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# Computational investigation of hydrogen storage on scandium–acetylene system

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## ABSTRACT

The hydrogen storage capacities of synthesized Scandium–Acetylene systems ( $\text{Sc}-\eta^2-\text{C}_2\text{H}_2$ ) and  $\text{HC}\equiv\text{C}-\text{ScH}$ ) are tested by using density functional theory (DFT) and the coupled-cluster theory (CCSD (T)) with 6–311++G (3df, 3pd) basis sets. Both the energy profile and natural bond orbital analysis predict that  $\text{Sc}-\eta^2-\text{C}_2\text{H}_2$  and  $\text{HC}\equiv\text{C}-\text{ScH}$  complexes are promising hydrogen storage materials. The  $\text{Sc}-\eta^2-\text{C}_2\text{H}_2$  and  $\text{HC}\equiv\text{C}-\text{ScH}$  complexes can trap up to six hydrogen molecules, reaching gravimetric uptake capacities as high as 14.56 wt%. Thermo-chemistry calculations indicate two  $\text{H}_2$  in  $\text{Sc}-\eta^2-\text{C}_2\text{H}_2(\text{H}_2)_6$  and four  $\text{H}_2$  in  $\text{HC}\equiv\text{C}-\text{ScH}(\text{H}_2)_6$  can be readily adsorbed at 77 K and desorbed at 298.15 K under atmospheric pressure, corresponding to the maximal reversible hydrogen storage abilities of 5.37 and 10.20 wt%, respectively. The further comparison between  $\text{HC}\equiv\text{C}-\text{ScH}(\text{H}_2)$  and  $\text{HC}\equiv\text{C}-\text{ScH}^- (2\text{H})$  reveals that the charged state of Sc atom has a great influence on the hydrogen adsorption state and adsorption energy. Moreover, dimers may form in case of scandium-acetylene systems. The most stable  $(\text{C}_2\text{H}_2\text{Sc})_2$  can adsorb ten  $\text{H}_2$  molecules, reaching the hydrogen storage capacity of 12.43 wt%. Thermo-chemistry calculations indicate the maximal reversible hydrogen storage capacities of  $\text{Sc}(\text{C}_2\text{H}_2)_2$  and  $(\text{C}_2\text{H}_2\text{Sc})_2$  are 7.67 and 7.85 wt%, respectively.

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## Introduction

With the increasing demand of energy and limitations of fossil fuels, viable hydrogen storage materials play an increasingly important role [1–6]. The traditional chemisorption materials (metal hydrides [7]) and physisorption materials (carbon-based nanostructures [8–10] and metal/covalent organic frameworks [11,12]) fail to meet the ultimate targets set by the U. S. Department of Energy (DOE) [13]. Chemisorption is seldom reversible while physisorption cannot achieve high hydrogen contents. Fortunately, the transition metal complex

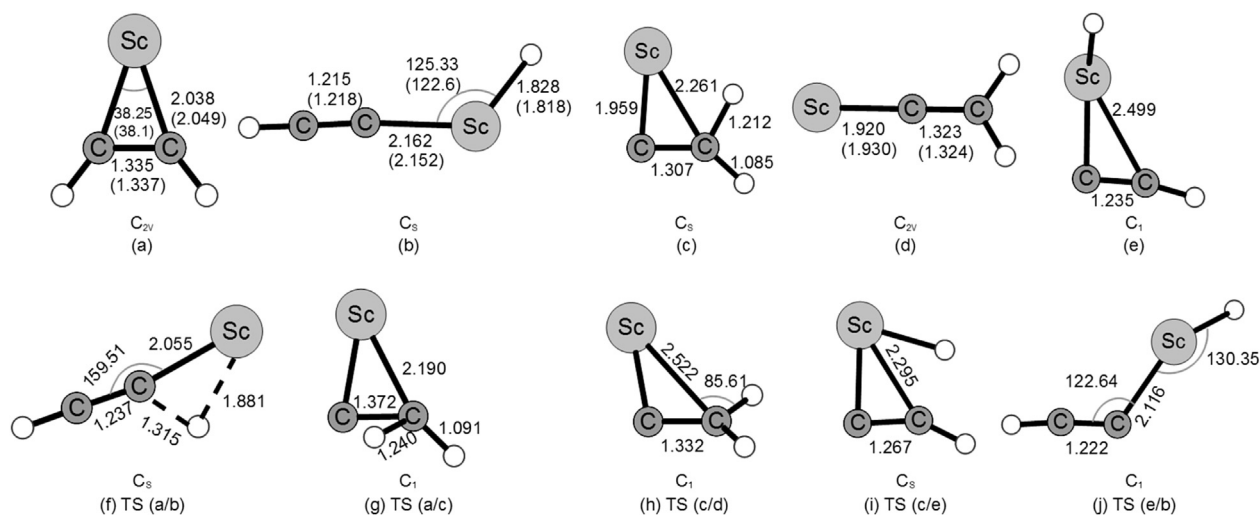
can coordinate multiple hydrogen molecules by the Kubas-typed orbital interaction (s or s\* orbits of  $\text{H}_2$  hybridize with 3d orbits of transition metals) [14–17]. This Kubas interaction, with binding intermediate between physisorption and chemisorption, has been widely employed to make new class of hydrogen storage materials [18–24]. Moreover, a single metallic cation also could adsorb up to six hydrogen molecules by electrostatic interaction [25]. Given the two interactions, many researchers have been trying to make adsorbents by decorating carbon-based nanostructures with transition metal [23,26,27]. Though a number of promising materials have been designed by theoretical studies, there

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**Fig. 1** – Optimized conformations of  $C_2H_2Sc$  complexes and transition states at wb97XD/6-311++G (3df, 3pd) level. The values in parentheses are B3LYP results in Ref. [44]. The bond lengths and angles are in Å and degrees. The symmetries are also shown.

were few materials applied experimentally due to the difficulty of synthesis [28,29]. Durgun [24,30] predicted the hydrogen storage capacities of transition-metal-ethylene complexes and shown that  $Ti_2-C_2H_4$  adsorbed up to ten hydrogen molecules with the average binding energy of 0.45 eV/ $H_2$ . Under this guidance, numerous studies on hydrogen adsorption capacities of organometallic compounds ( $TM-C_2H_4$  and  $TM-C_nH_n$ , TM stands for first transition metals; n refers to 1, 2, 3, 4, 5, 6, 8) were carried out theoretically to search for ideal hydrogen storage media [31–41]. As a matter of fact,  $H_2$  uptake capacities of  $Ti-C_2H_4$  complex (12 wt%) [42] and titanium benzene complexes (6 wt%) [43] have been observed in experiments. These experimental data were in excellent agreement with theoretical results [30,41]. These meaningful results encourage us to consider some realistic structures such as already synthesized organometallic compounds. So, the challenge is to find a synthesized organometallic compound with positively charged transition metal atom.

The Scandium–Acetylene systems are exactly what we've been trying hard to find due to their excellent performances: (i) Sc has the maximum number of available empty d orbitals, namely, more electrons from  $H_2$  can be filled in these orbitals. (ii) On the basis of density functional calculations, the charges in the  $C_2H_2Sc$  complexes transfer from Sc to the acetylene leaving the Sc atoms in cationic states. (iii) Above all, experiment based on controlled synthesis of  $Sc-\eta^2-C_2H_2$  and  $HC\equiv C-ScH$  has shown that they are very stable clusters [44]. Previously, computational investigations of hydrogen adsorptions on  $C_2H_2M$  ( $M=Li, Ti, Ni$ ) [32–34] have been reported.  $C_2H_2Li$  complex was not suitable for ideal hydrogen storage even at a very low temperature (50 K) [33];  $C_2H_2Ni$  could only adsorb maximum of two  $H_2$  molecules with average binding energy of 1.18 eV/ $H_2$ , then the molecules were remained strongly bound to the organometallic complex even at 600 K [34]; Both  $Ti-\eta^2-(C_2H_2)$  and  $HC\equiv C-TiH$  could adsorb six  $H_2$  molecules below temperatures 315 K and 275 K, respectively [32]. Unfortunately, dimers could form in case of  $C_2H_2Ti$  and

$C_2H_2Ni$  complexes [32,34], and the hydrogen storage capacities were substantially reduced from 14.06 wt% to 7.56 wt% and from 4.54 wt% to 3.45 wt%, respectively.

The aim of this work is to predict the hydrogen storage capacities of synthesized  $\pi$  and insertion complexes ( $Sc-\eta^2-C_2H_2$  and  $HC\equiv C-ScH$ ) in the gas phase using *ab initio* CCSD (T) calculations to guide potential experiment. Firstly, the experimental observations in Ref. [44] (the observed products in the matrix infrared spectra were  $Sc-\eta^2-C_2H_2$  and  $HC\equiv C-ScH$  rather than vinylidene product) have been reconfirmed by theoretical calculation; Secondly, stable structures of adsorbed complexes are displayed and the binding energies are calculated; Moreover, the nature of interactions between  $H_2$  and  $Sc-\eta^2-(C_2H_2)/HC\equiv C-ScH$  is profoundly anatomized; Thirdly, the effect of temperature and pressure on the adsorption energies is calculated to estimate the adsorption/desorption temperature at 1 atm and the maximal reversible hydrogen adsorption ability at 77–298.15 K. Finally, dimerization is studied. Our results may offer researchers a new strategy for the design of the hydrogen sorbents based on Kubas interaction and electrostatic interaction.

## Computational details

All geometries, harmonic vibrational frequencies, zero-point energies (ZPE) and the intrinsic reaction coordinate (IRC) calculations [45,46] were obtained using the range-separated hybrid density functional theory (wb97XD [47]) with the valence double diffuse and polarization function 6-311++G(3df, 3pd) basis sets. The wb97XD functional includes empirical dispersion and long range corrections [47], and it described binding energy between  $C_2H_2Ti$  and  $H_2$  molecules well [32]. The calculated bond length and frequency of  $H_2$  were 0.743 Å and 4428  $cm^{-1}$ , which agreed very well with experimental values of 0.741 Å and 4401  $cm^{-1}$  [48]. The three main vibrational normal modes,  $ScC_2$  stretches (565.1  $cm^{-1}$  and

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