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Transition metal-metal oxide hybrids as versatile materials for hydrogen storage

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ABSTRACT

Metal atom located on metal oxide (MMO) is a promising material with various applications such as hydrogen storage. As one of the metal oxides, niobium oxide (NbO) presents fascinating properties that make it a possibly applicable in MMOs. Here, we investigated the feasibility of transition metal-NbO hybrids as MMO materials for application in the hydrogen storage technology. In this respect, the hydrogen adsorption of transition metals (Fe, Ni, Cu, Pd, Ag, and Pt) decorated on the NbO nanocluster has been explored using density functional theory calculations. We found that the adsorption energy of the H_2 molecule on the NbO adsorbent is remarkably increased by locating the transition metals on the NbO metal oxide. Our results reveal that the transition metals decorated on the NbO nanocluster can act as active sites for hydrogen adsorption. Among the studied transition metals, Pt shows the highest hydrogen capacity up to 6.52 wt%.

1. Introduction

Recent studies in materials science have revealed an extensive attention toward finding of materials for energy resources. In this respect, hydrogen is considered as a main element for future energy resources because of its efficiency, abundance, and environmental friendliness [1]. To reach the aim of economic feasibility, hydrogen storage schemes with high gravimetric and volumetric densities, as defined by the DOE targets of 6.0 wt % mass ratio and 45 kg m^{-3} volumetric capacity by 2010, must be achieved, and hydrogen recycling should be carried out in a reversible manner under near ambient conditions [1,2] Thus, another essential criteria is the adsorption energy per H_2 molecule which should be within the range of -0.2 to -0.6 eV [3]. In recent years, plenty experimental and theoretical analyses have been performed to discovery suitable materials for high efficient hydrogen storage [4–8]. One class of candidates for the H_2 adsorption includes chemical hydrides [9–12], such as BH_3, NH_3, $B_{12}H_{12}$, AlH_3, MgH_2, $LiBH_4$, and $NaAlH_4$, where H_2 is adsorbed atomically. However, the difficult regeneration processes considerably prevent their practical applications. Another approach is adsorption of the H_2 on the carbon-based nanomaterials, silica-based materials, metal-organic frameworks (MOFs), and covalent-organic frameworks (COFs) [9,13–16]. In this method, the interaction between the considered materials and the H_2 is very weak and hence the H_2 releases at low temperatures. On the other side, such weak interactions need high pressures for sufficient storage. Recent works also show that the H_2 adsorption can be remarkably increased by the carbon-based nanomaterials supported with the alkali atoms (Li, Na, K, and Ca) [17–19] or transition metal (TM) atoms (Sc, Ti, and V) [20,21]. Nonetheless, hindering clustering of the supported atoms remains a problem [22,23]. Given this scenario, in the present study a new H_2 adsorption material has been suggested. MMOs are very important materials with the practical performances in oxygen reduction reactions (ORRs), petroleum purification, and energy storage [24–28]. The extensive applications of the MMOs arise mostly from the

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strong metal-metal oxide interactions, which can mainly enhance the reactivity of the decorated metal atoms towards guest molecules [27–42]. In recent years, the MMOs including platinum (Pt) decorated on transition metal oxides such as Nb, Ti, Ta, W, Ce, Ru, Ir, and Sn have been studied [33,41–57]. Recently, a fascinating finding has represented that the MMO material constructed by combining the niobium oxide (NbO) and the Pt via a modified arc plasma deposition method can shows tunable electronic properties [42]. Excellent stability in acid condition of the NbO make them versatile materials in fuel cells [57–65]. Moreover, the NbO has attracted an extensive attention due to its novel properties suitable for gas detecting, catalysis, electro-optical and field-emission devices, and micro-electronics [66–69]. Most of the recent researches limited their studies on the catalytic applications of the MMOs leaving the question of feasibility of these materials for application in other research area. The above studies on the MMOs give us a motivation: because the MMOs possess novel properties, whether these materials can be used to H_2 adsorption? To answer this question, in the present work, by studying the H_2 adsorption on the TM atoms (Fe, Ni, Pd, Pt, Cu, and Ag) decorated on the NbO nanocluster through DFT method, we have investigated the feasibility of these materials in hydrogen adsorption applications.

2. Computational details

All quantum chemical calculations were carried out using the general theoretical and computational method based on all electrons DFT with the generalized gradient approximation (GGA) in Perdew-Wang (PW91) functional form [70] and the LanL2DZ basis set, as implemented in GAUSSIAN 09 [71]. Since the PW91 method is unable of giving an accurate description of the weak interactions, we adopted a DFT + D (D stands for dispersion) method with the Grimme's van der Waals (vdW) correction [72,73] in the present work. Singlet and doublet states have been calculated using the restricted and unrestricted schemes for the closed-shell and open-shell computations, respectively. Further, the natural bond orbital (NBO) analysis [74] was utilized to obtain the given charge transfer in this work. The cohesive energies (E_{coh}) of a TM atom on the NbO nanocluster and the adsorption energy (E_{ads}) for the H_2 adsorbed on the MMOs are obtained using the following equations:

$$E_{coh} = \left(E_{tot} - \sum_j n_j E_j\right)/k \tag{1}$$

$$E_{ads} = E(H_2/MMO) - E(H_2) - E(MMO) \tag{2}$$

where E_{tot}, E_j, and n_j being the total energy of the MMO, the atomic energy and the amount of atoms type j (j = Nb, O, and TMs), and k is the total number of atoms present in the MMOs. Also, $E(H_2/MMO)$ and $E(H_2)$ are the total energies of the H_2/MMO complexes and isolated H_2 molecule, respectively. We have also evaluated the reactivity of the considered MMOs by use of chemical hardness descriptor. In the framework of DFT, chemical hardness (η) is defined as the second partial derivatives of the electronic energy with respect to the number of electrons at a constant external potential ($\nu(r)$) [75]:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(r)} \tag{3}$$

Therefore, Fuentealba and Parr [76] computed η (Eq. (4)) from the electron affinity (A), and the first and second ionization potential (I_1 and I_2):

$$\eta = 2(b - ac) \tag{4}$$

The coefficients a, b and c are related to A, I_1 and I_2 through:

$$c = \frac{I_2 - 2I_1 + A}{2I_2 - 2I_1 - A} \tag{5}$$

$$b = -\frac{I_1 - A}{2} - \left(\frac{I_1 + A}{2}\right)c \tag{6}$$

$$a = -\frac{I_1 + A}{2} + \left(\frac{I_2 - A}{2}\right)c \tag{7}$$

3. Results and discussion

3.1. Single H_2 molecule adsorption on pristine NbO nanocluster

First, the geometry and electronic properties of the pristine NbO nanocluster are investigated. Geometry optimization was performed for the pristine NbO nanocluster with the tetrahedral form with the chemical formula $Nb_{10}O_{20}$ that is shown in Fig. 1 panel (A). The angles in tetragon rings of the nanocluster vary from 73.8° to 108.2°. Three different O—Nb bonds are distinguished in the pristine NbO; at the edge (B1) (2.14 Å), at the center (B2) (2.07 Å), and at the surface (B3) (2.22 Å) of the nanocluster. The NBO analysis revealed a net charge of 0.83e from the Nb atom to the O atom in the pristine nanocluster, demonstrating an iconicity nature.

Here, we explored all the adsorption places: directly on top of a Nb or O atom, and above the midpoint of a bond connecting the Nb-O atoms, and found that the top of Nb and O atoms are the most stable site for the H_2 adsorption on the pristine nanocluster.