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# Two dimetalloenes with vanadium and chromium: Electronic structures and their promising application in hydrogen storage

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## ARTICLE INFO

### Article history:

Received 10 March 2015

Received in revised form

10 July 2015

Accepted 12 July 2015

### Keywords:

Sandwich-type dimetalloenes

Electronic structures

Hydrogen storage

## ABSTRACT

The hydrogen storage capacities of the two sandwich-type Cp<sub>2</sub>TM<sub>2</sub> [Cp = cyclopentadienyl (C<sub>5</sub>H<sub>5</sub>); TM = V or Cr] dimetalloenes were studied using first-principles calculations. According to the B3PW91 method in density functional theory (DFT), Cp<sub>2</sub>V<sub>2</sub> and Cp<sub>2</sub>Cr<sub>2</sub> could adsorb up to seven and six hydrogen molecules, respectively. The predicted hydrogen storage densities of Cp<sub>2</sub>V<sub>2</sub> and Cp<sub>2</sub>Cr<sub>2</sub> were 5.73 and 4.91 wt%, respectively. Additionally, because hydrogen binding energies bound by Kubas model were 0.39 and 0.43 eV/H<sub>2</sub>, respectively, both the Cp<sub>2</sub>V<sub>2</sub> and Cp<sub>2</sub>Cr<sub>2</sub> dimetalloenes were proven to be favourable for reversible adsorption and desorption of hydrogen molecules under ambient conditions.

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## Introduction

Currently, because of the unrecoverable environmental effect, it is unwise to continuously depend on fossil fuels that dominate our energy infrastructure [1,2]. To search a better energy source that can replace the fossil fuels is an important challenge for human beings [3–7]. Because of its environmental compatibility, large chemical energy per unit mass (142 MJ kg<sup>-1</sup>) and exploitable efficiency, hydrogen is the best candidate [8–13]. Hydrogen can be acquired from renewable energy sources [14–16], but the lack of a

convenient and efficient on-board system for hydrogen storage prohibits its use [17–20]. To satisfy the ideal hydrogen storage conditions, the medium should meet the following specifications: (1) a gravimetric density of 5.5 wt% and volumetric capacity of 40 g L<sup>-1</sup>, as set by the U.S. Department of Energy in 2014 [21], and (2) rapid adsorption and desorption kinetics at ambient conditions in a reversible manner so that it is compatible with current generation fuel cells [22,23]. In fact, both the compressed hydrogen storage and the liqueficient method cannot be applied due to their low densities and high costs [24]. Hydrogen storage in certain solid media has been widely accepted because

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<http://dx.doi.org/10.1016/j.ijhydene.2015.07.058>

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it is the safest and most effective technique among all existing methods [25,26].

At present, chemisorption and physisorption are the two common ways by which hydrogen is adsorbed on a solid material [27–38]. In the first method, the materials have large gravimetric capacities; therefore, the H<sub>2</sub> molecule becomes two isolated H atoms, which bind strongly to these complexes via chemical bonds, much like metal hydrides and complex hydrides. Therefore, the high hydrogen desorption temperature and sluggish kinetics result in significant challenges for practical applications [9,27–30]. The second way, physisorption, utilizes sorbent materials, including carbon-based materials [31,32], BN-based materials [33,34], graphene [35], and metal-organic frameworks (MOFs) [36,37], to obtain high gravimetric capacities and rapid kinetics. Unfortunately, the H<sub>2</sub> molecules bind on the surface of these substrates with a weak binding energy; therefore, hydrogen desorbs at cryogenic temperatures, hampering the use of this method for commercial applications.

A developing field that proposes a third way to strongly bind substrates to H<sub>2</sub> is an intermediate between chemisorption and physisorption, and it has garnered significant interest because the H<sub>2</sub> molecules can be adsorbed and desorbed by quasi-molecular binding under ambient conditions in a reversible manner [38,39]. There are two different explanations for this type of binding. Niu et al. [40] reported that the electric fields produced by positively charged metal ions can polarize H<sub>2</sub> molecules; however, Kubas [41] demonstrated that charge transfer from the H<sub>2</sub> molecule to the unfilled *d*-type orbitals of transition-metal atoms and then transfer from the transition-metal atom to the antibonding orbital of the H<sub>2</sub> molecule forms this quasi-molecular bonding. This interaction between H<sub>2</sub> molecules and transition metals (TMs) had been found in many hydrogen storage medium, lain between chemisorption and physisorption, with a rational binding energy range which was compatible with room temperature adsorption and desorption [42–50]. One of most common examples were fullerenes and nanotubes coated with Ti atom and they could strongly adsorb up to large quantities of H<sub>2</sub> molecules [42–45]. However, most TM atoms tended to form clusters on their surfaces after several charging–discharging processes and this disadvantage weakened the hydrogen storage ability [46,47]. Instead of aforementioned examples, some hydrocarbons decorated with TM atoms had already been investigated for the use as possible hydrogen storage medium [48–50]. A typical molecule was Ti-ethylene complex and the hydrogen storage density decreased from 14 wt% to 10 wt% to 6.1 wt% when the Ti atoms polymerized during recycling [49]. Hence, the exploration for novel and feasible high capacity hydrogen storage medium is still significant in this field.

The novel structures and potential hydrogen storage properties of metallocene, dimetallocene and multimetallocene complexes have been investigated. The hydrogen storage properties of metallocenes consisted of TMs and one cyclopentadienyl (Cp) ring have been studied by some research teams. For example, the hydrogen storage capacity of TiC<sub>5</sub>H<sub>5</sub> is 6.61 wt% and corresponds to the average binding energy per H<sub>2</sub> molecule of 0.72 eV [50]. FeC<sub>5</sub>H<sub>5</sub> and Fe<sub>2</sub>C<sub>5</sub>H<sub>5</sub> have high hydrogen storage capacities (7.63 and 10.15 wt%)

and the average adsorption energies are 0.49 and 0.73 eV/H<sub>2</sub> [51]. Lei et al. have reported that LaC<sub>5</sub>H<sub>5</sub>, EuC<sub>5</sub>H<sub>5</sub> and HoC<sub>5</sub>H<sub>5</sub> can bind six H<sub>2</sub> molecules, the corresponding gravimetric storage capacities are 5 wt% [52]. Unfortunately, in the aforementioned examples, the TMs and adsorbed H<sub>2</sub> molecules are exposed in surrounding space. When the real hydrogen storage systems formed, the TMs will prefer to cluster and those complexes may polymerize after H<sub>2</sub> molecules are desorbed [51,53,54]. So, the ability of those compounds to store H<sub>2</sub> molecules is reduced due to this drawback and it is necessary to sequentially search more feasible materials.

In our previous studies, some sandwich-type metallocene, dimetallocene and multimetallocene complexes have been researched. Ferrocene is one of the most typical representative metallocene of which one metal sandwiched between the two Cp rings has been studied at first. For ferrocene, the iron atom can only adsorb two H<sub>2</sub> molecules and the corresponding gravimetric hydrogen density is low (1.07 wt%). Because the distance between two Cp rings is slightly small (about 3.3 Å), a single iron atom can not open enough distance space between the two Cp rings to accommodate sufficient H<sub>2</sub> molecules [55]. Subsequently, the dimetallocenes (Cp<sub>2</sub>Sc<sub>2</sub> and Cp<sub>2</sub>Ti<sub>2</sub>) with a pair of metal atoms sandwiched between two Cp rings have been explored. With respect to first-principles calculations, the gravimetric hydrogen-storage capacity is 6.7 wt% for Cp<sub>2</sub>Ti<sub>2</sub> and 6.8 wt% for Cp<sub>2</sub>Sc<sub>2</sub>. Moreover, the multimetallocenes (e.g., CpTi<sub>3</sub>Cp and CpTi<sub>4</sub>Cp) complexes can further increase the H<sub>2</sub> adsorption capacity to 8.7 wt% and 10.4 wt%, respectively [56]. Recently, the sandwich-type ethylene dimetallocene complex Cp<sub>2</sub>Ti<sub>2</sub>C<sub>2</sub>H<sub>4</sub> has been indicated that the two Ti atoms can adsorb up to six H<sub>2</sub> molecules via the Kubas interaction, and the corresponding gravimetric hydrogen density of Cp<sub>2</sub>Ti<sub>2</sub>C<sub>2</sub>H<sub>4</sub> is 4.73 wt% [57]. Considering the significant challenge to synthesize multimetallocenes [58], dimetallocenes might be more promising systems for hydrogen-storage. Therefore, in this paper, we will focus on the dimetallocenes of the next two transition metals, V and Cr, expressed as Cp<sub>2</sub>V<sub>2</sub> and Cp<sub>2</sub>Cr<sub>2</sub>, because they also have empty *d* orbitals. Their structures and stabilities will be discussed first, followed by studies of their hydrogen storage properties.

## Computational methods

First-principles studies were performed using density functional theory (DFT). DFT has been recognized as a practical and effective computational tool, especially for organometallic compounds [59–61]. The B3PW91 method, a hybrid HF/DFT method that uses a combination of the Becke's three-parameter functional (B3) [62] and the Perdew and Wang functional (PW91), was employed for all computations, including the structures, frequencies and energies. This method contains the 6-31G\*\* basis set, which adds a standard *p*-polarization function to the H atoms based on the sufficient complete basis set 6-31G\* and includes moderately diffuse *d* orbitals [63]. This basis set was used for the structural optimized calculations.

The dispersion forces are important or even dominant in non-covalent interactions, which are caused by favourable

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