_3$ at a coverage of 1/4. The oxygen atom is seen to coordinate to two Zr atoms. Right: the chemisorption energy for oxygen at coverages 1/2 and 1/4 for all the nine XY₃ materials.



Fig. 10. The band structure for $\rm ZrBr_6$ with oxygen chemisorbed. To the left the coverage is 1/4 and to the right the coverage is 1/2.

 Ti_2ClBrI_4 in the β -TiCl₃-chain structure. Interestingly, alloying the TM atoms does also seem to be possible in this structure as materials like HfPdBr₆ and HfPtBr₆ are calculated to have formation energies less than 0.2 eV/atom above the convex hull. This class of materials could thus be interesting to further analyze.

In the present work we only consider the binding energies of gas atoms. A further assessment of these materials as catalysts would require an investigation of the relevant chemical processes including the activation barriers. Due to the particular one-dimensional structure a dissociation path will be different than for a three-dimensional material and this might also affect the relation between the transition state and the final states. Future work will show, if this can open new possibilities for catalyst materials.

CRediT authorship contribution statement

Hadeel Moustafa: Data curation, Investigation, Methodology, Software, Validation, Writing – original draft. Jens Jørgen Mortensen: Data curation, Methodology, Software, Writing – review & editing. Jan Rossmeisl: Conceptualization, Supervision, Writing – review & editing. Karsten Wedel Jacobsen: Conceptualization, Funding acquisition, Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All calculated atomic structures and energies are available at the Computational Materials Repository (CMR) at the url https://cmr.fysik. dtu.dk/ads1d/ads1d.html.

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