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# **On the reductive hydrogenation process of gas-phase metal dioxides. H<sub>2</sub> activation or reduction of the metal center, what is more important?**

Patricio González-Navarrete and Monica Calatayud\*

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## **Abstract**

A detailed CCSD(T)//B3LYP study is presented to unravel the gas-phase reductive hydrogenation process of dioxides MO<sub>2</sub> (M= Si, Ti, Zr, Sn, Hf, Ir Ce) according to the following reaction MO<sub>2</sub> + H<sub>2</sub> → M(OH)<sub>2</sub>. For the reductive hydrogenation process a heterolytic H-H bond cleavage is considered via hydride intermediates OMH(OH). A discussion concerning the effects of the reducibility of the metal centers and the structural aspects of the dioxides is presented. The results show that the activation of molecular hydrogen is directly related to the capability of the oxide to polarize the H<sub>2</sub> molecule prior to the H-H bond cleavage, although the formation of hydride intermediates do not necessarily guarantee further reduction of the metal center. The activation of the reduction reaction to form M(OH)<sub>2</sub> is found to be significantly larger than the activation to form the OMH(OH) intermediate. This gas-phase study aims to enhance the fundamental understanding of elementary steps in reductive hydrogenation processes of metal oxides.

**Keywords:** Reductive hydrogenation, metal dioxides, gas-phase, H<sub>2</sub>-activation

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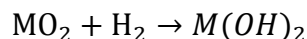
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## 1. Introduction

Hydrogen is at the present time one of the most vital energy resources.[1] Catalytic processes involving H<sub>2</sub> activation have been widely used in a wide range of chemical transformations.[2-7] Moreover, in recent years the increasing demand for clean energies indicates that future energy supply could, among other alternatives, be based on a dihydrogen technology.[8,9] Indeed, a comprehensive understanding of the chemistry behind hydrogenation processes needs to be developed in order to get insights into this area.[8] Certainly, one of the most challenging aspects of the H<sub>2</sub> molecule is the strength of the its  $\sigma$ -H-H bond,[1] and consequently, a spontaneous H<sub>2</sub> splitting could not be expected to take place under ambient conditions. In case of a heterolytic cleavage, the H<sub>2</sub> molecule must undergo polarization prior to its splitting, which can be assisted by main-group elements or metals. The formation of stable encounter complexes prior to the H-H bond cleavage is crucial to accomplish a noticeable electronic redistribution in H<sub>2</sub> molecule. In this sense, the polarization in encounter complexes requires the assistance of reaction centers. Polarizing effects can stem from: orbital overlaps, influence of strong coulombic fields, or spin polarization.[10] Thus, H<sub>2</sub> activation processes with high energy barriers are certainly associated with too small polarization. Likewise, given the importance of main-group elements or metal to accomplish an effective H<sub>2</sub> activation, metal oxides (MOs) in chemistry play an important role. In this regard, activation of H<sub>2</sub> by metal centers is a fundamental step in nearly all metal catalytic hydrogenation reactions.[11-14] Thus, the importance of MOs arises from their capabilities to assist and/or catalyze chemical processes owing to their acid-base and/or redox properties with applications in homogenous/heterogenous catalysis as well as support materials for different commercially relevant reactions.[15,16] In fact, the ability of metal cations to be reduced plays an important role in order to determine oxide chemical behaviors. The reducibility of metal cations has a strong influence in the physical-chemistry properties of materials, and therefore, to comprehend the nature associated with reduction mechanisms is required. The aim of this article is to provide insights into the hydrogenation process and its relationship with the reducibility of the metal center on dioxides. Indeed, the use of simple metal oxides model clusters in gas-phase has been broadly performed and served as an interesting way to gain a better understanding of the nature of active species in catalysis at strict molecular level.[17] Gas-phase metal oxides are generated experimentally by laser beam techniques, and recent studies increasingly look into the reactivity of the cluster

species formed for technologically important reactions[17-21] while the use of quantum chemical calculation provides a useful and complementary extension to unravel their intrinsic reactivity.

The present work corresponds to a theoretical study on the hydrogenation of dioxides MO<sub>2</sub> molecules (M = Si, Ti, Zr, Hf, Ir, Sn and Ce) according to the following reaction:



The MO<sub>2</sub> molecules were selected to enable the comparison of their calculated properties with the same stoichiometry. M is an element with a formal oxidation state of +IV in the oxide molecule, which is the highest that the central atom may reach. All the compositions correspond to stable macroscopic materials with stoichiometry MO<sub>2</sub>. The different nature of the central atom allows highlighting electronic effects: Si and Sn are p-block elements with s<sup>2</sup>p<sup>2</sup> electronic configurations; Ti, Zr, Hf are early transition metals with s<sup>2</sup>d<sup>2</sup> configuration, Ce is a lanthanide with s<sup>2</sup>f<sup>2</sup> configuration; Ir is a late transition metal with s<sup>2</sup>d<sup>7</sup> configuration. Despite the same stoichiometry and their macroscopic stability, the physico-chemical properties are very different: SiO<sub>2</sub> is a covalent non-reducible oxide, TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub> and SnO<sub>2</sub> are iono-covalent more or less reducible oxides, CeO<sub>2</sub> is mainly ionic and reducible, and IrO<sub>2</sub> has metallic character. The aim of the present work is to investigate the role of the central atom in the hydrogenation reaction for the gas-phase MO<sub>2</sub> molecules, getting rid of the structural factors such as polymorphism, surface orientation and termination. The results obtained are important *per se* in the field of gas-phase cluster reactivity, and although they are not intended to be directly extrapolated to more complex structural models, they might provide valuable insight on the role of the electronic configuration in the activation of H<sub>2</sub> in more complex systems.

The reaction mechanism of H<sub>2</sub> dissociation considers firstly the formation of hydrides species OMH(OH), that give rise in a second step to hydroxylated products M(OH)<sub>2</sub>. The former step involves H<sub>2</sub> polarization whereas the latter involves the reduction of the M atom from IV to II. The effect of the M atoms and their properties as regards H-H polarization and M reducibility, are analyzed. This article is structured as follows: first, the computational methods are described. The next section is devoted to results and discussions, and finally, the conclusions of the work are given.

## 2. Methodology.

Density functional theory (DFT) calculations have been performed using Gaussian 09.[22] The B3LYP[23,24] functional has been used for the exploration of reaction pathways associated with the hydrogenation process of dioxides. The structures have been optimized using Def2-TZVPP basis set[25-28] for Si, Ti, Zr, Hf, Ir, Sn and Ce atoms, and Def2-TZVPPD[29] for O and H atoms. The energies of the DFT optimized structures were improved with CCSD(T) single point calculations to account for dispersive interactions, known to fail in DFT. The def2-QZVPPD basis set[29] was employed for H, O, Si, Ti, Zr, Hf, Ir and Sn atoms, whereas for Ce calculations only DFT results have been analyzed since energy corrections could not be obtained. The energies reported refer CCSD(T) energies and are corrected by zero-point vibrational energy (ZPVE) contributions.

## 3. Results and discussions

The potential energy surfaces (PESs) considered involve two steps: i) the dissociation of the H<sub>2</sub> molecule giving rise to the formation of hydride intermediates OMH(OH), and ii) the formation of reduced dihydroxy species M(OH)<sub>2</sub>. A direct homolytic cleavage of H<sub>2</sub> yielding to OMH(OH) or M(OH)<sub>2</sub> species could not be predicted at any level of theory for any MO<sub>2</sub> + H<sub>2</sub> systems, as it proceeds with a higher activation energy in the gas-phase (see scheme 1). It is worth noting that an homolytic splitting entails the recurrent stabilization of the H· species from heterogeneous metal surfaces or, in the homogeneous phase, from suitable reaction centers allowing the formation of dihydride species[8] which are not available in a gas-phase performance; consequently, homolytic reaction pathways have been discarded in the present work. The formation of dihydride species via oxygen vacancies, although found for instance in ZrO<sub>2</sub> slab models,[30] has not been considered here due to the complexity of treating reduced gas-phase MO<sub>2</sub> species. Interestingly, although heterolytic H<sub>2</sub> dissociation is usually associated with irreducible oxides,[31-33] there are theoretical evidences of a heterolytic path on CeO<sub>2</sub> surfaces, which are reducible, involving CeH/OH pairs[34,35,33,36] Thus, the only hydrogenation process considered in this study is through a heterolytic step-wise reaction mechanism as displayed in scheme 1.

We have characterized the geometrical structures of the dioxides as well as their electronic structures, which are summarized in Table 1. The results show that TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub> and CeO<sub>2</sub> present C<sub>2v</sub> structures with closed shell singlet <sup>1</sup>A<sub>1</sub> as ground states; SiO<sub>2</sub>, SnO<sub>2</sub> are predicted with lineal structures in closed shell singlet state whereas IrO<sub>2</sub> is predicted to have a doublet ground state with a C<sub>2v</sub> symmetry as well.

An exploration of the frontier molecular orbitals (see Table 1), reveals that for, TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub> and CeO<sub>2</sub> their LUMOs are available with a<sub>1</sub> symmetry localized on the metal center which favor the stabilization of hydrides species after H<sub>2</sub> cleavage. The availability of *ns*, (*n-1*)*d* or (*n-2*)*f* orbitals on the metal atom, discarding then *np* orbitals which are higher in energy, makes the charge distribution of an excess electron different than in anions of polar molecules that do not contain a transition metal atom.[11,37] For IrO<sub>2</sub>, it displays its HOMO with a<sub>1</sub> symmetry due to its spin polarized nature. In addition, HOMO-LUMO (H-L) energy gaps are also reported in Table 1, which may be considered as a measure of the reducibility of the metal atoms.[38] Thus, SiO<sub>2</sub> and SnO<sub>2</sub> display the highest H-L energy gap indicating thus a plausible resistance of the metal center to be reduced as compared to the rest of MO<sub>2</sub> species. However, SnO<sub>2</sub> is classified as a reducible material [38] and differences in its reactivity as a molecular dioxide in gas-phase are explained in detail below.

The calculated reaction paths are shown in the supporting information. The results show that the formation of the encounter complexes MO<sub>2</sub>···H<sub>2</sub> is predicted to be exothermic for Ti, Zr, Hf, and Ce, whereas they are slightly endothermic for Si, Sn and Ir. The favorable interaction between H<sub>2</sub> molecule and Ti, Zr, Hf and Ce dioxides is predicted to be 6.0, 5.0, 8.7 and 2.0 kcal mol<sup>-1</sup>, respectively, more stable than their corresponding separated reactants (see Figure 1). In contrast, the formation of encounter complexes for Si, Ir, and Sn brings about quasi-equilibrium scenarios with stabilization energies close to zero, i.e. 0.5, 0.0 and 0.2 kcal mol<sup>-1</sup>, respectively, regarding separated reactants. Note that the latter group of dioxides display a linear configuration, and clearly, an unfavorable interaction towards the formation of encounter complexes is observed. Likewise, the preliminary stabilization of encounter complexes acts in favor of the dissociation of H<sub>2</sub>; this is reflected in their corresponding activation energies summarized in Figure 2. Thus, Ti, Zr, and Hf encounter complexes give rise to activation energies significantly lower than those calculated for Si, Ir and Sn dioxides. Moreover, encounter complexes and corresponding transition states of Si, Ir, and Sn

dioxides have been predicted above the line of separated reactants, in line with an unfavorable H<sub>2</sub> activation.

For dioxides of group IV, H<sub>2</sub> activation energy barrier decreases as the size of the metal center increases.[11] On the contrary, linear dioxides give rise to higher activation energies as previously mentioned. Despite the presence of localized spin density on the metal center on IrO<sub>2</sub>, it does not improve the H<sub>2</sub> activation, indicating thus that the H<sub>2</sub> activation could be related to the polarity of the reactive sites instead of the radical nature of the metal center. A deeper analysis reveals a direct relationship between polarities of dioxides and the stabilization energy of encounter complexes as depicted in Figure 3a. An increment of dipole moment in dioxides gives rise to more stable encounter complexes, whereas linear dioxides do not show favorable interactions with the H<sub>2</sub> molecule. Accordingly, polar encounter complexes promote electronic redistributions of the H<sub>2</sub> molecule resulting in heterolytic H-H cleavages towards H<sup>+</sup> and H<sup>-</sup>, and therefore, lower activation energies can be observed for Ti, Zr, and Hf dioxides (see Figure 3b), for which values range between 1.6 - 8.0 kcal mol<sup>-1</sup>. In contrast, linear dioxides bring about higher activation energies for which values range between 16.0 - 24.6 kcal mol<sup>-1</sup>. Interestingly, an exception is found for the case of CeO<sub>2</sub>, for which H<sub>2</sub> activation energy barrier is predicted to be 21.0 kcal mol<sup>-1</sup>. Despite CeO<sub>2</sub> is predicted with a dipole moment higher than Si, Ir, and Sn dioxides, its H<sub>2</sub> activation is predicted slightly lower than that calculated for SnO<sub>2</sub> and higher than those predicted for SiO<sub>2</sub> and IrO<sub>2</sub>. Note that TiO<sub>2</sub>, ZrO<sub>2</sub> and HfO<sub>2</sub> are predicted to have higher dipole moments, and consequently, their H<sub>2</sub> activations are considerably lower in energy than that predicted for CeO<sub>2</sub>. The difference in the reactivity presented by CeO<sub>2</sub> could be attributed to orientation of its frontier molecular orbitals. By and large, the heterolytic H-H cleavage observed in the systems studied here takes place by means of a Lewis base-transition metal (LB-TM) catalytic assistance,[1,39-41] where the metal accepts the hydride (LUMO) and the assisting Lewis base attracts the proton (HOMO), see Scheme 2. Main group elements with lone pair(s), such as nitrogen, oxygen, or sulfur, are considered as the assisting Lewis base. Thus, despite the fact that CeO<sub>2</sub> possesses a main group with lone pairs (terminal oxygen atoms), those lone pairs are not well-oriented in order to facilitate the H-H cleavage, as depicted in Table 1 and scheme 2. This could explain its higher H<sub>2</sub> activation energy barrier, since the system requires a redistribution of lone pairs to accomplish the acceptance of the proton.

On the other hand, the stabilization of hydride intermediates  $\text{OMH}(\text{OH})$  ranges between  $-33.0$  and  $-50.2 \text{ kcal mol}^{-1}$  as depicted in Figure 4; note that  $\text{OCeH}(\text{OH})$  is predicted  $1.0 \text{ kcal mol}^{-1}$  above the line of separated reactants. Apparently, there is not any correlation between  $\text{H}_2$  activation and the stability of their corresponding  $\text{OMH}(\text{OH})$  intermediates. For example, note that  $\text{OMH}(\text{OH})$  ( $\text{M} = \text{Sn, Ti and Zr}$ ) intermediates present similar stabilities despite their dissimilar  $\text{H}_2$  activation energies barriers. In addition,  $\text{OSnH}(\text{OH})$  and  $\text{OIrH}(\text{OH})$  are slightly more stable than  $\text{OTiH}(\text{OH})$  and  $\text{OZrH}(\text{OH})$ , although  $\text{H}_2$  activations by  $\text{TiO}_2$  and  $\text{ZrO}_2$  are kinetically more favorable than that predicted for  $\text{SnO}_2$ . Nevertheless, a linear response might be observed between the stability of  $\text{OMH}(\text{OH})$  species and their corresponding  $\text{H}_2$  activation energies accounting for the Hammond's postulate (see Figure 5) just considering the dioxides from group IV and  $\text{CeO}_2$  and excluding  $\text{SiO}_2$ ,  $\text{IrO}_2$  and  $\text{SnO}_2$ .

The last step is the interconversion of  $\text{OMH}(\text{OH})$  into  $\text{M}(\text{OH})_2$  and corresponds to the rate-limiting step of the process in all the cases studied. The activation energies for these steps are summarized in Figure 6. Indeed, this interconversion may be considered as a measure of the capability of the metal center to be reduced. As depicted in Figure 6, the  $\text{OSiH}(\text{OH})$  is predicted with the highest energy barrier associated with the interconversion process. Likewise,  $\text{SiO}_2$  and  $\text{OSiH}(\text{OH})$  display the highest H-L energy gap (see Table 1 and Table 2), with  $4.84$  and  $5.77 \text{ kcal mol}^{-1}$ , respectively, indicating thus a clear resistance of the metal center to be reduced as compared to the rest of dioxides. On the contrary,  $\text{IrO}_2$  is predicted to be the most reducible dioxide, while  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{SnO}_2$  and  $\text{CeO}_2$  have been calculated to be reducible with activation energy barriers for the interconversion processes ranging between  $34.5$  and  $47.0 \text{ kcal mol}^{-1}$ . Despite the fact that  $\text{SnO}_2$  and  $\text{IrO}_2$  systems are predicted with favorable energy barriers for the interconversion process, they have been calculated kinetically unfavorable towards H-H bond activations in the first step of their processes. Does this mean that  $\text{IrO}_2$  and  $\text{SnO}_2$  must be considered as irreducible systems in gas-phase? Since the homolytic cleavage of H-H bond is less plausible under ambient conditions in gas-phase, the transformation of  $\text{MO}_2 + \text{H}_2$  into  $\text{M}(\text{OH})_2$  inevitably should occur via a heterolytic H-H bond cleavage as mentioned above. In order to accomplish this heterolytic H-H bond cleavage, the system certainly requires a favorable  $\text{H}_2$  activation, which stems from a preceding polarization of the  $\text{H}_2$  molecule in order to guarantee the formation of a hydride species  $\text{OMH}(\text{OH})$ . Due to the linear geometry of



IrO<sub>2</sub> and SnO<sub>2</sub>, inefficient H-H activation is observed albeit the reducibility of the metal centers remains unbroken. Therefore, to understand hydrogenation processes of the metal oxides in gas-phase with the aim of producing hydroxylated species M-OH, it is necessary to take into account, firstly, the capability of the metal center to be reduced (for example considering the H-L energy gap of the oxides), and secondly, the capability of the metal oxides to polarize H<sub>2</sub> molecules (dipole moment) prior to the H-H bond cleavage. In other words, the intrinsic property of the metal center does not ensure by itself a successful formation of OH-M-OH species, and consequently, a reductive hydrogenation could be accomplished by a complementary and synergistic approach taking into account both factors. In particular, OMH(OH) (M= Ti, Zr, Ce) intermediates give rise to M(OH)<sub>2</sub> species with activation energies rather similar ~ 43 kcal mol<sup>-1</sup>, whereas OMH(OH) (M= Sn, Hf) are predicted with activation energies of ~ 35 kcal mol<sup>-1</sup>. Likewise, OIrH(OH) is predicted with the lowest interconversion process with an energy barrier of 25.1 kcal mol<sup>-1</sup>. Likewise, it is worth noting that all those hydride intermediates display a H-L energy gap lower than that calculated for OSiH(OH), see Table 2. Finally, the formation of M(OH)<sub>2</sub> and their relative energies are depicted in Figure 7. Note that all the M(OH)<sub>2</sub> species are depicted in their corresponding ground states; in particular, only Ti(OH)<sub>2</sub> and Ce(OH)<sub>2</sub> undergo spin crossing after overcoming the energy barriers associated with the interconversion process. A deeper analysis of electronic structure and the potential energy surfaces associated with the interconversion processes of Ti, Zr and Hf has been described in detail elsewhere [11].

#### 4. Conclusions

A detailed computational DFT study on the key steps associated with hydrogenation of gas-phase dioxides (MO<sub>2</sub>, M = Si, Ti, Zr, Hf, Ir, Sn and Ce) according to the following reaction  $MO_2 + H_2 \rightarrow M(OH)_2$  has been carried out. Hydrogen activation, effects of the reducibility of the metal centers and the structural aspects of the dioxides have been discussed. The results show that the activation molecular hydrogen is directly related to the capability of the oxide to polarize the H<sub>2</sub> molecule prior to the H-H bond cleavage. Because in gas-phase conditions the H<sub>2</sub> activation preferably takes place by means of a heterolytic H-H bond cleavage, a favorable formation of hydride intermediates OMH(OH) does not necessarily guarantee a subsequent reduction of the metal center. Thus, a reductive hydrogenation could be accomplished by complementary effects

considering the ability of reactive sites to polarize the H<sub>2</sub> molecule and the reducibility of the metal center. These results could be used to enhance the fundamental understanding of elementary steps in reductive hydrogenation processes of metal oxides in order to assist the design of tailor-made catalysts for real applications in the condensed phase.

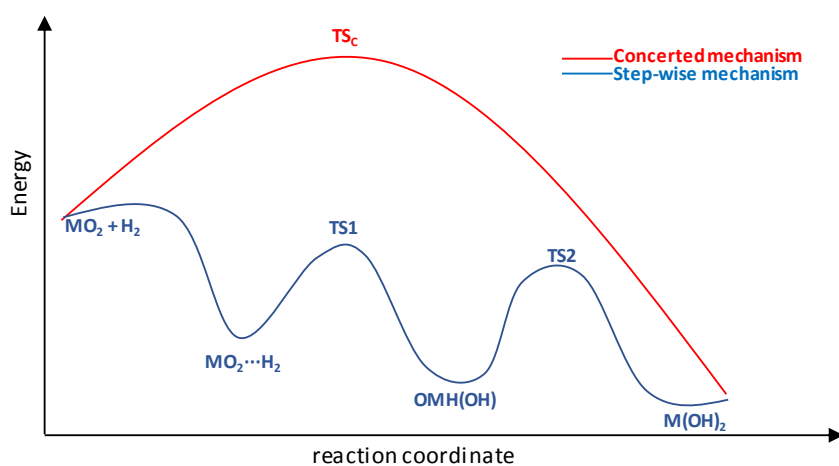
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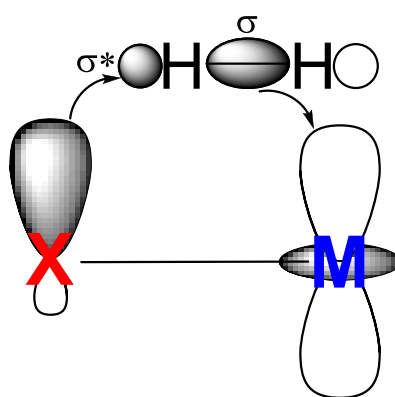
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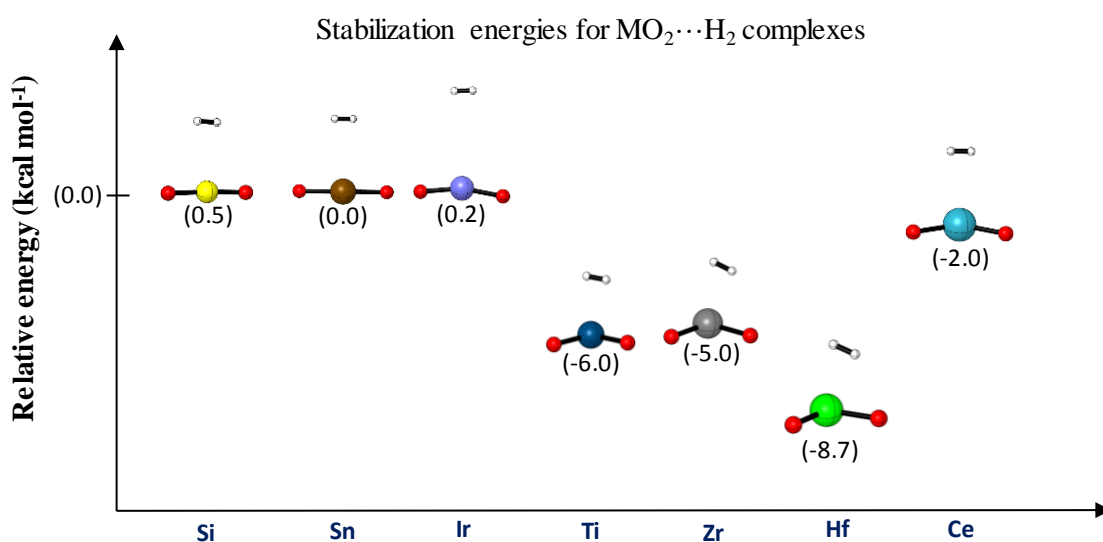
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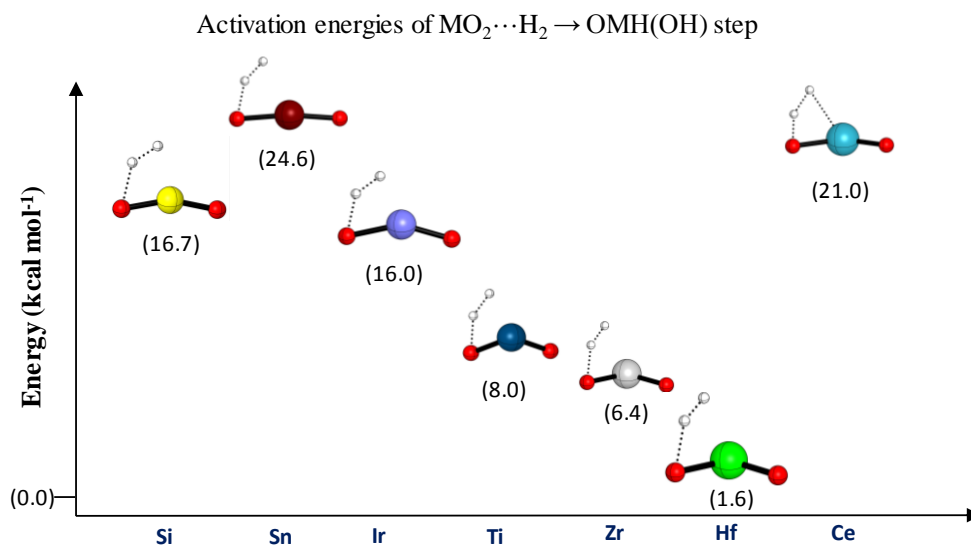
Scheme 1



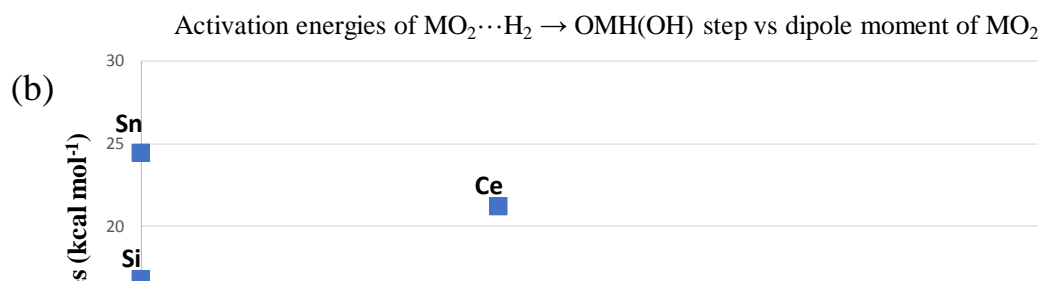
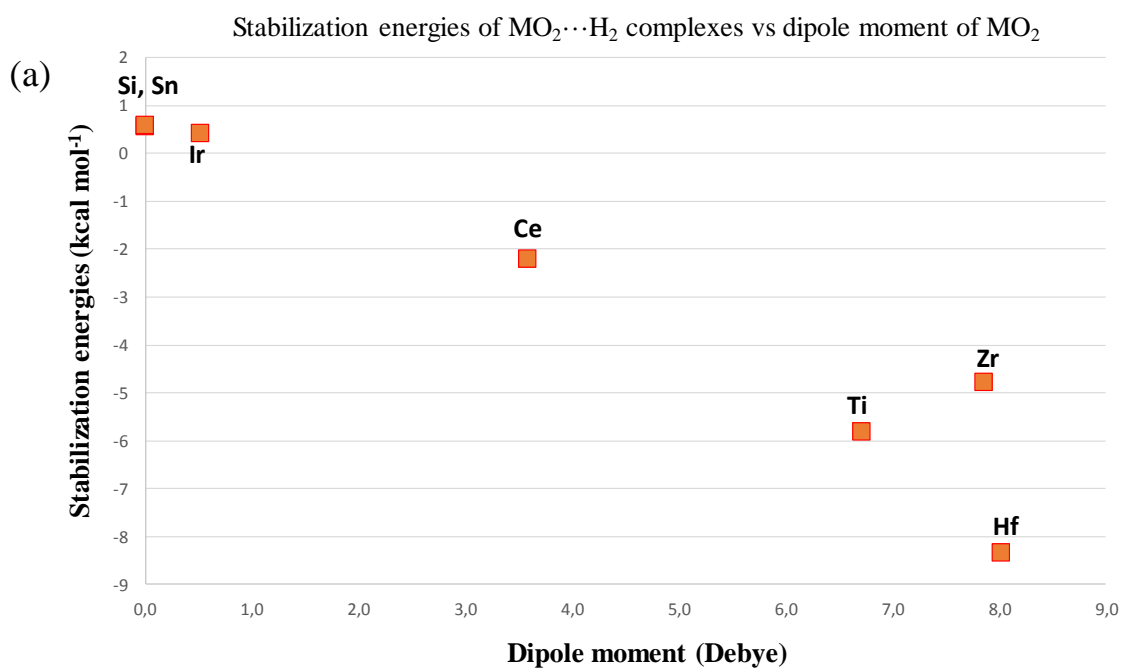
## Scheme 2



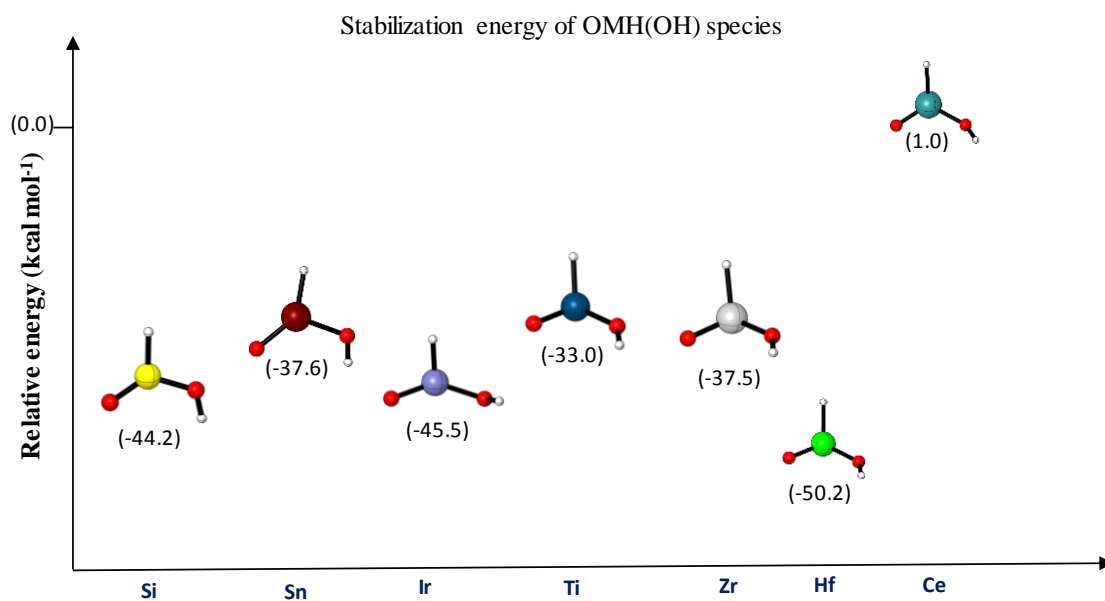
**Figure 1.** Stabilization energies for  $\text{MO}_2 \cdots \text{H}_2$  complexes calculated at the CCSD(T)//B3LYP level of theory (except for Ce). Relative energies regarding separated reactants ( $\text{MO}_2 + \text{H}_2$ ) are corrected for ZPVE contributions.



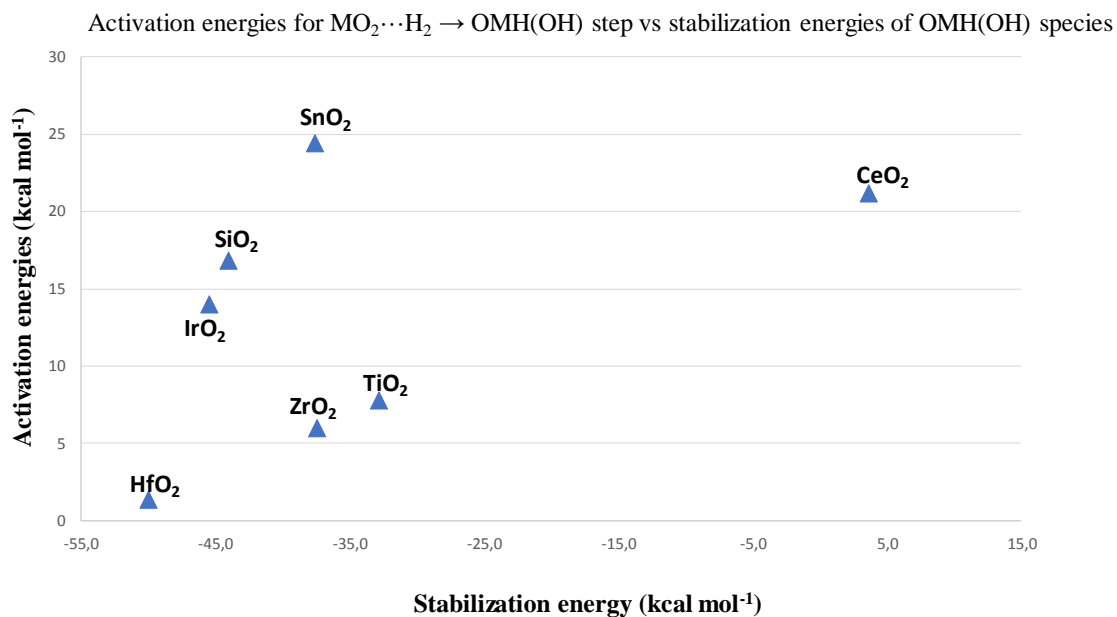
**Figure 2.** Activation energies of  $\text{MO}_2 \cdots \text{H}_2 \rightarrow \text{OMH}(\text{OH})$  step with their corresponding transition states calculated at the CCSD(T)//B3LYP level of theory (except for Ce). Energies are corrected for ZPVE contributions.



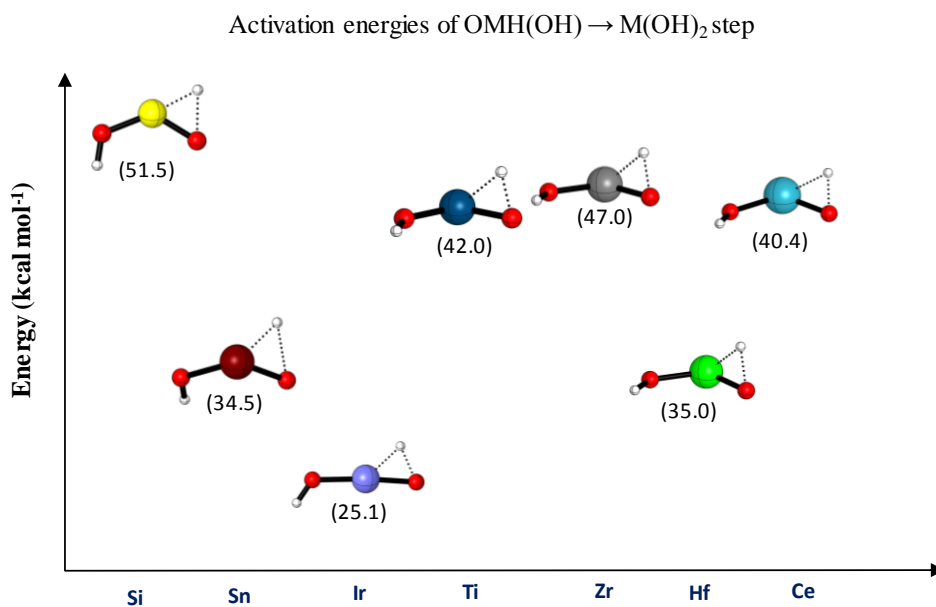
**Figure 3.** (a) Stabilization energies of  $\text{MO}_2 \cdots \text{H}_2$  complexes vs dipole moment of  $\text{MO}_2$  species. (b)  $\text{H}_2$  activation energy barrier by  $\text{MO}_2$  vs dipole moment of  $\text{MO}_2$  species. Energies calculated at the CCSD(T)//B3LYP level of theory (except for Ce) and corrected for ZPVE contributions.



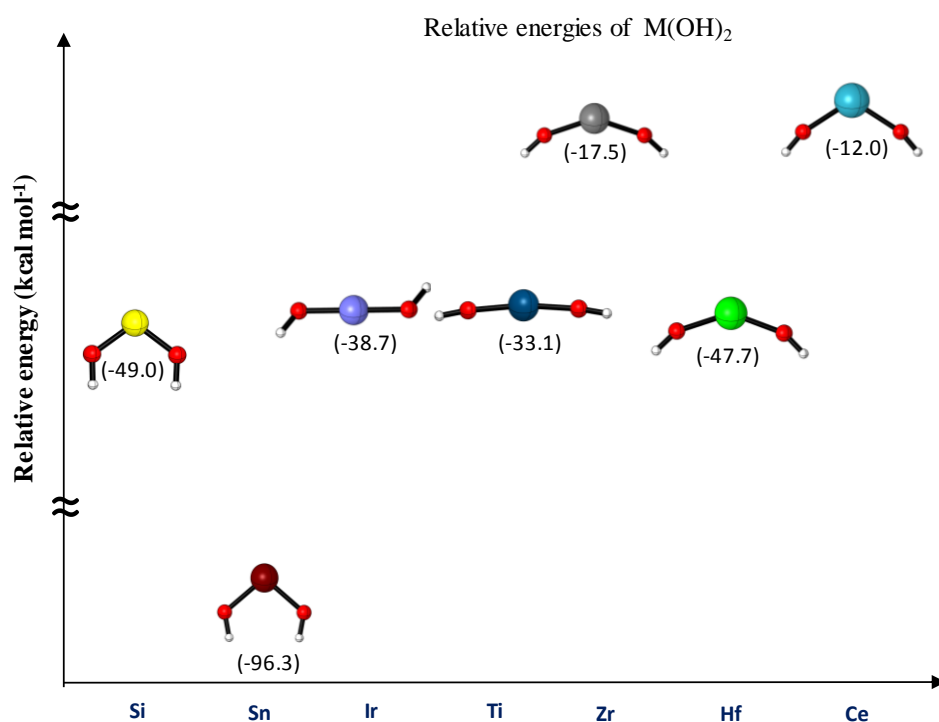
**Figure 4.** Stabilization energies of OMH(OH) species calculated at the CCSD(T)//B3LYP level of theory (except for Ce). Relative energies regarding separated reactants ( $\text{MO}_2 + \text{H}_2$ ) are corrected for ZPVE contributions.



**Figure 5.** Stabilization energies of  $\text{OMH(OH)}$  species calculated at the CCSD(T)//B3LYP level of theory except for Ce. Relative energies regarding separated reactants ( $\text{MO}_2 + \text{H}_2$ ) are corrected for ZPVE contributions.



**Figure 6.** Activation energies of  $\text{OMH(OH)} \rightarrow \text{M(OH)}_2$  step with their corresponding transition states calculated at the CCSD(T)//B3LYP level of theory, except for Ce. Energies are corrected for ZPVE contributions.


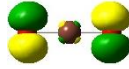
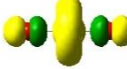
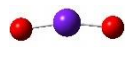
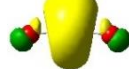
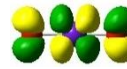


**Figure 7.** Relative energies for  $M(OH)_2$  species calculated at the CCSD(T)//B3LYP level of theory (except for Ce). Relative energies regarding separated reactants ( $MO_2 + H_2$ ) are corrected for ZPVE contributions.

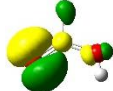
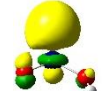
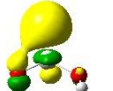

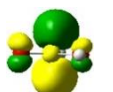

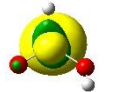


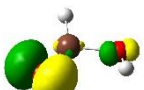
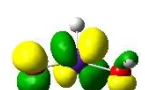
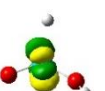
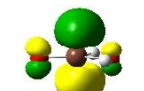
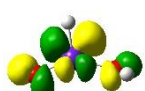
**Table 1.** Geometrical parameters for  $MO_2$  species calculated at B3LYP level of theory as well as their corresponding frontier molecular orbitals and HOMO-LUMO (H-L) energy gaps (in kcal mol<sup>-1</sup>)

$MO_2$		Distance M-O	Angle O-M-O	HOMO	LUMO	H-L Gap
$SiO_2$		1.527	180.0			4.84
$TiO_2$		1.641	111.8			3.22
$ZrO_2$		1.773	108.3			2.76
$HfO_2$		1.788	107.9			2.30
$CeO_2$		1.819	144.8			3.68



SnO <sub>2</sub>		1.813	180.0			3.92
IrO <sub>2</sub>		1.695	166.0			2.07

**Table 2.** Frontier molecular orbitals and HOMO-LUMO (H-L) energy gaps (in kcal mol<sup>-1</sup>) calculated at B3LYP level of theory for OMH(OH) species.

OMH(OH)	Si	Ti	Zr	Hf
HOMO				
LUMO				
H-L gap	5.77	4.03	3.91	4.03
OMH(OH)	Ce	Sn	Ir	
HOMO				
LUMO				
H-L gap	2.94	4.23	2.86	